would be the ground state.[19,20]

Concluding Remarks

In this paper a unique linear trinuclear Fe(II) compound is described that can provide a suitable basis for further research, especially on the electronic properties of such a trinuclear system. The mechanism of the spin transition in the crystalline state is not yet understood. Sorai and Seki[21,22] have suggested, on the basis of precise heat capacity measurements on $[Fe(phen)_2(NCS)_2]$, that a cooperative spin transition takes place in this system through a significant coupling between the electronic state and the vibrational modes of the lattice surroundings. The suggestion of a cooperative spin transition has been well supported by the metal dilution studies on $[Fe(2\text{-pic})_3]Cl_2\cdot C_2H_5OH$ by Sorai et al.[23] and Gütlich et al.[24] The different chemical environments in the outer two metal ions and in the central one allow the selective substitution of the terminal Fe atoms by for instance Mn or Zn. This may give more information on the different mechanisms of the cooperative spin transitions, as well as allowing the detailed study of the magnetic exchange through the triazole ligand. These investigations are in progress.

Acknowledgment. The magnetic susceptibility measurements between 80 and 300 K were carried out by B. van der Griendt. The investigations were supported by the Netherlands Organization for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. $[Fe_3(Ettrz)_6(H_2O)_6](CF_3SO_3)_6$, 84823-79-0.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters at 300 and 105 K (10 pages). Ordering information is given on any current masthead page.

---

(21) Sorai, M.; Seki, S. *J. Phys. Chem. Solids* **1974**, *35*, 555.
(22) Sorai, M.; Seki, S. *J. Phys. Soc. Jpn.* **1972**, *33*, 575.
(23) Sorai, M.; Ensling, J.; Gütlich, P. *Chem. Phys.* **1976**, *18*, 199.
(24) Gütlich, P.; Link, R.; Steinhauser, H. G. *Inorg. Chem.* **1978**, *17*, 2509.

Notes

Contribution from the Departments of Chemistry,
The Ohio State University, Columbus, Ohio 43210,
and University of Toronto, Toronto, Ontario M5S 1A1, Canada

Xα–SW Calculations for Naked Actinide Dimers: On the Existence of ϕ Bonds between Metal Atoms

Bruce E. Bursten*[†] and Geoffrey A. Ozin[‡]

Received February 24, 1984

Multiple bonding in dimeric transition-metal systems involves diatomic interactions between the available d orbitals on each atom.[1] With the use of d orbitals, for which $l = 2$, these interactions can be of σ ($m_l = 0$), π ($m_l = 1$), or δ ($m_l = 2$) diatomic symmetry, leading to bond orders as high as 6 in naked metal dimers such as Mo_2.[2] It occurred to us that dimers of the actinide elements would likely involve diatomic interactions between f orbitals. As shown in Figure 1, these not only could generate bonds of σ, π, and δ symmetry but also could lead to ϕ bonds (between f orbitals with $m_l = 3$) as well. The possibility of "ϕ-back-bonding" in actinocene complexes has been successfully investigated with use of nonrelativistic and relativistic Xα–SW molecular orbital calculations,[3,4] and in this note we report preliminary Xα–SW calculations on the naked actinide dimers U_2 and Np_2 to demonstrate for the first time the existence of ϕ bonds between metal atoms.[5]

In order for ϕ bonds to exist in actinide dimers, it is apparent that two conditions must be satisfied. First, since the ϕ bond is expected to be the weakest of the f–f interactions, the 5f orbitals must be low enough in energy that the ϕ bonds are lower in energy than the 6d–6d bonding interactions. We were encouraged in this regard by our studies of organouranium(IV) complexes,[15] in which the 5f orbitals are greatly stabilized relative to the 6d and 7s orbitals. Second, the diatomic interactions must be strong enough to give an energetic separation between the ϕ bonds and antibonds. Although the 5f orbitals in higher oxidation state actinide complexes are quite contracted, it was our feeling that this might not be the case for U(0) and Np(0) and that appreciable ϕ interaction might result.

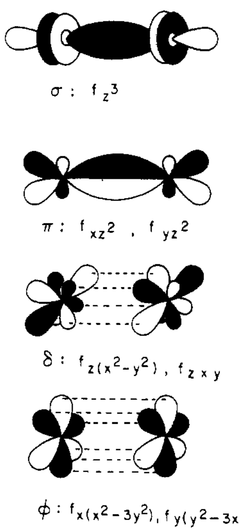

Figure 1. Qualitative diagram of f–f diatomic bonding interactions. The f orbitals that may form each type of bond are indicated below each.

[†] The Ohio State University.
[‡] University of Toronto.

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.
(2) Bursten, B. E.; Cotton, F. A.; Hall, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 6348-9.
(3) Rösch, N.; Streitwieser, A., Jr. *J. Organomet. Chem.* **1978**, *145*, 195-200.
(4) Rösch, N.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 7237-40.
(5) Calculational details: A bond length of 2.2 Å was assumed for both U_2 and Np_2; this is ca. 0.6 and 0.4 Å shorter than the M–M distances in elemental U[6,7] and Np[8], respectively. Xα–SW calculations were performed in a fashion analogous to that for previous calculations on metal dimers[9-13] using an α value of 0.692 for both U and Np. A Watson sphere[14] with charge 2+ was used in order to stabilize unoccupied orbitals.
(6) Jacob, C. W.; Warren, B. E. *J. Am. Chem. Soc.* **1937**, *59*, 2588-91.
(7) Sturcken, E. F. *Acta Crystallogr.* **1960**, *13*, 852.
(8) Zachariasen, W. H. *Acta Crystallogr.* **1952**, *5*, 660-4.
(9) Norman, J. G., Jr.; Kolari, H. J.; Gray, H. B.; Trogler, W. C. *Inorg. Chem.* **1977**, *16*, 987-93.
(10) Klotzbücher, W.; Ozin, G. A.; Norman, J. G., Jr.; Kolari, H. J. *Inorg. Chem.* **1977**, *16*, 2871-7.

0020-1669/84/1323-2910$01.50/0 © 1984 American Chemical Society

Table I. Nonrelativistic Xα–SW Valence Molecular Orbitals for Np_2[d]

		sphere distribn[a]			Np contribns[b]			
orbital	ϵ, eV	Np	INT	OUT	s	p	d	f
$2\delta_u$	−7.16	38	32	31	-	-	84	16
$3\sigma_g$	−7.37	41	0	59	5	0	84	11
$3\pi_u$	−8.50	31	14	55	-	5	62	33
$2\pi_u$	−9.92	32	40	29	-	15	73	12
$\boldsymbol{\sigma_u}$	−10.11	86	7	7	0	0	10	89
$2\delta_g$	−10.15	39	35	26	-	-	53	47
$\boldsymbol{\pi_g}$	−10.16	92	4	4	-	0	6	94
$\boldsymbol{\delta_u}$	−10.57	93	4	3	-	-	2	98
$\boldsymbol{\phi_g}$	−10.99	95	4	1	-	-	-	100
$2\sigma_g$	−11.02	38	28	34	6	0	9	85
$\boldsymbol{\phi_u}$[c]	−11.29	92	7	1	-	-	-	100
$\boldsymbol{\delta_g}$	−12.06	81	16	3	-	-	7	93
$\boldsymbol{\pi_u}$	−12.98	96	2	2	-	1	13	86
$\boldsymbol{\sigma_g}$	−13.98	78	15	7	0	1	21	78

[a] Percent contributions from inside the Np atomic sphere, in the intersphere region (INT), and outside the outer sphere (OUT). [b] Percent contribution of partial waves centered at the Np atoms. A dash indicates a contribution of zero due to symmetry. [c] Highest occupied molecular orbital. [d] Bold-faced orbitals are those arising from primarily 5f–5f interactions.

The nonrelativistic Xα–SW molecular orbitals for Np_2 are tabulated in Table I. It is seen that the 5f–5f interactions dominate the lower valence MOs and that, assuming it is closed-shell, the molecule has a valence configuration of $\sigma_g^2\pi_u^4\delta_g^4\phi_u^4$, i.e., a septuple bond consisting of one σ, two π, two δ, and two ϕ bonds. The nonrelativistic results for U_2 parallel those of Np_2, leading to a $\sigma_g^2\pi_u^4\delta_g^4\phi_u^2$ configuration. At higher energy are found the antibonding counterparts (ϕ_g, δ_u, π_g, and σ_u) of the 5f–5f bonds. The amount of s, p, and d character in these eight orbitals is small even when allowed by symmetry. The more diffuse 6d-based orbitals appear at higher energy. Also evident in both calculations is the $2\sigma_g$ orbital, which is only slightly higher in energy than the ϕ_u orbital. This orbital is quite diffuse and consists of a mix of metal $5f_{z^3}$ partial waves with an s partial wave on the outer sphere. It is not yet clear whether or not this orbital is an artifact of the calculational procedures. Upon the inclusion of relativistic corrections,[16] this orbital drops below the δ_g orbital, but a transfer of two electrons from the ϕ_u to the $2\sigma_g$ orbital results in destabilization of the latter to such an extent that it should no longer be occupied. Despite these orbital instabilities, the relativistic corrections do not significantly change the relative ordering or energetics of the eight 5f–5f bonding and antibonding orbitals, and with the exception of the $2\sigma_g$ orbital discussed above, the 5f–5f bonding orbitals are the lowest valence orbitals of the molecules.

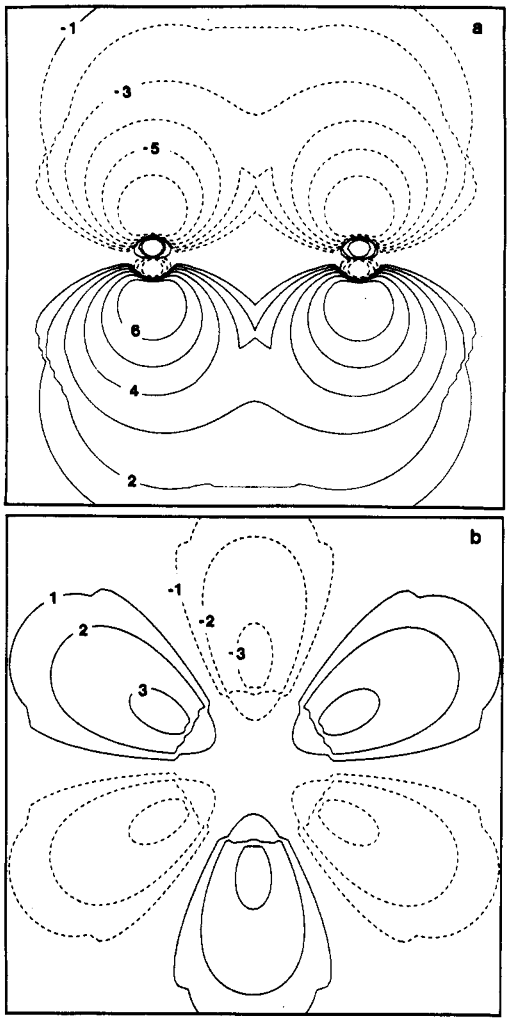

Figure 2. Contour diagrams of the ϕ_u orbital of Np_2 from the nonrelativistic Xα–SW calculation: (a) a plane containing the molecule; (b) a plane bisecting the molecule. The contour values are ±1, ±2, ±3, ±4, ±5, ±6 = ±0.005, ±0.010, ±0.020, ±0.040, ±0.080, ±0.160, respectively.

Contour plots of one of the ϕ_u orbitals of Np_2 from the converged nonrelativistic calculation are shown in Figure 2. As expected, the ϕ_u orbital consists of two "face-to-face" $f_{x(x^2-3y^2)}$ orbitals. The interaction of these is apparently quite weak; in both the nonrelativistic and the relativistic calculations on U_2 and Np_2, the energetic separation of the ϕ_u and ϕ_g orbitals is ca. 0.3 eV. For Np_2 this may mean that $\sigma_g^2\pi_u^4\delta_g^4\phi_u^2\phi_g^2$, or some other excited, higher spin configuration, might be preferred over the assumed closed-shell configuration. For U_2, however, the spin quantum number cannot be increased by promoting a ϕ_u electron to the ϕ_g orbital, and it may be the case that the $\sigma_g^2\pi_u^4\delta_g^4\phi_u^2$ configuration is preferred, albeit slightly, over one in which the ϕ bond is destroyed. The bond energy of U_2 has been estimated to be 218 ± 21 kJ/mol,[17] but the ϕ bond, if it exists, would doubtless make little or no contribution to this, just as the δ bonds of naked transition-metal dimers contribute little or nothing to the bond strengths of those systems.[12] It is also apparent that if U_2 is open shell, spin–orbit effects will be sizable,[18] and we are currently investigating the magnitudes of these effects.

In summary, it appears likely that the bonding in U_2 and Np_2 involves 5f–5f interactions, leading to the intuitive orbital energetic ordering $\sigma_g < \pi_u < \delta_g < \phi_u < \phi_g < \delta_u < \pi_g < \sigma_u$. Further studies are necessary to ascertain the dependence of the 5f–5f bonding upon the bond lengths of the molecules and upon the inclusion of spin–orbit and other relativistic effects, and these are currently in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Natural Sciences and Engineering Research Council of Canada for partial support of this research.

Registry No. U_2, 37205-83-7; Np_2, 76971-78-3.

---

(11) Ozin, G. A.; Huber, H.; McIntosh, D.; Mitchell, S.; Norman, J. G., Jr.; Noodleman, L. *J. Am. Chem. Soc.* **1979**, *101*, 3504–11.

(12) Bursten, B. E.; Cotton, F. A. *Symp. Faraday Soc.* **1980**, *No. 14*, 180–93.

(13) Nagarathna, H. M.; Montano, P. A.; Naik, V. M. *J. Am. Chem. Soc.* **1983**, *105*, 2938–43.

(14) Watson, R. E. *Phys. Rev.* **1958**, *111*, 1108.

(15) Bursten, B. E.; Fang, A. *J. Am. Chem. Soc.* **1983**, *105*, 6495–6.

(16) Wood, J. H.; Boring, A. M. *Phys. Rev. B*: *Condens. Matter* **1978**, *18*, 2701–11.

(17) Gingerich, K. A. *Symp. Faraday Soc.* **1980**, *No. 14*, 109–25.

(18) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271–5.