



# Cyanide linkage isomerism in cerium(III) and uranium(III) complexes. A relativistic DFT study

Yamina Bouzidi, Lotfi Belkhiri, Michel Ephritikhine, Jean-François Halet,  
Abdou Boucekkine

## ► To cite this version:

Yamina Bouzidi, Lotfi Belkhiri, Michel Ephritikhine, Jean-François Halet, Abdou Boucekkine. Cyanide linkage isomerism in cerium(III) and uranium(III) complexes. A relativistic DFT study. Journal of Organometallic Chemistry, 2017, 847, pp.82-89. 10.1016/j.jorgchem.2017.03.002 . cea-01487700

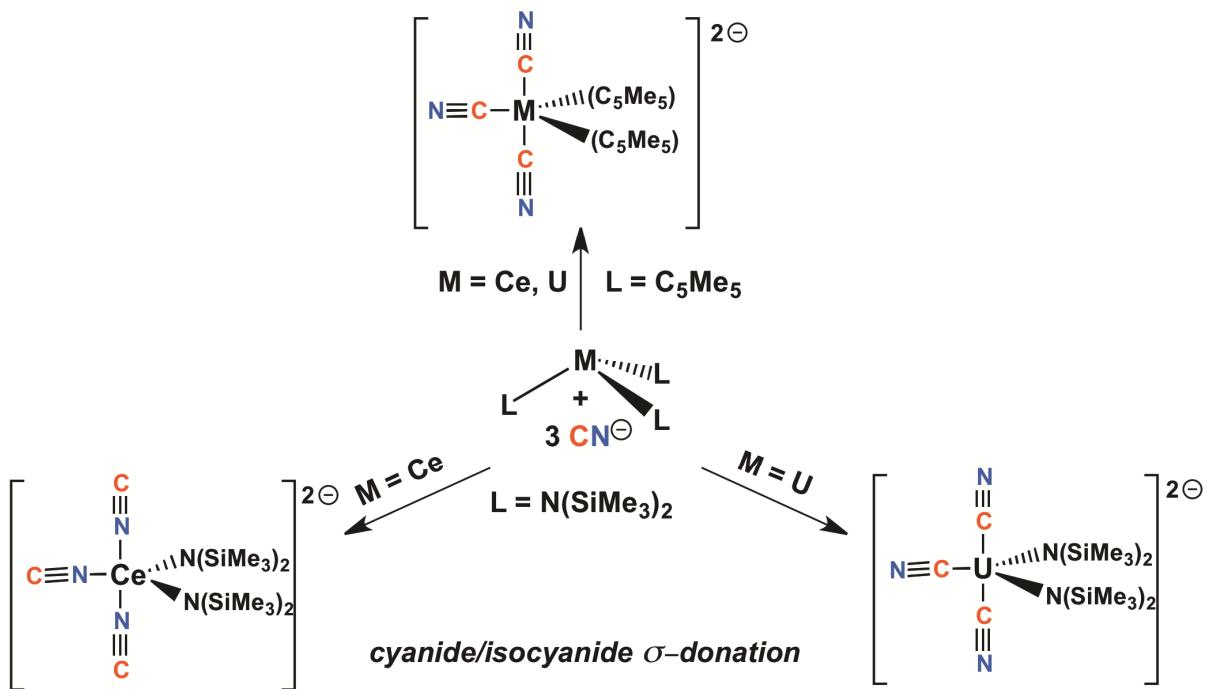
HAL Id: cea-01487700

<https://cea.hal.science/cea-01487700>

Submitted on 2 Oct 2017

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



# Cyanide linkage isomerism in cerium(III) and uranium(III) complexes. A relativistic DFT study

Yamina Bouzidi <sup>a,b</sup>, Lotfi Belkhiri <sup>b,\*</sup>, Michel Ephritikhine <sup>c</sup>,  
Jean-François Halet <sup>d,\*</sup>, and Abdou Boucekkine <sup>d,\*</sup>

<sup>a</sup> Département de Chimie, Université de Batna 1, 05000 Batna, Algeria

<sup>b</sup> URCHEMS, Département de Chimie, Université des Frères Mentouri Constantine 1, 25017 Constantine, Algeria

<sup>c</sup> NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France

<sup>d</sup> Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1, 35042 Rennes Cedex, France

## ABSTRACT

The chemistry of cyanide complexes of the *f*-elements has witnessed significant recent advances, showing in particular the remarkable ability of the cyanide ligand to stabilize uranium compounds in their +3 to +6 oxidation states and its capacity to adopt two distinct ligation modes, namely cyanide M–CN or isocyanide M–NC, towards trivalent f-ions. Here, we have theoretically investigated the tris(cyanide) complexes  $[ML_2X_3]^{2-}$  ( $M = Ce^{3+}, U^{3+}$ ; L = C<sub>5</sub>H<sub>4</sub>Me, N(SiMe<sub>3</sub>)<sub>2</sub>; X = CN, NC), using relativistic DFT computations, focusing on cyanide (CN<sup>−</sup>) and isocyanide (NC<sup>−</sup>) coordination competition and differences between their electronic structures. X-ray crystal data reveal distinct coordination modes of the CN ligand towards uranium and cerium metal centers. Interestingly, in the case of the cerium complexes, and contrarily to the uranium ones, the coordination mode of the cyanide ligand depends on the co-ligand L attached to the metal. The observed coordination in these tris(cyanide) complexes is driven by the binding energies of the CN<sup>−</sup>/NC<sup>−</sup> ligands to the metals. The solvent is shown to play a determining role for the chosen coordination. The developed methodology can help to confirm the cyanide or isocyanide coordination mode when X-ray crystal data are not conclusive or to predict the configuration of a complex to be synthesized. Another application is in the field of lanthanide(III)/actinide(III) differentiation.

**Keywords:** Cyanide, *f*-complexes, Ln(III)/An(III) differentiation, CN-coordination isomerism, DFT calculations, solvation effects

\* Corresponding authors. E-mail address: lotfi.belkhiri@umc.edu.dz (L. Belkhiri), halet@univ-rennes1.fr (J.-F. Halet), abdou.boucekkine@univ-rennes1.fr (A. Boucekkine)

Dedicated to our good friend and colleague John Gladysz on the occasion of his 65<sup>th</sup> Birthday.

## 1. Introduction

Since the first synthesis of *f*-element cyanide complexes in the early seventies [1], the cyanide CN<sup>-</sup> ligand has gained a prominent position in both *d*- and *f*-coordination chemistry mainly because of its strong coordinating ability, its capacity to stabilize a wide range of oxidation states and to adopt different ligation modes, thus giving a rich variety of homo and heteropolymeric compounds with interesting stereochemistry and properties [2]. This is attributed to the strong  $\sigma$ -donor character of the cyanide and isocyanide ligands, *via* donation from either the C-localized orbital of CN<sup>-</sup> (carbon lone pair) or the N-localized one of NC<sup>-</sup> with nitrogen major character [2b]. Therefore, this field is currently attracting attention in various domains, especially in *d*-metal coordination chemistry, with applications in biology and materials science, exemplified with the discovery of molecular-based assemblies with cyanide bridges, giving magnetic materials and providing significant insights into magneto-structural correlations [3].

However, *f*-element cyanide complexes have received much less attention, while the lanthanide and actinide chemistry experienced a spectacular development during the last decades [4,5]. Indeed, the different binding modes of cyanide or isocyanide CN<sup>-</sup>/NC<sup>-</sup> anions towards trivalent *f*-ions was reported recently, revealing a potential application in lanthanide(III)/actinide(III) differentiation [5a,6,7]. Thus, a number of mono and polycyanide complexes of cerium and uranium have been isolated and crystallographically characterized, starting from the metallocene complexes  $[M(Cp^*)_2(CN)_3]^{2-}$  ( $M = Ce, U$ ; Cp<sup>\*</sup> = C<sub>5</sub>Me<sub>5</sub>) which were the first trivalent molecular polycyanide compounds of an *f*-element to have been structurally characterized [2b], followed by the successive syntheses of the mononuclear  $[MN^*_3(CN)]^-$ ,  $[MN^*_3(CN)_2]^{2-}$ ,  $[MN^*_2(CN)_3]^{2-}$  and cyanido-bridged dinuclear  $[(MN^*_3)_2(\mu-CN)]^-$  ( $M = Ce, U$ ; N<sup>\*</sup> = N(SiMe<sub>3</sub>)<sub>2</sub>) anionic compounds [2a]. It is worth noting that the bis(silylamine) ligand N<sup>\*</sup> seems to play a crucial role in stabilizing these polycyanide complexes. It was observed in these latter species that the cerium(III) complexes are

isomorphous but not isostructural to their uranium(III) counterparts because of the distinct cyanide or isocyanide M–CN/NC linkage in the crystal. This striking difference between the cyanide and isocyanide ligation modes in the uranium and cerium compounds was tentatively explained by the fact that the U(III) ion is softer than the Ce(III) ion in the *hard and soft (Lewis) acids and bases* (HSAB) classification and will have a greater affinity for the softer carbon end of the CN ligand [2b].

Synergetic studies at both experimental and theoretical levels were carried out investigating the fundamental chemical differences between the 4f elements, lanthanides (Ln), and the 5f elements, actinides (An), in this field [8-10]. In particular, the coordination competition between cyanide ( $\text{CN}^-$ ) and isocyanide ( $\text{NC}^-$ ) has been studied theoretically in the case of uranyl derivatives [2b, 8, 9], and also for pentacyanide and isocyanide complexes of (IV), U(V) and U(VI) of general formula  $[\text{X}_2\text{U}(\text{CN})_5]^{q-}$  ( $\text{X} = \text{O}, \text{Cp} = \text{C}_5\text{H}_5$ ) [2b,8]. Indeed, it has been shown that cyanide coordination is preferred, although the isocyanide form is also a stable configuration [8]. Two structurally stable structures have been predicted with cyanide linkage mode for the  $[\text{UO}_2(\text{CN})_5]^{4-}$  and  $[\text{Cp}_2\text{U}(\text{CN})_5]^-$  uranyl and Cp-type systems.

In this context, we reported recently a theoretical study on the preferential ligation modes of the cyanide and isocyanide ligands in the Ce(III)/U(III) bis(cyanide)  $[\text{MN}^*{}_{\text{3}}(\text{CN})_2]^{2-}$  complexes [10a]. Based on X-ray data and computational DFT analysis, the preference in M–CN/NC ligation modes has been rationalized by considering the electronic structures and the ligand-to-metal binding energies. Specifically, it has been found that the stronger  $\sigma$ -donating ability of the cyanide ligand toward uranium and not cerium is related to the better energy matching between 6d/5f uranium metal and ligand orbitals [11]. The same observation has been made in the case of U(III) and U(IV) bis(silylamine) mono and bis(cyanide) complexes  $[\text{UN}^*{}_{\text{3}}\text{X}]^{q-}$  and  $[\text{UN}^*{}_{\text{3}}\text{X}_2]^{q-}$  ( $q = 2, 1; \text{X} = \text{CN}, \text{NC}$ ), the covalency contribution to the bonding being also at work (orbital mixing) [10b].

Although the cyanide M–CN ligation mode is ubiquitous for various uranium complexes in different oxidation states (III-VI) [12], the preference for cyanide or isocyanide coordination could remain controversial for some systems. Indeed, as noted by previous theoretical studies [8,9], controversy still exists about the preference for the C or N coordination in the case of uranyl ion derivatives, where the cyanide complexes might be more stable than their isocyanide congeners, noting that the energy difference is only 3.3 kcal. $\text{mol}^{-1}$  [9c].

In the present study, we have investigated using relativistic density functional theory (DFT), the electronic structures of several analogous tris(cyanide) complexes of cerium(III) and uranium(III), with different cyanide and isocyanide ligation modes. The target systems are the bis(cyclopentadienyl) and bis(silylamine) tris(cyanide) compounds  $[M(Cp^*)_2(CN)_3]^{2-}$  and  $[MN^*_2(CN)_3]^{2-}$  ( $M = Ce, U$ ), which have been synthesized recently and crystallographically characterized [10a]. Unexpected coordination modes have been observed. For the bis(cyclopentadienyl) complexes, the X-ray crystal structures show the unambiguous M-C bonding mode of the CN ion. On the contrary, the observed structures of the bis(silylamine) Ce(III) and U(III) complexes exhibit distinct coordination modes of the cyanide CN ligand, through the N or C atom to the Ce(III) or U(III) ions, respectively. Our aim is to rationalize these particular coordinations, especially in the context of Ln(III)/An(III) differentiation.

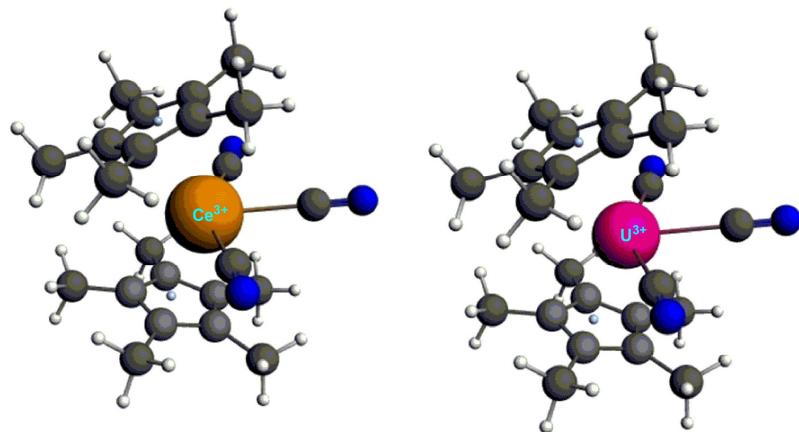
## 2. Results and discussion

“The determining factor (*vide infra*) leading to the M-CN or M-NC coordination mode is the binding energy between the metal fragment and the CN or NC ligand [10a,b]. As shown below, these binding energies differences between isomers range from *ca.* 4 to 14 kcal/mol, except for the  $[UN^*_2X_3]^{2-}$  case for which these binding energies differences are much smaller.

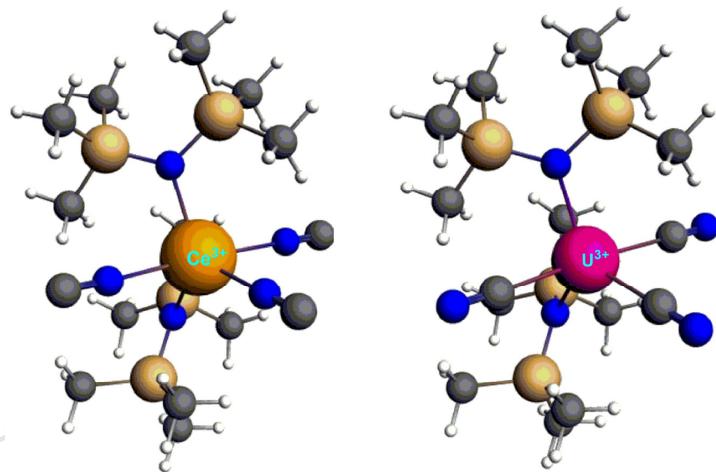
### 2.1. DFT molecular geometry optimization of the tris(cyanide) complexes

We consider the actual complexes of general formula  $[ML_2X_3]^{2-}$  ( $M = Ce^{3+}/U^{3+}$ ;  $L = Cp^*/N^*$  and  $X = CN/NC$ ) and their hypothetical isomers. All structures were fully optimized using the BP86 functional coupled to the polarized double- $\zeta$  Slater basis set (DZP) in the framework of the relativistic zeroth-order regular approximation (ZORA). The solvent (THF) was treated using the COSMO solvation model, implemented in the ADF program (see Computational details). As previously stated [13,14], ZORA/BP86/DZP computed geometries of *f*-elements complexes are generally in good agreement with X-ray crystal structures. Computed bond lengths M-X, M-L ( $L = Cp^*$  and  $N^*$ ) and C-N/N-C of the optimized structures (Fig. 1 and 2) are reported in Table 1 for the actual complexes  $[MCp^*_2(CN)_3]^{q-}$  ( $M = Ce^{3+}, U^{3+/4+}$ ;  $q = 2, 1$ ) (**1a**) and (**1b**) (complexes **6** and **5** in ref. 2b), and their hypothetical isomers  $[MCp^*_2(NC)_3]^{q-}$ . The computed parameters for the isocyanide cerium(III)  $[CeN^*_2(NC)_3]^{2-}$  (**2a**) and cyanide uranium(III)  $[UN^*_2(CN)_3]^{2-}$  (**2b**) complexes (respectively

complexes **4a** and **4b** in reference 10a) and their hypothetical isomers, are also given in Table 1.



**Fig. 1.** ZORA/BP86/DZP optimized geometry of the bis(cyclopentadienyl) tris(cyanide)  $[MCp^*_2X_3]^{2-}$  complexes ( $M = Ce^{3+}, U^{3+}$ ;  $X = CN$ ) **1a** (left) and **1b** (right). The blue, black, and white spheres are nitrogen, carbon, and hydrogen atoms, respectively.



**Fig. 2.** ZORA/BP86/DZP optimized structures of the bis(silylamine) tris(cyanide/isocyanide) complexes  $[MN^*_2X_3]^{2-}$  complexes ( $M = Ce^{3+}, U^{3+}$ ;  $X = CN, NC$ ), **2a** (left) and **2b** (right). The orange, blue, black, and white spheres are silicon, nitrogen, carbon, and hydrogen atoms, respectively.

The computed geometries of the actual  $[MCp^*_2(CN)_3]^{2-}$  Ce<sup>III</sup>-CN and U<sup>III/IV</sup>-CN compounds are in good agreement with the available X-ray data, noting however a slight discrepancy of *ca.* 0.06 Å for the metal-ligand bond distance in the case of the bis(silylamine) Ce<sup>III</sup>-NC derivative (Table 1). This good agreement shows once again the reliability of the ZORA/BP86/DZP method in computing molecular *f*-complex geometries. Notably, the

shortening of the metal-ligand bond distances when going from U(III) to U(IV), in line with uranium ionic radii variation [15], is well predicted by computation.

**Table 1**

Relevant optimized averaged metal-ligand bond distances ( $\text{\AA}$ ) at the ZORA/BP86/DZP level and X-Ray data where available (in bold) for the  $[\text{ML}_2\text{X}_3]^{q^-}$  complexes ( $\text{M} = \text{Ce}^{3+}$ ,  $\text{U}^{3+}$  and  $\text{U}^{4+}$ ;  $\text{X} = \text{CN/NC}$ ;  $\text{L} = \text{Cp}^*/\text{N}^*$ ;  $q = 2, 1$ ) in the gas phase and in solution (in italics).

Complex	$\langle \text{M-C/N} \rangle$	$\Delta (\text{\AA})^a$	$\langle \text{C-N/N-C} \rangle$	$\langle \text{M-L} \rangle$
$[\text{MCp}^*_2\text{X}_3]^{q^-}$				
$\text{Ce}^{3+}$	2.665/2.535		1.178/1.182	2.621/2.638
	2.655/2.546		1.176/1.177	2.586/2.583
	<b>2.666/-</b>		<b>1.158/-</b>	<b>2.562/-</b>
$\text{U}^{3+}$	2.612/2.492	0.053/0.043	1.178/1.183	2.571/2.560
	2.585/2.489	0.070/0.057	1.177/1.180	2.509/2.534
	<b>2.640/-</b>		<b>1.156/-</b>	<b>2.534/-</b>
$\text{U}^{4+}$	2.501/2.389		1.175/1.185	2.482/2.507
	2.520/2.424		1.176/1.180	2.476/2.493
	<b>2.520/-</b>		<b>1.158/-</b>	<b>2.446/-</b>
$[\text{MN}^*_2\text{X}_3]^{q^-}$				
$\text{Ce}^{3+}$	2.666/2.511		1.176/1.183	2.413/2.427
	2.657/2.523		1.175/1.179	2.379/2.387
	<b>-/2.580</b>		<b>-/1.164</b>	<b>-/2.390</b>
$\text{U}^{3+}$	2.605/2.462	0.061/0.049	1.178/1.185	2.377/2.394
	2.593/2.472	0.064/0.051	1.176/1.181	2.348/2.358
	<b>2.600/-</b>		<b>1.148/-</b>	<b>2.334/-</b>
$\text{U}^{4+}$	2.512/2.374		1.175/1.186	2.239/2.253
	2.543/2.416		1.175/1.182	2.198/2.220

<sup>a</sup> Metric difference between Ce–C/N and U–C/N bond distances.

It is worth noting that the comparison between the two Ce(III) and U(III) analogous complexes  $[\text{MCp}^*_2(\text{CN})_3]^{2-}$  in Table 1 reveals a significant shortening of the computed metal-ligand bond distances when going from the cerium to the uranium species. Indeed, the M–CN bond distances in the  $[\text{MCp}^*_2(\text{CN})_3]^{2-}$  gas phase species are equal to 2.665 for Ce vs. 2.612  $\text{\AA}$  for U, and 2.535 vs. 2.492  $\text{\AA}$  for the corresponding M–NC ones in  $[\text{MCp}^*_2(\text{NC})_3]^{2-}$ . This bond length shortening is also observed for the solvated species with a greater contraction of the U(III)–CN/NC bond distances comparatively to the Ce(III) species. The metric difference  $\Delta$  between the Ce–C/N and U–C/N bond distances computed at the ZORA/BP86/DZP level is predicted to be larger for the cyanide CN than for the isocyanide NC ligand (0.053 vs. 0.043

$\text{\AA}$ ), which is slightly amplified by solvation (0.070 vs. 0.057  $\text{\AA}$ ), suggesting that the former, *i.e.*, the cyanide form, leads to a more covalent bonding than the isocyanide one. These features illustrate the distinct coordination modes of these two ligands towards the Ce(III) and U(III) ions, as experimentally observed.

The U–CN/NC bond length shortening relatively to Ce–CN/NC is also observed for the U–L ( $L = \text{Cp}^*$  and  $\text{N}^*$ ) coordination. Moreover, no significant difference is computed for C–N/N–C distances when moving from Ce(III) to U(III) complexes, suggesting that no  $M \rightarrow X \pi$  back-donation occurs, and that the M–X bond is essentially  $\sigma$  in character. The electronic structure analysis will shed light on these points.

## 2.2. Electronic structures of the tris(cyanide) complexes

As reported previously for the bis(cyanide) compounds  $[\text{MN}_3^*\text{X}_2]^{2-}$  ( $M = \text{Ce}^{\text{III}}$  and  $\text{U}^{\text{III}}$ ,  $X = \text{C}-\text{N}/\text{N}-\text{C}$ ) [10a], the better energy matching of the C-localized  $\sigma$  lone pair orbital of the cyanide ligand with the  $\text{U}^{\text{III}}(5f)$  metal-based orbitals makes it a much more effective donor than the N-localized  $\sigma$  orbital, which is much lower in energy [9]. This feature was also reported to explain the cyanide U(III)–CN and isocyanide U(IV)–NC coordination mode in the  $[\text{UN}_3^*\text{X}_2]^{2-/1-}$  complexes [10b]. To investigate further the electronic structure and metal-ligand bonding, natural bond order/natural population analyses (NBO/NPA) [16a] (see Appendix A, computational details) were performed on the optimized geometries of the cyanide and isocyanide systems at the ZORA/BP86/DZP level. The NPA approach proved to probe the covalency in *f*-element complexes with results in better agreement with experimental trends [16b,c,d] than the Mulliken population analysis (MPA) [16e], especially in the context of lanthanide(III)/actinide(III) differentiation [10,11,16f].

NPA results for the complexes  $[\text{ML}_2\text{X}_3]^{2-}$  ( $M = \text{Ce}^{3+}$ ,  $\text{U}^{3+}$ ;  $L = \text{Cp}^*/\text{N}^*$ ;  $X = \text{CN}/\text{NC}$ ) under consideration are given in Table 2. Natural metal ( $q_M$ ), carbon and nitrogen atomic net charges as well as the metallic spin population  $\rho_M$  are reported.  $\rho_M$  is computed to be the difference between the total  $\alpha$  and  $\beta$  spin electronic populations. In the case of the bis(cyclopentadienyl)  $\text{MCp}_2^*(\text{CN})_3$  complexes, examination of the NPA results (Table 2) indicates a small difference between the metal natural charges ( $q_M$ ) for the cyanide M–CN and isocyanide M–NC complexes (+1.53/+1.74) for  $\text{Ce}^{3+}$  and (+0.73/+1.03 for  $\text{U}^{3+}$ ) which are consistent with the slightly stronger  $\sigma$ -donation of the cyanide ligand to the U(III) ion, since

the ligand-to-metal donation is stronger when the positive metallic net charge becomes smaller, in agreement with previous findings [10a]. This difference becomes more pronounced when the two Ce(III)/U(III)–X systems are compared (namely +1.53 for cerium vs. +0.73 for uranium, in the case of a CN coordination), which could account for Ce(III)/U(III) differentiation. In the case of the bis(silylamine)  $MN_2^*$  complexes, the metal natural charge ( $q_M$ ) for the cyanide U–CN is lower than for the isocyanide U–NC (namely +1.30 vs. +1.54) indicating a stronger ligand-to-metal donation, and it is also lower than for the cyanide Ce–CN ones (*i.e.*, +1.71) consistent with the U–CN/NC bond length shortening relatively to Ce–CN/NC. It is noteworthy that solvation effects do not modify the trends observed for the isolated complexes.

**Table 2**

ZORA/BP86/DZP NPA results for the  $[MCp^*_2X_3]^{2-}$  and  $[MN^*_2X_3]^{2-}$  ( $M = Ce^{3+}, U^{3+}$ , X = CN/NC) complexes in the gas phase and in solution (in italics).

M–(CN/NC) Structure	NPA spin population		NPA net charge	
	$\rho_M$	$q_M$	$\langle C-N \rangle$	$\langle N-C \rangle$
$[MCp^*_2X_3]^{2-}$				
Ce(III)	0.989/0.993	+1.53/+1.74	-0.12: -0.57	-0.81: +0.04
	<i>0.985/0.981</i>	<i>+1.49/+1.72</i>	<i>-0.28: -0.63</i>	<i>-0.76: -0.01</i>
U(III)	2.913/2.898	+0.73/+1.03	-0.23: -0.56	-0.71: +0.05
	<i>2.874/2.873</i>	<i>+0.56/+1.01</i>	<i>+0.05: -0.63</i>	<i>-0.66: -0.04</i>
$[MN^*_2X_3]^{2-}$				
Ce(III)	1.019/1.018	+1.71/+1.88	-0.17: -0.54	-0.85: +0.09
	<i>1.003/1.016</i>	<i>+1.66/+1.86</i>	<i>-0.11: -0.61</i>	<i>-0.80: +0.02</i>
U(III)	2.949/2.921	+1.30/+1.54	-0.11: -0.53	-0.85: +0.10
	<i>2.929/2.901</i>	<i>+1.23/+1.50</i>	<i>-0.04: -0.59</i>	<i>-0.70: +0.03</i>

Comparison of the charge distribution on the C–N coordination reveals a slightly but significantly lower C cyanide natural charge in U(III) than in Ce(III) species, especially for the bis(silylamine)  $MN_2^*$  complexes (e.g., -0.11 vs. -0.17), which sustains its stronger  $\sigma$ -donation for the actinide system (in vacuum). These trends seem to be amplified by solvation, since the negative net charge borne by the C cyanide in the U(III) system decreases significantly (-0.11 vs. -0.04), sustaining its stronger  $\sigma$ -donation towards the actinide ion. Interestingly, the total charges of the C–N moiety in the case of Ce(III) and U(III) cyanide coordination are equal to -0.69 vs. -0.79 for the  $MCp^*_2$  complexes and -0.71 vs. -0.64 for

the  $MN_2^*$  ones, respectively. Similarly, the total charges of the N–C isocyanide for the Ce(III) and U(III) systems, equal to  $-0.77$  vs.  $-0.66$  and  $-0.76$  vs.  $-0.75$  for the two  $MCp^*_2$  and  $MN_2^*$  systems, respectively, show that the isocyanide donation ability is similar in the bis(silylamide) complexes. Thus, it seems that the stronger C cyanide covalent bonding towards  $UN_2^*$  moieties contributes to the chosen coordination mode of this species. The covalent factors, presumably slight, likely to originate mainly from the cyanide and/or isocyanide  $\sigma$ -donation abilities and the better energy matching between metallic orbitals d/f and ligand orbitals, are responsible for the Ce(III)/U(III) differentiation, this point being supported by bond order (BO) calculations. To further assess these electronic factors, *i.e.*, the ionic and/or covalent contribution to the cyanide/isocyanide coordination preference, the Nalewajski-Mrozek (NM) bond indices [17a,b] and Mayer bond orders [17c] for the M–CN/NC and C–N/N–C bonds were computed and are reported in Table 3.

**Table 3**

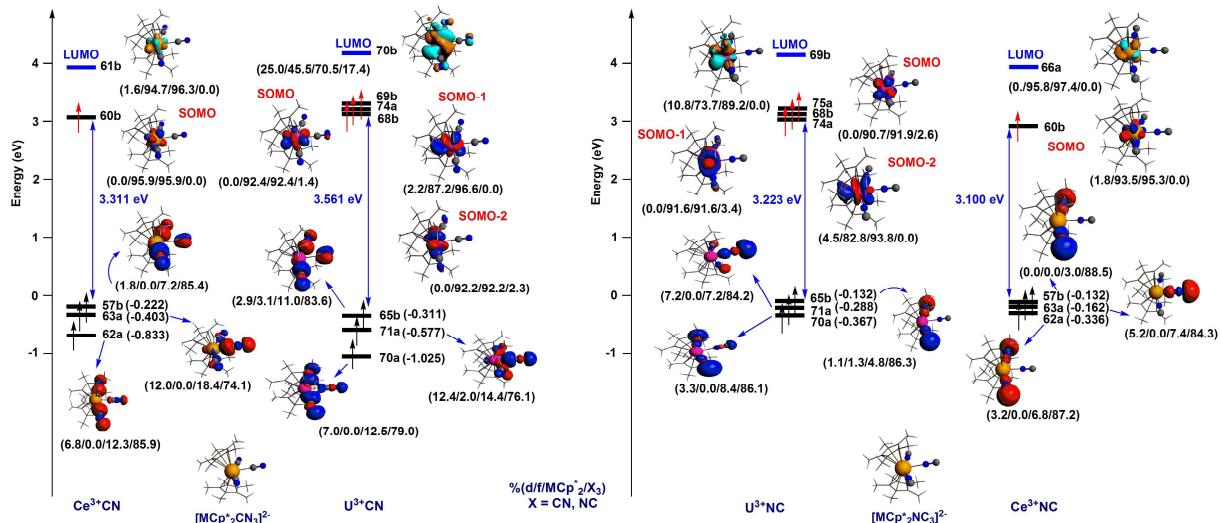
ZORA/BP86/DZP Mayer bond orders and Nalewajski–Mrozek (NM) bond indices for the  $[ML_2X_3]^{2-}$  ( $M = Ce^{3+}, U^{3+}$ ;  $L = Cp^*, N^*$ ;  $X = CN/NC$ ) complexes in the gas phase and in solution (in italics).

Compound	M–(CN/NC) (Å)	Mayer bond order		NM bond index	
		$\langle M-C/N \rangle$	$\langle C-N/N-C \rangle$	$\langle M-C/N \rangle$	$\langle C-N/N-C \rangle$
$[MCp^*_2X_3]^{2-}$	Ce(III)	2.665/2.535 2.655/2.546	0.447/0.387 0.431/0.361	2.814/2.665 2.835/2.755	0.695/0.642 0.687/0.612
	U(III)	2.612/2.492 2.585/2.489	0.529/0.466 0.530/0.445	2.759/2.624 2.780/2.712	0.837/0.801 0.859/0.785
	Ce(III)	2.666/2.511 2.657/2.523	0.440/0.396 0.426/0.364	2.829/2.633 2.841/2.723	0.838/0.952 0.796/0.894
	U(III)	2.605/2.462 2.593/2.472	0.540/0.491 0.532/0.467	2.777/2.585 2.790/2.670	0.885/0.868 0.882/0.830
As expected, the NM approach, which accounts for both ionic and covalent contributions, gives greater metal-ligand bond orders, up to two times, than Mayer ones which essentially takes into account covalent contributions. It is noteworthy that NM and Mayer analyses give larger M–CN/NC BOs for uranium complexes than for their cerium congeners, correlating well with structural features and NPA results. For the C–N/N–C bonds, the covalent character is high, so that the NM and Mayer indices get closer. It is worth noting that for all systems, Mayer analysis, consistently gives M–C cyanide bond orders higher than M–N isocyanide ones, <i>e.g.</i> 0.447 vs. 0.387 and 0.529 vs. 0.446 for $CeCp^*_2$ and $UCp^*_2$ systems, respectively.					

These trends, namely higher BOs for M–C cyanide than for isocyanide M–N coordination, are corroborated by the NM results for the bis(cyclopentadienyl)  $\text{MCp}^*_2$  systems. On the other hand, this is the opposite is computed for the bis(silylamide)  $\text{MN}^*_2$  species. Indeed, the isocyanide Ce–N NM is predicted to be higher than the Ce–C cyanide one (0.952 vs. 0.838) in the  $\text{CeN}^*_2$  system, whereas the opposite is computed for the  $\text{UN}^*_2$  congeners, the U–C NM being slightly but significantly higher than the U–N one (0.885 vs. 0.868), in accordance with the experimental observation. The NM approach correlates well with the experimental structural data and as stated recently by other works, [10,17d] appears to be more reliable because it both accounts for ionic and covalent contribution. Notably, the slight difference between the cyanide M–C and isocyanide M–N Nalewajski-Mrozek BOs reflects the subtle balance between the ionic/covalent contributions in their coordination preference. It is noteworthy that the computed COSMO/THF results performed to take account of the solvation species in solution are in line with the gas phase ones and confirm the crucial role of the bis(silylamide)  $\text{MN}^*_2$  co-ligand in the Ln(III)/An(III) differentiation.

### 2.3. Molecular orbital (MO) analysis of the tris(cyanide) complexes

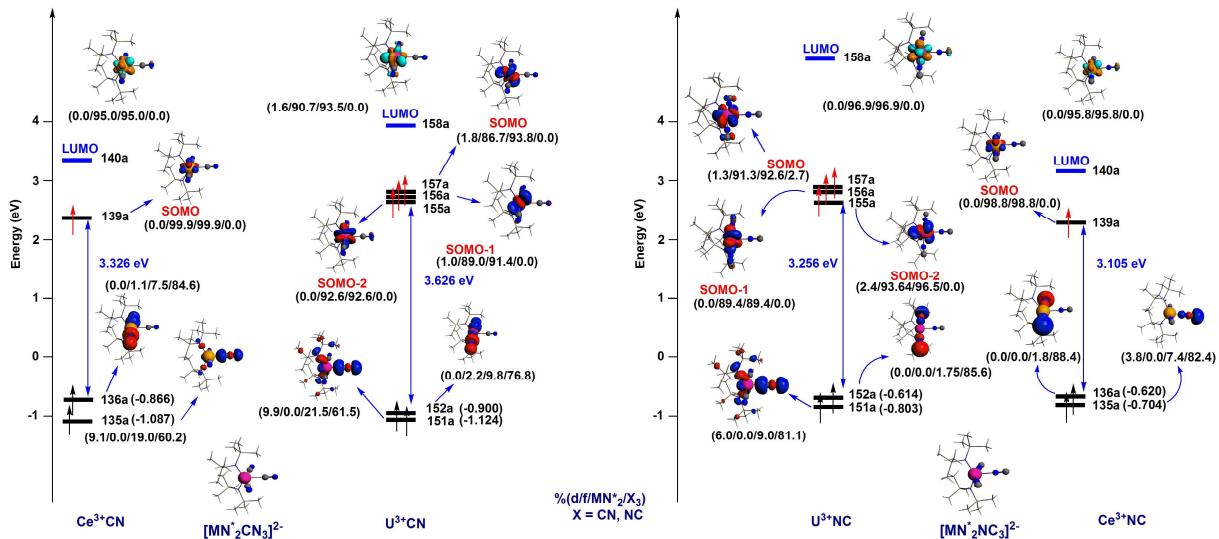
MO frontier diagrams of the trivalent complexes  $[\text{ML}_2\text{X}_3]^{2-}$  ( $\text{M} = \text{Ce}^{3+}$  or  $\text{U}^{3+}$ ;  $\text{L} = \text{Cp}^*$  or  $\text{N}^*$ ;  $\text{X} = \text{CN}/\text{NC}$ ) are given in Fig. 3 and 4. For the sake of simplicity, only  $\alpha$  spin-MOs are shown. Different sets of MOs appear. For all cyanide and isocyanide complexes, the diagrams show that the highest occupied  $\alpha$  spin-orbitals, *i.e.*, the SOMO, SOMO-1 and SOMO-2 in  $\text{U}(\text{III})$  ( $f^3$ ) complexes and the SOMO in the  $\text{Ce}(\text{III})$  ( $f^1$ ) counterpart are essentially metallic in character, with a strong  $f$  orbital contribution. In the case of the  $\text{U}(\text{III})$  systems, a weak cyanide or isocyanide ligand contribution of *ca.* 4% is observed in the SOMOs. However, neither presence of metal-to-ligand  $\pi$  back-donation nor  $\pi$  interaction appears between the metal center and the cyanide or isocyanide ligands, since the participation of the C-localized orbital of  $\text{CN}^-$  or N-localized orbital of  $\text{NC}^-$  is null. This confirms the fact that these ligands remain mainly  $\sigma$  donors in character in these species.



**Fig. 3.** ZORA/BP86/DZP  $\alpha$  spin-MO diagram for M–CN (left) and M–NC (right)  $[\text{MCp}^*_2\text{X}_3]^{2-}$  ( $\text{X} = \text{CN/NC}$ ) complexes ( $C_2$  symmetry). From the left to the right, the M  $d$ , M  $f$ , ML<sub>2</sub>, and X<sub>3</sub> percentage contributions are given in brackets. Contour values are  $\pm 0.03$  (e/bohr<sup>3</sup>)<sup>1/2</sup>.

More interestingly, the sets of occupied M–CN/NC MOs, deeper in energy, exhibit mainly the  $\sigma$  donation character of the CN or NC ligand. First of all, the comparison of the electronic structure of the cyanide U–CN and Ce–CN compounds with that of their isocyanide congeners in the  $[\text{MCp}^*_2\text{X}_3]^{2-}$  complexes (Fig. 3), reveals that the metal  $d/f$  orbitals weight is slightly larger for the cyanide M–CN complexes than for their M–NC analogues, as it can be seen in the  $\sigma$ -donating 62a, 63a, 57b and 70a, 71a, 65b MOs, namely 7.2–18.4 vs. 11.1–14.4 % for Ce–CN and U–CN, respectively. This weight is reduced to 3.0–7.4 vs. 4.8–8.4 % for Ce–NC and U–NC, respectively, for the same MO bonding sets. It is worth noting that the 6d/5f actinide orbitals both contribute more significantly to the U–CN bonding. This is in agreement with the coordination preference of uranium.

Moving back to the bis(silylamine) MN\*<sub>2</sub> systems, the MO diagram of Fig. 4 shows that the metal  $d/f$  orbitals contributions within the bonding  $\sigma$ -donating pair U–CN/NC, *i.e.*, 151a, 152a MOs are in the range 9.8–21.5 vs. 1.7–9.0% for U–CN and U–NC, respectively, in line with NM bond orders and NPA analyses discussed above, and correlating well with the observed cyanide UN\*<sub>2</sub>–CN coordination. Furthermore, these bonding  $\sigma$ -donating pairs, *i.e.*, 151a, 152a MOs, are slightly lower in energy for the U–CN coordination than for the hypothetical U–NC one, namely –0.90 and –1.12 vs. –0.61 and –0.80 eV, respectively, sustaining the stronger interaction between the 6d/5f U(III) orbitals and C-cyanide ones due to a better energy matching [11].



**Fig. 4.** ZORA/BP86/DZP  $\alpha$  spin-MO diagram for M–CN (left) and M–NC (right)  $[\text{MN}^*\text{}_2\text{X}_3]^{2-}$  ( $\text{X} = \text{CN/NC}$ ) complexes ( $C_1$  symmetry). From the left to the right, the M  $d$ , M  $f$ , ML<sub>2</sub>, and X<sub>3</sub> percentage contributions are given in brackets. Contour values are  $\pm 0.03$  (e/bohr<sup>3</sup>)<sup>1/2</sup>.

Considering the bis(silylamide) Ce–CN/NC pair, as shown by the MO analysis (Fig. 4), the 135a and 136a MOs exhibit metal contributions of 19.0 and 7.5 % vs. 7.4 and 1.8 % mainly 5d orbitals, for Ce–CN and Ce–NC bonding, respectively. Moreover, the Ce–CN bonding levels are slightly lower in energy than the Ce–NC congeners (*i.e.*, –0.87 and –1.09 vs. –0.62 and –0.70 eV, respectively) and the small gap between the SOMO and the Ce–CN/NC pair  $\sigma$ -donating MOs (3.33 vs. 3.11 eV) suggest that the preferred CN/NC coordination is, in this case, under ionic or/and covalent subtle control, as noted by NPA and NM bond orders analysis (see above Tables 2 and 3).

As shown by the MO analysis (Fig. 3 and 4), the isocyanide M–NC interaction seems to be weaker than the cyanide M–CN interaction, as corroborated by metallic percentages in bonding M–CN/NC MOs, which are greater in the latter. This could explain the energy stability difference between the cyanide and isocyanide systems and the coordination mode preference to the uranium(III) and cerium(III) centers.

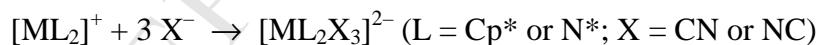
As indicated by the electronic structure and MO analysis, the variations in structural and bonding parameters of the considered complexes could be explained by the  $\sigma$ -donating abilities of the cyanide and isocyanide ligands and the occurrence of a higher covalent character of the bonding in the case of the U(III) complexes. However, even though structural parameters and electronic factors can account for the latter effects [18], they cannot always

permit to differentiate the CN/NC coordination mode preference for actinide(III) and lanthanide(III) systems in terms of their relative stabilities, as recently noted [10a].

The chosen coordination mode is mainly driven by a good match between the energies of the metal AOs within the  $\text{MCp}^*_2$  and  $\text{MN}^*_2$  fragments, and the carbon or nitrogen lone pair energies of the cyanide ligand. The energies of the metal orbitals involved in bonding with the cyanide ligand are lower by *ca.* 1 eV for the  $\text{CeN}^*_2$  fragment relatively to  $\text{CeCp}^*_2$ . Let us remind that the nitrogen lone pair of the cyanide ligand is lower in energy than the carbon lone pair. This result would explain why in the cerium compounds the cyanide coordination is observed with the  $\text{Cp}^*_2$  co-ligands and the isocyanide with the  $\text{N}^*_2$  ones. On the contrary, the cyanide coordination in the case of the uranium complexes is not uniquely driven by this sole factor, since it is observed for the two complexes under consideration. The investigation of the bonding energies is required to clarify this issue.

#### 2.4. Energy decomposition analysis

In order to get some additional information on the energy factors driving the preferred coordination of the cyanide or isocyanide ligands to the cerium or uranium atoms in the actual  $[\text{ML}_2\text{X}_3]^{2-}$  complexes ( $\text{M} = \text{Ce}^{3+}$  or  $\text{U}^{3+}$ ;  $\text{L} = \text{Cp}^*$  or  $\text{N}^*$ ;  $\text{X} = \text{CN/NC}$ ) and their hypothetical isomers, an energy decomposition analysis was carried out (see Appendix A, computational details). The bonding energies of the ligands to the metal centers were calculated according to the following fragmentation scheme:



These total bonding energies ( $\text{TBE}_{\text{frag}}$ ) computed at the spin unrestricted ZORA/BP86/DZP level (see Appendix) are given in Table 4.

**Table 4**

Energy decomposition analysis at the ZORA/BP86/DZP level for the complexes  $[\text{ML}_2\text{X}_3]^{2-}$  ( $\text{M} = \text{Ce}^{3+}$  or  $\text{U}^{3+}$ ;  $\text{L} = \text{Cp}^*$  or  $\text{N}^*$ ;  $\text{X} = \text{CN(left)/NC(right)}$ ) in the gas phase and in solution (in *italics*).

ion	$E_{\text{Pauli}}$ (eV)	$E_{\text{elstat}}$ (eV)	$E_{\text{st}}$ (eV)	$E_{\text{orb}}$ (eV)	$E_{\text{solvat}}$ (eV)	$\text{TBE}_{\text{frag}}$ (eV)	$\Delta E$ (kcal/mol)
$[\text{MCp}^*_2\text{X}_3]^{2-}$							
$\text{Ce}^{3+}$	6.001/6.314	-16.928/-16.225	-10.927/-9.910	-6.700/-7.257	-	-17.628/-17.186	0.0/10.1

5.856/6.011	-16.265/-16.286	-10.409/-10.275	-6.852/-6.713	-4.651/-4.629	-21.885/-21.589	0.0/6.8
-------------	-----------------	-----------------	---------------	---------------	-----------------	---------

<b>U<sup>3+</sup></b>	7.788/8.383	-17.873/-17.869	-10.084/-9.485	-7.945/-8.209	-	-18.030/-17.695	0.0/7.7
	8.209/8.369	-18.001/-17.868	-9.791/-9.498	-8.276/-8.099	-4.637/-4.572	-22.677/-22.142	0.0/12.3
<b>[MN*<sub>2</sub>X<sub>3</sub>]<sup>2-</sup></b>							
<b>Ce<sup>3+</sup></b>	5.703/6.297	-16.935/-17.821	-11.231/-11.523	-7.143/-7.458	-	-18.375/-18.981	13.9/0.0
	5.599/5.865	-17.319/-17.635	-11.719/-11.769	-6.719/-6.943	-4.506/-4.405	-22.915/-23.087	4.0/0.0
<b>U<sup>3+</sup></b>	8.247/8.874	-18.634/-18.916	-10.387/-10.041	-8.439/-8.849	-	-18.826/-18.891	1.5/0.0
	7.943/8.369	-18.619/-18.851	-10.676/-10.489	-8.107/-8.300	-4.458/-4.381	-23.212/-23.132	0.0/1.8

Considering first the computed energy for isolated complexes (namely in vacuum), it can be seen that the TBE<sub>frag</sub> for the cyanide M–CN coordination of the MCp\*<sub>2</sub> complexes are significantly higher (in absolute value) than the isocyanide M–NC ones, as shown by their relative stability  $\Delta E$ , in agreement with the experimental observation, *i.e.*, the actual structures. We note that for the MN\*<sub>2</sub> complexes, the most stable species is correctly predicted for the isocyanide Ce–NC species but not for the cyanide U–CN species. Indeed, the relative stability given by  $\Delta E$  clearly highlights the difference in M–CN/NC coordination between the Ce(III) and U(III) ions, in agreement with the experimental findings, except for the UN\*<sub>2</sub> complex, where  $\Delta E$  in vacuum indicates a U–NC coordination, noting that the energy difference is small, 1.50 kcal/mol only.

As expected, considering the different energy terms (Table 4), the steric term ( $E_{st}$ ) is slightly more destabilizing for the U(III) than for the Ce(III) species, especially in the bis(silylamide) MN\*<sub>2</sub>, due to the shorter metal–ligand distances in the former. Notably, in the bis(cyclopentadienyl) MCp\*<sub>2</sub> series, the steric term, which is the sum of the Pauli repulsion (repulsion between electron pairs) and the stabilizing electrostatic interactions, reveals that the isocyanide binding mode for the two Ce(III) and U(III) ions is less sterically favored than the cyanide binding mode. This is due to a higher Pauli repulsion related to smaller M–N bond lengths than M–C ones.

More interestingly, the steric term in the bis(silylamide) MN\*<sub>2</sub> species reveals that the isocyanide Ce–NC binding mode is slightly more sterically favored than the cyanide Ce–CN one (*i.e.*, -11.52 vs. -11.23 eV) whereas the opposite is observed for the U–CN/NC

coordination (*i.e.*,  $-10.38$  vs.  $-10.04$  eV), confirming the preference for the cyanide coordination mode.

The orbital term  $E_{\text{orb}}$  (stabilizing energy due to orbital mixing) is slightly larger in the M–NC case than in the M–CN one. However, the difference is small and is due to the competitive contribution of the covalent (orbital mixing) and the polarization factors, these latter being larger for the smaller M–NC bond distances [10]. Indeed, we must keep in mind that the orbital  $E_{\text{orb}}$  part includes both a polarization term due to the rearrangement of the metal and ligand charge distribution with complexation, and covalency if their orbitals overlap [19]. Unfortunately, these two terms cannot be evaluated separately [19b]. Moreover, the polarization component is likely not the same for the C or N coordination modes, so that difference in  $E_{\text{orb}}$  cannot be directly related to difference in covalency. Furthermore, as stated by others authors [9,11], the best energy matching between the *d/f* orbitals and the upper C-cyanide or the lower N-isocyanide  $\sigma$ -donating MO is likely to play a crucial role in this coordination preference.

In addition to the gas phase analysis we have also computed the complexation energies incorporating the effect of the solvent (THF) using the COSMO solvation approach (Table 4). Indeed, the main trends observed for isolated complexes are maintained in solution. Interestingly, in the case of the uranium  $[\text{UN}^*\text{X}_3]^{2-}$  species, the U–CN coordination appears now to be favored relatively to the U–NC one, by 1.8 kcal/mol, in agreement with experimental data [10a]. This theoretical result is in line with the fact that the synthesis of this complex was made in solution. It is noteworthy that using the most extended basis set available in the ADF program for all atoms, *i.e.* the ZORA/TZ2P one, the coordination preference of the cyanide towards U(III) is confirmed for the bis(silylamine) complex. Indeed, the same trend is obtained, *i.e.* the cyano isomer is more stable than the isocyano one (by 1.2 kcal/mol at the TZ2P level *vs.* 1.8 kcal/mol at the DZP one) when the solvent effect is taken into account, the opposite being obtained in the gas phase.

### 3. Conclusion

The observed distinct coordination modes of cyanide and isocyanide ligands towards cerium(III) and uranium(III) in the tris(cyanide) complexes  $[\text{ML}_2\text{X}_3]^{2-}$  ( $\text{M} = \text{Ce}^{3+}/\text{U}^{3+}$ ;  $\text{L} = \text{Cp}^*/\text{N}^*$ ;  $\text{X} = \text{CN/NC}$ ) were investigated using relativistic DFT/ZORA/BP86 computations both in the gas phase and solution. The coordination modes, M–CN or M–NC, were well

rationalized by the consideration of the binding energies of the cyanide and isocyanide ligands to the metal ions and by the confrontation of the DFT optimized geometries to the X-ray crystal data. The effects of cyanide and isocyanide coordination on structural properties of the complexes, especially in the bis(silylamine) compounds  $[MN^{*2}X_3]^{2-}$ , have been rationalized considering electronic indices like NPA charges and bond orders. Furthermore, the variations in structural and bonding parameters of the considered complexes could be explained by an MO analysis. The coordination preference of the cyanide and isocyanide ligands towards the  $[MCp^{*2}]$  and  $[MN^{*2}]$  moieties results mainly from the best energy matching between the  $d/f$  metallic orbitals and the upper energy C-cyanide or the lower N-isocyanide  $\sigma$ -donating MOs. More generally, MO analysis shows that the stronger  $\sigma$ -donating ability of the cyanide ligand towards actinide bis(silylamine) systems over their cerium congeners is related to the higher covalent bonding character which plays a significant role in metal-ligand coordination preference.

The calculated total bonding energies between the  $[MCp^{*2}]$  and  $[MN^{*2}]$  ( $M = Ce, U$ ) metallic fragments and the CN/NC ligands could permit prediction of the M–CN/NC coordination preference towards the Ce(III)/U(III) pair. Indeed, considering the experimental and hypothetical structures in their gas and solvated phases, it was found that the  $TBE_{frag}$  bonding energies for the cyanide M–CN coordination in the  $MCp^{*2}$  complexes are significantly higher (in absolute value) than the isocyanide M–NC ones, as shown by their relative stability  $\Delta E$ , agreeing well with the experimental structures. In the  $MN^{*2}$  series, the isocyanide Ce–NC coordination was clearly predicted more stable than the Ce–CN one, whereas the correct cyanide coordination of the uranium complex is found only if solvent effects are taken into account. This result is rather rewarding since the latter uranium complex has been synthesized in solution. The developed methodology seems able to predict the correct isomer with confidence in all cases. Nevertheless, the preferred cyanide or isocyanide coordination mode is driven by a subtle balance between steric, ionic or/and covalent factors, as well as solvent effects, so that it could be difficult to predict with certainty, on the basis of the theoretical computation alone, the preferred coordination mode, especially when the binding energies are not very different [10].

## Appendix A. Computational details

All molecular geometries of the tris(cyanide) complexes  $[ML_2X_3]^{2-}$  ( $M = Ce^{3+}/U^{3+}$ ;  $X = CN/NC$ ;  $L = Cp^*/N^*$ ) were fully optimized, starting from crystal structures where available, at the scalar relativistic DFT level of theory using the Amsterdam Density Functional (ADF2014.07) program package [20].

Scalar relativistic effects were taken into account via the Zeroth Order Regular Approximation (ZORA) [20e-g]. The Vosko–Wilk–Nusair functional (VWN) [21a] for the Local Density Approximation (LDA) and gradient corrections for exchange and correlation of Becke and Perdew (BP86 functional) [21b,c] were used for geometry optimization and analytical computation of the frequencies of the normal modes of vibration. Double- $\zeta$  Slater-type valence orbitals (STO) augmented by one set of polarization functions were used for all atoms. For all elements, the basis sets were taken from the ADF/ZORA/DZP database. Several theoretical studies have shown that such a ZORA/BP86/DZP approach reproduces the experimental geometries and ground state properties of *f*-element compounds with a satisfying accuracy [14]. Finally, for all complexes, we considered the highest ( $2S+1$ ) spin state as the ground state configuration, *i.e.*, doublet ( $f^1$ ) spin states for the Ce(III) and quartet ( $f^3$ ) for U(III) systems.

In order to provide a better understanding of the metal-ligand bonding, a Natural Population Analysis (NPA) [16a] was carried out. It has been shown that such an approach provides reliable results for *f*-element complexes [16b,c,d,f].

As the ADF program supplies an energy decomposition of the metal-ligand bonding into chemically useful terms, spin-unrestricted fragment calculations were carried out considering the two molecular moieties in interaction, *i.e.*,  $ML_2$  and  $X_3$  ( $X = CN/NC$ ) for the  $[ML_2X_3]^{2-}$  complexes ( $M = Ce$  or  $U$ ;  $L = N^*$  or  $Cp^*$ ). This energy decomposition, which is based on the transition-state method developed by Morokuma [22a,b] and Ziegler *et al.* [22c], provides insights into the balance of the different bonding electronic or electrostatic factors at work between the isolated cation or metallic moiety and the ligands in a complex. Thus, within this scheme, the resulting total bonding energy  $TBE_{frag}$  between two fragments can be decomposed into two terms as  $TBE_{frag} = E_{steric} + E_{orb}$ , where  $E_{steric}$  is, in our case, the steric interaction energy between the  $MCp^*_2$  or  $MN^*_2$  ( $Cp^* = C_5Me_5$  and  $N^* = N(SiMe_3)_2$ ) metallic fragment and the CN or NC ligand and  $E_{orb}$  is the orbital (covalent) contribution to the metal–CN/NC bond. The steric energy term ( $E_{steric}$ ) is itself decomposed into a destabilizing term

$E_{\text{Pauli}}$ , the electronic repulsion due to the Pauli principle, and  $E_{\text{elstat}}$ , the stabilizing electrostatic energy between the two fragments  $E_{\text{steric}} = E_{\text{Pauli}} + E_{\text{elstat}}$ . The bonding energies have been computed at the ZORA/BP86/DZP level.  $\Delta E$  in Table 4 is the energy difference between the two M-CN and M-NC isomers (differences of their  $\text{TBE}_{\text{frag}}$ ).

## Appendix B. Supplementary material

Cartesian coordinates of DFT optimized geometries.

## Acknowledgments

The authors are grateful to Algerian CNEPRU (project 2015-2018: E00920140093), for financial support. GENCI-IDRIS and GENCI-CINES for an allocation of computing time (Grant No. 2015-2016-080649). The COST CM-1006 action is also acknowledged.

## References

- (1) (a) B.L. Kalsotra, B.D. Jain, R.K. Multani, *J. Inorg. Nucl. Chem.* 34 (1972) 2265–2269. (b) B. Kanellakopulos, E. Dornberger, H. Billich, *J. Organomet. Chem.* 76 (1974) C42–C44.
- (2) (a) J.C. Berthet, P. Thuéry, M. Ephritikhine, *Dalton Trans.* 44 (2015) 7727–7742 and references therein. (b) J. Maynadié, J.C. Berthet, P. Thuéry, M. Ephritikhine, *Organometallics* 26 (2007) 2623–2629.
- (3) (a) M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain, *Coord. Chem. Rev.* 1023 (1999) 190–192. (b) M. Ohba, H. Ōkawa, *Coord. Chem. Rev.* 198 (2000) 313–328. (c) P. Przychodzen, T. Korzeniak, R. Podgajny, B. Sieklucka, *Coord. Chem. Rev.* 250 (2006) 2234–2260. (d) S. Tanase, J. Reedijk, *Coord. Chem. Rev.* 250 (2006) 2501–2510. (e) S. Wang, X.H. Ding, Y.H. Li, W. Huang, *Coord. Chem. Rev.* 256 (2012) 439–464.
- (4) (a) A. Boucekkine, L. Belkhiri, *f-Element Complexes*. In *Comprehensive Inorganic Chemistry II*, J. Reedijk, K. Poeppelmeier, Eds. Elsevier: Oxford. 9 (2013) 277–319. W.J. Evans, *Organometallics* 35 (2016) 3088–3100. (b) F.T. Edelmann, *Coord. Chem.*

- Rev. 318 (2016) 29–130. F.T. Edelmann, Coord. Chem. Rev. 284 (2015) 124–205. (c) T.J. Marks, Organometallics 32 (2013) 1133–1136.
- (5) (a) M. Ephritikhine, Dalton Trans. 21 (2006), 2501–2516. (b) S.T. Liddle, D.P. Mills, Dalton Trans. (2009) 5592–5605. (c) O.P. Lam, K. Meyer, Polyhedron, 32 (2012) 1–9. (d) R.J. Baker, Coord. Chem. Rev. 256 (2012) 2843–2871. (e) T.W. Hayton, Chem. Commun. 49 (2013) 2956–2973. (f) M.B. Jones, A.J. Gaunt, Chem. Rev. 113 (2013) 1137–1198.
- (6) (a) K.L. Nash, In *Handbook on the Chemistry and Physics of Rare Earths*, K.A. Jr. Gschneidner, L. Eyring, G.R. Choppin, G.H. Lander, Eds. Elsevier Science: Amsterdam, The Netherlands, (1994), Vol. 18, Chapter 121. (b) *The Chemistry of the Actinide and Trans-actinide Elements*, 3rd ed., L.R. Morss, N.M. Edelstein, F. Fuger, Eds. Springer: Dordrecht, The Netherlands, (2006).
- (7) A.E.V. Gorden, M.A. DeVore, II, B.A. Maynard, Inorg. Chem. 52 (2013) 3445–3458.
- (8) N. Iché-Tarrat, N. Barros, C.J. Marsden, L. Maron, Chem. Eur. J. 14 (2008) 2093–2099.
- (9) (a) C. Clavaguera-Sarrio, S. Hoyau, N. Ismail, C.J.J. Marsden, Phys. Chem. A. 107 (2003) 4515–4525. (b) J.L. Sonnenberg, P.J. Hay, R.L. Martin, B.E. Bursten, Inorg. Chem. 44 (2005) 2255–2262. (c) D.P. Hernández, R. Ramírez-Tagle, E. Codorniu-Hernández, L.A. Montero-Cabrera, R. Arratia-Pérez, Polyhedron 29 (2010) 975–984.
- (10) (a) A. Hervé, Y. Bouzidi, J.C. Berthet, L. Belkhiri, P. Thuéry, A. Boucekkine, M. Ephritikhine, Inorg. Chem. 53 (2014) 6995–7013. (b) A. Hervé, Y. Bouzidi, J. C. Berthet, L. Belkhiri, P. Thuéry, A. Boucekkine, M. Ephritikhine, Inorg. Chem. 54 (2015) 2474–2490.
- (11) P.L. Arnold, Z.R. Turner, N. Kaltsoyannis, P. Pelekanaki, R.M. Bellabarba, R.P. Tooze, Chem. Eur. J. 16. 16 (2010) 9623–9629.
- (12) M. Straka, M. Patzschke, P. Pyykkö, Theor. Chem. Acc. 109 (2003) 332–340.
- (13) (a) Q.Y. Wu, C.Z. Wang, J.H. Lan, C.L. Xiao, X.K. Wang, Y.L. Zhao, Z.F. Chai, W. Q. Shi, Inorg. Chem. 53 (2014) 9607–9614. (b) B. Averkiev, M. Mantina, R. Valero, I. Infante, A. Kovacs, D. Truhlar, L. Gagliardi, Theor. Chem. Acc. 129 (2011) 657–666.
- (14) (a) M. Roger, L. Belkhiri, T. Arliguie, P. Thuery, A. Boucekkine, M. Ephritikhine, Organometallics 27 (2008) 33–42. (b) A.J. Gaunt, S.D. Reilly, A.E. Enriquez, B.J. Scott, J.A. Ibers, P. Sekar, K.I. M. Ingram, N. Kaltsoyannis, M. P. Neu, Inorg. Chem. 47 (2008) 29–41. (c) M. Roger, L. Belkhiri, P. Thuery, S. E. Bouaoud, A. Boucekkine, M. Ephritikhine, Inorg. Chem. 48 (2009) 221–230. (d) S. Meskaldji, L. Belkhiri,; T.

- Arliguie, M. Fourmigue, M. Ephritikhine, A. Boucekkine, Inorg. Chem. 49 (2010) 3192–3200. (e) S. Meskaldji, A. Zaiter, L. Belkhiri, A. Boucekkine, Theor. Chem. Acc. 131 (2012) 1151–1159. (f) B. Teyar, L. Belkhiri, K. Costuas, A. Boucekkine, K. Meyer, Inorg. Chem. 55 (2016) 2870–2881.
- (15) R.D. Shannon, Acta Crystallogr, Sect. A. 32 (1976) 751–767.
- (16) (a) A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899–926. (b) A.E. Clark, J.L. Sonnenberg, P.J. Hay, R.L. Martin, J. Chem. Phys. 121 (2004) 2563–2570. (c) M. Straka, P. Hrobarik, M. Kaupp, J. Am. Chem. Soc. 127 (2005) 2591–2599. (d) H. Wu, Q.-Y. Wu, C-Z. Wang, J-H. Lan, Zi-R. Liu, Z-F. Chai, W-Q. Shi, Dalton Trans. 45 (2016) 8107–8117. (e) R.S. Mulliken, J. Chem. Phys. 23 (1955) 1833–1840. (f) P. Yang, I. Warnke, R.L. Martin, P.J. Hay, Organometallics 27 (2008) 1384–1392.
- (17) (a) R.F. Nalewajski, J. Mrozek, Int. J. Quant. Chem. 51 (1994) 187–200. (b) R.F. Nalewajski, J. Mrozek, A. Michalak, Int. J. Quant. Chem. 6 (1997) 589–601. (c) I. Mayer, Chem. Phys. Lett. 7 (1983) 270–274. (d) B. Sadhu, M. Sundararajan, T. Bandyopadhyay, Inorg. Chem. 55 (2016) 598–609.
- (18) M.L. Neidig, D.L. Clark, R.L. Martin, Coord. Chem. Rev. 257 (2013) 394–406.
- (19) (a) B. Vlaisavljevich, P. Miro, C.J. Cramer, L. Gagliardi, I. Infante, S.T. Liddle, Chem. Eur. J. 17 (2011) 8424–8433. (b) L. Petit, C. Adamo, P. Maldivi, Inorg. Chem. 45(2006) 8517–8522. (c) D. Manna, S. Mula, A. Bhattacharyy, S. Chattopadhyay, T. K. Ghanty, Dalton Trans. 44 (2015) 1332–1340.
- (20) (a) G. te Velde, F.M. Bickelhaupt, S.J.A.V. Gisbergen, C. Fonseca Guerra, E.J. Baerends, J.G. Snijders, T. Ziegler, Chemistry with ADF, J. Comput. Chem. 22 (2001) 931–967. (b) C. Fonseca Guerra, J.G. Snijders, G. te Velde, E.J. Baerends, Theor. Chem. Acc. 99 (1998) 391–403. (c) ADF2014, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>. (d) A.D. Becke, J. Chem. Phys. 88 (1988) 2547–2553. (e) E.V. Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 99 (1993) 4597–4610. (f) E.V. Lenthe, E.J. Baerends, J.G. Snijders, J. Chem. Phys. 101 (1994) 9783–9792. (g) E.V. Lenthe, A.E. Ehlers, E. J. Baerends, J. Chem. Phys. 110 (1999) 8943–8953.
- (21) (a) S.D. Vosko, L. Wilk, M. Nusair, Can. J. Chem. 58 (1980) 1200–1211. (b) A.D. Becke, Phys. Rev. A. 38 (1988) 3098–3100. (c) J.P. Perdew, Phys. Rev. B 34 (1986) 7406. J.P. Perdew, in *Electronic Structure of Solids'91*, Ed. P. Ziesche, H. Eschrig, Akademie Verlag, Berlin, 11 (1991). (d) J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244–13249. (e) J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77

- (1996) 3865–3868. (f) J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
- (22) (a) K. Morokuma, J. Chem. Phys. 55 (1971) 1236–1244. (b) K. Kitaura, K. Morokuma, Int. J. Quant.Chem. 10 (1976) 325–340. (c) T. Ziegler, A. Rauk, Theor. Chim. Acta. 46 (1977) 1–10.

# Cyanide linkage isomerism in cerium(III) and uranium(III) complexes. A relativistic DFT study

Yamina Bouzidi<sup>a,b</sup>, Lotfi Belkhiri<sup>b,\*</sup>, Michel Ephritikhine<sup>c</sup>,  
Jean-François Halet<sup>d,\*</sup>, and Abdou Boucekkine<sup>d,\*</sup>

<sup>a</sup> Département de Chimie, Université de Batna 1, 05000 Batna, Algeria

<sup>b</sup> URCHEMS, Département de Chimie, Université des Frères Mentouri Constantine 1,  
25017 Constantine, Algeria

<sup>c</sup> NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette,  
France

<sup>d</sup> Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes  
1, 35042 Rennes Cedex, France

## Highlights

- Different ligation modes of cyanide/isocyanide ligands towards trivalent Ce(III)/U(III) ions.
- Relativistic DFT/ZORA investigation accounting solvation effects.
- Dependence of the M–CN/NC coordination preference on the steric, ionic, covalent factors, co-ligand, and solvation effects.

## Cyanide linkage isomerism in cerium(III) and uranium(III) complexes. A relativistic DFT study

Yamina Bouzidi <sup>a,b</sup>, Lotfi Belkhiri <sup>b,\*</sup>, Michel Ephritikhine <sup>c</sup>,  
Jean-François Halet <sup>d,\*</sup>, and Abdou Boucekkine <sup>d,\*</sup>

<sup>a</sup> Département de Chimie, Université de Batna 1, 05000 Batna, Algeria

<sup>b</sup> URCHEMS, Département de Chimie, Université des Frères Mentouri Constantine 1,  
25017 Constantine, Algeria

<sup>c</sup> NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette,  
France

<sup>d</sup> Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes  
1, 35042 Rennes Cedex, France

### Supplementary Information

## Cartesian coordinates of DFT optimized geometries.

$[\text{MCp}^*\text{X}_3]^0 / q=2-,1-/X=\text{CN,NC}/\text{GAZ}$						
$[\text{Ce(III)}\text{Cp}^*\text{CN}_3]^2-$				$[\text{Ce(III)}\text{Cp}^*\text{NC}_3]^2-$		
1 Ce	0.000000000000	0.000000000000	0.662157345200	1 Ce	0.000000000000	0.000000000000
2 N	0.000000000000	0.000000000000	4.473082654000	2 C	0.000000000000	0.000000000000
3 N	-0.603426950800	3.736948879000	1.406183130000	3 C	-0.369424745800	3.662852699000
4 C	0.000000000000	0.000000000000	3.295433151000	4 N	0.000000000000	0.000000000000
5 C	-0.417392077300	2.585003675000	1.241293223000	5 N	-0.253396091900	2.503149597000
6 C	0.2047694898000	0.343201361900	-1.382503998000	6 C	2.039385842000	0.200771171200
7 C	2.130878980000	1.521198489000	-0.581825116900	7 C	2.187950419000	1.379417240000
8 C	2.628106787000	1.141088081000	0.701578806600	8 C	2.669558318000	0.987747457600
9 C	2.853257207000	-0.265610856700	0.690675451800	9 C	2.817518516000	-0.430856334500
10 C	2.493862205000	-0.762946573500	-0.598896747200	10 C	2.430028796000	-0.918002202200
11 C	1.763758775000	0.309156840900	-2.856446193000	11 C	1.754127382000	0.169934613600
12 H	2.680382217000	0.494954075400	-3.449472830000	12 H	2.684186600000	0.271383501500
13 H	1.030792118000	1.071770170000	-3.158556435000	13 H	1.088167717000	0.987568192300
14 H	1.369676232000	-0.665466803000	-3.178561441000	14 H	1.279571213000	-0.771541507400
15 C	1.916794684000	2.926203279000	-1.065870868000	15 C	2.046311331000	2.788255056000
16 H	1.514268595000	3.573179139000	-0.274856437100	16 H	1.695030545000	3.462182308000
17 H	1.198637064000	2.965456791000	-1.898583752000	17 H	1.316559507000	2.860820959000
18 H	2.861825480000	3.371929563000	-1.433355235000	18 H	3.008713897000	3.177968823000
19 C	2.930879266000	2.072843034000	1.839840410000	19 C	3.046120978000	1.915449612000
20 H	2.782777209000	1.582003551000	2.812127215000	20 H	2.919127271000	1.436812229000
21 H	2.269486591000	2.949340862000	1.825595948000	21 H	2.416256343000	2.815095989000
22 H	3.977936681000	2.430004259000	1.800274464000	22 H	4.102987391000	2.234978837000
23 C	3.439587092000	-1.069484386000	1.815420425000	23 C	3.375816230000	-1.258270554000
24 H	4.545724150000	-1.073911782000	1.771362271000	24 H	4.478192557000	-1.335862379000
25 H	3.091512981000	-2.110833485000	1.787791054000	25 H	2.961021238000	-2.275037557000
26 H	3.147052070000	-0.665089863100	2.794494635000	26 H	3.132332912000	-0.827100924000
27 C	2.720429876000	-2.159634770000	-1.100494159000	27 C	2.585843711000	-2.327725755000
28 H	2.020262807000	-2.423856496000	-1.907678999000	28 H	1.913818845000	-2.543422017000
29 H	2.575483748000	-2.904209797000	-0.306837864500	29 H	2.348655216000	-3.057660065000
30 H	3.743248668000	-2.278947694000	-1.508034534000	30 H	3.618698961000	-2.518689391000
31 N	0.603426950800	-3.736948879000	1.406183130000	31 C	0.369424745800	-3.662852699000
32 C	0.417392077300	-2.585003675000	1.241293223000	32 C	0.253396091900	-2.503149597000
33 C	-0.2047694898000	-0.343201361900	-1.382503998000	33 C	-2.039385842000	-0.200771171200
34 C	-2.130878980000	-1.521198489000	-0.581825116900	34 C	-2.187950419000	-1.379417240000
35 C	-2.628106787000	-1.141088081000	0.701578806600	35 C	-2.669558318000	-0.987747457600
36 C	-2.853257207000	0.265610856700	0.690675451800	36 C	-2.817518516000	0.430856334500
37 C	-2.493862205000	0.762946573500	-0.598896747200	37 C	-2.430028796000	0.918002202200
38 C	-1.763758775000	-0.309156840900	-2.856446193000	38 C	-1.754127382000	-0.169934613600
39 H	-2.680382217000	-0.494954075400	-3.449472830000	39 H	-2.684186600000	-0.271383501500
40 H	-1.030792118000	-1.071770170000	-3.158556435000	40 H	-1.088167717000	-0.987568192300
41 H	-1.369676232000	0.665466803000	-3.178561441000	41 H	-1.279571213000	0.771541507400
42 C	-1.916794684000	-2.926203279000	-1.065870868000	42 C	-2.046311331000	-2.788255056000
43 H	-1.514268595000	-3.573179139000	-0.274856437100	43 H	-1.695030545000	-3.462182308000
44 H	-1.198637064000	-2.965456791000	-1.898583752000	44 H	-1.316559507000	-2.860820959000
45 H	-2.861825480000	-3.371929563000	-1.433355235000	45 H	-3.008713897000	-3.177968823000
46 C	-2.930879266000	-2.072843034000	1.839840410000	46 C	-3.046120978000	-1.915449612000
47 H	-2.782777209000	-1.582003551000	2.812127215000	47 H	-2.919127271000	-1.436812229000
48 H	-2.269486591000	-2.949340862000	1.825595948000	48 H	-2.416256343000	-2.815095989000
49 H	-3.977936681000	-2.430004259000	1.800274464000	49 H	-4.102987391000	-2.234978837000
50 C	-3.439587092000	1.069484386000	1.815420425000	50 C	-3.375816230000	1.258270554000
51 H	-4.545724150000	1.073911782000	1.771362271000	51 H	-4.478192557000	1.335862379000
52 H	-3.091512981000	2.110833485000	1.787791054000	52 H	-2.961021238000	2.275037557000
53 H	-3.147052070000	0.665089863100	2.794494635000	53 H	-3.132332912000	0.827100924000
54 C	-2.720429876000	2.159634770000	-1.100494159000	54 C	-2.585843711000	2.327725755000
55 H	-2.020262807000	2.423856496000	-1.907678999000	55 H	-1.913818845000	2.543422017000
56 H	-2.575483748000	2.904209797000	-0.306837864500	56 H	-2.348655216000	3.057660065000
57 H	-3.743248668000	2.278947694000	-1.508034534000	57 H	-3.618698961000	-2.518689391000
$[\text{U(III)}\text{Cp}^*\text{CN}_3]^2-$				$[\text{U(III)}\text{Cp}^*\text{NC}_3]^2-$		
1 U	0.000000000000	0.000000000000	0.693105122500	1 U	0.000000000000	0.000000000000
2 N	0.000000000000	0.000000000000	4.456691964000	2 C	0.000000000000	0.000000000000
3 N	-0.397896091000	3.690327760000	1.515900192000	3 C	-0.387448409300	3.590307312000
4 C	0.000000000000	0.000000000000	3.278936557000	4 N	0.000000000000	0.000000000000
5 C	-0.254902033200	2.536504041000	1.323045130000	5 N	-0.280052445400	2.439791998000
6 C	2.368842994000	-0.921176233800	-0.605739074300	6 C	2.369944770000	-0.891760009600
7 C	1.976424121000	0.212236714200	-1.381308185000	7 C	1.980304733000	0.258166036900
8 C	2.148022431000	1.379076393000	-0.576063082800	8 C	2.164071410000	1.409075622000

$[\mathbf{U(IV)Cp^*}_2\mathbf{CN}_3]^-$					
1 U	0.000000000000	0.000000000000	0.498247659300		
2 N	-0.006121805906	-3.596980631000	1.269106245000		
3 N	0.000000000000	0.000000000000	4.171972244000		
4 N	0.006121805906	3.596980631000	1.269106245000		
5 C	-0.009639042411	-2.439685628000	1.059658680000		
6 C	0.000000000000	0.000000000000	2.997217064000		
7 C	0.009639042411	2.439685628000	1.059658680000		
8 C	-2.667769700000	0.712457745500	0.745934941600		
9 C	-2.668050356000	-0.714247608400	0.730830216300		
10 C	-2.275947090000	-1.143844297000	-0.573170776300		
11 C	-0.2019662334000	0.021287448080	-1.361539616000		
12 C	-2.276253382000	1.169769389000	-0.548906811300		
13 C	-3.109315756000	1.567249268000	1.896421385000		
14 H	-4.207119027000	1.682650979000	1.890345956000		
15 H	-2.658040153000	2.565864142000	1.855182271000		
16 H	-2.826465783000	1.124382182000	2.860664679000		
17 C	-3.110530665000	-1.592779751000	1.862876005000		
18 H	-2.817501567000	-1.176304580000	2.835698150000		
19 H	-2.669213834000	-2.594263470000	1.794874757000		
20 H	-4.209326609000	-1.697590965000	1.861140125000		
21 C	-2.324782642000	-2.547916531000	-1.097389569000		
$[\mathbf{U(IV)Cp^*}_2\mathbf{NC}_3]^-$					
9 C	2.651100472000	0.971260239100	0.731526509300		
10 C	2.783244110000	-0.448290372900	0.687293182600		
11 C	2.512063446000	-2.282511665000	-1.151083997000		
12 H	1.772090349000	-2.487573038000	-1.939912690000		
13 H	2.356988200000	-3.038797109000	-0.370709183000		
14 H	3.514094643000	-2.441693440000	-1.596054335000		
15 C	1.737864494000	0.285648155000	-2.841716736000		
16 H	1.100223011000	1.130819928000	-3.138835065000		
17 H	1.249391645000	-0.631489810800	-3.199481124000		
18 H	2.687728868000	0.386424910100	-3.405919230000		
19 C	2.036996262000	2.832018480000	-0.991524179400		
20 H	2.961560847000	3.173712719000	-1.496276135000		
21 H	1.829416700000	3.508129872000	-0.152701927000		
22 H	1.208775025000	2.961707716000	-1.704665955000		
23 C	3.029797979000	1.856227814000	1.883017532000		
24 H	2.910141544000	1.335949993000	2.843519408000		
25 H	2.392715090000	2.749966842000	1.924544408000		
26 H	4.083743004000	2.187142527000	1.809446979000		
27 C	3.346869970000	-1.310371413000	1.779114497000		
28 H	4.448766930000	-1.387721653000	1.701942406000		
29 H	2.927882378000	-2.324668596000	1.743591448000		
30 H	3.110855741000	-0.905355151300	2.773161912000		
31 C	0.387448409300	-3.590307312000	1.404297020000		
32 C	0.280052445400	-2.439791998000	1.149287192000		
33 C	-2.369944770000	0.891760090600	-0.606668924500		
34 C	-1.980304733000	-0.258166036900	-1.361038308000		
35 C	-2.164071410000	-1.409075622000	-0.534932961900		
36 C	-2.651100472000	-0.971260239100	0.731526509300		
37 C	-2.783244110000	0.448290372900	0.687293182600		
38 C	-2.512063446000	2.282511665000	-1.151083997000		
39 H	-1.772090349000	2.487573038000	-1.939912690000		
40 H	-2.356988200000	3.038797109000	-0.370709183000		
41 H	-3.514094643000	2.441693440000	-1.596054335000		
42 C	-1.737864494000	-0.285648155000	-2.841716736000		
43 H	-1.100223011000	-1.130819928000	-3.138835065000		
44 H	-1.249391645000	0.631489810800	-3.199481124000		
45 H	-2.687728868000	-0.386424910100	-3.405919230000		
46 C	-2.036996262000	-2.832018480000	-0.991524179400		
47 H	-2.961560847000	-3.173712719000	-1.496276135000		
48 H	-1.829416700000	-3.508129872000	-0.152701927000		
49 H	-1.208775025000	-2.961707716000	-1.704665955000		
50 C	-3.029797979000	-1.856227814000	1.883017532000		
51 H	-2.910141544000	-1.335949993000	2.843519408000		
52 H	-2.392715090000	-2.749966842000	1.924544408000		
53 H	-4.083743004000	-2.187142527000	1.809446979000		
54 C	-3.346869970000	1.310371413000	1.779114497000		
55 H	-4.448766930000	1.387721653000	1.701942406000		
56 H	-2.927882378000	2.324668596000	1.743591448000		
57 H	-3.110855741000	0.905355151300	2.773161912000		

$[MN^{*2}X_3]^q / q=2-, 1-, X=CN, NC, GAZ$			
$[Ce(III)N^{*2}CN_3]^{2-}$			
1 Ce 13.490106620000	22.521990030000	0.130086868000	
2 Si 16.183970060000	24.031669560000	1.867627026000	
3 Si 16.000453060000	24.858052630000	-1.036970627000	
4 Si 11.569644710000	20.979705460000	-2.409344487000	
5 Si 14.431817110000	20.009631850000	-2.320757126000	
6 C 14.608299590000	20.486856770000	1.490309387000	
7 C 11.685862530000	22.601184380000	2.024665652000	
8 C 12.180530040000	24.589817230000	-0.990801766500	
9 N 15.442192240000	23.927297210000	0.307092500100	
10 N 13.166854510000	21.035876060000	-1.744084474000	
11 N 15.120157300000	19.575999270000	2.031710109000	
12 N 10.870267570000	22.629245990000	2.871789423000	
13 N 11.654547110000	25.505325190000	-1.510362883000	
14 C 14.968927980000	23.564149590000	3.242300904000	
15 H 14.075454980000	24.205785870000	3.257827189000	
16 H 15.473633200000	23.672297340000	4.217356126000	
17 H 14.632029430000	22.518055830000	3.176960965000	
18 C 16.799336890000	25.784694750000	2.334174613000	
19 H 17.575395600000	26.163449470000	1.652083936000	
20 H 17.229854790000	25.762303000000	3.349581831000	
21 H 15.969138580000	26.506817850000	2.336243794000	
22 C 17.692250120000	22.887038500000	2.048232925000	
23 H 17.377856760000	21.838449770000	1.935614470000	
24 H 18.159969350000	22.997066110000	3.040931610000	
25 H 18.454768920000	23.100921560000	1.284058291000	
26 C 15.568923480000	26.707623750000	-0.922181641900	
27 H 14.476536370000	26.822435220000	-0.853927899600	
28 H 15.911769390000	27.245173160000	-1.822140483000	
29 H 16.023880640000	27.188378010000	-0.044317531080	
30 C 17.898015150000	24.760233380000	-1.279242689000	
31 H 18.449094280000	25.156375750000	-0.412481745200	
32 H 18.205144820000	25.341487160000	-2.164931301000	
22 H -3.296197040000	-2.737472924000	-1.587310447000	
23 H -2.188837746000	-3.285727271000	-0.298752673300	
24 H -1.541846946000	-2.739980285000	-1.844823252000	
25 C -1.795823978000	0.038190528340	-2.845315079000	
26 H -1.246112610000	-0.847171464300	-3.192166812000	
27 H -1.236040911000	0.925774336600	-3.170476317000	
28 H -2.759127166000	0.050792277940	-3.386303545000	
29 C -2.332184466000	2.583892064000	-1.044242142000	
30 H -1.545072981000	2.799171998000	-1.780269176000	
31 H -2.208236675000	3.305334660000	-0.228740314500	
32 H -3.301726522000	2.775655072000	-1.537050363000	
33 C 2.667769700000	-0.712457745500	0.745934941600	
34 C 2.276253382000	-1.169769389000	-0.548906811300	
35 C 2.019662334000	-0.021287448080	-1.361539616000	
36 C 2.275947090000	1.143844297000	-0.573170776300	
37 C 2.668050356000	0.714247608400	0.730830216300	
38 C 3.109315756000	-1.567249268000	1.896421385000	
39 H 4.207119027000	-1.682650979000	1.890345956000	
40 H 2.658040153000	-2.565864142000	1.855182271000	
41 H 2.826465783000	-1.124382182000	2.860664679000	
42 C 2.332184466000	-2.583892064000	-1.044242142000	
43 H 3.301726522000	-2.775655072000	-1.537050363000	
44 H 1.545072981000	-2.799171998000	-1.780269176000	
45 H 2.208236675000	-3.305334660000	-0.228740314500	
46 C 1.795823978000	-0.038190528340	-2.845315079000	
47 H 2.759127166000	-0.050792277940	-3.386303545000	
48 H 1.246112610000	0.847171464300	-3.192166812000	
49 H 1.236040911000	-0.925774336600	-3.170476317000	
50 C 2.324782642000	2.547916531000	-1.097389569000	
51 H 3.296189704000	2.737472924000	-1.587310447000	
52 H 2.188837746000	3.285727271000	-0.298752673300	
53 H 1.541846946000	2.739980285000	-1.844823252000	
54 C 3.110530665000	1.592779751000	1.862876005000	
55 H 2.817501567000	1.176304580000	2.835698150000	
56 H 2.669213834000	2.594263470000	1.794874757000	
57 H 4.209326609000	1.697590965000	1.861140125000	
22 H -3.366636630000	-2.704123019000	-1.578714393000	
23 H -2.346689957000	-3.293110021000	-0.239695619500	
24 H -1.602857477000	-2.800192006000	-1.758591963000	
25 C -1.853483917000	-0.013989423750	-2.830915273000	
26 H -1.290312087000	-0.898607150200	-3.158042188000	
27 H -1.304583077000	0.875102772200	-3.169780338000	
28 H -2.814059476000	-0.025472879730	-3.377141667000	
29 C -2.398653819000	2.551669350000	-1.077650250000	
30 H -1.589873781000	2.782296804000	-1.784893325000	
31 H -2.338065400000	3.294014941000	-0.274711533100	
32 H -3.354547996000	2.694731973000	-1.611881410000	
33 C 2.657116844000	-0.719974661500	0.770092334400	
34 C 2.314772174000	-1.152357206000	-0.549290486600	
35 C 2.077947405000	0.005562485418	-1.347685065000	
36 C 2.316890683000	1.154846233000	-0.537087348300	
37 C 2.658319790000	0.708038772100	0.777365803700	
38 C 3.077674098000	-1.600039448000	1.908817966000	
39 H 4.171481773000	-1.749516208000	1.901360640000	
40 H 2.596923398000	-2.584762020000	1.856004983000	
41 H 2.807602339000	-1.160744176000	2.877877024000	
42 C 2.398653819000	-2.551669350000	-1.077650250000	
43 H 3.354547996000	-2.694731973000	-1.611881410000	
44 H 1.589873781000	-2.782296804000	-1.784893325000	
45 H 2.338065400000	-3.294014941000	-0.274711533100	
46 C 1.853483917000	0.013989423750	-2.830915273000	
47 H 2.814059476000	0.025472879730	-3.377141667000	
48 H 1.290312087000	0.898607150200	-3.158042188000	
49 H 1.304583077000	-0.875102772200	-3.169780338000	
50 C 2.407735286000	2.559213812000	-1.050313443000	
51 H 3.366636630000	2.704123019000	-1.578714393000	
52 H 2.346689957000	3.293110021000	-0.239695619500	
53 H 1.602857477000	2.800192006000	-1.758591963000	
54 C 3.080251472000	1.576936010000	1.923845886000	
55 H 2.846473903000	1.109629338000	2.889053509000	
56 H 2.570447974000	2.548297252000	1.902850304000	
57 H 4.168670305000	1.758999353000	1.893938093000	

33 H	18.219074290000	23.717954720000	-1.429129147000		33 H	18.255316770000	23.795447110000	-1.392609522000
34 C	15.251289010000	24.281973060000	-2.681458937000		34 C	15.307324020000	24.270609030000	-2.688530971000
35 H	15.443209750000	23.223961320000	-2.904976551000		35 H	15.586655690000	23.235182310000	-2.927748454000
36 H	15.691449430000	24.877996950000	-3.498520421000		36 H	15.709507300000	24.915739200000	-3.48799317000
37 H	14.164089590000	24.446437410000	-2.702862778000		37 H	14.211202090000	24.348730390000	-2.719686415000
38 C	10.980229670000	19.227371550000	-2.910378424000		38 C	10.970202050000	19.220150180000	-2.917387932000
39 H	11.603087170000	18.7724997470000	-3.695238988000		39 H	11.603555590000	18.763613280000	-3.692962506000
40 H	9.948231816000	19.285955500000	-3.295703389000		40 H	9.943170421000	19.276427640000	-3.316280682000
41 H	10.978096200000	18.548577370000	-2.044403772000		41 H	10.957942490000	18.543380920000	-2.049731922000
42 C	11.380122100000	22.056429070000	-3.966069510000		42 C	11.375593310000	22.049360900000	-3.976063569000
43 H	11.568247570000	23.110722810000	-3.712900569000		43 H	11.570123310000	23.099069150000	-3.727570095000
44 H	10.360610780000	21.983652150000	-4.380267658000		44 H	10.357226700000	21.975816070000	-4.393693540000
45 H	12.091361990000	21.759734290000	-4.751553127000		45 H	12.088069450000	21.740050180000	-4.757274189000
46 C	10.280286310000	21.585665330000	-1.162540074000		46 C	10.245259660000	21.579576030000	-1.183834044000
47 H	10.274730200000	20.998053400000	-0.232573943400		47 H	10.235996410000	20.994015890000	-0.252533786800
48 H	9.278347138000	21.498952650000	-1.616228020000		48 H	9.248533407000	21.483904120000	-1.647089275000
49 H	10.411692990000	22.644717150000	-0.891713034300		49 H	10.371975970000	22.638806240000	-0.914561003600
50 C	14.579848920000	20.001362430000	-4.230931745000		50 C	14.570017850000	20.003926100000	-4.210492384000
51 H	13.668076340000	19.623558200000	-4.718578077000		51 H	13.665574120000	19.618818320000	-4.706088416000
52 H	15.419373820000	19.360957240000	-4.550053266000		52 H	15.418016520000	19.372364380000	-4.524793764000
53 H	14.764213880000	21.017315990000	-4.612512126000		53 H	14.747775610000	21.022748950000	-4.587833060000
54 C	14.243487960000	18.191602660000	-1.791657411000		54 C	14.222260100000	18.185171360000	-1.781308826000
55 H	14.230596640000	18.131635670000	-0.692832765500		55 H	14.203222490000	18.117780970000	-0.683015324000
56 H	15.092898840000	17.589368350000	-2.155180181000		56 H	15.074038610000	17.585940270000	-2.144626239000
57 H	13.317118320000	17.739883880000	-2.174374335000		57 H	13.297954170000	17.734544500000	-2.170831618000
58 C	16.140837760000	20.532277690000	-1.686343719000		58 C	16.117992670000	20.525028540000	-1.659497078000
59 H	16.415280920000	21.558511860000	-1.965910813000		59 H	16.393378620000	21.552855750000	-1.932562829000
60 H	16.899544910000	19.857423320000	-2.117169797000		60 H	16.876538500000	19.851873880000	-2.093538856000
61 H	16.205180490000	20.443959840000	-0.592038388900		61 H	16.178334010000	20.433524310000	-0.565709433600
<b>[U(III)N*<sub>2</sub>CN<sub>3</sub>]<sup>2-</sup></b>								
1 U	9.870916846000	7.217636646000	4.891487284000		1 U	9.861076137000	7.194637680000	4.882952268000
2 Si	10.886976370000	9.675800247000	2.439903953000		2 Si	10.864918380000	9.655939107000	2.443029080000
3 Si	7.988545376000	9.718245472000	3.321013915000		3 Si	7.978844037000	9.768608085000	3.32980513000
4 Si	12.295229180000	8.288082051000	7.336557932000		4 Si	12.278679690000	8.260311010000	7.335784161000
5 Si	12.469356030000	5.409775118000	6.411824719000		5 Si	12.490135410000	5.384883170000	6.426952779000
6 N	11.602668170000	5.417610807000	2.017356773000		6 C	11.449234590000	5.421042793000	2.110827894000
7 N	7.239924675000	4.563263773000	5.051036423000		7 C	7.340282422000	4.581213136000	4.861991834000
8 N	8.031916513000	8.877748319000	7.773417763000		8 C	8.009716864000	8.707257677000	7.646615481000
9 N	9.598507450000	9.075952960000	3.431636829000		9 N	9.566858336000	9.077103083000	3.432693486000
10 N	11.756021680000	6.991958200000	6.318685332000		10 N	11.744628510000	6.948854107000	6.339396215000
11 C	11.058883660000	5.961620942000	2.092708930000		11 N	10.983655200000	5.999356907000	3.034945521000
12 C	8.065685108000	5.401268862000	5.000409349000		12 N	8.162999523000	5.432470024000	4.863120685000
13 C	8.550806670000	8.350282651000	6.856958208000		13 N	8.612350638000	8.266425377000	6.725793201000
14 C	10.971949200000	11.589510660000	2.419840142000		14 C	10.995616850000	11.567895490000	2.422744965000
15 H	11.121156060000	11.982636800000	3.437404900000		15 H	11.156651270000	11.956905990000	3.440115077000
16 H	10.059612840000	12.048602790000	2.014084414000		16 H	10.091886100000	12.050094150000	2.020099364000
17 H	11.821582600000	11.927125010000	1.799697953000		17 H	11.849776850000	11.883973380000	1.799798166000
18 C	10.762649740000	9.120227653000	0.625053507100		18 C	10.731178910000	9.105100283000	0.627476298600
19 H	11.616577250000	9.503774500000	0.041793893470		19 H	11.588717570000	9.475518206000	0.040996553100
20 H	9.837230063000	9.467069318000	0.143111957300		20 H	9.809261594000	9.467837647000	0.150672302400
21 H	10.787204090000	8.020548999000	0.580820469800		21 H	10.736465750000	8.005469083000	0.580779930500
22 C	12.604479730000	9.110591115300	3.011435499000		22 C	12.573775630000	9.067089666000	3.018001768000
23 H	12.834938190000	9.401007398000	4.045092749000		23 H	12.833968700000	9.422425732000	4.024390106000
24 H	13.363847550000	9.573027928000	2.357606895000		24 H	13.332435780000	9.458974327000	2.318540294000
25 H	12.711945460000	8.019806302000	2.929423796000		25 H	12.648557680000	7.970463954000	3.008290122000
26 C	7.459677648000	10.211000840000	1.546099335000		26 C	7.464558171000	10.300177420000	1.563997034000
27 H	8.088094371000	11.001224450000	1.108993647000		27 H	8.124132920000	11.067177560000	1.130865838000
28 H	6.421718659000	10.584043570000	1.569014770000		28 H	6.443191157000	10.716180600000	1.594054513000
29 H	7.488766980000	9.342360429000	0.871043788200		29 H	7.455437998000	9.437073710000	0.881339882300
30 C	7.751521257000	11.273796890000	4.388446756000		30 C	7.792885756000	11.322395350000	4.415217856000
31 H	7.902729238000	11.020432290000	5.448600948000		31 H	7.954747913000	11.058484350000	5.471198736000
32 H	6.732263481000	11.680013630000	4.276882442000		32 H	6.782446512000	11.754781610000	4.322690981000
33 H	8.467178778000	12.064719930000	4.117992211000		33 H	8.524109404000	12.096916430000	4.138699513000
34 C	6.683532848000	8.463154380000	3.868964124000		34 C	6.629610730000	8.554156659000	3.867919867000
35 H	6.667800543000	7.565398086000	3.234337637000		35 H	6.620480341000	7.642910714000	3.251964685000
36 H	5.688889096000	8.938415864000	3.807476946000		36 H	5.646112249000	9.045055988000	3.762963436000
37 H	6.811763174000	8.133020203000	4.911316078000		37 H	6.728712541000	8.248109647000	4.919570303000
38 C	14.203064800000	8.455312279000	7.369952233000		38 C	14.185111000000	8.457786813000	7.358781077000
39 H	14.699210880000	7.555074008000	7.763452891000		39 H	14.697552100000	7.569944219000	7.759323255000
40 H	14.500225830000	9.306346244000	8.005799677000		40 H	14.470877870000	9.320141099000	7.984616152000
41 H	14.595098960000	8.636278250000	6.357322464000		41 H	14.569604120000	8.635111627000	6.342296132000

42 C	11.730087100000	8.109861088000	9.142685905000		42 C	11.732040630000	8.096269392000	9.151303571000
43 H	10.629975370000	8.097805299000	9.176936668000		43 H	10.632794710000	8.057727882000	9.197390146000
44 H	12.080644930000	8.963059384000	9.747364409000		44 H	12.067652000000	8.965756880000	9.741309173000
45 H	12.102386610000	7.185991631000	9.607952370000		45 H	12.130798940000	7.187621685000	9.625526499000
46 C	11.666583820000	9.990972253000	6.788619355000		46 C	11.624998340000	9.949587565000	6.774545114000
47 H	11.985872460000	10.264256750000	5.773807291000		47 H	11.941404280000	10.219203740000	5.757344589000
48 H	12.066566770000	10.751499210000	7.481842846000		48 H	12.013837680000	10.721060270000	7.461715818000
49 H	10.569376230000	10.047410030000	6.832634028000		49 H	10.526771960000	9.989357699000	6.815505182000
50 C	14.040656520000	5.259492296000	5.351150797000		50 C	14.045339410000	5.257707529000	5.338175740000
51 H	13.784575530000	5.409747127000	4.291495301000		51 H	13.771438830000	5.408278979000	4.282976061000
52 H	14.495735350000	4.260133720000	5.453770778000		52 H	14.517056390000	4.264899606000	5.430322863000
53 H	14.794250500000	6.010076109000	5.632948414000		53 H	14.791681060000	6.018930968000	5.611468572000
54 C	11.284397900000	4.049962053000	5.840519942000		54 C	11.317274660000	4.000703302000	5.888419359000
55 H	10.369249940000	4.000760918000	6.447714374000		55 H	10.408787390000	3.96025336000	6.507141677000
56 H	11.799891820000	3.077228923000	5.923667585000		56 H	11.838141790000	3.032038231000	5.985947564000
57 H	10.984852720000	4.160700527000	4.787449155000		57 H	11.004483780000	4.096901364000	4.838514827000
58 C	12.975412080000	4.883225869000	8.183296729000		58 C	13.045643450000	4.879294866000	8.191405054000
59 H	13.729651270000	5.544251612000	8.635268194000		59 H	13.794073110000	5.560721524000	8.623335959000
60 H	13.400656620000	3.865824202000	8.149162926000		60 H	13.492926230000	3.871414693000	8.155376179000
61 H	12.101713060000	4.858955106000	8.851630443000		61 H	12.186543180000	4.841038155000	8.878317728000
<b>[U(IV)N<sup>2</sup><sub>2</sub>CN<sub>3</sub>]<sup>1-</sup></b>								
1 U	9.975455302000	7.306725179000	4.879117340000		1 U	9.937883397000	7.282841429000	4.899762000000
2 Si	10.923643780000	9.647472487000	2.474381091000		2 Si	10.878127960000	9.641462564000	2.490337497000
3 Si	7.985110042000	9.710432446000	3.383663218000		3 Si	7.944664927000	9.685712383000	3.391897049000
4 Si	12.292233630000	8.332291992000	7.282584159000		4 Si	12.339154120000	8.333438082000	7.247289579000
5 Si	12.418904110000	5.389254442000	6.390207217000		5 Si	12.442554930000	5.399485456000	6.381924242000
6 N	11.550533080000	5.447871223000	2.080727094000		6 C	11.287098220000	5.501948617000	2.116293070000
7 N	7.411293603000	4.721465691000	4.885366118000		7 C	7.462449476000	4.774374789000	5.092484934000
8 N	8.116595862000	8.806445081000	7.715078538000		8 C	8.241223468000	8.819900038000	7.639355200000
9 N	9.620112956000	9.032986788000	3.498677255000		9 N	9.579527837000	9.017523200000	3.510735692000
10 N	11.711537380000	7.009770810000	6.261677412000		10 N	11.728930750000	7.012786464000	6.244544649000
11 C	11.031294670000	6.017238305000	2.967494680000		11 N	10.925234080000	6.073770713000	3.08972674000
12 C	8.238858080000	5.555772963000	4.886235477000		12 N	8.287114587000	5.622317374000	5.003804731000
13 C	8.662837513000	8.330911455000	6.790082390000		13 N	8.786037057000	8.381209262000	6.682070248000
14 C	11.005816400000	11.543292240000	2.531108044000		14 C	10.963278510000	11.536446630000	2.572413950000
15 H	11.157185280000	11.904638360000	3.558981429000		15 H	11.111560190000	11.882114820000	3.605849702000
16 H	10.096237920000	12.019908660000	2.138418878000		16 H	10.054640260000	12.018659440000	2.184156542000
17 H	11.853113050000	11.896669430000	1.922163020000		17 H	11.811822550000	11.898277750000	1.970119082000
18 C	10.752695000000	9.091025722000	0.679310513800		18 C	10.703208260000	9.120698887000	0.682675958300
19 H	11.615878360000	9.444656038000	0.093332832670		19 H	11.581879880000	9.459636321000	0.111134426300
20 H	9.841626480000	9.473442893000	0.200476186800		20 H	9.808683655000	9.538039345000	0.202299230600
21 H	10.739136240000	7.992243259000	0.627732364100		21 H	10.657926620000	8.024310478000	0.608095183500
22 C	12.615392050000	9.026227950000	3.059063069000		22 C	12.571881840000	9.002290455000	3.047004608000
23 H	12.863913100000	9.293733913000	4.094531848000		23 H	12.802872019000	9.191260534000	4.102971052000
24 H	13.374722650000	9.501277989000	2.416072720000		24 H	13.334695520000	9.531041581000	2.452010902000
25 H	12.728853860000	7.939904347000	2.939038889000		25 H	12.691403060000	7.928400081000	2.853825874000
26 C	7.508995600000	10.186719310000	1.608260992000		26 C	7.463935286000	10.146376060000	1.613166638000
27 H	8.142098625000	10.975323190000	1.178211324000		27 H	8.086878217000	10.942476080000	1.182267038000
28 H	6.473443694000	10.563893150000	1.615837058000		28 H	6.423157302000	10.508753510000	1.615477218000
29 H	7.539043115000	9.316725114000	0.936799547000		29 H	7.510398701000	9.274579585000	0.945248256500
30 C	7.819335826000	11.248447080000	4.467713796000		30 C	7.757553777000	11.233882960000	4.459011072000
31 H	7.959500377000	10.985841940000	5.526347611000		31 H	7.925892826000	10.992118890000	5.518091154000
32 H	6.815448401000	11.689061020000	4.360632846000		32 H	6.740060077000	11.645152860000	4.364589470000
33 H	8.556848342000	12.019547740000	4.203406906000		33 H	8.467803167000	12.020854340000	4.168581698000
34 C	6.707185876000	8.437869784000	3.933482535000		34 C	6.671868273000	8.408750899000	3.947198631000
35 H	6.693968939000	7.540651036000	3.299002979000		35 H	6.684220081000	7.499138806000	3.330248463000
36 H	5.714711296000	8.912721352000	3.857954399000		36 H	5.673811136000	8.865439515000	3.841938728000
37 H	6.816547201000	8.113499761000	4.978170557000		37 H	6.771538873000	8.106867545000	4.998538778000
38 C	14.186864430000	8.451211589000	7.244113047000		38 C	14.237713230000	8.407174444000	7.230349365000
39 H	14.677881390000	7.555484554000	7.650547040000		39 H	14.708967810000	7.514829100000	7.665795595000
40 H	14.516351500000	9.311554339000	7.848489580000		40 H	14.573970580000	9.277420332000	7.816890421000
41 H	14.556310560000	8.600668234000	6.218820972000		41 H	14.621890470000	8.525784881000	6.2065301047000
42 C	11.722975470000	8.160763470000	9.072789230000		42 C	11.759398590000	8.196014329000	9.039379236000
43 H	10.624234610000	8.136093085000	9.116440178000		43 H	10.660918380000	8.222601540000	9.086039148000
44 H	12.064599150000	9.028347240000	9.659479480000		44 H	12.142682630000	9.045952063000	9.626141331000
45 H	12.111737470000	7.254550578000	9.555760865000		45 H	12.103165750000	7.271630159000	9.522256312000
46 C	11.649540540000	10.008485850000	6.677870411000		46 C	11.771195080000	10.028896930000	6.616441178000
47 H	11.992629500000	10.284085380000	5.671853123000		47 H	12.307626380000	10.353486000000	5.715023900000
48 H	12.039311830000	10.772991350000	7.370330071000		48 H	11.993816760000	10.763002820000	7.408191814000
49 H	10.553487040000	10.081909530000	6.711193285000		49 H	10.690936170000	10.092224640000	6.428519194000
50 C	13.965641900000	5.244664225000	5.315645968000		50 C	13.979881800000	5.245223140000	5.293421821000

<b>[MCp*<sub>2</sub>X<sub>3</sub>]<sup>q</sup> / q=2-, -1- / X=CN ,NC/ COSMO</b>																					
<b>[Ce(III)Cp*<sub>2</sub>CN<sub>3</sub>]<sup>2-</sup></b>				<b>[Ce(III)Cp*<sub>2</sub>NC<sub>3</sub>]<sup>2-</sup></b>																	
51 H 13.706939040000 5.376269313000 4.255120779000	51 H 13.718103030000 5.409900234000 4.238394348000	52 H 14.423171350000 4.249100442000 5.429239968000	52 H 14.416042730000 4.237540702000 5.379136951000	53 H 14.722190870000 5.996381754000 5.581823480000	53 H 14.754285730000 5.973535249000 5.572492748000	54 C 11.169211080000 4.088020242000 5.840945254000	54 C 11.199518300000 4.077884871000 5.863985898000	55 H 10.267775940000 4.065180439000 6.469290402000	55 H 10.293453760000 4.076617212000 6.486454376000	56 H 11.658022820000 3.103274269000 5.927834961000	56 H 11.686705820000 3.096882433000 5.990996722000	57 H 10.852167570000 4.182853704000 4.792470450000	57 H 10.890490600000 4.143589361000 4.812143151000	58 C 12.893937930000 4.929667853000 8.170404929000	58 C 12.934891590000 4.951730030000 8.161325651000	59 H 13.667416460000 5.580257000000 8.601904049000	59 H 13.694595160000 5.617496603000 8.593100472000	60 H 13.292267810000 3.901915885000 8.169663511000	60 H 13.352556000000 3.931833652000 8.161769332000	61 H 12.020154610000 4.945297538000 8.837154686000	61 H 12.061133200000 4.951238936000 8.828615668000

57 H	-3.724000679000	2.288121730000	-1.502010132000	57 H	-3.591644264000	2.515209641000	-1.444787207000
<b>[U(III)Cp*<sub>2</sub>CN<sub>3</sub>]<sup>2-</sup></b>							
1 U	0.000000000000	0.000000000000	0.579911769800	1 U	0.000000000000	0.000000000000	0.632549000000
2 N	0.000000000000	0.000000000000	4.360438248000	2 C	0.000000000000	0.000000000000	4.305505000000
3 N	-0.409575461800	3.580387961000	1.628155337000	3 C	-0.323763000000	3.547740000000	1.502163000000
4 C	0.000000000000	0.000000000000	3.184891866000	4 N	0.000000000000	0.000000000000	3.127746000000
5 C	-0.274055746700	2.447833806000	1.332904663000	5 N	-0.242201000000	2.410313000000	1.196694000000
6 C	2.351421602000	-0.907100117800	-0.625649931900	6 C	2.372926000000	-0.938348000000	-0.561304000000
7 C	1.969696628000	0.241507952700	-1.386657103000	7 C	1.973458000000	0.171150000000	-1.369432000000
8 C	2.124901975000	1.392868297000	-0.550878552000	8 C	2.133244000000	1.360683000000	-0.592400000000
9 C	2.606340728000	0.952008249200	0.721227810300	9 C	2.623614000000	0.983607000000	0.694370000000
10 C	2.752611768000	-0.465785304000	0.673137043100	10 C	2.770333000000	-0.433988000000	0.713505000000
11 C	2.477261201000	-2.304750947000	-1.158473425000	11 C	2.529574000000	-2.351079000000	-1.039098000000
12 H	1.741260528000	-2.505667487000	-1.952212177000	12 H	1.772842000000	-2.613123000000	-1.793693000000
13 H	2.310079990000	-3.051661349000	-0.370542882600	13 H	2.415952000000	-3.068147000000	-0.216162000000
14 H	3.479239138000	-2.477587096000	-1.593958236000	14 H	3.522115000000	-2.506425000000	-1.502334000000
15 C	1.741151936000	0.270133517100	-2.869763100000	15 C	1.743990000000	0.125427000000	-2.851718000000
16 H	1.093969402000	1.105241560000	-3.173531971000	16 H	1.092489000000	0.940146000000	-3.196469000000
17 H	1.273762183000	-0.654403331100	-3.236974386000	17 H	1.280802000000	-0.818917000000	-3.169874000000
18 H	2.696599330000	0.388160032000	-3.416607750000	18 H	2.698856000000	0.218803000000	-3.404202000000
19 C	1.998142002000	2.818348615000	-1.003010422000	19 C	1.993188000000	2.761382000000	-1.108843000000
20 H	2.942504506000	3.181828089000	-1.450723774000	20 H	2.939552000000	3.117279000000	-1.557743000000
21 H	1.730194961000	3.481764677000	-0.170211319100	21 H	1.706601000000	3.457214000000	-0.309845000000
22 H	1.213148522000	2.935855657000	-1.765799995000	22 H	1.217679000000	2.832146000000	-1.885863000000
23 C	3.007651389000	1.832611213000	1.868640072000	23 C	3.005912000000	1.917388000000	1.805033500000
24 H	2.839798085000	1.332923783000	2.833486842000	24 H	2.843414000000	1.456053000000	2.789662000000
25 H	2.419829728000	2.760029252000	1.883910594000	25 H	2.403580000000	2.834901000000	1.779310000000
26 H	4.079427802000	2.101333586000	1.808275544000	26 H	4.072805000000	2.200603000000	1.738736000000
27 C	3.342680512000	-1.315818644000	1.759540943000	27 C	3.327132000000	-1.241997000000	1.848832000000
28 H	4.447895703000	-1.309722491000	1.710572206000	28 H	4.428160000000	-1.320174000000	1.781444000000
29 H	2.997258827000	-2.355286995000	1.686606454000	29 H	2.910193000000	-2.257821000000	1.856071000000
30 H	3.049470505000	-0.953406119200	2.755919585000	30 H	3.083371000000	-0.788742000000	2.820261000000
31 N	0.409575461800	-3.580387961000	1.628155337000	31 C	0.323763000000	-3.547740000000	1.502163000000
32 C	0.274055746700	-2.447833806000	1.332904663000	32 N	0.242201000000	-2.410313000000	1.196694000000
33 C	-2.351421602000	0.907100117800	-0.625649931900	33 C	-2.372926000000	0.938348000000	-0.561304000000
34 C	-1.969696628000	-0.241507952700	-1.386657103000	34 C	-1.973458000000	-0.171150000000	-1.369432000000
35 C	-2.124901975000	-1.392868297000	-0.550878552000	35 C	-2.133244000000	-1.360683000000	-0.592400000000
36 C	-2.606340728000	-0.952008249200	0.721227810300	36 C	-2.623614000000	-0.983607000000	0.694370000000
37 C	-2.752611768000	0.465785304000	0.673137043100	37 C	-2.770333000000	0.433988000000	0.713505000000
38 C	-2.477261201000	2.304750947000	-1.158473425000	38 C	-2.529574000000	2.351079000000	-1.039098000000
39 H	-1.741260528000	2.505667487000	-1.952212177000	39 H	-1.772842000000	2.613123000000	-1.793693000000
40 H	-2.310079990000	3.051661349000	-0.370542882600	40 H	-2.415952000000	3.068147000000	-0.216162000000
41 H	-3.479239138000	-2.477587096000	-1.593958236000	41 H	-3.522115000000	2.506425000000	-1.502334000000
42 C	-1.741151936000	-0.270133517100	-2.869763100000	42 C	-1.743990000000	-0.125427000000	-2.851718000000
43 H	-1.093969402000	-1.105241560000	-3.173531971000	43 H	-1.092489000000	-0.940146000000	-3.196469000000
44 H	-1.273762183000	0.654403331100	-3.236974386000	44 H	-1.280802000000	0.818917000000	-3.169874000000
45 H	-2.696599330000	-0.388160032000	-3.416607750000	45 H	-2.698856000000	-0.218803000000	-3.404202000000
46 C	-1.998142002000	-2.818348615000	-1.003010422000	46 C	-1.993188000000	-2.761382000000	-1.108843000000
47 H	-2.942504506000	-3.181828089000	-1.450723774000	47 H	-2.939552000000	-3.117279000000	-1.557743000000
48 H	-1.730194961000	-3.481764677000	-0.170211319100	48 H	-1.706601000000	-3.457214000000	-0.309845000000
49 H	-1.213148522000	-2.935855657000	-1.765799995000	49 H	-1.217679000000	-2.832146000000	-1.885863000000
50 C	-3.007651389000	-1.832611213000	1.868640072000	50 C	-3.005912000000	-1.917388000000	1.805035000000
51 H	-2.839798085000	-1.332923783000	2.833486842000	51 H	-2.843414000000	-1.456053000000	2.789662000000
52 H	-2.419829728000	-2.760029252000	1.883910594000	52 H	-2.403580000000	-2.834901000000	1.779310000000
53 H	-4.079427802000	-2.101333586000	1.808275544000	53 H	-4.072805000000	-2.200603000000	1.738736000000
54 C	-3.342680512000	1.315818644000	1.759540943000	54 C	-3.327132000000	1.241997000000	1.848832000000
55 H	-4.447895703000	1.309722491000	1.710572206000	55 H	-4.428160000000	1.320174000000	1.781444000000
56 H	-2.997258827000	2.355286995000	1.686606445000	56 H	-2.910193000000	2.257821000000	1.856071000000
57 H	-3.049470505000	0.953406119200	2.755919585000	57 H	-3.083371000000	0.788742000000	2.820261000000
<b>[U(IV)Cp*<sub>2</sub>CN<sub>3</sub>]<sup>1-</sup></b>							
1 U	0.000000000000	0.000000000000	0.423341000000	1 U	0.000000000000	0.000000000000	0.569583000000
2 N	-0.039158000000	-3.518341000000	1.560553000000	2 C	-0.001737000000	-3.480360000000	1.500258000000
3 N	0.000000000000	0.000000000000	4.116776000000	3 C	0.000000000000	0.000000000000	4.178328000000
4 N	0.039158000000	3.518341000000	1.560553000000	4 C	0.001737000000	3.480360000000	1.500258000000
5 C	-0.028795000000	-2.390420000000	1.227273000000	5 N	-0.000431000000	-2.354196000000	1.146471000000
6 C	0.000000000000	0.000000000000	2.941015000000	6 N	0.000000000000	0.000000000000	2.998262000000
7 C	0.028795000000	2.390420000000	1.227273000000	7 N	0.000431000000	2.354196000000	1.146471000000
8 C	-2.696104000000	0.664290000000	0.814012000000	8 C	-2.676426000000	0.715516000000	0.639185000000
9 C	-2.660852000000	-0.757250000000	0.664620000000	9 C	-2.676843000000	-0.713623000000	0.639919000000

$[\text{MN}^*\text{z}\text{X}_3]^q / q=2, -1, / \text{X}=\text{CN, NC} / \text{COSMO}$					
$[\text{Ce(III)}\text{N}^*\text{z}\text{CN}_3]^{2-}$			$[\text{Ce(III)}\text{N}^*\text{z}\text{NC}_3]^{2-}$		
10 C -2.251310000000	-1.050415000000	-0.676298000000	10 C -2.214792000000	-1.156785000000	-0.638784000000
11 C -2.042382000000	0.195957000000	-1.354274000000	11 C -1.925714000000	-0.000329000000	-1.430184000000
12 C -2.328105000000	1.253744000000	-0.434616000000	12 C -2.213961000000	1.157115000000	-0.639878000000
13 C -3.188608000000	1.398277000000	2.027653000000	13 C -3.202465000000	1.587106000000	1.743857000000
14 H -4.286488000000	1.503204000000	1.999737000000	14 H -4.295154000000	1.709610000000	1.652503000000
15 H -2.757476000000	2.404869000000	2.092502000000	15 H -2.749923000000	2.585536000000	1.720012000000
16 H -2.931144000000	0.866288000000	2.952420000000	16 H -3.004918000000	1.155098000000	2.733893000000
17 C -3.158025000000	-1.739007000000	1.686952000000	17 C -3.203555000000	-1.583840000000	1.745436000000
18 H -2.851078000000	-1.458877000000	2.703622000000	18 H -3.012096000000	-1.147241000000	2.734671000000
19 H -2.783229000000	-2.750400000000	1.495955000000	19 H -2.746382000000	-2.580328000000	1.727322000000
20 H -4.260614000000	-1.775008000000	1.674248000000	20 H -4.295292000000	-1.711719000000	1.650030000000
21 C -2.193075000000	-2.408282000000	-1.317968000000	21 C -2.228072000000	-2.570123000000	-1.149228000000
22 H -3.139930000000	-2.629758000000	-1.839004000000	22 H -3.164564000000	-2.771568000000	-1.697147000000
23 H -2.023131000000	-3.199154000000	-0.578172000000	23 H -2.152539000000	-3.296321000000	-0.332016000000
24 H -1.395190000000	-2.481167000000	-2.071642000000	24 H -1.400678000000	-2.767940000000	-1.845122000000
25 C -1.767820000000	0.368031000000	-2.822731000000	25 C -1.696841000000	-0.000806000000	-2.915460000000
26 H -1.219699000000	-0.482211000000	-3.248611100000	26 H -1.148383000000	-0.888614000000	-3.254262000000
27 H -1.195610000000	1.281490000000	-3.038303000000	27 H -1.145259000000	0.885106000000	-3.254074000000
28 H -2.715147000000	0.450137000000	-3.382193000000	28 H -2.663732000000	0.000938000000	-3.447898000000
29 C -2.413837000000	2.708707000000	-0.795397000000	29 C -2.225506000000	2.569966000000	-1.151797000000
30 H -1.626680000000	3.012354000000	-1.499768000000	30 H -1.396224000000	2.766800000000	-1.845746000000
31 H -2.329791000000	3.350430000000	0.088267000000	31 H -2.151952000000	3.297084000000	-0.335199000000
32 H -3.380849000000	2.921181000000	-1.282068000000	32 H -3.160475000000	2.771109000000	-1.702467000000
33 C 2.696014000000	-0.664290000000	0.814012000000	33 C 2.676426000000	-0.715516000000	0.639185000000
34 C 2.328105000000	-1.253744000000	-0.434616000000	34 C 2.213961000000	-1.157115000000	-0.639878000000
35 C 2.042382000000	-0.195957000000	-1.354274000000	35 C 1.925714000000	0.000932900000	-1.430184000000
36 C 2.251310000000	1.050415000000	-0.676298000000	36 C 2.214792000000	1.156785000000	-0.638784000000
37 C 2.660085200000	0.757250000000	0.664620000000	37 C 2.676843000000	0.713623000000	0.639919000000
38 C 3.188608000000	-1.398277000000	2.027653000000	38 C 3.202465000000	-1.587106000000	1.743857000000
39 H 4.286488000000	-1.503204000000	1.999737000000	39 H 4.295154000000	-1.709610000000	1.652503000000
40 H 2.757476000000	-2.404869000000	2.092502000000	40 H 2.749923000000	-2.585536000000	1.720012000000
41 H 2.931144000000	-0.866288000000	2.952420000000	41 H 3.004918000000	-1.155098000000	2.733893000000
42 C 2.413837000000	-2.708707000000	-0.795397000000	42 C 2.225506000000	-2.569966000000	-1.151797000000
43 H 3.380849000000	-2.921181000000	-1.282068000000	43 H 3.160475000000	-2.771109000000	-1.702467000000
44 H 1.626680000000	-3.012354000000	-1.499768000000	44 H 3.196224000000	-2.766800000000	-1.845746000000
45 H 2.329791000000	-3.350430000000	0.088267000000	45 H 2.151952000000	-3.297084000000	-0.335199000000
46 C 1.767820000000	-0.368031000000	-2.822731000000	46 C 1.696841000000	0.000806000000	-2.915460000000
47 H 2.715147000000	-0.450137000000	-3.382193000000	47 H 2.663732000000	-0.000938000000	-3.447898000000
48 H 2.129699000000	0.482211000000	-3.248611000000	48 H 1.148383000000	0.888614000000	-3.254262000000
49 H 1.195610000000	-1.281490000000	-3.038303000000	49 H 1.145259000000	-0.885106000000	-3.254074000000
50 C 2.193075000000	2.408282000000	-1.317968000000	50 C 2.280720000000	2.570123000000	-1.149228000000
51 H 3.139930000000	2.629758000000	-1.839004000000	51 H 3.164564000000	2.771568000000	-1.697147000000
52 H 2.023131000000	3.199154000000	-0.578172000000	52 H 2.152539000000	3.296321000000	-0.332016000000
53 H 1.395190000000	2.481167000000	-2.071642000000	53 H 1.400678000000	2.767940000000	-1.845122000000
54 C 3.158025000000	1.739007000000	1.686952000000	54 C 3.203555000000	1.583840000000	1.745436000000
55 H 2.851078000000	1.458877000000	2.703622000000	55 H 3.012096000000	1.472410000000	2.734671000000
56 H 2.783229000000	2.750400000000	1.495955000000	56 H 2.746382000000	2.580328000000	1.727322000000
57 H 4.260614000000	1.775008000000	1.674248000000	57 H 4.295292000000	1.711719000000	1.650030000000

21 H	16.077179190000	26.507874670000	2.297269091000		21 H	16.071858950000	26.492646370000	2.282533264000
22 C	17.671078460000	22.824012900000	2.031116451000		22 C	17.657073260000	22.808744270000	1.999243904000
23 H	17.312341370000	21.788308460000	1.932217363000		23 H	17.299019660000	21.773544120000	1.896337268000
24 H	18.155548800000	22.927756450000	3.015875866000		24 H	18.147292620000	22.907829410000	2.981550899000
25 H	18.427896960000	23.000117300000	1.251774542000		25 H	18.409401430000	22.988545120000	1.216537838000
26 C	15.572667060000	26.706818890000	-0.915816875000		26 C	15.533911880000	26.681135980000	-0.938097435300
27 H	14.485489490000	26.820483050000	-0.785692056200		27 H	14.447093360000	26.797771040000	-0.809077284800
28 H	15.868675140000	27.245661250000	-1.830824517000		28 H	15.830953350000	27.214708590000	-1.855882268000
29 H	16.076483450000	27.179913830000	-0.060769553950		29 H	16.037704080000	27.158279770000	-0.085289245330
30 C	17.869840360000	24.732960450000	-1.380425171000		30 C	17.833062550000	24.710255620000	-1.381459948000
31 H	18.456221660000	25.118715200000	-0.532368747100		31 H	18.417256760000	25.099248820000	-0.533712254600
32 H	18.151124510000	25.313460110000	-2.274283147000		32 H	18.114386160000	25.289259230000	-2.276445934000
33 H	18.169205120000	23.686533960000	-1.543904556000		33 H	18.135880300000	23.664322600000	-1.542782726000
34 C	15.142835870000	24.283845840000	-2.659145057000		34 C	15.125642180000	24.258019320000	-2.682219083000
35 H	15.317929560000	23.225301420000	-2.901490212000		35 H	15.306247460000	23.200769810000	-2.919369116000
36 H	15.536352060000	24.877135590000	-3.500806235000		36 H	15.530786880000	24.854886210000	-3.516034041000
37 H	14.055877110000	24.454205500000	-2.625718430000		37 H	14.038636160000	24.421580750000	-2.657969343000
38 C	11.017727260000	19.228278330000	-2.970969516000		38 C	11.057099360000	19.246045680000	-2.981707392000
39 H	11.654643530000	18.796488330000	-3.757276126000		39 H	11.707390260000	18.823606470000	-3.761998273000
40 H	9.989032774000	19.278186400000	-3.364776192000		40 H	10.034346230000	19.296478940000	-3.390665747000
41 H	11.019082870000	18.537251510000	-2.114756249000		41 H	11.047712350000	18.546374560000	-2.132600205000
42 C	11.392655190000	22.085622860000	-3.971028968000		42 C	11.425257200000	22.116374430000	-3.944228571000
43 H	11.573242750000	23.135057910000	-3.693607049000		43 H	11.606046610000	23.162302810000	-3.654703592000
44 H	10.378335170000	22.012349490000	-4.396336023000		44 H	10.413628780000	22.048788390000	-4.376754421000
45 H	12.116613740000	21.808721530000	-4.752202710000		45 H	12.154149830000	21.8477221650000	-4.723478828000
46 C	10.280699810000	21.547521450000	-1.182442323000		46 C	10.281695390000	21.532713320000	-1.175889360000
47 H	10.274719870000	20.922828390000	-0.277164063600		47 H	10.280455500000	20.904114750000	-0.272911288900
48 H	9.283628253000	21.478723790000	-1.649453422000		48 H	9.290790255000	21.439361820000	-1.651458466000
49 H	10.416516220000	22.594047510000	-0.870219052900		49 H	10.389498030000	22.581025210000	-0.860524657600
50 C	14.674621600000	20.021820220000	-4.204640817000		50 C	14.686025210000	20.060362350000	-4.171961134000
51 H	13.780449110000	19.641545700000	-4.721986380000		51 H	13.791794570000	19.682490280000	-4.690484088000
52 H	15.527014990000	19.387089610000	-4.497406069000		52 H	15.538163940000	19.426446660000	-4.467807897000
53 H	14.864986350000	21.041285280000	-4.573641829000		53 H	14.877059580000	21.080913570000	-4.53775337000
54 C	14.256121630000	18.207878350000	-1.770772811000		54 C	14.283886600000	18.232627120000	-1.751327843000
55 H	14.188895550000	18.161971490000	-0.673045614800		55 H	14.206656370000	18.176105840000	-0.654928271100
56 H	15.126283810000	17.610294890000	-2.088268973000		56 H	15.161141350000	17.643826620000	-2.065926477000
57 H	13.351412640000	17.748257110000	-2.193988472000		57 H	13.386392560000	17.770297520000	-2.186661175000
58 C	16.123053720000	20.569342430000	-1.586013495000		58 C	16.150234240000	20.594053440000	-1.567184725000
59 H	16.400776630000	21.600596440000	-1.845463558000		59 H	16.422218860000	21.626118530000	-1.826940088000
60 H	16.913306200000	19.912676460000	-1.985261134000		60 H	16.934155710000	19.936277180000	-1.977341531000
61 H	16.146472460000	20.471248000000	-0.489998860000		61 H	16.179620460000	20.498022320000	-0.47238148600
<b>[U(III)N*<sub>2</sub>CN<sub>3</sub>]<sup>2-</sup></b>								
1 U	9.865108125000	7.196436014000	4.887045754000		1 U	9.848699368000	7.187468814000	4.887482808000
2 Si	10.956692310000	9.614008972000	2.493877250000		2 Si	10.935164690000	9.627198803000	2.490260305000
3 Si	8.039157364000	9.741004467000	3.349834560000		3 Si	8.031232992000	9.754262572000	3.358834680000
4 Si	12.234809420000	8.361749759000	7.285351697000		4 Si	12.247827970000	8.328156880000	7.287802802000
5 Si	12.482969790000	5.456371461000	6.411009943000		5 Si	12.472899130000	5.433050715000	6.402059490000
6 N	11.270075660000	5.222982565000	1.972658145000		6 C	11.200506960000	5.325775487000	2.039673269000
7 N	7.291939496000	4.495111074000	4.877864688000		7 C	7.316433030000	4.595540576000	4.833028653000
8 N	7.795759376000	8.515907391000	7.771455120000		8 C	7.904918961000	8.429582887000	7.734344115000
9 N	9.632714523000	9.053138267000	3.467248885000		9 N	9.621600611000	9.063677926000	3.476051662000
10 N	11.728840000000	7.020337594000	6.304944243000		10 N	11.728919100000	7.000131428000	6.297183921000
11 C	10.807435710000	5.795962023000	2.889803973000		11 N	10.854450240000	5.931849862000	2.992004493000
12 C	8.097369042000	5.353732434000	4.879621534000		12 N	8.137882219000	5.442700379000	4.871857108000
13 C	8.390960971000	8.090877375000	6.850029332000		13 N	8.528716680000	8.113596097000	6.782748913000
14 C	11.156560210000	11.510196960000	2.547820917000		14 C	11.102976450000	11.528242630000	2.501541327000
15 H	11.321854510000	11.856256010000	3.579540233000		15 H	11.262164960000	11.897302420000	3.526398342000
16 H	10.269855090000	12.032964350000	2.158578604000		16 H	10.210702440000	12.031940060000	2.100040080000
17 H	12.023006190000	11.820893680000	1.941170055000		17 H	11.966411010000	11.8373252440000	1.889545146000
18 C	10.796850540000	9.113063843000	0.668807494400		18 C	10.781474150000	9.087304768000	0.675172979800
19 H	11.686241540000	9.434213457000	0.102377867600		19 H	11.662098690000	9.415333184000	0.098783835570
20 H	9.909441615000	9.552173285000	0.191800652100		20 H	9.882986827000	9.499365523000	0.194374580300
21 H	10.721291690000	8.016954084000	0.602195839300		21 H	10.728683090000	7.988897898000	0.627685684000
22 C	12.618754700000	8.899621241000	3.058562736000		22 C	12.618444970000	8.970259121000	3.063247584000
23 H	12.868821190000	9.143138645000	4.099905597000		23 H	12.875558300000	9.271652427000	4.087567238000
24 H	13.414148210000	9.319047162000	2.419264235000		24 H	13.395913820000	9.375134952000	2.393506058000
25 H	12.648944940000	7.805828710000	2.947466775000		25 H	12.668887740000	7.873781126000	3.008022436000
26 C	7.569831394000	10.349232980000	1.603464137000		26 C	7.541747195000	10.311602390000	1.599751525000
27 H	8.232764536000	11.142514580000	1.228274513000		27 H	8.205359530000	11.087536390000	1.190685345000

28 H	6.545168059000	10.755795940000	1.630122695000		28 H	6.519971954000	10.725850710000	1.624797498000	
29 H	7.584696360000	9.521146991000	0.879301630700		29 H	7.542984265000	9.459664547000	0.903226453100	
30 C	7.824106005000	11.224285040000	4.515713632000		30 C	7.835609010000	11.274251590000	4.481402260000	
31 H	7.932835100000	10.894159630000	5.559728546000		31 H	7.989206692000	10.980507830000	5.530782211000	
32 H	6.826107936000	11.677831400000	4.399491180000		32 H	6.827491984000	11.710322140000	4.387539370000	
33 H	8.581555429000	11.998412780000	4.320966885000		33 H	8.573377044000	12.052054390000	4.233167325000	
34 C	6.704853218000	8.473113322000	3.793767663000		34 C	6.685294763000	8.517177212000	3.855162484000	
35 H	6.700526859000	7.621160798000	3.098095492000		35 H	6.683069802000	7.626676884000	3.209684705000	
36 H	5.719701015000	8.967642925000	3.737456853000		36 H	5.705122204000	9.014850693000	3.752719475000	
37 H	6.803742732000	8.074337395000	4.814830887000		37 H	6.768679318000	8.177727717000	4.897674540000	
38 C	14.121063860000	8.639495064000	7.234647676000		38 C	14.139988220000	8.573844787000	7.256742311000	
39 H	14.679406270000	7.772739842000	7.619014347000		39 H	14.682165470000	7.699198372000	7.647096312000	
40 H	14.396320780000	9.514210584000	7.846421117000		40 H	14.422288250000	9.445228802000	7.870292046000	
41 H	14.460589530000	8.824260407000	6.204017177000		41 H	14.490695500000	8.752769732000	6.228607586000	
42 C	11.740563050000	8.176057727000	9.109753982000		42 C	11.734490730000	8.139079807000	9.10770530000	
43 H	10.648168810000	8.060796859000	9.178300743000		43 H	10.640349510000	8.034714691000	9.165925848000	
44 H	12.028166500000	9.075723073000	9.678559598000		44 H	12.027031470000	9.031476235000	9.684962299000	
45 H	12.213226360000	7.304547605000	9.584255895000		45 H	12.192748990000	7.259087069000	9.580818062000	
46 C	11.450644200000	9.993824705000	6.726508507000		46 C	11.510045860000	9.986303674000	6.739961043000	
47 H	11.687479420000	10.260711270000	5.688026858000		47 H	11.762936720000	10.257399810000	5.706088315000	
48 H	11.831168040000	10.803985440000	7.371399293500		48 H	11.908594520000	10.777627620000	7.397647243000	
49 H	10.356095570000	9.975771427000	6.832632480000		49 H	10.414773520000	9.992702357000	6.834730331000	
50 C	13.977531990000	5.311181608000	5.249440837000		50 C	13.993241080000	5.291748616000	5.272193400000	
51 H	13.647829650000	5.408036102000	4.204157009000		51 H	13.689165080000	5.429359229000	4.223685762000	
52 H	14.474233770000	4.333952380000	5.365369273000		52 H	14.4675267670000	4.301069969000	5.366623526000	
53 H	14.716508560000	6.101250515000	5.449872917000		53 H	14.742793630000	6.060058122000	5.514707855000	
54 C	11.273760840000	4.074119125000	5.951701317000		54 C	11.276488730000	4.050321723000	5.905510802000	
55 H	10.415578450000	4.033928139000	6.638443202000		55 H	10.386443170000	4.022861361000	6.551188219000	
56 H	11.806434540000	3.109262203000	6.011425286000		56 H	11.801447890000	3.084538790000	6.006467010000	
57 H	10.881816120000	4.160651862000	4.926805078000		57 H	10.936148300000	4.126275913000	4.862744975000	
58 C	13.104919820000	5.003287922000	8.156773298000		58 C	13.056212950000	4.955213977000	8.155970984000	
59 H	13.870669040000	5.695935818000	8.535933949000		59 H	13.815236540000	5.640338286000	8.561237159000	
60 H	13.551806560000	3.995636034000	8.128332790000		60 H	13.500130100000	3.946311949000	8.124329990000	
61 H	12.275455440000	4.984009659000	8.879302002000		61 H	12.210517010000	4.929772629000	8.859467086000	
<b>[U(IV)N*<sub>2</sub>CN<sub>3</sub>]<sup>-</sup></b>									
1 U	10.034757000000	7.375728000000	4.883747000000		1 U	10.129239000000	7.415174000000	4.858136000000	
2 Si	10.988535000000	9.659384000000	2.507023000000		2 Si	10.843132000000	9.658875000000	2.448480000000	
3 Si	8.009379000000	9.738781000000	3.370051000000		3 Si	7.899819000000	9.754898000000	3.387831000000	
4 Si	12.302155000000	8.389186000000	7.255806000000		4 Si	12.374722000000	8.341086000000	7.246608000000	
5 Si	12.448598000000	5.412881000000	6.397459000000		5 Si	12.506271000000	5.360874000000	6.440021000000	
6 N	11.091554000000	5.287196000000	1.971327000000		6 C	11.220797000000	5.353626000000	2.096381000000	
7 N	7.462411000000	4.743698000000	4.915227000000		7 C	7.576979000000	4.927480000000	5.074283000000	
8 N	7.929479000000	8.412284000000	7.792674000000		8 C	8.184567000000	8.699944000000	7.605877000000	
9 N	9.649742000000	9.050717000000	3.512916000000		9 N	9.531602000000	9.047924000000	3.477664000000	
10 N	11.722496000000	7.036682000000	6.250258000000		10 N	11.792882000000	6.981742000000	6.262061000000	
11 C	10.777231000000	5.914599000000	2.914040000000		11 N	10.891767000000	6.026501000000	3.011230000000	
12 C	8.283725000000	5.585856000000	4.905267000000		12 N	8.428758000000	5.732048000000	4.915072000000	
13 C	8.567050000000	8.109714000000	6.852838000000		13 N	8.822177000000	8.332762000000	6.680940000000	
14 C	11.093493000000	11.538284000000	2.630639000000		14 C	10.989414000000	11.540756000000	2.546751000000	
15 H	11.236627000000	11.868908000000	3.672134000000		15 H	11.147549000000	11.875906000000	3.582360000000	
16 H	10.191006000000	12.036527000000	2.242340000000		16 H	10.098128000000	12.052747000000	2.156175000000	
17 H	11.953355000000	11.897872000000	2.038966000000		17 H	11.852063000000	11.874645000000	1.947947000000	
18 C	10.817372000000	9.129265000000	0.707444000000		18 C	10.657508000000	9.121613000000	0.650087000000	
19 H	11.703215000000	9.466679000000	0.141809000000		19 H	11.548163000000	9.423724000000	0.076541000000	
20 H	9.924346000000	9.548996000000	0.221343000000		20 H	9.778301000000	9.569010000000	0.166646000000	
21 H	10.770227000000	8.030190000000	0.637321000000		21 H	10.567176000000	8.027366000000	0.585947000000	
22 C	12.650534000000	8.955986000000	3.105524000000		22 C	12.493747000000	8.946481000000	3.060305000000	
23 H	12.897090000000	9.184575000000	4.151835000000		23 H	12.775142000000	9.254450000000	4.076161000000	
24 H	13.432540000000	9.422028000000	2.478786000000		24 H	13.271643000000	9.352750000000	2.391902000000	
25 H	12.724778000000	7.867361000000	2.957967000000		25 H	12.569414000000	7.852276000000	2.981400000000	
26 C	7.587660000000	10.237461000000	1.597846000000		26 C	7.438903000000	10.268629000000	1.625048000000	
27 H	8.238868000000	11.029580000000	1.196689000000		27 H	8.085428000000	11.056715000000	1.213897000000	
28 H	6.552381000000	10.622741000000	1.587049000000		28 H	6.409634000000	10.663374400000	1.639907000000	
29 H	7.630879000000	9.376233000000	0.912530000000		29 H	7.455475000000	9.412193000000	0.935352000000	
30 C	7.844169000000	11.248980000000	4.491556000000		30 C	7.779362000000	11.272691000000	4.505365000000	
31 H	7.956883000000	10.959398000000	5.548544000000		31 H	7.962165000000	10.997586000000	5.554428000000	
32 H	6.845899000000	11.703775000000	4.369695000000		32 H	6.772028000000	11.714485000000	4.440975000000	
33 H	8.598914000000	12.017451000000	4.262044000000		33 H	8.506025000000	12.048156000000	4.222205000000	
34 C	6.735383000000	8.441352000000	3.890628000000		34 C	6.611827000000	8.488458000000	3.929384000000	
35 H	6.760498000000	7.536231000000	3.264821000000		35 H	6.611614000000	7.600943000000	3.280620000000	

36 H	5.735429000000	8.897216000000	3.776096000000	36 H	5.616761000000	8.958020000000	3.857822000000
37 H	6.815837000000	8.127469000000	4.942958000000	37 H	6.746153000000	8.155298000000	4.967082000000
38 C	14.180391000000	8.523966000000	7.150696000000	38 C	14.261309000000	8.471087000000	7.222738000000
39 H	14.690956000000	7.632656000000	7.548497000000	39 H	14.753942000000	7.608722000000	7.694941000000
40 H	14.518570000000	9.393094000000	7.741487000000	40 H	14.569269000000	9.372548000000	7.776889000000
41 H	14.519304000000	8.668474000000	6.112018000000	41 H	14.643110000000	8.562641000000	6.194977000000
42 C	11.756527000000	8.214771000000	9.050334000000	42 C	11.777951000000	8.225471000000	9.031385000000
43 H	10.657027000000	8.164120000000	9.110883000000	43 H	10.679924000000	8.179799000000	9.068654000000
44 H	12.087217000000	9.100273000000	9.620420000000	44 H	12.101539000000	9.117889000000	9.590201000000
45 H	12.174526000000	7.321838000000	9.538121000000	45 H	12.178428000000	7.342127000000	9.547007000000
46 C	11.586487000000	10.039652000000	6.640731000000	46 C	11.731920000000	9.982403000000	6.528132000000
47 H	11.877718000000	10.306283000000	5.614908000000	47 H	12.399876000000	10.389616000000	5.757196000000
48 H	11.989661000000	10.823787000000	7.307347000000	48 H	11.718014000000	10.708814000000	7.357906000000
49 H	10.489252000000	10.086034000000	6.719107000000	49 H	10.702846000000	9.982696000000	6.134531000000
50 C	13.961485000000	5.280307000000	5.275187000000	50 C	14.040476000000	5.200830000000	5.350868000000
51 H	13.668814000000	5.388484000000	4.218582000000	51 H	13.781200000000	5.342136000000	4.291064000000
52 H	14.436816000000	4.291352000000	5.395031000000	52 H	14.483238000000	4.197943000000	5.460440000000
53 H	14.714384000000	6.050404000000	5.505226000000	53 H	14.810024000000	5.940679000000	5.615543000000
54 C	11.184180000000	4.104054000000	5.882347000000	54 C	11.252170000000	4.050674000000	5.919894000000
55 H	10.280972000000	4.103329000000	6.511238000000	55 H	10.361211000000	4.052802000000	6.563504000000
56 H	11.669759000000	3.117943000000	5.996019000000	56 H	11.733698000000	3.063739000000	6.017768000000
57 H	10.864638000000	4.173723000000	4.830998000000	57 H	10.924268000000	4.149509000000	4.876240000000
58 C	12.957259000000	5.008165000000	8.171102000000	58 C	12.983063000000	4.969110000000	8.228492000000
59 H	13.727273000000	5.684086000000	8.574283000000	59 H	13.757675000000	5.636298000000	8.632024000000
60 H	13.375223000000	3.985644000000	8.183449000000	60 H	13.384275000000	3.942745000000	8.261537000000
61 H	12.093445000000	5.024263000000	8.854382000000	61 H	12.110656000000	5.006633000000	8.896714000000