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A Comprehensive Theoretical View of the Bonding in Actinide Molecular Complexes

Laurence Petit,[†,‡] Laurent Joubert,[†] Pascale Maldivi,*[,‡] and Carlo Adamo*[,†]

Laboratoire d'Electrochimie et de Chimie Analytique, CNRS UMR-7575, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, F-75231 Paris Cedex 05, France, and Laboratoire de Reconnaissance Ionique, DRFMC/LCIB (UMR_E 3 CEA-UJF), CEA-Grenoble, 17 rue des Martyrs, F-38054 Grenoble Cedex 9, France

Received October 10, 2005; E-mail: maldivi@drfmc.ceng.cea.fr; carlo-adamo@enscp.fr

Research devoted to the comparative coordination chemistry of trivalent lanthanide (Ln) and actinide (An) is generally related to the management of nuclear spent fuel. Since the main objective is to develop highly selective extractants, the understanding of their chemical interaction with heavy metals is crucial. In this regard, a high selectivity is related to a possible modulation of the covalent character, pointing out the role of d and f orbitals. These orbitals may indeed be involved in the "classical" Dewar−Chatt−Duncanson (D−C−D) orbital model of donation/back-donation.[1]

Numerous experimental and theoretical works[2−9] have been therefore published in the past two decades and have thoroughly discussed low-valent lanthanides and uranium molecular species. For instance, structural and atomic charge analyses suggest that bonds in Ln(III) systems are purely ionic, whereas significant electron back-donation occurs with U(III) when bound to π-acceptor ligands.

Although heavier actinides, such as Am(III), are effectively involved in the spent fuel, the theoretical description of the Am−ligand bonding remains ambiguous.[5,6] This, associated with the lack of experimental data, does not allow a clear-cut vision of covalency effects in Am(III) complexes. There is thus a strong need, because of the major interest of this key element, to apply more sophisticated analyses directly related to the molecular wave function or electron density. Yet, the most commonly used methods rest on arbitrary partitions of the wave function and hence may be sometimes troublesome.[10] Quantum chemical topologies (QCT), such as the electronic density (AIM) or electron localization function (ELF) gradient field analyses, are instead based on more soundly theoretical grounds,[11,13] but their interpretation may appear less straightforward to the chemist.

In this work, we show that whereas standard approaches (i.e., structural, population, and orbital analyses) are relevant for studying Ln(III) and U(III) systems, they fail in describing consistently Am(III) systems. In contrast, QCT analyses clearly point out back-donation in Am complexes, although to a lesser extent than in U(III) analogues. We based our study on model complexes of general formula F_3MCO, with M = Nd, Am, and U. I_3AmCO and I_3UCO were also investigated to ensure the validity of our results. To this end, the already-characterized Nd and U systems[7] were taken as references, and values were compared to available experimental data.[2]

All wave function calculations were performed with the Gaussian 03 package.[14] Since we were not interested in spectroscopic properties, the spin−orbit coupling was not taken into account.[8] As already reported, the DFT route with the BP86[15] functional and a quasi-relativistic pseudopotential scheme indeed provides a proper description of the bonding in rare earth complexes[7,8] and was thus applied through this work. Subsequent QCT calculations were made using the Topmod package[16] (see Supporting Information for more details).

The first step consists of analyzing structural parameters (see Table SI1). As expected, the U−C bond length is much shorter (2.43 Å) than the Nd−C bond (2.88 Å) due to a back-bonding interaction from 5f(U) to π*(CO). It should be stressed that our computed U−C distances are in full agreement with the range of experimental values (2.38−2.48 Å) found in analogous Cp_3UCO-type experimental complexes.[2] These trends are also consistent with the variation of the CO stretching mode, ν_{CO}. While the free carbonyl ν_{CO} is calculated at 2115 cm^{-1}, it reaches 2170 cm^{-1} in F_3NdCO and decreases in F_3UCO (1964 cm^{-1}), the latter being close to experimental data.[2] These variations agree with a weak donation effect from CO in the case of the Nd(III) system, whereas back-donation is predominant in F_3UCO. The behavior of the Am derivatives is less straightforward; the Am−C distance (2.66 Å) in F_3AmCO is indeed intermediate between Nd and U, but the corresponding ν_{CO} (2125 and 2104 cm^{-1}) for F_3AmCO and I_3AmCO respectively closely surrounds that of the free carbonyl.

These structural trends are substantiated by the analysis of the electronic densities (atomic charges and spin populations) reported in Table 1. Back-donation is quite evident for U with a higher atomic charge and a lower spin population (<3, value for the free ion) than for Nd. At the same time, a large negative charge is localized on the carbonyl group for the U complex. In contrast, the F_3AmCO behavior is still unclear with similar charges to the Nd derivative and a metal spin population very close to the free ion value (about 6 au). The iodide derivative, I_3AmCO, computed in the same manner, strengthens this ambiguity. Although they show correct global trends, all methodologies do not give similar results. On one hand, the Mulliken charges[17] are, in general, very low (Table 1) compared to the expected values. The covalent character in such a scheme is indeed often overestimated because of the unweighted partition of the electronic density.[10] On the other hand, NPA,[18] AIM,[11] and ELF[12,13] partition schemes exhibit consistent trends, with small numerical discrepancies. In particular, the close agreement between AIM and ELF charges evolution deserves to be underlined; despite their different theoretical background (electronic density vs electron localization function), they provide very similar descriptions for strongly polarized interactions.

To explain differences between metal centers, Figure 1 compares (n−2)f orbital levels for F_3M species. If close enough to π*(CO), the last alpha occupied orbitals with predominant f character can be involved in the back-donation process. As expected, 4f(Nd) are found to be too contracted, while larger 5f(U) orbitals feature a smaller gap (2.5 eV) with π*(CO), favorable for interactions. The case of Am is again subtle since its 5f levels are energetically close to the Nd ones, thus explaining why classical bonding analysis methods are inadequate for such a compound.

[†] Ecole Nationale Supérieure de Chimie de Paris.
[‡] DRFMC/LCIB.

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Table 1. Comparison of Mulliken, NPA, AIM, and ELF Charge and Spin Population Analyses[a]

	Mulliken			NPA			AIM			ELF		
	q_M	q_{CO}	n_M	q_M	q_{CO}	n_M	q_M	q_{CO}	n_M	q_M	q_{CO}	n_M
F_3−Nd−CO	1.06	0.05	3.14	2.32	0.02	3.00	2.07	0.05	3.02	2.29	0.01	3.00
F_3−Am−CO	1.14	0.13	6.02	2.30	−0.02	5.94	2.09	0.00	5.90	2.27	−0.06	5.88
F_3−U−CO	1.19	−0.09	2.66	2.47	−0.34	2.56	2.40	−0.33	2.48	2.55	−0.48	2.44
I_3−Am−CO	0.30	0.19	6.50	1.73	−0.06	6.38	1.40	−0.07	6.32		−0.10	
I_3−U−CO	0.21	0.08	3.00	1.75	−0.16	2.92	1.59	−0.20	2.82		−0.30	

[a] q_M and q_{CO}, in $|e^-|$, and related atomic spin population ($n_M = n_\alpha - n_\beta$) of the metal (n_M, in e^-). Note that ELF values for iodide compounds are not reported due to technical problems.

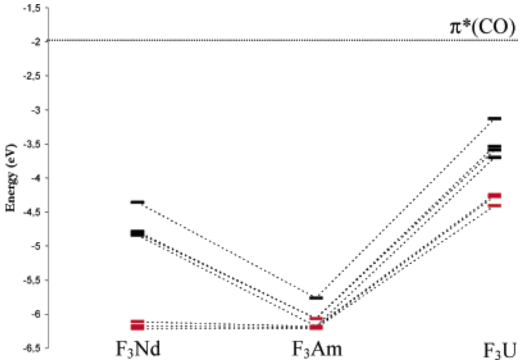

Figure 1. Diagram of (n−2)f (F_3M) orbitals (occupied levels in red) in comparison with the π^*(CO).

Table 2. CO → M Donation and M → CO Back-Donation Contributions (in e^-)

complex	CO→M (AIM)	M→CO (AIM)	CO→M (ELF)	M→CO (ELF)
F_3−Nd−CO	0.06	0.01	0.02	0.01
F_3−Am−CO	0.10	0.10	0.03	0.09
F_3−U−CO	0.17	0.50	0.04	0.52
I_3−Am−CO	0.00	0.07	0.00	0.10
I_3−U−CO	0.08	0.28	0.00	0.30

Beyond the population analysis, the QCT approach leads to a more physical description of metal−ligand interactions (see Supporting Information for further details).[19,20] In particular, the strongly polarized character of M−C interactions is herein confirmed by a low value of the electronic density at the M−C bond critical point (BCP) together with a local charge depletion, that is, $\Delta\rho_{BCP} > 0$ (see Table SI2). This conclusion is supported by the absence of any bonding basin in the ELF partition scheme. Although being mainly ionic, the M−C bond can present donation and back-donation that can be assessed separately (Table 2). With the aim to bridge the gap between the D−C−D orbital model and QCT, we can indeed consider the contributions of the π canonical orbitals involved in the back-donation process to the AIM or ELF topological basins of the CO ligand.[19] Therefore, we can deduce the σ contributions (donation) from the total electronic population of these basins. In this manner, a slight donation (0.06 e^-, AIM) is observed for the Nd(III) complex, while higher donation together with predominant back-donation (up to 0.52 e^-) is revealed in U(III) systems. More interesting is that such effects also appear for the F_3AmCO, where there is a similar amount (0.10 $|e^-|$, AIM) of donation and back-donation. From a topological viewpoint, charge transfer (donation and back-donation) should not be confused with covalency. Physically, only a fraction of electrons is indeed shared between the two atoms, thus really contributing to covalency, while the remaining part is localized on the carbon atom.[20] In this perspective, where covalency is viewed as a “shared interaction”,[20] the delocalization index δ(M,C)[21] provides a quantitative measure of electron pair sharing between M and C atoms. It is worth noting that corresponding values (see Table SI2) are consistent with the previous analysis. Only a weak donation is found for F_3NdCO and logically results in a low value of δ(M,C), that is, 0.20/ 0.14 (AIM/ELF), very close to a purely ionic interaction. In F_3UCO, where back-donation is predominant, δ(M,C) markedly increases up to 0.94/0.96 in F_3UCO and 0.80/0.68 in I_3UCO, the higher back-donation with fluorides being assigned to a better electrostatic interaction between F and M atoms. Low back-donation is still observed in Am(III) complexes, with a delocalization index of 0.40/ 0.32 in F_3AmCO.

Overall, our results well underline how topological and more “classical” orbital analyses provide an overall coherent picture of metal−ligand bonding in heavy-metal complexes. Low magnitude covalent interactions, such as back-donation in Am complexes, are described unambiguously for the first time, with the help of topological approaches. Furthermore, despite their intrinsic differences, ELF and AIM approaches may help to reexamine classical chemical concepts by using descriptors for the analysis of chemical interactions.

Supporting Information Available: Complete refs 3 and 14, computational details, Tables SI1 (structural parameters) and SI2 (topological data). This material is available free of charge via the Internet at http://pubs.acs.org.

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