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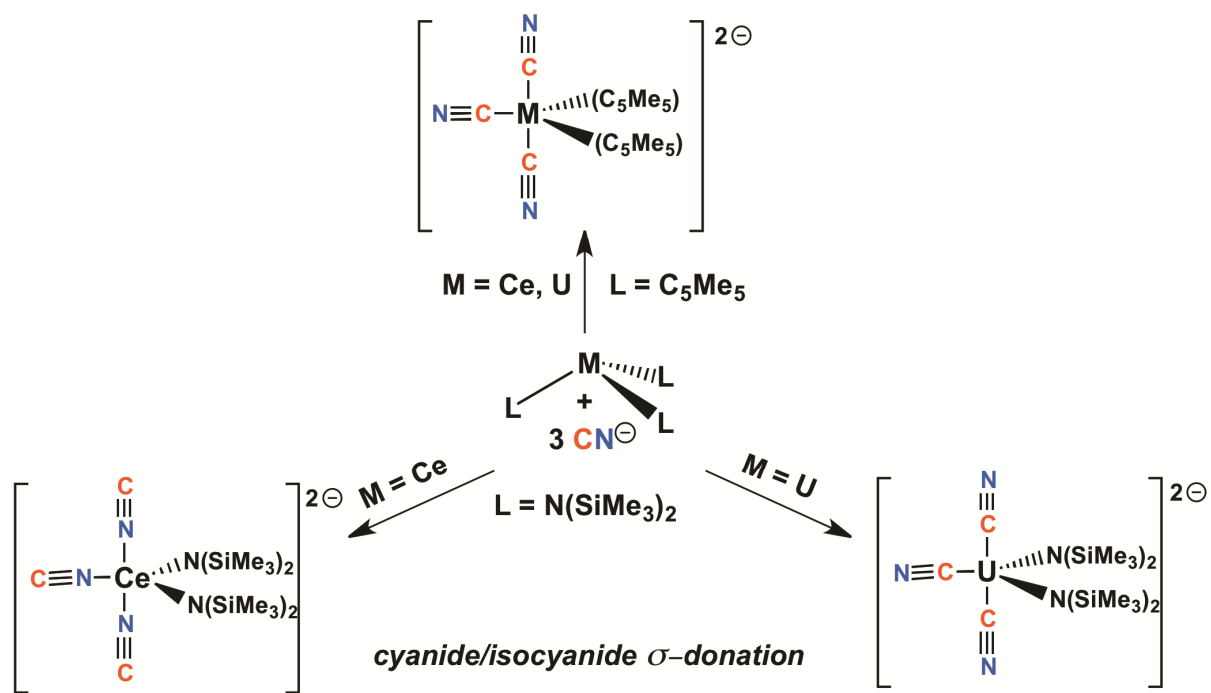
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Cyanide linkage isomerism in cerium(III) and uranium(III) complexes. A relativistic DFT study

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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 $[ML_2X_3]^{2-}$ ($M = Ce^{3+}, U^{3+}$; $L = C_5H_4Me, N(SiMe_3)_2$; $X = CN, NC$), using relativistic DFT computations, focusing on cyanide (CN) and isocyanide (NC⁻) 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⁻/NC⁻ 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

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

1. Introduction

Since the first synthesis of *f*-element cyanide complexes in the early seventies [1], the cyanide CN⁻ 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 heteropolynuclear compounds with interesting stereochemistry and properties [2]. This is attributed to the strong σ -donor character of the cyanide and isocyanide ligands, *via* donation from either the C-localized orbital of CN⁻ (carbon lone pair) or the N-localized one of NC⁻ 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⁻/NC⁻ 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* = C₅Me₅) 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(μ -CN)]⁻ (M = Ce, U; N* = N(SiMe₃)₂) anionic compounds [2a]. It is worth noting that the bis(silylamide) ligand N* 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 4*f* elements, lanthanides (Ln), and the 5*f* elements, actinides (An), in this field [8-10]. In particular, the coordination competition between cyanide (CN⁻) and isocyanide (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 [X₂U(CN)₅]^{q-} (X = O, Cp = C₅H₅) [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 [UO₂(CN)₅]⁴⁻ and [Cp₂U(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) [MN*₃(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 σ -donating ability of the cyanide ligand toward uranium and not cerium is related to the better energy matching between 6*d*/5*f* uranium metal and ligand orbitals [11]. The same observation has been made in the case of U(III) and U(IV) bis(silylamide) mono and bis(cyanide) complexes [UN*₃X]^{q-} and [UN*₃X₂]^{q-} (q = 2, 1; X = CN, 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.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(silylamide) tris(cyanide) compounds $[M(\text{Cp}^*)_2(\text{CN})_3]^{2-}$ and $[\text{MN}^*_2(\text{CN})_3]^{2-}$ ($M = \text{Ce}, \text{U}$), 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(silylamide) 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 $[\text{UN}^*_2\text{X}_3]^{2-}$ 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 $[\text{ML}_2\text{X}_3]^{2-}$ ($M = \text{Ce}^{3+}/\text{U}^{3+}$; $L = \text{Cp}^*/\text{N}^*$ and $X = \text{CN}/\text{NC}$) and their hypothetical isomers. All structures were fully optimized using the BP86 functional coupled to the polarized double- ζ 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 ($L = \text{Cp}^*$ and N^*) and C–N/N–C of the optimized structures (Fig. 1 and 2) are reported in Table 1 for the actual complexes $[\text{MCp}^*_2(\text{CN})_3]^{q-}$ ($M = \text{Ce}^{3+}, \text{U}^{3+/4+}$; $q = 2, 1$) (**1a**) and (**1b**) (complexes **6** and **5** in ref. 2b), and their hypothetical isomers $[\text{MCp}^*_2(\text{NC})_3]^{q-}$. The computed parameters for the isocyanide cerium(III) $[\text{CeN}^*_2(\text{NC})_3]^{2-}$ (**2a**) and cyanide uranium(III) $[\text{UN}^*_2(\text{CN})_3]^{2-}$ (**2b**) complexes (respectively

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

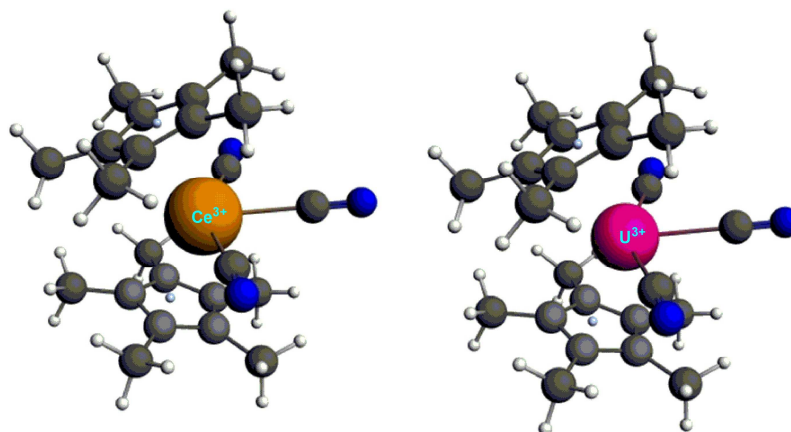


Fig. 1. ZORA/BP86/DZP optimized geometry of the bis(cyclopentadienyl) tris(cyanide) $[\text{MCp}^*_2\text{X}_3]^{2-}$ complexes ($\text{M} = \text{Ce}^{3+}, \text{U}^{3+}$; $\text{X} = \text{CN}$) **1a** (left) and **1b** (right). The blue, black, and white spheres are nitrogen, carbon, and hydrogen atoms, respectively.

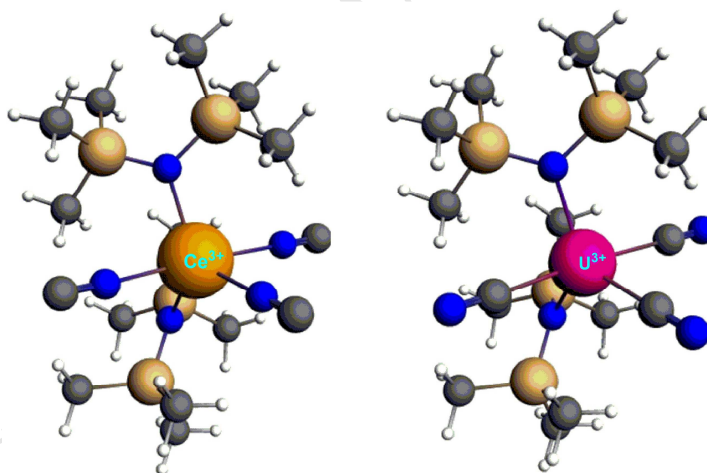


Fig. 2. ZORA/BP86/DZP optimized structures of the bis(silylamide) tris(cyanide/isocyanide) complexes $[\text{MN}^*_2\text{X}_3]^{2-}$ complexes ($\text{M} = \text{Ce}^{3+}, \text{U}^{3+}$; $\text{X} = \text{CN}, \text{NC}$), **2a** (left) and **2b** (right). The orange, blue, black, and white spheres are silicon, nitrogen, carbon, and hydrogen atoms, respectively.

The computed geometries of the actual $[\text{MCp}^*_2(\text{CN})_3]^{2-}$ $\text{Ce}^{\text{III}}\text{-CN}$ and $\text{U}^{\text{III/IV}}\text{-CN}$ 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(silylamide) $\text{Ce}^{\text{III}}\text{-NC}$ 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 (Å) at the ZORA/BP86/DZP level and X-Ray data where available (in bold) for the $[\text{ML}_2\text{X}_3]^{q-}$ complexes ($\text{M} = \text{Ce}^{3+}$, U^{3+} and 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	$\langle \text{M}-\text{C/N} \rangle$	Δ (Å) ^a	$\langle \text{C}-\text{N/N}-\text{C} \rangle$	$\langle \text{M}-\text{L} \rangle$
$[\text{MCp}^*_2\text{X}_3]^{q-}$				
Ce^{3+}	2.665/2.535		1.178/1.182	2.621/2.638
	<i>2.655/2.546</i>		<i>1.176/1.177</i>	<i>2.586/2.583</i>
	2.666/-		1.158/ -	2.562/ -
U^{3+}	2.612/2.492	0.053/0.043	1.178/1.183	2.571/2.560
	<i>2.585/2.489</i>	<i>0.070/0.057</i>	<i>1.177/1.180</i>	<i>2.509/2.534</i>
	2.640/ -		1.156/ -	2.534/ -
U^{4+}	2.501/2.389		1.175/1.185	2.482/2.507
	<i>2.520/2.424</i>		<i>1.176/1.180</i>	<i>2.476/2.493</i>
	2.520/ -		1.158/ -	2.446 / -
$[\text{MN}^*_2\text{X}_3]^{q-}$				
Ce^{3+}	2.666/2.511		1.176/1.183	2.413/2.427
	<i>2.657/2.523</i>		<i>1.175/1.179</i>	<i>2.379/2.387</i>
	- /2.580		- /1.164	- /2.390
U^{3+}	2.605/2.462	0.061/0.049	1.178/1.185	2.377/2.394/
	<i>2.593/2.472</i>	<i>0.064/0.051</i>	<i>1.176/1.181</i>	<i>2.348/2.358</i>
	2.600/ -		1.148/ -	2.334/ -
U^{4+}	2.512/2.374		1.175/1.186	2.239/2.253
	<i>2.543/2.416</i>		<i>1.175/1.182</i>	<i>2.198/2.220</i>
	-		-	-

^a 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 Å for U, and 2.535 vs. 2.492 Å 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 Δ 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

Å), which is slightly amplified by solvation (0.070 vs. 0.057 Å), 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 = Cp* and 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→X π back-donation occurs, and that the M–X bond is essentially σ 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 = Ce^{III} and U^{III}, X = C–N/N–C) [10a], the better energy matching of the C-localized σ lone pair orbital of the cyanide ligand with the U^{III}(5*f*³) metal-based orbitals makes it a much more effective donor than the N-localized σ 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 = Ce³⁺, U³⁺; L = Cp*/N*; X = CN/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 ρ_M are reported. ρ_M is computed to be the difference between the total α and β 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 Ce³⁺ and (+0.73/+1.03 for U³⁺) which are consistent with the slightly stronger σ -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(silylamide) 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	
	ρ_M	q_M	$\langle C-N \rangle$	$\langle N-C \rangle$
	$[MCp^*_2X_3]^{2-}$			
Ce(III)	0.989/0.993 <i>0.985/0.981</i>	+1.53/+1.74 <i>+1.49/+1.72</i>	–0.12: –0.57 <i>–0.28: –0.63</i>	–0.81: +0.04 <i>–0.76: –0.01</i>
U(III)	2.913/2.898 <i>2.874/2.873</i>	+0.73/+1.03 <i>+0.56/+1.01</i>	–0.23: –0.56 <i>+0.05: –0.63</i>	–0.71: +0.05 <i>–0.66: –0.04</i>
	$[MN^*_2X_3]^{2-}$			
Ce(III)	1.019/1.018 <i>1.003/1.016</i>	+1.71/+1.88 <i>+1.66/+1.86</i>	–0.17: –0.54 <i>–0.11: –0.61</i>	–0.85: +0.09 <i>–0.80: +0.02</i>
U(III)	2.949/2.921 <i>2.929/2.901</i>	+1.30/+1.54 <i>+1.23/+1.50</i>	–0.11: –0.53 <i>–0.04: –0.59</i>	–0.85: +0.10 <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(silylamide) MN_2^* complexes (e.g., –0.11 *vs.* –0.17), which sustains its stronger σ -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 σ -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 σ -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		
		<M–C/N>	<C–N/N–C>	<M–C/N>	<C–N/N–C>	
$[MCp^*_2X_3]^{2-}$	Ce(III)	2.665/2.535	0.447/0.387	2.814/2.665	0.695/0.642	3.165/3.114
		<i>2.655/2.546</i>	<i>0.431/0.361</i>	<i>2.835/2.755</i>	<i>0.687/0.612</i>	<i>3.168/3.156</i>
	U(III)	2.612/2.492	0.529/0.466	2.759/2.624	0.837/0.801	3.117/3.059
		<i>2.585/2.489</i>	<i>0.530/0.445</i>	<i>2.780/2.712</i>	<i>0.859/0.785</i>	<i>3.100/3.054</i>
$[MN^*_2X_3]^{2-}$	Ce(III)	2.666/2.511	0.440/0.396	2.829/2.633	0.838/0.952	3.192/3.109
		<i>2.657/2.523</i>	<i>0.426/0.364</i>	<i>2.841/2.723</i>	<i>0.796/0.894</i>	<i>3.190/3.152</i>
	U(III)	2.605/2.462	0.540/0.491	2.777/2.585	0.885/0.868	3.130/3.043
		<i>2.593/2.472</i>	<i>0.532/0.467</i>	<i>2.790/2.670</i>	<i>0.882/0.830</i>	<i>3.123/3.078</i>

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, *e.g.* 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) MCp^*_2 systems. On the other hand, this is the opposite is computed for the bis(silylamide) 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 CeN^*_2 system, whereas the opposite is computed for the 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) 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 U^{3+} ; $\text{L} = \text{Cp}^*$ or N^* ; $\text{X} = \text{CN}/\text{NC}$) are given in Fig. 3 and 4. For the sake of simplicity, only α spin-MOs are shown. Different sets of MOs appear. For all cyanide and isocyanide complexes, the diagrams show that the highest occupied α spin-orbitals, *i.e.*, the SOMO, SOMO-1 and SOMO-2 in U(III) (f^3) complexes and the SOMO in the Ce(III) (f^1) counterpart are essentially metallic in character, with a strong f orbital contribution. In the case of the U(III) systems, a weak cyanide or isocyanide ligand contribution of *ca.* 4% is observed in the SOMOs. However, neither presence of metal-to-ligand π back-donation nor π interaction appears between the metal center and the cyanide or isocyanide ligands, since the participation of the C-localized orbital of CN^- or N-localized orbital of NC^- is null. This confirms the fact that these ligands remain mainly σ donors in character in these species.

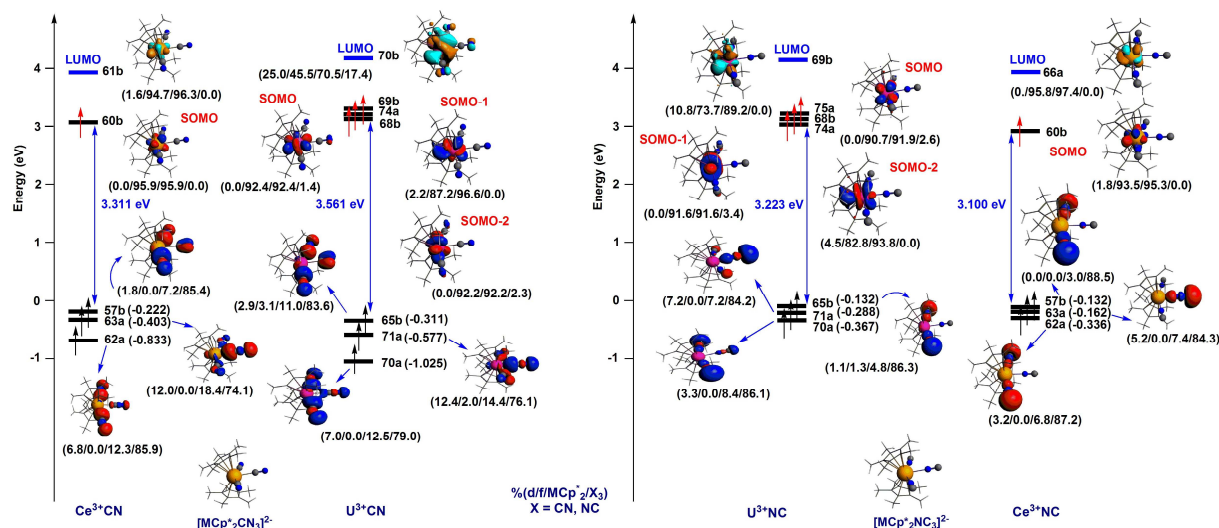


Fig. 3. ZORA/BP86/DZP α spin-MO diagram for M–CN (left) and M–NC (right) $[\text{MCp}^*_2\text{X}_3]^{2-}$ ($\text{X} = \text{CN}/\text{NC}$) complexes (C_2 symmetry). From the left to the right, the M d , M f , ML_2 , and X_3 percentage contributions are given in brackets. Contour values are ± 0.03 (e/bohr^3) $^{1/2}$.

More interestingly, the sets of occupied M–CN/NC MOs, deeper in energy, exhibit mainly the σ 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 σ -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(silylamide) MN^*_2 systems, the MO diagram of Fig. 4 shows that the metal d/f orbitals contributions within the bonding σ -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^*_2 –CN coordination. Furthermore, these bonding σ -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].

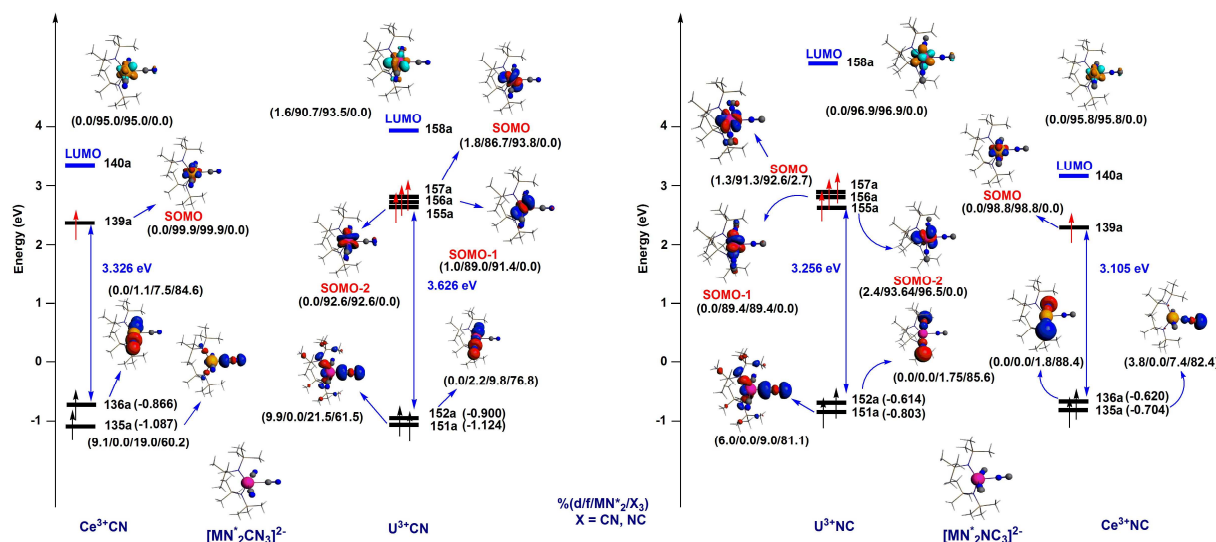


Fig. 4. ZORA/BP86/DZP α spin-MO diagram for M–CN (left) and M–NC (right) $[\text{MN}^*_2\text{X}_3]^{2-}$ ($X = \text{CN}/\text{NC}$) complexes (C_1 symmetry). From the left to the right, the M d , M f , ML_2 , and X_3 percentage contributions are given in brackets. Contour values are ± 0.03 (e/bohr^3)^{1/2}.

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 σ -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.

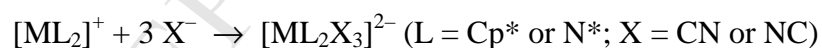
As indicated by the electronic structure and MO analysis, the variations in structural and bonding parameters of the considered complexes could be explained by the σ -donating abilities of the cyanide and isocyanide ligands and the occurrence of a higher covalent character of the bonding in the case 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 MCp^*_2 and 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 CeN^*_2 fragment relatively to 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 Cp^*_2 co-ligands and the isocyanide with the 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 U^{3+} ; $\text{L} = \text{Cp}^*$ or 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 (TBE_{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 U^{3+} ; $\text{L} = \text{Cp}^*$ or N^* ; $\text{X} = \text{CN(left)/NC(right)}$) in the gas phase and in solution (in italics).

ion	E_{Pauli} (eV)	E_{elstat} (eV)	E_{st} (eV)	E_{orb} (eV)	E_{solvat} (eV)	TBE_{frag} (eV)	ΔE (kcal/mol)
$[\text{MCp}^*_2\text{X}_3]^{2-}$							
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
U³⁺	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
[MN*₂X₃]²⁻							
Ce³⁺	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
U³⁺	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_{frag} for the cyanide M–CN coordination of the MCp^*_2 complexes are significantly higher (in absolute value) than the isocyanide M–NC ones, as shown by their relative stability ΔE , in agreement with the experimental observation, *i.e.*, the actual structures. We note that for the MN^*_2 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 ΔE 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^*_2 complex, where ΔE 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^*_2 , due to the shorter metal–ligand distances in the former. Notably, in the bis(cyclopentadienyl) MCp^*_2 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^*_2 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_{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_{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_{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 σ -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 $[\text{UN}^*_2\text{X}_3]^{2-}$ 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(silylamide) complex. Indeed, the same trend is obtained, *i.e.* the cyano isomer is more stable than the isocyno 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 $[\text{ML}_2\text{X}_3]^{2-}$ ($\text{M} = \text{Ce}^{3+}/\text{U}^{3+}$; $\text{L} = \text{Cp}^*/\text{N}^*$; $\text{X} = \text{CN}/\text{NC}$) 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(silylamide) compounds $[\text{MN}^*_2\text{X}_3]^{2-}$, 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 $[\text{MCp}^*_2]$ and $[\text{MN}^*_2]$ 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 σ -donating MOs. More generally, MO analysis shows that the stronger σ -donating ability of the cyanide ligand towards actinide bis(silylamide) 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 $[\text{MCp}^*_2]$ and $[\text{MN}^*_2]$ ($\text{M} = \text{Ce}, \text{U}$) 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 ΔE , 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 $[\text{ML}_2\text{X}_3]^{2-}$ ($\text{M} = \text{Ce}^{3+}/\text{U}^{3+}$; $\text{X} = \text{CN}/\text{NC}$; $\text{L} = \text{Cp}^*/\text{N}^*$) 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- ζ 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 ($\text{X} = \text{CN}/\text{NC}$) for the $[\text{ML}_2\text{X}_3]^{2-}$ complexes ($\text{M} = \text{Ce}$ or U ; $\text{L} = \text{N}^*$ 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 $\text{TBE}_{\text{frag}} = E_{\text{steric}} + E_{\text{orb}}$, where E_{steric} is, in our case, the steric interaction energy between the MCp^*_2 or MN^*_2 ($\text{Cp}^* = \text{C}_5\text{Me}_5$ and $\text{N}^* = \text{N}(\text{SiMe}_3)_2$) 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_{Pauli} , the electronic repulsion due to the Pauli principle, and E_{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. ΔE in Table 4 is the energy difference between the two M-CN and M-NC isomers (differences of their TBE_{frag}).

Appendix B. Supplementary material

Cartesian coordinates of DFT optimized geometries.

Acknowledgments

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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. Edelman, 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

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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

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Supplementary Information

Cartesian coordinates of DFT optimized geometries.

$[\text{Mcp}^*_2\text{X}_3]^q / q=2, -1 / \text{X}=\text{CN}, \text{NC} / \text{GAZ}$			
$[\text{Ce(III)Cp}^*_2\text{CN}_3]^{2-}$		$[\text{Ce(III)Cp}^*_2\text{NC}_3]^{2-}$	
1 Ce	0.000000000000	0.000000000000	0.662157345200
2 N	0.000000000000	0.000000000000	4.473082654000
3 N	-0.603426950800	3.736948879000	1.406183130000
4 C	0.000000000000	0.000000000000	3.295433151000
5 C	-0.417392077300	2.585003675000	1.241293223000
6 C	2.047694898000	0.343201361900	-1.382503998000
7 C	2.130878989000	1.521198489000	-0.581825116900
8 C	2.628106787000	1.141088081000	0.701578806600
9 C	2.853257207000	-0.265610856700	0.690675451800
10 C	2.493862205000	-0.762946573500	-0.598896747200
11 C	1.763758775000	0.309156840900	-2.856446193000
12 H	2.680382217000	0.494954075400	-3.449472830000
13 H	1.030792118000	1.071770170000	-3.158556435000
14 H	1.369676232000	-0.665466803000	-3.178561441000
15 C	1.916794684000	2.926203279000	-1.065870868000
16 H	1.514268595000	3.573179139000	-0.274856437100
17 H	1.198637064000	2.965456791000	-1.898583752000
18 H	2.861825480000	3.371929563000	-1.433355235000
19 C	2.930879266000	2.072843034000	1.839840410000
20 H	2.782777209000	1.582003551000	2.812127215000
21 H	2.269486591000	2.949340862000	1.825595948000
22 H	3.977936681000	2.430004259000	1.800274464000
23 C	3.439587092000	-1.069484386000	1.815420425000
24 H	4.545724150000	-1.073911782000	1.771362271000
25 H	3.091512981000	-2.110833485000	1.787791054000
26 H	3.147052070000	-0.665089863100	2.794494635000
27 C	2.720429876000	-2.159634770000	-1.100494159000
28 H	2.020262807000	-2.423856496000	-1.907678999000
29 H	2.575483748000	-2.904209797000	-0.306837864500
30 H	3.743248668000	-2.278947694000	-1.508034534000
31 N	0.603426950800	-3.736948879000	1.406183130000
32 C	0.417392077300	-2.585003675000	1.241293223000
33 C	-2.047694898000	-0.343201361900	-1.382503998000
34 C	-2.130878989000	-1.521198489000	-0.581825116900
35 C	-2.628106787000	-1.141088081000	0.701578806600
36 C	-2.853257207000	0.265610856700	0.690675451800
37 C	-2.493862205000	0.762946573500	-0.598896747200
38 C	-1.763758775000	-0.309156840900	-2.856446193000
39 H	-2.680382217000	-0.494954075400	-3.449472830000
40 H	-1.030792118000	-1.071770170000	-3.158556435000
41 H	-1.369676232000	0.665466803000	-3.178561441000
42 C	-1.916794684000	-2.926203279000	-1.065870868000
43 H	-1.514268595000	-3.573179139000	-0.274856437100
44 H	-1.198637064000	-2.965456791000	-1.898583752000
45 H	-2.861825480000	-3.371929563000	-1.433355235000
46 C	-2.930879266000	-2.072843034000	1.839840410000
47 H	-2.782777209000	-1.582003551000	2.812127215000
48 H	-2.269486591000	-2.949340862000	1.825595948000
49 H	-3.977936681000	-2.430004259000	1.800274464000
50 C	-3.439587092000	1.069484386000	1.815420425000
51 H	-4.545724150000	1.073911782000	1.771362271000
52 H	-3.091512981000	2.110833485000	1.787791054000
53 H	-3.147052070000	0.665089863100	2.794494635000
54 C	-2.720429876000	2.159634770000	-1.100494159000
55 H	-2.020262807000	2.423856496000	-1.907678999000
56 H	-2.575483748000	2.904209797000	-0.306837864500
57 H	-3.743248668000	2.278947694000	-1.508034534000
$[\text{U(III)Cp}^*_2\text{CN}_3]^{2-}$		$[\text{U(III)Cp}^*_2\text{NC}_3]^{2-}$	
1 U	0.000000000000	0.000000000000	0.6931105122500
2 N	0.000000000000	0.000000000000	4.456691964000
3 N	-0.397896091000	3.690327760000	1.515900192000
4 C	0.000000000000	0.000000000000	3.278936557000
5 C	-0.254902033200	2.536504041000	1.323045130000
6 C	2.368842994000	-0.921176233800	-0.605739074300
7 C	1.976424121000	0.212236714200	-1.381308185000
8 C	2.148022431000	1.379076393000	-0.576063082800
1 U	0.000000000000	0.000000000000	0.664625353000
2 C	0.000000000000	0.000000000000	4.319730655000
3 C	-0.387448409300	3.590307312000	1.404297020000
4 N	0.000000000000	0.000000000000	3.137208501000
5 N	-0.280052445400	2.439791998000	1.149287192000
6 C	2.369944770000	-0.891760090600	-0.606689245000
7 C	1.980304733000	0.258166036900	-1.361038308000
8 C	2.164071410000	1.409075622000	-0.534932961900

9 C	2.646523899000	0.965499386700	0.696375330900	9 C	2.651100472000	0.971260239100	0.731526509300
10 C	2.783486533000	-0.452699697700	0.678056838400	10 C	2.783244111000	-0.448290372900	0.687293182600
11 C	2.493121756000	-2.327449838000	-1.116241867000	11 C	2.512063446000	-2.282511665000	-1.151083997000
12 H	1.756929473000	-2.537286360000	-1.906811341000	12 H	1.772090349000	-2.487573038000	-1.939912690000
13 H	2.318651656000	-3.064254534000	-0.320989344100	13 H	2.356988820000	-3.038797109000	-0.370709183000
14 H	3.496228466000	-2.512212720000	-1.548513178000	14 H	3.514094643000	-2.441693440000	-1.596054335000
15 C	1.727054677000	0.210613090100	-2.860127156000	15 C	1.737864494000	0.285648155000	-2.841716736000
16 H	1.079352277000	1.042645681000	-3.170092250000	16 H	1.100223011000	1.130819928000	-3.138835065000
17 H	1.247166951000	-0.718308643000	-3.199123445000	17 H	1.249391645000	-0.631489810800	-3.199481124000
18 H	2.674238336000	0.310463056600	-3.428608545000	18 H	2.687728868000	0.386424910100	-3.405919230000
19 C	2.003768574000	2.795448616000	-1.050808283000	19 C	2.036996262000	2.832018480000	-0.991524179400
20 H	2.936306663000	3.158107351000	-1.526229732000	20 H	2.961560847000	3.173712719000	-1.496276135000
21 H	1.749241946000	3.473785938000	-0.226398547800	21 H	1.829416700000	3.508129872000	-0.152701927000
22 H	1.199337394000	2.895438300000	-1.795439488000	22 H	1.208775025000	2.961707716000	-1.704665955000
23 C	3.039607845000	1.867050548000	1.830940262000	23 C	3.029797979000	1.856227814000	1.883017532000
24 H	2.890782213000	1.376174611000	2.802861891000	24 H	2.910141544000	1.335949993000	2.843519408000
25 H	2.433863666000	2.782933925000	1.843928191000	25 H	2.392715090000	2.749966842000	1.924544408000
26 H	4.105523584000	2.158486432000	1.762000830000	26 H	4.083743004000	2.187142527000	1.809446979000
27 C	3.351280454000	-1.290282041000	1.787255845000	27 C	3.346869970000	-1.310371413000	1.779111497000
28 H	4.457413109000	-1.313605179000	1.745736130000	28 H	4.448766930000	-1.387721653000	1.701942406000
29 H	2.983213090000	-2.322979698000	1.737479598000	29 H	2.927882378000	-2.324668596000	1.743591448000
30 H	3.063722520000	-0.901022300500	2.774549461000	30 H	3.110855741000	-0.905355151300	2.773161912000
31 N	0.397896091000	-3.690327760000	1.515900192000	31 C	0.387448409300	-3.590307312000	1.404297020000
32 C	0.254902033200	-2.536504041000	1.323045130000	32 N	0.280052445400	-2.439791998000	1.149287192000
33 C	-2.368842994000	0.921176233800	-0.605739074300	33 C	-2.369944770000	0.891760090600	-0.606668924500
34 C	-1.976424121000	-0.212236714200	-1.381308185000	34 C	-1.980304733000	-0.258166036900	-1.361038308000
35 C	-2.148022431000	-1.379076393000	-0.576630828000	35 C	-2.164071410000	-1.409075622000	-0.534932961900
36 C	-2.646523899000	-0.965499386700	0.696375330900	36 C	-2.651100472000	-0.971260239100	0.731526509300
37 C	-2.783486533000	0.452699697700	0.678056838400	37 C	-2.783244111000	0.448290372900	0.687293182600
38 C	-2.493121756000	-2.327449838000	-1.116241867000	38 C	-2.512063446000	-2.282511665000	-1.151083997000
39 H	-1.756929473000	2.537286360000	-1.906811341000	39 H	-1.772090349000	2.487573038000	-1.939912690000
40 H	-2.318651656000	3.064254534000	-0.320989344100	40 H	-2.356988820000	3.038797109000	-0.370709183000
41 H	-3.496228466000	2.512212720000	-1.548513178000	41 H	-3.514094643000	2.441693440000	-1.596054335000
42 C	-1.727054677000	-0.210613090100	-2.860127156000	42 C	-1.737864494000	-0.285648155000	-2.841716736000
43 H	-1.079352277000	1.042645681000	-3.170092250000	43 H	-1.100223011000	-1.130819928000	-3.138835065000
44 H	-1.247166951000	0.718308643000	-3.199123445000	44 H	-1.249391645000	0.631489810800	-3.199481124000
45 H	-2.674238336000	-0.310463056600	-3.428608545000	45 H	-2.687728868000	-0.386424910100	-3.405919230000
46 C	-2.003768574000	-2.795448616000	-1.050808283000	46 C	-2.036996262000	-2.832018480000	-0.991524179400
47 H	-2.936306663000	3.158107351000	-1.526229732000	47 H	-2.961560847000	3.173712719000	-1.496276135000
48 H	-1.749241946000	-3.473785938000	-0.226398547800	48 H	-1.829416700000	-3.508129872000	-0.152701927000
49 H	-1.199337394000	-2.895438300000	-1.795439488000	49 H	-1.208775025000	-2.961707716000	-1.704665955000
50 C	-3.039607845000	-1.867050548000	1.830940262000	50 C	-3.029797979000	-1.856227814000	1.883017532000
51 H	-2.890782213000	-1.376174611000	2.802861891000	51 H	-2.910141544000	-1.335949993000	2.843519408000
52 H	-2.433863666000	-2.782933925000	1.843928191000	52 H	-2.392715090000	-2.749966842000	1.924544408000
53 H	-4.105523584000	-2.158486432000	1.762000830000	53 H	-4.083743004000	-2.187142527000	1.809446979000
54 C	-3.351280454000	1.290282041000	1.787255845000	54 C	-3.346869970000	1.310371413000	1.779111497000
55 H	-4.457413109000	1.313605179000	1.745736130000	55 H	-4.448766930000	1.387721653000	1.701942406000
56 H	-2.983213090000	2.322979698000	1.737479598000	56 H	-2.927882378000	2.324668596000	1.743591448000
57 H	-3.063722520000	0.901022300500	2.774549461000	57 H	-3.110855741000	0.905355151300	2.773161912000
[U(IV)Cp* ₂ CN ₃] ⁻¹				[U(IV)Cp* ₂ NC ₃] ⁻¹			
1 U	0.000000000000	0.000000000000	0.498247659300	1 U	0.000000000000	0.000000000000	0.530890778500
2 N	-0.006121805906	-3.596980631000	1.269106245000	2 C	0.012301319410	-3.545588480000	1.061853406000
3 N	0.000000000000	0.000000000000	4.171972244000	3 C	0.000000000000	0.000000000000	4.081818081000
4 N	0.006121805906	3.596980631000	1.269106245000	4 C	-0.012301319410	3.545588480000	1.061853406000
5 C	-0.009639042411	-2.439685628000	1.059658680000	5 N	0.003140854492	-2.383955272000	0.828748276200
6 C	0.000000000000	0.000000000000	2.997217064000	6 N	0.000000000000	0.000000000000	2.896467294000
7 C	0.009639042411	2.439685628000	1.059658680000	7 N	-0.003140854492	2.383955272000	0.828748276200
8 C	-2.667769700000	0.712457745500	0.745934941600	8 C	-2.657116844000	0.719974661500	0.770092334400
9 C	-2.668050356000	-0.714247608400	0.730830216300	9 C	-2.658319790000	-0.708038772100	0.777365803700
10 C	-2.275947090000	-1.143844297000	-0.573170776300	10 C	-2.316890683000	-1.154846233000	-0.537087348300
11 C	-2.019662334000	0.021287448080	-1.361539616000	11 C	-2.077947405000	-0.005562485418	-1.347685065000
12 C	-2.276253382000	1.169769389000	-0.548906811300	12 C	-2.314772174000	1.152357206000	-0.549290486600
13 C	-3.109315756000	1.567249268000	1.896421385000	13 C	-3.077674098000	1.600039448000	1.908817966000
14 H	-4.207119027000	1.682650979000	1.890345956000	14 H	-4.171481773000	1.749516208000	1.901360640000
15 H	-2.658040153000	2.565864142000	1.855182271000	15 H	-2.596923398000	2.584762020000	1.856004983000
16 H	-2.826465783000	1.124382182000	2.860664679000	16 H	-2.807602339000	1.160744176000	2.877877024000
17 C	-3.110530665000	-1.592779751000	1.862876005000	17 C	-3.080251472000	-1.576936010000	1.923845886000
18 H	-2.817501567000	-1.176304580000	2.835698150000	18 H	-2.846473903000	-1.109629338000	2.889053509000
19 H	-2.669213834000	-2.594263470000	1.794874757000	19 H	-2.570447974000	-2.548297252000	1.902805304000
20 H	-4.209326609000	-1.697590965000	1.861140125000	20 H	-4.168670305000	-1.758999353000	1.893938093000
21 C	-2.324782642000	-2.547916531000	-1.097389569000	21 C	-2.407735286000	-2.559213812000	-1.050313443000

22 H	-3.296189704000	-2.737472924000	-1.587310447000	22 H	-3.366636630000	-2.704123019000	-1.578714393000
23 H	-2.188837746000	-3.285727271000	-0.298752673300	23 H	-2.346689957000	-3.293110021000	-0.239695619500
24 H	-1.541846946000	-2.739980285000	-1.844823252000	24 H	-1.602857477000	-2.800192006000	-1.758591963000
25 C	-1.795823978000	0.038190528340	-2.845315079000	25 C	-1.853483917000	-0.013989423750	-2.830915273000
26 H	-1.246112610000	-0.847171464300	-3.192166812000	26 H	-1.290312087000	-0.898607150200	-3.158042188000
27 H	-1.236040911000	0.925774336600	-3.170476317000	27 H	-1.304583077000	0.875102772200	-3.169780338000
28 H	-2.759127166000	0.050792277940	-3.386303545000	28 H	-2.814059476000	-0.025472879730	-3.377141667000
29 C	-2.332184466000	2.583892064000	-1.044242142000	29 C	-2.398653819000	2.551669350000	-1.077650250000
30 H	-1.545072981000	2.799171998000	-1.780269176000	30 H	-1.589873781000	2.782296804000	-1.784893325000
31 H	-2.208236675000	3.305334660000	-0.228740314500	31 H	-2.338065400000	3.294014941000	-0.274711533100
32 H	-3.301726522000	2.775655072000	-1.537050363000	32 H	-3.354547996000	2.694731973000	-1.611881410000
33 C	2.667769700000	-0.712457745500	0.745934941600	33 C	2.657116844000	-0.719974661500	0.770092334400
34 C	2.276253382000	-1.169769389000	-0.548906811300	34 C	2.314772174000	-1.152357206000	-0.549290486600
35 C	2.019662334000	-0.021287448080	-1.361539616000	35 C	2.077947405000	0.005562485418	-1.347685065000
36 C	2.275947090000	1.143844297000	-0.573170776300	36 C	2.316890683000	1.154846233000	-0.537087348300
37 C	2.668050356000	0.714247608400	0.730830216300	37 C	2.658319790000	0.708038772100	0.777365803700
38 C	3.109315756000	-1.567249268000	1.896421385000	38 C	3.077674098000	-1.600039448000	1.908817966000
39 H	4.207119027000	-1.682650979000	1.890345956000	39 H	4.171481773000	-1.749516208000	1.901360640000
40 H	2.658040153000	-2.565864142000	1.855182271000	40 H	2.596923980000	-2.584762020000	1.856004983000
41 H	2.826465783000	-1.124382182000	2.860664679000	41 H	2.807602339000	-1.160744176000	2.877877024000
42 C	2.332184466000	-2.583892064000	-1.044242142000	42 C	2.398653819000	-2.551669350000	-1.077650250000
43 H	3.301726522000	-2.775655072000	-1.537050363000	43 H	3.354547996000	-2.694731973000	-1.611881410000
44 H	1.545072981000	-2.799171998000	-1.780269176000	44 H	1.589873781000	-2.782296804000	-1.784893325000
45 H	2.208236675000	-3.305334660000	-0.228740314500	45 H	2.338065400000	-3.294014941000	-0.274711533100
46 C	1.795823978000	-0.038190528340	-2.845315079000	46 C	1.853483917000	0.013989423750	-2.830915273000
47 H	2.759127166000	-0.050792277940	-3.386303545000	47 H	2.814059476000	0.025472879730	-3.377141667000
48 H	1.246112610000	0.847171464300	-3.192166812000	48 H	1.290312087000	0.898607150200	-3.158042188000
49 H	1.236040911000	-0.925774336600	-3.170476317000	49 H	1.304583077000	-0.875102772200	-3.169780338000
50 C	2.324782642000	2.547916531000	-1.097389569000	50 C	2.407735286000	2.559213812000	-1.050313443000
51 H	3.296189704000	2.737472924000	-1.587310447000	51 H	3.366636630000	2.704123019000	-1.578714393000
52 H	2.188837746000	3.285727271000	-0.298752673300	52 H	2.346689957000	3.293110021000	-0.239695619500
53 H	1.541846946000	2.739980285000	-1.844823252000	53 H	1.602857477000	2.800192006000	-1.758591963000
54 C	3.110530665000	1.592779751000	1.862876005000	54 C	3.080251472000	1.576936010000	1.923845886000
55 H	2.817501567000	1.176304580000	2.835698150000	55 H	2.846473903000	1.109629338000	2.889053509000
56 H	2.669213834000	2.594263470000	1.794874757000	56 H	2.570447974000	2.548297252000	1.902850304000
57 H	4.209326609000	1.697590965000	1.861140125000	57 H	4.168670305000	1.758993535000	1.893398093000
[MN*₂X₃]^q /q=2-,-1- /X=CN,NC /GAZ							
[Ce(III)N*₂CN₃]²⁻				[Ce(III)N*₂NC₃]²⁻			
1 Ce	13.490106620000	22.521990030000	0.130086868000	1 Ce	13.466098780000	22.519003230000	0.156744398900
2 Si	16.183970060000	24.031669560000	1.867627026000	2 Si	16.202908360000	24.02449040000	1.862395869100
3 Si	16.000453060000	24.858052630000	-1.036970627000	3 Si	15.997065980000	24.865717960000	-1.024682780000
4 Si	11.569644710000	20.979705460000	-2.409344487000	4 Si	11.553493270000	20.974560370000	-2.412704224000
5 Si	14.431871110000	20.009631850000	-2.320751726000	5 Si	14.409736670000	20.007919270000	-2.300370781000
6 C	14.608299590000	20.486856770000	1.490309387000	6 N	14.524235740000	20.592630810000	1.420146387000
7 C	11.685862530000	22.601184380000	2.024665652000	7 N	11.746333320000	22.631010720000	1.920673239000
8 C	12.180530040000	24.589817230000	-0.990801766500	8 N	12.289375080000	24.459234590000	-0.970115351800
9 N	15.442192240000	23.927297210000	0.307092500100	9 N	15.445746030000	23.919774630000	0.311563038000
10 N	13.166854510000	21.035876060000	-1.744084474000	10 N	13.140988870000	21.030997440000	-1.729664804000
11 N	15.120157300000	19.57599270000	2.031710109000	11 C	14.958356150000	19.654137750000	1.994709667000
12 N	10.870267570000	22.629245990000	2.871789423000	12 C	10.921811340000	22.684377160000	2.767911719000
13 N	11.654547110000	25.505325190000	-1.510362883000	13 C	11.751158850000	25.400367520000	-1.443529654000
14 C	14.968927980000	23.564149590000	3.242300904000	14 C	15.018705030000	23.525188870000	3.253836382000
15 H	14.075454980000	24.205785870000	3.257827189000	15 H	14.108578690000	24.142866800000	3.278353814000
16 H	15.473633220000	23.672297340000	4.217356126000	16 H	15.532077720000	23.652253430000	4.22054591000
17 H	14.632029430000	22.518055830000	3.176960965000	17 H	14.710751330000	22.470967180000	3.191098854000
18 C	16.799336890000	25.784694750000	2.334174613000	18 C	16.792925900000	25.783871150000	2.341035436000
19 H	17.575395600000	26.163449470000	1.652083936000	19 H	17.547954600000	26.188210970000	1.650208060000
20 H	17.229854790000	25.762303000000	3.349581831000	20 H	17.241844080000	25.758531200000	3.348446402000
21 H	15.969138580000	26.506817850000	2.336243794000	21 H	15.947557770000	26.487979150000	2.366539423000
22 C	17.692250120000	22.887038500000	2.048232925000	22 C	17.735930820000	22.906155160000	2.017799619000
23 H	17.377856760000	21.838449770000	1.935614470000	23 H	17.443309590000	21.854857540000	1.877097928000
24 H	18.159969350000	22.997066110000	3.040931610000	24 H	18.201022110000	22.999565750000	3.013428973000
25 H	18.454768920000	23.100921560000	1.284058291000	25 H	18.494340460000	23.154423600000	1.260103933000
26 C	15.568923480000	26.707623750000	-0.922181641900	26 C	15.513286660000	26.703524490000	-0.912934310300
27 H	14.476536370000	26.822435220000	-0.853927899600	27 H	14.417308250000	26.790587680000	-0.859569545900
28 H	15.911769390000	27.245173160000	-1.822140483000	28 H	15.855975610000	27.254388950000	-1.805026826000
29 H	16.023880640000	27.188378010000	-0.044317531080	29 H	15.943039300000	27.191018610000	-0.025534837900
30 C	17.898015150000	24.760233380000	-1.279242689000	30 C	17.901455220000	24.827309250000	-1.242809859000
31 H	18.449094280000	25.156375750000	-0.412481745200	31 H	18.434450870000	25.239416950000	-0.372316266100
32 H	18.205144820000	25.341487160000	-2.164931301000	32 H	18.196908810000	25.418768620000	-2.126000465000

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	14.495733530000	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	3.960253336000	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	6.835268194000	59 H	13.794073110000	5.560721524000	6.823335959000
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
[U(IV)N⁺₂CN₃]¹⁻				[U(IV)N⁺₂NC₃]¹⁻			
1 U	9.975453302000	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	7.242789579000
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	3.089726674000
12 C	8.238858808000	5.555772963000	4.886235477000	12 N	8.287114587000	5.622317374000	5.003804731000
13 C	8.662837513000	8.330911455000	6.790082339000	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	6.079310513800	18 C	10.703208260000	9.120698887000	6.082675958300
19 H	11.615878380000	9.444656038000	0.093332832670	19 H	11.581897880000	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	12.802870190000	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	2.85382874000
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	4.467137960000	30 C	7.757553770000	11.233882960000	4.459011072000
31 H	7.959500377000	10.985841940000	5.526347611000	31 H	7.925892826000	10.992111889000	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	7.230493650000
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	6.206530147000
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	11.992629250000	10.284085380000	5.671853123000	47 H	12.307626380000	10.353648600000	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	13.979888180000	5.245223140000	5.293421821000

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
[Mcp*₂X₃]^q/q=2-,1- /X=CN,NC/ COSMO							
[Ce(III)Cp*₂CN₃]²⁻				[Ce(III)Cp*₂NC₃]²⁻			
1 Ce	0.000000000000	0.000000000000	0.599294960700	1 Ce	0.000000000000	0.000000000000	0.640904058200
2 N	0.000000000000	0.000000000000	4.414545948000	2 C	0.000000000000	0.000000000000	4.354278349000
3 N	-0.598670714500	3.658093434000	1.603483091000	3 C	-0.357973822400	3.594981095000	1.557398063000
4 N	0.000000000000	0.000000000000	3.238714979000	4 N	0.000000000000	0.000000000000	3.177841918000
5 C	-0.413534165400	2.528389585000	1.332254660000	5 N	-0.248458457700	2.471195795000	1.223175672000
6 C	2.034381957000	0.336330697400	-1.391454542000	6 C	2.032489992000	0.204528477500	-1.382955553000
7 C	2.113706309000	1.513579110000	-0.589827427200	7 C	2.183011932000	1.376916152000	-0.584897381700
8 C	2.610183119000	1.135217715000	0.693581442700	8 C	2.659886789000	0.977248122900	0.700309107700
9 C	2.835036877000	-0.270175294600	0.684584044100	9 C	2.803003142000	-0.438402111100	0.696017771300
10 C	2.477463149000	-0.768393198800	-0.604268040100	10 C	2.416506044000	-0.918358113800	-0.592266161600
11 C	1.761073458000	0.304688677500	-2.866682112000	11 C	1.768631176000	0.185772785100	-2.859545028000
12 H	2.685696042000	0.485553337100	-3.444557270000	12 H	2.709399861000	0.284191792900	-3.432298155000
13 H	1.038365661000	1.073196702000	-3.175064365000	13 H	1.115499240000	1.010915247000	-3.175100695000
14 H	1.365092530000	-0.665871594300	-3.196401232000	14 H	1.292670571000	-0.749074827900	-3.186044875000
15 C	1.892672540000	2.918537588000	-1.068817943000	15 C	2.042784882000	2.788065896000	-1.072497543000
16 H	1.505343033000	3.562424047000	-0.268374513100	16 H	1.744337176000	3.466021481000	-0.263232124700
17 H	1.164822504000	2.960281555000	-1.892076250000	17 H	1.279676287000	2.875963793000	-1.859499143000
18 H	2.832130878000	3.362887920000	-1.445620063000	18 H	2.993785886000	3.155810082000	-1.498931686000
19 C	2.929998307000	2.066423942000	1.825740766000	19 C	3.034059601000	1.892570165000	1.828548357000
20 H	2.786688781000	1.578106848000	2.799474343000	20 H	2.882880630000	1.409409280000	2.803751968000
21 H	2.278458846000	2.949831934000	1.813381870000	21 H	2.421212748000	2.803243976000	1.824538153000
22 H	3.978982640000	2.410659904000	1.773239709000	22 H	4.095951481000	2.191566994000	1.763433010000
23 C	3.436954196000	-1.068859514000	1.803024417000	23 C	3.353533402000	-1.267718420000	1.818388901000
24 H	4.540945734000	-1.047275279000	1.756099342000	24 H	4.457360016000	-1.303702803000	1.782535751000
25 H	3.112295332000	-2.116610954000	1.765389042000	25 H	2.976134132000	-2.297317507000	1.775112273000
26 H	3.136009897000	-0.678008580700	2.784898270000	26 H	3.064483887000	-0.862973642700	2.798462312000
27 C	2.700982157000	-2.166884915000	-1.101226860000	27 C	2.563645826000	-2.327163434000	-1.085206375000
28 H	2.005410950000	-2.430497364000	-1.911417582000	28 H	1.884447135000	-2.538923470000	-1.923538754000
29 H	2.555465507000	-2.907091587000	-0.303602415200	29 H	2.337751653000	-3.057208786000	-0.297381319400
30 H	3.724000679000	-2.288121730000	-1.502010132000	30 H	3.591644264000	-2.515209641000	-1.444787207000
31 N	0.598670714500	-3.658093434000	1.603483091000	31 C	0.357973822400	-3.594981095000	1.557398063000
32 C	0.413534165400	-2.528389585000	1.332254660000	32 N	0.248458457700	-2.471195795000	1.223175672000
33 C	-2.034381957000	-0.336330697400	-1.391454542000	33 C	-2.032489992000	-0.204528477500	-1.382955553000
34 C	-2.113706309000	-1.513579110000	-0.589827427200	34 C	-2.183011932000	-1.376916152000	-0.584897381700
35 C	-2.610183119000	-1.135217715000	0.693581442700	35 C	-2.659886789000	-0.977248122900	0.700309107700
36 C	-2.835036877000	0.270175294600	0.684584044100	36 C	-2.803003142000	0.438402111100	0.696017771300
37 C	-2.477463149000	0.768393198800	-0.604268040100	37 C	-2.416506044000	0.918358113800	-0.592266161600
38 C	-1.761073458000	-0.304688677500	-2.866682112000	38 C	-1.768631176000	-0.185772785100	-2.859545028000
39 H	-2.685696042000	-0.485553337100	-3.444557270000	39 H	-2.709399861000	-0.284191792900	-3.432298155000
40 H	-1.038365661000	-1.073196702000	-3.175064365000	40 H	-1.115499240000	-1.010915247000	-3.175100695000
41 H	-1.365092530000	0.665871594300	-3.196401232000	41 H	-1.292670571000	0.749074827900	-3.186044875000
42 C	-1.892672540000	-2.918537588000	-1.068817943000	42 C	-2.042784882000	-2.788065896000	-1.072497543000
43 H	-1.505343033000	-3.562424047000	-0.268374513100	43 H	-1.744337176000	-3.466021481000	-0.263232124700
44 H	-1.164822504000	-2.960281555000	-1.892076250000	44 H	-1.279676287000	-2.875963793000	-1.859499143000
45 H	-2.832130878000	-3.362887920000	-1.445620063000	45 H	-2.993785886000	-3.155810082000	-1.498931686000
46 C	-2.929998307000	-2.066423942000	1.825740766000	46 C	-3.034059601000	-1.892570165000	1.828548357000
47 H	-2.786688781000	-1.578106848000	2.799474343000	47 H	-2.882880630000	-1.409409280000	2.803751968000
48 H	-2.278458846000	-2.949831934000	1.813381870000	48 H	-2.421212748000	-2.803243976000	1.824538153000
49 H	-3.978982640000	-2.410659904000	1.773239709000	49 H	-4.095951481000	-2.191566994000	1.763433010000
50 C	-3.436954196000	1.068859514000	1.803024417000	50 C	-3.353533402000	1.267718420000	1.818388901000
51 H	-4.540945734000	1.047275279000	1.756099342000	51 H	-4.457360016000	1.303702803000	1.782535751000
52 H	-3.112295332000	2.116610954000	1.765389042000	52 H	-2.976134132000	2.297317507000	1.775112273000
53 H	-3.136009897000	0.678008580700	2.784898270000	53 H	-3.064483887000	0.862973642700	2.798462312000
54 C	-2.700982157000	2.166884915000	-1.101226860000	54 C	-2.563645826000	2.327163434000	-1.085206375000
55 H	-2.005410950000	2.430497364000	-1.911417582000	55 H	-1.884447135000	2.538923470000	-1.923538754000
56 H	-2.555465507000	2.907091587000	-0.303602415200	56 H	-2.337751653000	3.057208786000	-0.297381319400

57 H	-3.7240006790000	2.288121730000	-1.502010132000	57 H	-3.591644264000	2.515209641000	-1.444787207000
[U(III)Cp*₂CN₃]²⁻				[U(III)Cp*₂NC₃]²⁻			
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	1.805035000000
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	1.686606445000	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
[U(IV)Cp*₂CN₃]¹⁻				[U(IV)Cp*₂NC₃]¹⁻			
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	-2.696014000000	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

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