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Actinide Chemistry

Polyimido Uranium(IV) Clusters: Imidometalates with an $M_7(\mu_3\text{-}N)_6(\mu_2\text{-}N)_6$ Core Analogous to the Anderson-Type Polyoxometalate Motif**

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Much recent work has been directed to the construction of polyoxo actinide clusters, which are of broad interest for their relevance in the nuclear industry and the natural environment as well as in the field of materials and catalysis.[1–4] The variety and scope of such polynuclear compounds should be considerably enlarged by replacing the oxo group O^{2-} with the isoelectronic imido group RN^{2-}. Novel structures, reactions, and physicochemical properties should emerge, which would be strongly influenced and controlled by the nature of the organic substituent R.[5–7]

In stark contrast to the large number of imido complexes of the main groups and d transition metals, such compounds of the f elements are much less common. In the lanthanide series, there is only one terminal imido complex,[8] while the few others are di- and tetranuclear compounds in which the NR groups act as bridging or capping ligands.[9] The inverse situation is observed with the imido uranium compounds, since several mononuclear bis(cyclopentadienyl) complexes in the oxidation states +4, +5, or +6 were prepared[10] as well as the imido analogues of the uranyl ion, $[U(NR)_2]^{2+}$ and $[U(NR)(O)]^{2+}$.[11] Structural comparisons, reactivity studies, and theoretical calculations indicate that the U–N bonds have a more covalent character than the corresponding U–O bonds.[11] Polynuclear uranium imido complexes are scarce; they are limited to a few dimeric, dinuclear derivatives,[12] such as $[\{(MeC_5H_4)_2U(\mu\text{-}NR)\}_2]$ (R = Ph or $SiMe_3$).[12a] Herein we present the synthesis and X-ray crystal structures of novel uranium clusters in which four or seven metal centers are linked by μ_2- and μ_3-imido ligands and which exhibit unprecedented frameworks.

Our initial objective was to prepare an imido analogue of a polyoxo uranium cluster containing the $U_6(\mu_3\text{-}O)_8$ core, in which the uranium atoms were found in the +4 and/or +5 oxidation state,[2,4] by following the strategy developed by Power and co-workers, that is, the introduction of the RN^{2-} group by means of the imide transfer Grignard reagent $[\{PhNMg(thf)\}_6]$.[13] Reaction of six equivalents of UCl_4 and 8/6 equivalents of the hexameric magnesium imide in pyridine at 20 °C led to the reproducible formation of the tetranuclear $[U_4(NPh)_6Cl_4(py)_8]$ (**1**, py = pyridine), which was deposited as dark brown crystals of the solvate **1**·2 py upon slow diffusion of pentane into the pyridine solution; dark brown crystals of **1**·2 py and $[U_4(NPh)_6Cl_4(py)_6]$ (**2**) were obtained after two days when the reaction mixture was heated under reflux. Changing the pyridine solvent to thf has a dramatic influence on both the aggregation process and the structure of the products, since brown crystals of the heptanuclear compounds $[Mg(thf)_5][U_7(NPh)_{12}Cl_6(thf)_6]$ (**3**) and $[Mg_2Cl_3(thf)_6][U_7(NPh)_{12}Cl_5(thf)_6]$·2 thf (**4**·2 thf) were deposited from the orange solution after heating at reflux for three days. The tetra- and heptanuclear complexes were synthesized on a preparative scale by using the right stoichiometry of reactants, according to Equations (1) and (2). The crystalline products were quickly separated from the hot solution by filtration, thus avoiding crystallization of $MgCl_2$ at lower temperature; desolvation of the crystals occurred upon drying under vacuum, affording brown powders whose elemental analyses correspond to the formulas $[U_4(NPh)_6Cl_4(py)_7]$ and $[U_7(NPh)_{12}Cl_6(thf)_6Mg]$ in 20 and 64 % yield, respectively.

$$4\,UCl_4 + [\{PhNMg(thf)\}_6] \xrightarrow[100\,^\circ C]{\text{pyridine}} [U_4(NPh)_6Cl_4(py)_n] + 6\,MgCl_2 \qquad (1)$$

$$\mathbf{1}\; n = 8$$

$$\mathbf{2}\; n = 6$$

$$7\,UCl_4 + 2\,[\{PhNMg(thf)\}_6] \xrightarrow[100\,^\circ C]{\text{thf}} \underset{\mathbf{3}}{[Mg(thf)_5][U_7(NPh)_{12}Cl_6(thf)_6]} + 11\,MgCl_2 \qquad (2)$$

The air- and moisture-sensitive complexes **1**–**4** were characterized by their X-ray crystal structures (see below). In the ^1H NMR spectra, no signals were observed in pyridine for the heptanuclear compounds or for the poorly soluble tetranuclear complexes. This lack of signals in the NMR spectra was also noticed with the polyoxo uranium clusters $[U_6O_{13}(1,2,4\text{-}tBu_3C_5H_2)_4(bpy)_2]$[3] and $[U_6O_8(OTf)_8(py)_8]$[4] (bpy = 2,2′-bipyridine, OTf = $CF_3SO_3^-$) and can be explained by the fluxionality of the complexes related to rapid ligand exchange reactions or disruption of the clusters in solution. IR spectroscopy is of limited utility in imido chemistry, since the ν(MN) frequencies are strongly coupled to those of other ligands in the complex, and no general trend has emerged in the assignment of terminal and bridging imido groups.[7] The IR spectra of **1** and of $[U_7(NPh)_{12}Cl_6(thf)_6Mg]$ show strong bands characteristic of the ν(C=C) stretching mode in the aromatic region at 1575 and 1578 cm^{-1}, respectively.[9] The other frequencies lie in the 400–1240 cm^{-1} region.

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Views of the centrosymmetric tetranuclear clusters **1** and **2** are shown in Figures 1 and 2, respectively; the structures differ by the distinct number of pyridine molecules coordinated to U1 (three in **1** and two in **2**) and the presence in **2** of an additional $U1\cdots C_{ipso}$ interaction. Both complexes possess a central U_4N_6 core that can be described as a "deck chair" or as two *seco*-heterocubes sharing a U_2N_2 face. The U1, U2, and U2′ atoms are capped by the μ_3-N1Ph ligand, while the μ_2-N2Ph and μ_2-N3Ph ligands are in bridging position between U1 and U2 or U2′. This geometry of the U_4N_6 framework, which corresponds to that of the polyoxo $M_4(\mu_2\text{-}O)_4(\mu_3\text{-}O)_2$ core in a series of antimony compounds of general formula $[Sb_4O_6X_8]$[14] and in the uranium complex $[U_4O_6Cp^*{}_2Cl_4(NHSPh)_6]$ ($Cp^* = C_5Me_5$),[15] is quite rare for imido complexes. To the best of our knowledge, it is limited to a few heteronuclear compounds with the $M_2M'_2N_6$ core (M = Sn and M′ = Si; M = Te and M′ = Li or In).[6,16] In **1** and **2**, the μ_3-N1Ph and μ_2-N2Ph ligands exhibit contacts as short as approximately 2.95 Å between their *ipso* carbon atoms C1 and C7 and the U2 atoms, while a short distance of 2.815(4) Å is found only in **2** between U1 and the *ipso* carbon C13 of the μ_2-N3Ph ligand. This supplementary $U\cdots C_{ipso}$ interaction in **2**, by comparison with **1**, should compensate the dissociation from U1 of one of the three pyridine ligands. The presence of $U\cdots C_{ipso}$ interactions render the corresponding U-μ_2-NPh-U bridges unsymmetrical, with two unequal U−N bonds of 2.17(2) and 2.33(3) Å (average values). These values are quite similar to those of 2.156(8) and 2.315(8) Å in the dimeric complex $[\{(MeC_5H_4)_2U(\mu\text{-}NPh)\}_2]$, for which a $U\cdots C_{ipso}$ separation of 3.09(1) Å was measured.[12a] In contrast, the U1-N3-U2′ bridge in **1** is symmetrical, with an average U−N bond length of 2.26(3) Å, which can be compared with that of 2.22(1) Å in $[\{(MeC_5H_4)_2U(\mu\text{-}NSiMe_3)\}_2]$.[12a] The average U−N bond length involving the μ_3-N1Ph ligand, 2.40(4) Å for both complexes, is expectedly larger (by ca. 0.15 Å) than that of the μ_2-NPh groups. However, the μ_3-N1Ph ligation is symmetrical in **1**, with a mean U−N1 bond length of 2.395(12) Å, while in **2** the U1−N1 distance of 2.328(4) Å is significantly smaller than the average U2−N1 and U2′−N1 bond lengths of 2.439(6) Å.

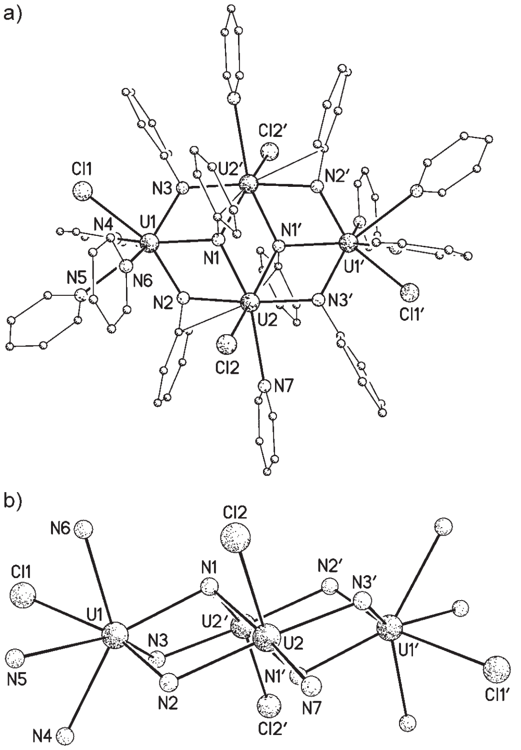

Figure 1. Two views of **1** with carbon atoms omitted in (b). Symmetry code: ′ = 2−*x*, 2−*y*, −*z*. Selected bond lengths [Å] and angles [°]: U1–N1 2.398(6), U1–N2 2.190(6), U1–N3 2.282(6), U1–N4 2.631(6), U1–N5 2.730(6), U1–N6 2.669(6),U1–Cl1 2.715(2), U2–N1 2.379(6), U2–N1′ 2.409(6), U2–N2 2.309(6), U2–N3′ 2.231(6), U2–N7 2.772(6), U2–Cl2 2.7219(17); N1-U1-N2 74.9(2), N1-U1-N3 74.82(19), N1-U2-N1′ 75.0(2), N1-U2-N2 73.2(2), N1′-U2-N3′ 75.5(2), N2-U2-N3′ 172.7(2).

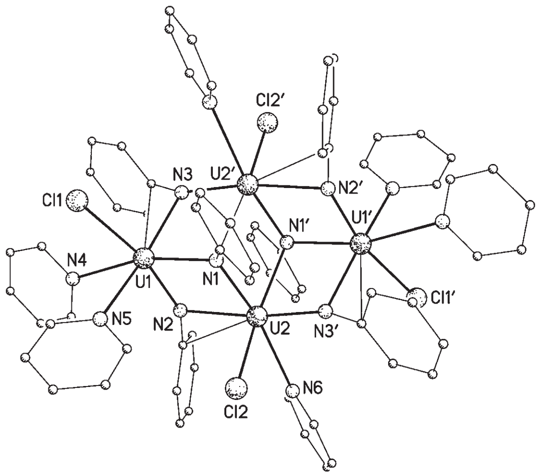

Figure 2. View of **2**. Symmetry code: ′ = 2−*x*, 1−*y*, 1−*z*. Selected bond lengths [Å] and angles [°]: U1–N1 2.328(4), U1–N2 2.149(4), U1–N3 2.302(4), U1–N4 2.625(4), U1–N5 2.648(4), U1–Cl1 2.7383(13), U2–N1 2.433(4), U2–N1′ 2.444(4), U2–N2 2.373(4), U2–N3′ 2.170(4), U2–N6 2.693(4), U2–Cl2 2.7161(12); N1-U1-N2 78.76(14), N1-U1-N3 76.09(13), N1-U2-N1′ 76.99(14), N1-U2-N2 72.57(13), N1′-U2-N3′ 76.16(13), N2-U2-N3′ 167.96(15).

The U−N(py) bond lengths vary from 2.625(4) to 2.772(6) Å and average 2.70(5) and 2.66(3) Å in **1** and **2**, respectively; these values are at the upper limit of those reported for other U^{IV} complexes, which are in the range 2.54–2.70 Å.[17] The U−Cl bonds, which average 2.723(9) Å in both complexes, are unexceptional.

Views of the anion $[U_7(NPh)_{12}Cl_6(thf)_6]^{2-}$ in **3** are shown in Figure 3. The heptanuclear complex has crystallographically imposed S_6 point symmetry. The central U2 atom is linked to the six uranium centers U1 through six μ_3-N1Ph ligands, and the hexagonal skeleton of U1 atoms is held by six peripheral μ_2-N2Ph groups. This structure can also be described as the association of two $U_4(NPh)_6$ moieties sharing a common edge (for example N1-U2-N1C) and with two additional linkages by μ_2-NPh groups (U1 and U1E by N2Ph, and U1B and U1C by N2CPh).

While homo- and heterometallic compounds containing the symmetrical M_7O_{12}[18] or $M_6M'O_{12}$ core are well documented, in particular the hetero-polyoxometalates of the Anderson type,[19] **3** is the first complex exhibiting the

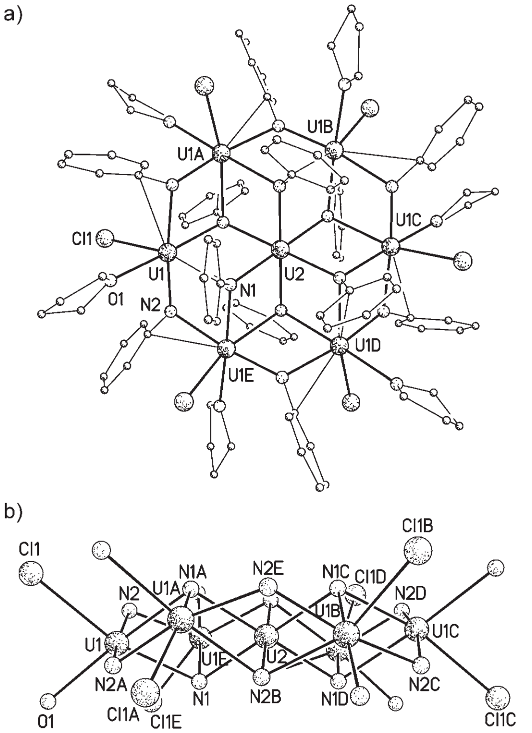

Figure 3. Views of the anion $[\mathrm{U_7(NPh)_{12}Cl_6(thf)_6}]^{2-}$ in **3** along (a) and perpendicular to (b) the S_6 axis. The labels A–E represent the positions generated by the symmetry axis. Carbon atoms have been omitted in view (b). Selected bond lengths [Å] and angles [°]: U1–N1 2.441(8), U1–N1A 2.486(8), U1–N2 2.201(9), U1–N2A 2.283(8), U1–O1 2.481(9), U1–Cl1 2.724(3), U2–N1 2.323(8); N1-U1-N1A 74.6(4), N1-U1-N2 75.0(3), N2-U1-N2A 167.7(3), N1-U1-Cl1 159.4(2), N1A-U1-O1 174.7(3), N1-U2-N1A 80.0(3), N1-U2-N1D 100.0(3).

analogous $\mathrm{M_7(\mu_3\text{-}N)_6(\mu_2\text{-}N)_6}$ structural motif. No uranate derivative involving an anionic $\mathrm{U_7O_{12}}$ core has been reported.[1f] Short contacts of 2.959(8) and 3.040(11) Å are present between U1 and the *ipso* C1 and C7 atoms of the μ_3-N1Ph and μ_2-N2Ph ligands. The U-N2-U bridge, with U–N bonds of 2.201(9) and 2.283(8) Å, is more symmetrical than in **1** and **2**, while the μ_3-N1Ph ligation has the same geometry as in **2**; the U2–N1 bond of 2.323(8) Å is approximately 0.15 Å shorter than the U1–N1 distances. The average U–μ_2-N and U–μ_3-N distances of 2.24(4) and 2.42(7) Å are similar to those in **1** and **2**.

The structure of the anion $[\mathrm{U_7(NPh)_{12}Cl_5(thf)_6}]^-$ in **4**, represented in Figure 4, exhibits the same $\mathrm{U_7(\mu_3\text{-}N)_6(\mu_2\text{-}N)_6}$ core as **3** but is devoid of any even approximate symmetry element. Each of the atoms U1–U5 is in close contact (less than or equal to 3.05 Å) with an *ipso* carbon atom of a μ_3-NPh ligand, except U2, which interacts with the *ipso* atom C43 of the μ_2-N8Ph group. In contrast, U6 is bound to the two neighboring μ_3-NPh ligands, which adopt an η^3 ligation mode involving the N, C_{ipso}, and one of the C_{ortho} atoms; the interaction with the N5Ph group (U–C_{ipso} 2.772(8) Å and U–C_{ortho} 2.857(8) Å) is much stronger than the corresponding interaction with the N6Ph ligand (U–C_{ipso} 3.040(8) Å and U–C_{ortho} 3.036(8) Å). This η^3 bonding mode, which, to the best of our knowledge, is unprecedented for the arylimide ligand, is reminiscent of that known for some benzyl, arylthiolate, and arylamide complexes.[20] The η^3 coordination of two NPh groups to U6 is likely a compensation for the missing chloride ligand on this metal center. The ligation of the μ_3-NPh ligands is more symmetrical than in **3**, since the average distance of 2.38(2) Å between the central U7 and μ_3-N atoms is much closer to that of 2.42(4) Å between the peripheral U and μ_3-N atoms; however, the average U–μ_2-N and U–μ_3-N distances are similar to those in **3**. The neighboring U···U separations average 3.740(6) Å in **3** and 3.72(3) Å in **4,** with variations from 3.6628(5) to 3.7669(5) Å for the latter compound.

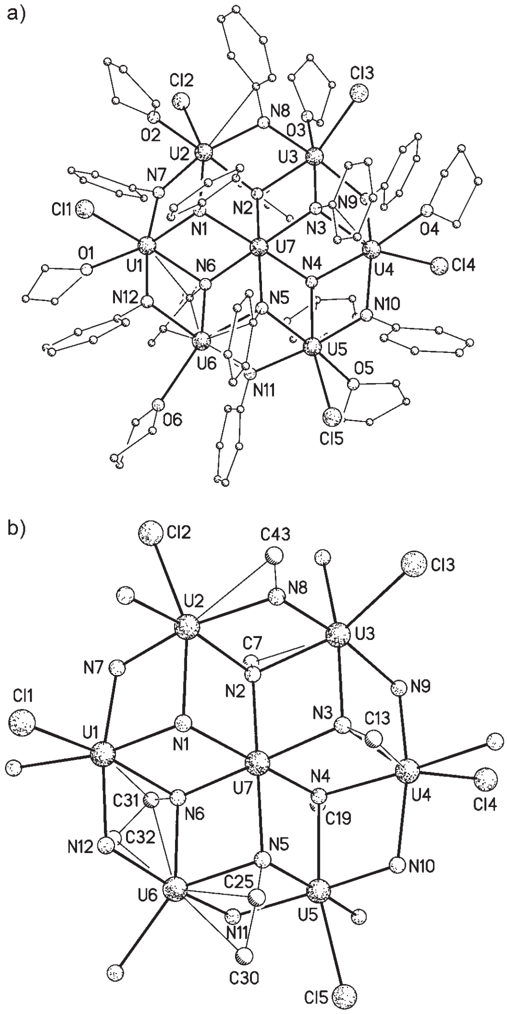

Figure 4. Views of the anion $[\mathrm{U_7(NPh)_{12}Cl_5(thf)_6}]^-$ in **4**. In view (b), only the *ipso* and *ortho* carbon atoms interacting with the metal centers are represented. Average bond lengths [Å]: ⟨U–μ_2N⟩ 2.26(4), ⟨U–μ_3N⟩ 2.41(4), ⟨U–O⟩ 2.52(3), ⟨U–Cl⟩ 2.714(17).

The formation of these polynuclear complexes demonstrates the potential of the imido ligand to expand the molecular chemistry of actinides with attractive perspectives for the synthesis of clusters. Further work, including theoretical studies, is in progress to extend the variety of imido polynuclear compounds of uranium either by changing the nature of R in RN^{2-}, the ancillary ligands, and the oxidation state of the metal center. Of interest is the generalization of this work to the whole f-element series. Current investigations with trivalent lanthanides reveal the formation of clusters with novel shapes; these results on the 4f elements will be reported in a forthcoming paper.

Experimental Section

All manipulations were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk vessel and vacuum line techniques or in a glove box.

$[U_4(NPh)_6Cl_4(py)_n]$ ($n = 8$ **1**, $n = 6$ **2**): A flask was charged with UCl_4 (200 mg, 0.52 mmol) and PhNMg(thf) (149 mg, 0.79 mmol), and pyridine (15 mL) was condensed in. After stirring for 7 h at 100 °C, brown crystals of **1** and **2** were deposited from the red-brown solution; the quantity of crystals increased after further heating for two days at 100 °C. The crystals were quickly separated from the warm solution by filtration and dried under vacuum, affording a brown powder analyzing as $[U_4(NPh)_6Cl_4(py)_7]$ (59 mg, 0.025 mmol, 20 %). Elemental analysis (%) calcd for $C_{71}H_{65}Cl_4N_{13}U_4$: C 38.53, H 2.98, N 8.27; found: C 38.65, H 2.99, N 8.42. IR: $\tilde{\nu} = 1575$ (s), 1242 (vs), 1216 (vs), 1166 (m), 1142 (w), 1068 (w), 1036 (s), 1025 (m), 868 (vs), 825 (w), 800 (w), 774 (m), 753 (s), 692 (vs), 619 (w), 603 (m), 535 (s), 514 (s), 478 cm^{-1} (s).

$[Mg(thf)_5][U_7(NPh)_{12}Cl_6(thf)_6]$ **3**: A flask was charged with UCl_4 (200 mg, 0.52 mmol) and PhNMg(thf) (169.3 mg, 0.90 mmol), and thf (15 mL) was condensed in. The color of the suspension rapidly turned orange-brown, and a brown microcrystalline powder of **3** was deposited after 1 h. The suspension was further stirred for three days at 100 °C to increase the quantity of product. The powder of **3** was quickly separated from the warm solution by filtration, washed with Et_2O/thf (1:3, ca. 20 mL), and dried under vacuum, affording a brown powder analyzing as $[U_7(NPh)_{12}Cl_6(thf)_6Mg]$ (165 mg, 0.05 mmol, 64 %). Elemental analysis (%) calcd for $C_{96}H_{108}Cl_6MgN_{12}O_6U_7$: C 33.62, H 3.17, N 4.90, Mg 0.71; found: C 33.36, H 3.07, N 5.04, Mg 0.84. IR: $\tilde{\nu} = 1758$ (s), 1220 (vs), 1154 (m), 1070 (w) 1022 (s), 993 (w), 852 (s), 825 (s), 755 (s), 695 (s), 619 (w), 593 (w), 577 (w), 535 (s), 497 cm^{-1} (s). In an NMR tube, dark crystals of **3** and **4** were obtained by heating a thf solution of UCl_4 and PhNMg(thf) (1.5 equiv) at reflux.

Crystallography: Data were collected at 100(2) K on a Nonius Kappa-CCD area-detector diffractometer and processed with HKL2000. Absorption effects were corrected empirically. The structures were solved by direct methods and refined by full- or blocked-matrix least-squares on F^2 with SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC 682429, 682430, 682431, 682432 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) L. Soderholm, P. M. Almond, S. Skanthakumar, R. E. Wilson, P. C. Burns, *Angew. Chem.* **2007**, *120*, 304; *Angew. Chem. Int. Ed.* **2008**, *47*, 298; b) S. V. Krivovichev, V. Kahlenberg, I. G. Tananaev, R. Kaindl, E. Mersdorf, B. F. Myasoedov, *J. Am. Chem. Soc.* **2005**, *127*, 1072; c) S. V. Krivovichev, V. Kahlenberg, R. Kaindl, E. Mersdorf, I. G. Tananaev, B. F. Myasoedov, *Angew. Chem.* **2005**, *117*, 1158; *Angew. Chem. Int. Ed.* **2005**, *44*, 1134; d) P. C. Burns, K.-A. Kubatko, G. Sigmon, B. J. Fryer, J. E. Gagnon, M. R. Antonio, L. Soderholm, *Angew. Chem.* **2005**, *117*, 2173; *Angew. Chem. Int. Ed.* **2005**, *44*, 2135; e) T. Albrecht-Schmitt, *Angew. Chem.* **2005**, *117*, 4914; *Angew. Chem. Int. Ed.* **2005**, *44*, 4836; f) I. Grenthe, J. Drożdżyński, T. Fujino, E. C. Buck, T. E. Albrecht-Schmitt, S. F. Wolf in *The Chemistry of the Actinide and Transactinide Elements*, *Vol. 1*, 3rd ed. (Eds.: L. R. Morss, N. Edelstein, J. Fuger, J. J. Katz), Springer, Dordrecht, **2006**, chap. 5, p. 253.

[2] G. Nocton, F. Burdet, J. Pécaut, M. Mazzanti, *Angew. Chem.* **2007**, *119*, 7718; *Angew. Chem. Int. Ed.* **2007**, *46*, 7574.

[3] P. B. Duval, C. J. Burns, D. L. Clark, D. E. Morris, B. L. Scott, J. D. Thompson, E. L. Werkema, L. Jia, R. A. Andersen, *Angew. Chem.* **2001**, *113*, 3461; *Angew. Chem. Int. Ed.* **2001**, *40*, 3357.

[4] J. C. Berthet, P. Thuéry, M. Ephritikhine, *Chem. Commun.* **2005**, 3415.

[5] G. M. Aspinall, M. C. Copsey, A. P. Leedham, C. A. Russell, *Coord. Chem. Rev.* **2002**, *227*, 217.

[6] J. K. Brask, T. Chivers, *Angew. Chem.* **2001**, *113*, 4082; *Angew. Chem. Int. Ed.* **2001**, *40*, 3960.

[7] a) W. A. Nugent, J. M. Mayer, *Metal–Ligand Multiple Bonds*, Wiley-Interscience, New York, **1988**; b) D. E. Wigley, *Prog. Inorg. Chem.* **1994**, *42*, 239.

[8] T. K. Panda, S. Randoll, C. H. Hrib, P. G. Jones, T. Bannenberg, M. Tamm, *Chem. Commun.* **2007**, 5007.

[9] G. R. Giesbrecht, J. C. Gordon, *Dalton Trans.* **2004**, 2387.

[10] C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2007**, *129*, 11914, and references therein.

[11] T. W. Hayton, J. M. Boncella, B. L. Scott, E. R. Batista, *J. Am. Chem. Soc.* **2006**, *128*, 12622, and references therein.

[12] a) J. G. Brennan, R. A. Andersen, A. Zalkin, *J. Am. Chem. Soc.* **1988**, *110*, 4554; b) R. C. Schnabel, B. L. Scott, W. H. Smith, C. J. Burns, *J. Organomet. Chem.* **1999**, *591*, 14; c) J. L. Steward, R. A. Andersen, *New J. Chem.* **1995**, *19*, 587; d) P. B. Duval, C. J. Burns, W. E. Buschmann, D. L. Clark, D. E. Morris, B. L. Scott, *Inorg. Chem.* **2001**, *40*, 5491.

[13] W. J. Grigsby, T. Hascall, J. J. Ellison, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1996**, *35*, 3254.

[14] Y. Kusaka, Y. Ozawa, A. Yagasaki, *Inorg. Chem.* **2001**, *40*, 2634.

[15] R. E. Cramer, K. A. N. S. Ariyaratne, J. W. Gilje, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1856.

[16] a) M. Veith, R. Lisowski, *Angew. Chem.* **1988**, *100*, 1124; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1087; b) T. Chivers, X. Gao, M. Parvez, *Angew. Chem.* **1995**, *107*, 2756; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2549; c) T. Chivers, G. Schatte, *Eur. J. Inorg. Chem.* **2002**, 2266.

[17] J. C. Berthet, P. Thuéry, M. Ephritikhine, *Inorg. Chem.* **2005**, *44*, 1142.

[18] a) M. Tesmer, B. Müller, H. Vahrenkamp, *Chem. Commun.* **1997**, 721; b) M. A. Bolcar, S. M. J. Aubin, K. Folting, D. N. Hendrickson, G. Christou, *Chem. Commun.* **1997**, 1485; c) G. L. Abbati, A. Cornia, A. C. Fabretti, A. Caneschi, D. Gatteschi, *Inorg. Chem.* **1998**, *37*, 3759; d) G. Labat, C. Boskovic, H. U. Güdel, *Acta Crystallogr. Sect. E* **2005**, *61*, m611.

[19] M. T. Pope in *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**.

[20] a) P. Legzdins, R. H. Jones, E. C. Phillips, V. C. Yee, J. Trotter, F. W. B. Einstein, *Organometallics* **1991**, *10*, 986; b) M. Roger, N. Barros, T. Arliguie, P. Thuéry, L. Maron, M. Ephritikhine, *J. Am. Chem. Soc.* **2006**, *128*, 8790; c) A. R. Johnson, W. M. Davis, C. C. Cummins, *Organometallics* **1996**, *15*, 3825.