

Theoretical studies of the structures and electronic properties of $\text{U}(\text{NH}_2)_3$ and $\text{Np}(\text{NH}_2)_3$

P. Jeffrey Hay and Richard L. Martin

Theoretical Division, MS B268, Los Alamos National Laboratory, Los Alamos, NM 87545 (USA)

Abstract

The electronic structure of the model compounds $\text{U}(\text{NH}_2)_3$ and $\text{Np}(\text{NH}_2)_3$ is investigated with the aid of *ab initio* electronic structure techniques. The electronic ground states and equilibrium geometries of these complexes are determined using multiconfiguration SCF techniques. The ground state and low-lying excited states of $\text{U}(\text{NH}_2)_3$ are found to arise from the $(5f)^2 (6d)^1$ and $(5f)^3$ configurations on the metal. The lowest state of the $(5f)_2 (6d)^1$ and $(5f)^3$ configurations are comparable in energy. $\text{Np}(\text{NH}_2)_3$ utilizes the $(5f)^4$ configuration, with the $(5f)^3 (6d)^1$ configuration lying about 2 eV higher in energy. Comparisons are made to the AnL_3 counterparts with $\text{L} = \text{CH}_3$.

1. Introduction

In recent years low-valent actinide complexes have been isolated as synthetic strategies have been devised for stabilizing complexes with low coordination numbers. Traditionally actinides have been encountered in high oxidation states and high coordination numbers ranging from 8 to 12. Members of the AnL_3 family of three-coordinate actinide complexes now include $\text{L} = \text{alkyl}$ [1, 2], amide [3], aryloxy [4] and cyclopentadienide [5] species. Calculations have been performed on several of these compounds using approaches based on density functional theory [6, 7] and multiconfiguration SCF *ab initio* methods [8]. We report here preliminary results on the model amide systems $\text{U}(\text{NH}_2)_3$ and $\text{Np}(\text{NH}_2)_3$, where the electronic properties and equilibrium structures are examined. This work complements our earlier study of the $\text{An}(\text{CH}_3)_3$ series [8].

2. Details of the calculations

Calculations were carried out in a $(6s\ 5p\ 2d\ 4f)$ gaussian basis contracted to $[3s\ 3p\ 2d\ 2f]$ to represent the 6s and 7s, 6p and 7p, 6d and 5f electrons of the U and Np atoms. Relativistic effective core potentials (ECPs) [9] were used to represent the inner core electrons corresponding to the configuration $[\text{Xe}]\ (4f)^{14}\ (5d)^{10}$. For N and H $(9s\ 5p)\text{--}[3s\ 2p]$ and $(4s)\text{--}[2s]$ contracted bases were used [10].

Complete active space self-consistent field calculations (CAS-SCF) were carried out on each molecular species corresponding to the configurations [valence]

$(5f)^3$ or [valence] $(5f)^2 (6d)^1$ for the case of U and $(5f)^4$ or $(5f)^3 (6d)^1$ for the case of Np. All orbitals in the [valence] configuration were held doubly occupied, while all excitations of three electrons in seven 5f orbitals were included for the $(5f)^3$ case. This is referred to as a 3-in-7 CAS-SCF. In the $(5f)^2 (6d)^1$ case all excitations of three electrons in seven 5f orbitals and one 5d orbital were originally included, but only four 5f orbitals and one 5d orbital were actually populated. Subsequent calculations utilized this smaller 3-in-5 CAS-SCF method. Geometries were optimized using analytic gradient techniques. Configuration interaction (CI) calculations were carried out using the CAS-SCF orbitals and improved virtual orbitals (IVOs) for additional excited orbitals. All calculations used the MESA electronic structure programs [11].

3. Results and discussion

We consider first the $\text{U}(\text{NH}_2)_3$ species, which one might expect to be qualitatively similar to the $\text{U}(\text{CH}_3)_3$ species, for which the electronic ground state was found to have the form [valence] $(5f)^3$. The doubly occupied orbitals describing the U–C and C–H bonds, as well as the U 6s and 6p and C 1s core orbitals, are denoted by [valence], and the three unpaired electrons occupying 5f orbitals are denoted by $(5f)^3$. The ground state of $\text{U}(\text{CH}_3)_3$ was not well represented by a single configuration but required a multiconfiguration representation involving excitations of three electrons among all seven 5f orbitals. For the amide analog, it was found that the $(5f)^3$ and $(5f)^2 (6d)^1$ configurations are very com-

parable in energy, and in each case a multiconfiguration description is required. A qualitative molecular orbital scheme for the two molecules is shown in Fig. 1. The 6d orbital is z^2 in character (with some 7s and 7p_z hybridization) where the z-axis lies along the three-fold rotation axis.

From CI calculations including excitations of three electrons into all 5f and 6d orbitals, the $(5f)^3$ state is found to lie 0.3 eV (2400 cm⁻¹) lower in energy (see Table 1). For both the $(5f)^2(6d)^1$ and $(5f)^3$ states, however, there exists a dense manifold of closely spaced states ranging from energies almost degenerate with the lowest state to several eV above the lowest state (Fig. 2). For high-spin $S=3/2$ states, there would be 21 $(5f)^2(6d)^1$ states and 35 $(5f)^3$ states. Starting at 0.6 eV there begins the low-spin $S=1/2$ manifold of states arising from the $(5f)^2(6d)^1$ configuration.

The geometrical parameters of the lowest $(5f)^2(6d)^1$ and $(5f)^3$ states were optimized using analytic MC-SCF

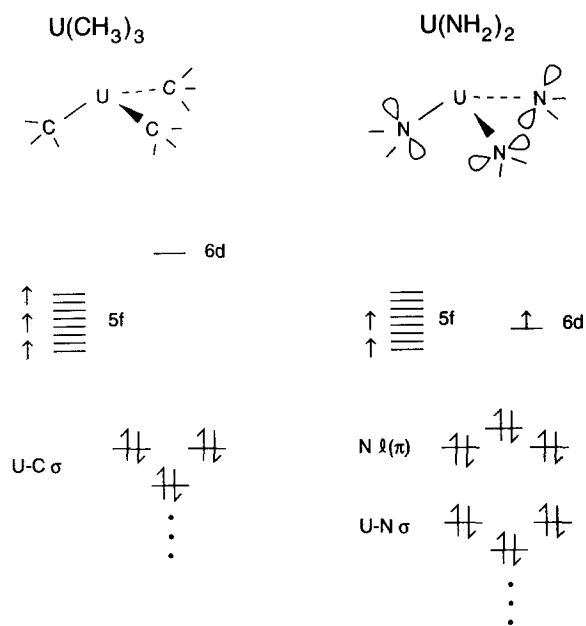


Fig. 1. Schematic molecular orbital diagram for $U(CH_3)_3$ and $U(NH_2)_3$.

TABLE 1. Summary of electronic properties of $An(NH_2)_3$ complexes

Electronic configuration		Energy of lowest state (eV)	(cm ⁻¹)
$U(NH_2)_3$			
$(5f)^2(6d)^1$	$S=3/2$	0.0	0
$(5f)^2(6d)^1$	$S=1/2$	0.57	4600
$(5f)^3$	$S=3/2$	-0.3	-2400
$Np(NH_2)_3$			
$(5f)^4$	$S=2$	0.0	0
$(5f)^3(6d)^1$	$S=2$	2.27	18300

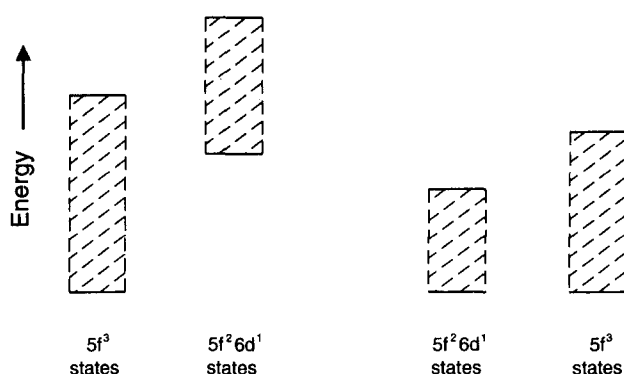


Fig. 2. Schematic diagram for the $(5f)^2(6d)^1$ and $(5f)^3$ states of $U(CH_3)_3$ and $U(NH_2)_3$.

TABLE 2. Calculated and experimental structural parameters for $An(NH_2)_3$ complexes

Parameter	An=U $(5f)^2(6d)^1$	An=U $(5f)^3$	An=Np $(5f)^4$
R(An-N) (Å)	2.242	2.329	2.316
$\angle X-An-N^a$	104.6	95.6	91.7
$\angle N-An-N$ (°)	113.8	119.1	119.9
$\angle An-N-H$ (°)	125.9	126.4	126.4
R(N-H) (Å)	1.007	1.009	1.009
NH ₂ twist angle ^b (°)	57.8	90.0	89.0

^aX denotes the three-fold rotation axis.

^bA twist angle of 0° corresponds to upright NH₂ groups.

gradient techniques and are summarized in Table 2. A pyramidal structure is found for the $(5f)^2(6d)^1$ state with the U-N bonds at an angle of 104.6° from the three-fold axis (where 90° corresponds to a structure with the U-N bonds coplanar). For the $(5f)^3$ state the U-N bonds make an angle of 95.6° from the three-fold axis. In the $(5f)^2(6d)^1$ state the NH₂ groups are twisted about 60° from the upright perpendicular position. The difference in energy between the fully optimized structure and the structure with the U-N bonds all coplanar at an angle of 90° relative to the three-fold axis, however, is less than 1 kcal mol⁻¹. This contrasts with barriers of about 3 kcal mol⁻¹ calculated for the AnL_3 species with L = CH₃.

For the $Np(NH_2)_3$ species, the $(5f)^4$ state is lower by 2.2 eV relative to the excited $(5f)^3(6d)^1$ state, and again a dense manifold of states is associated with each configuration. A nearly planar structure (Table 2) is found for this molecule, with the Np-N bonds bent only 2° out of planarity and the N-H bonds lying in the plane of the molecule.

As one proceeds along the actinide series one finds the 5f levels dropping in energy relative to the 6d levels. At the beginning of the series, one finds the ordering 6d < 5f for low-lying states of Th compounds. By the time one reaches Pu, the opposite ordering 5f < 6d is

found; all of the low-lying states involve only 5f orbitals, and the importance of 6d orbitals has been dramatically reduced. The change in ground state from nearly degenerate $(5f)^3$ and $(5f)^2(6d)^1$ manifolds in $U(NH_2)_3$ compared to $(5f)^4 < (5f)^3(6d)^1$ in $Np(NH_2)_3$ reflects this trend.

The lower energy of the $(5f)^2(6d)^1$ state relative to the $(5f)^3$ state in $U(NH_2)_3$ compared to $U(CH_3)_3$ is not as easily ascribed to a single effect. Schneider *et al.* [7] found considerable interaction between the 5f manifold and the N π lone pairs that could account for the destabilization of the $(5f)^3$ state, but the present calculations do not show a significant interaction. A more extensive analysis of the bonding and geometries of AnL_3 species will appear in subsequent papers.

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