Actinide Chemistry

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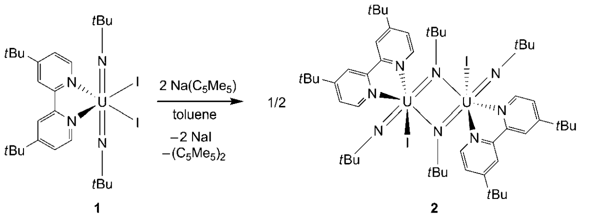
Cation–Cation Interactions, Magnetic Communication, and Reactivity of the Pentavalent Uranium Ion $[U(NtBu)_2]^+$**

*Liam P. Spencer, Eric J. Schelter, Ping Yang, Robyn L. Gdula, Brian L. Scott, Joe D. Thompson, Jaqueline L. Kiplinger, Enrique R. Batista, and James M. Boncella**

Pentavalent uranium complexes have long attracted attention as a means to probe the role of the f^1 electronic configuration in actinide chemistry. Studies of the $[UO_2]^+$ ion have been essential to this area as a result of its role in nuclear fuel reprocessing, its speciation in the environment, and its potential to perform electrochemical catalysis.[1] Despite this interest, well-characterized examples of the $[UO_2]^+$ ion are exceedingly rare, which has limited their use to illustrate important fundamental concepts in actinide chemistry. Although some of the structurally characterized $[UO_2]^+$ complexes are monomeric,[2a,b] many are oligomeric, for example, the uranyl(V) coordination polymer $\{[UO_2py_5][KI_2py_2]\}_n$,[2c,d] the tetrameric complex $[UO_2(dbm)_2]_4[K_6py_{10}]\cdot I_2\cdot py_3$[2e] (py = pyridine, dbm = dibenzoylmethanate), and the dimeric complex $[\{UO_2(dbm)_2K([18]crown\text{-}6)\}_2]$.[2f] These oligomers demonstrate that the $[UO_2]^+$ ion can assume many oxygen-bridged architectures. Although these complexes have been used to probe the role of cation–cation oligomeric interactions in structural uranyl(V) chemistry, very little is known about the reactivity and magnetic interactions between such f^1 actinide centers in polynuclear complexes. These properties can be further addressed by the study of other families of pentavalent actinide complexes that are similar in molecular and electronic structure to the $[UO_2]^+$ ion.

Despite the potential that $[U(NR)_2]^+$ ions offer to pentavalent uranium chemistry, imido analogues of the $[UO_2]^+$ ion are unknown. Herein, we describe the synthesis of the dimeric pentavalent bis(imido) uranium complex $[\{U(NtBu)_2(I)(tBu_2bpy)\}_2]$ (tBu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl), the first complex of the $[U(NR)_2]^+$ ion. We demonstrate with magnetic susceptibility measurements and DFT calculations that this f^1–f^1 system exhibits magnetic coupling at low temperatures. Furthermore, this dimeric species can undergo two-electron oxidative addition reactions to form new bis(imido) uranium(VI) complexes that are inaccessible by other synthetic procedures.

We described the synthesis and reactivity of the bis(imido) uranium(VI) ion, $[U(NR)_2]^{2+}$,[3a] in particular towards imido exchange and iodide metathesis reactions.[3b,c] During studies on the organouranium(VI) complex $[(C_5Me_5)_2U(NtBu)_2]$,[3d] we discovered that the reaction between two equivalents of NaC_5Me_5 and $[U(NtBu)_2(I)_2(tBu_2bpy)]$ (**1**; tBu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) does not provide the expected uranium(VI) species. Instead, the addition of a toluene solution of NaC_5Me_5 to **1** provides the bis(imido) uranium(V) dimeric complex $[\{U(NtBu)_2(I)(tBu_2bpy)\}_2]$ (**2**) in reasonable yield, in addition to dicyclopentadiene [Eq. (1)]. The use of the cyclopentadienyl anion as a reductant has precedent in the reduction of $[UO_2]^{2+}$ to $[UO_2]^+$ and in complexes such as $U(C_5Me_5)_3$ that can engage in sterically induced reduction reactions to eliminate $(C_5Me_5)_2$.[2d,4] Complex **2** was identified by ^1H NMR spectroscopy, single crystal X-ray diffraction, and elemental analysis. The ^1H NMR spectrum of **2** is consistent with a paramagnetic uranium(V) complex with broad resonances at $\delta = -18.54$ ppm and 44.42 ppm, which are due to the *tert*-butylimido groups. Two broad singlets were also detected at $\delta = -3.11$ ppm and 2.32 ppm, which are attributable to the *tert*-butyl groups on the bipyridyl ligand.



(1)

The molecular structure of **2** in the solid state (Figure 1) features the first structurally characterized pentavalent bis(imido) uranium(V) ion. This binuclear motif is not common in uranium chemistry; there are only a few reported binuclear, dimeric derivatives.[2f,5] Interestingly, the solid-state molecular structure of **2** has a cation–cation interaction between $[U(NR)_2]^+$ units that is to our knowledge the first structurally characterized example of an actinide complex with two bridging An=N(R)−An units and two An=N(R) ligands. These interactions are reminiscent of the An=O bridging interactions found in the dimeric uranyl(V) species $[UO_2(dbm)_2K([18]crown\text{-}6)]_2$.[2f] Complex **2** has a pseudo-octahedral geometry at each uranium center, which consists of two axial bis(imido) ligands and bipyridyl, iodide, and bridging imido equatorial ligands. A nearly linear bis(imido) N=U=N bond (average = 170.1(2)°) is present in **2**, along with

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[*] L. P. Spencer, E. J. Schelter, P. Yang, R. L. Gdula, B. L. Scott, J. D. Thompson, J. L. Kiplinger, E. R. Batista, J. M. Boncella
Los Alamos National Laboratory
MS J514, Los Alamos, NM 87544 (USA)
Fax: (+1) 505-667-9905
E-mail: boncella@lanl.gov

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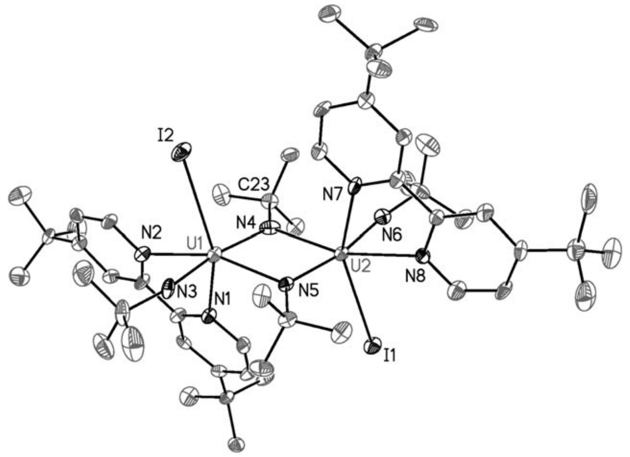


Figure 1. Structure of $[\{U(NtBu)_2(I)(tBu_2bpy)\}_2]$ (**2**) with ellipsoids set at 50% probability. Selected bond distances [Å] and angles [°]: U1–N1 2.536(5), U1–N2 2.650(5), U1–N3 1.895(5), U1–N4 2.067(5), U1–N5 2.380(5), U2–N4 2.387(5), U2–N5 2.078(5), U2–N6 1.901(5), U1–I2 3.1385(6); N3-U1-N4 170.6(2), U1-N4-U2 106.7(2), U1-N4-C23 130.5(4), U2-N4-C23 122.8(4), N4-U1-N5-U2 2.8(2).

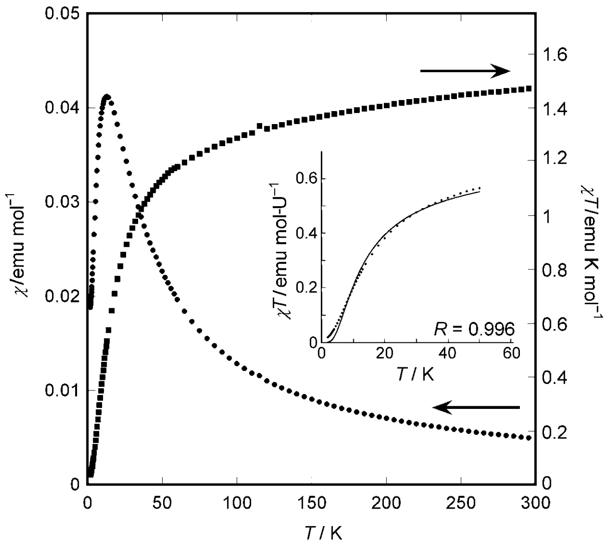


Figure 2. Molar temperature-dependent magnetic behavior of **2** recorded in the range 2–300 K.

non-bridging U$-$N$_{\text{imido}}$ bonds (average = 1.898(5) Å) that are slightly longer than the U$-$N$_{\text{imido}}$ bonds found in *trans*-bis(imido) uranium(VI) complexes,[3] and shorter than U$-$N$_{\text{imido}}$ bonds found in other uranium(V) imido complexes.[6] The U_2N_2 core features a set of U$-$N bonds, U1–N4 (2.067(5) Å) and U2–N5 (2.078(5) Å), that are on average about 0.3 Å shorter than U1–N5 (2.380(5) Å) and U2–N4 (2.387(5) Å). These shorter bonds are slightly longer than many of the U$-$N$_{\text{imido}}$ bond distances found in other uranium(V) imido complexes (1.910(6)–2.047(8) Å)[6] but significantly shorter than the U$-$N$_{\text{amido}}$ bond found in the uranium(V) amido complex $[\{(Me_3Si)_2N\}_3U{=}N(SiMe_3)]$ (U$-$N$_{\text{amido}}$=2.295(10) Å).[6d] This result suggests that there is metal–ligand multiple bond character present in this set of U$-$N bonds. In contrast, the average bond length in the other set of uranium–nitrogen bond distances, U1–N5 and U2–N4 (average 2.384(5) Å), is slightly longer than the U$-$N$_{\text{amido}}$ bonds observed in $[\{(Me_3Si)_2N\}_3U{=}N(SiMe_3)]$, and is consistent with a U$-$N bond with single-bond character. Furthermore, the U_2N_2 parallelogram defined by the atoms U1-N4-U2-N5 is nearly planar (N4-U1-N5-U2 = 2.8(2)°), as are the bridging nitrogen imido atoms as defined by the sum of the angles (360°) about atoms N4 and N5.

Temperature-dependent magnetic data were collected for complex **2** in the temperature range 2–300 K to detect the presence of interacting $^2F_{5/2}$ U^{V}–5f^1 spin centers (Figure 2). The molar χT versus T data reach a value of 1.48 emu K mol^{-1} at 300 K. This value is close to the expected value of $2 \times 0.69 = 1.38$ emu K mol^{-1} for a $J = 5/2$, $g_J = 0.857$ ion, which assumes complete population of the crystal field doublets at this temperature. The slightly larger than expected value is due to van Vleck temperature-independent paramagnetism (TIP) from excited-state mixing, as evidenced by the positive slope in the high temperature region of the χT versus T plot. Ignoring any effects of magnetic coupling (see below), the TIP for **1** can be roughly estimated from the slope of χT versus T between 140–300 K as 7.7×10^{-4} emu mol^{-1}. Recently reported organometallic uranium(V) imido complexes also exhibit such TIP.[6b]

The χ versus T data clearly indicate the presence of an antiferromagnetic interaction between the metal ions by the appearance of a maximum at 13 K. Observation of a clear signature of magnetic coupling is exceedingly rare in actinide molecular chemistry, as the magnetic response of paramagnetic actinide complexes is usually dominated by single-ion magnetic effects. The interaction in **2** is reminiscent of magnetic data reported for the bimetallic 5f^1–5f^1 complex $[(MeC_5H_4)_3U]_2[\mu\text{-}1,4\text{-}N_2C_6H_4]$ (**3**),[6i] as well as the structurally related $[\{UO_2(dbm)_2K(18C6)\}_2]$ (**4**).[2f] As with **3**, $1/\chi$ versus T data for **2** in the range 140–280 K are linear, allowing Curie–Weiss fitting $\chi = C/(T-\theta)$. Parameters per uranium ion (for ease in comparison) obtained from a linear fit of the $1/\chi$ versus T data in this range are $C = 0.80$ emu K mol^{-1}, $\mu_{\text{eff}} = 2.53\,\mu_B$, and $\theta = -27$ K (see the Supporting Information, Figure S1, for the linear fit of $1/\chi$ versus T). Table 1 shows a comparison of these results with compound **3**. Both the larger μ_{eff} value and smaller negative Weiss constant between **2** and **3** provide evidence that the magnetic coupling interaction in **2** is weaker than that observed in **3**. The $1/\chi$ versus T data for **4** are not linear over this temperature range, making comparison of **2** with this complex difficult; however a similar temperature-dependent character of the χ versus T data (see below) is present in **2** and **4**.

Table 1: Magnetism studies for complexes **2** and **3**.

	C[a,b]	μ_{eff} (μ_B)[a]	θ [K][a]	J [cm^{-1}]
2	0.80	2.53	−27	−12[c]
3	0.54	2.08	−147	−19

[a] Determined per mol of uranium from a linear fit of $1/\chi$ versus T over the range 280–40 K. [b] emu K per mol of uranium. [c] Estimate based on uniaxial crystal field of **3**; see text for details.

The nominal uniaxial crystal field present in **2** allows for modeling of the χT data to estimate the exchange energy in a similar way to that reported for **3**. The truncation of parameters by this symmetry assumption is supported by reported uranium(V) imido complexes, whose magnetic properties are rather insensitive to the identity of auxiliary ligands.[6b] The data were modeled according to the following effective spin, Ising expression ($\check{S}_{z1}=\check{S}_{z2}={}^1\!/_2$, $g_{\perp}=0$) [Eqs. (2) and (3), and Figure 2, inset]:[7]

$$\hat{H} = -2J\check{S}_{z1}\check{S}_{z2} + g_{\parallel}\mu_B H_z(\check{S}_{z1}+\check{S}_{z2}) \tag{2}$$

$$\chi T = \left(\frac{1}{3}\right)\frac{Ng_{\parallel}^2\mu_{\mathrm{B}}^2}{2k}\left(1+e^{\frac{-J}{kT}}\right)^{-1} + \chi_{\mathrm{TIP}}T \tag{3}$$

This model produced best-fit parameters $g_{\parallel}=4.52$ and $J=-12\ \mathrm{cm}^{-1}$ using $\chi_{\mathrm{TIP}}=3.85\times10^{-4}$ emu per mol of uranium. Critically, the value of $g_{\parallel}$ obtained is close to the expected value for the $\pm 5/2$ Kramer's doublet as the ground state, namely $g_{\parallel}=5g_J=4.29$. The appearance of this g value provides validation of the symmetry assumption and assignment of the ground-state $\pm 5/2$ doublet. The data indicate a smaller exchange interaction in **2** than **3** (Table 1), despite the shorter U−U distance in **2** (3.58 Å) compared to **3**, (ca. 9.6 Å) estimated from twice the metal to aryl ring-centroid distance in [1,2,4-*t*$\mathrm{Bu_3C_5H_2)_2U{=}N}$(*p*-tolyl)].[8] This result is consistent with the very different exchange pathways operative in these molecules: dative interactions of side-on U−N interactions in **2** (Figure 1) versus a covalent 1,4-phenylenediimide bridging ligand that is aligned directly with the magnetic easy axes of the uranium ions in **3**.

Temperature-dependent magnetic susceptibility data reported for **4** also indicate the presence of an antiferromagnetic interaction.[2f] Given our success using the Ising model described above, the approach could also reasonably be applied to **4** to ascertain the strength of the magnetic coupling interaction in that complex. Qualitatively, the interaction in **4** appears weaker than **2** judging from the appearance of a maximum at approximately 5 K in that complex compared to 13 K in **2**.

Further insight on the antiferromagnetic interaction between metal centers was attained from hybrid DFT calculations. These calculations were performed on the model complex [{U(N*t*Bu)$_2$(I)$_2$(bpy)}$_2$] (**5**) to investigate the molecular orbital interactions in the $\mathrm{U_2N_2}$ core, the relative energy differences, and spin densities of the singlet and triplet spin states. The structure of **5** predicted by DFT calculations is in good agreement with the experimental values of **2** (see the Supporting Information, Table S3), with deviations between experimental and theoretical values similar to other uranium(V) imido complexes at a similar level of computational theory.[6a,b] The ground state of **5** at its optimal configuration (0 K) was calculated to be a broken-symmetry singlet state, and the lowest triplet was found to be 1.6 kcal mol^{-1} higher in energy. A natural orbital analysis shows that the unpaired spin density is localized in the uranium center as f^1_{φ}–f^1_{φ} (see the Supporting Information, Figure S2). The Mulliken spin-density population analysis of the singlet and triplet state of **5** is given in Table 2. The singlet state of **5** has 1.13 unpaired electrons on both uranium centers with oppositely oriented spins, whereas the triplet state exhibits the same number of electrons but with parallel spins. A spin density so close to unity indicates that most of it comes from the unpaired electrons, and the bonding orbitals contribute only a small amount to the net spin polarization. Furthermore, the bridging and non-bridging imido nitrogen atoms possess very little spin density, as do the iodide and nitrogen-containing bpy ligands. The spin density in the bridging nitrogen atoms is reduced in the singlet state because the two uranium centers compete out of phase for the bonding interaction whereas this does not happen to the non-bridging atoms that can change the spin state.

Table 2: Net spin density calculations for singlet- and triplet-state configurations of **5**.[a]

	U1	U2	N4[b]	N5[b]	N3[c]	N6[c]
singlet	+1.13	−1.13	+0.09	−0.09	−0.12	+0.12
triplet	+1.14	+1.12	−0.13	−0.12	−0.12	−0.12

[a] Labeling follows that of Figure 1. [b] Bridging imido ligands. [c] Terminal imido ligands.

The bonding interaction between the two [U(N*t*Bu)$_2$]$^+$ centers consists in symmetric and antisymmetric combinations of the six U−N molecular bonding orbitals of [U(N*t*Bu)$_2$]$^{2+}$ (see the Supporting Information, Figure S3). The natural orbital with largest interaction (symmetric combination of π_u molecular orbitals) decomposed into its fragments is shown in Figure 3. The [U(N*t*Bu)$_2$]$^+$ orbital shown in Figure 3 A is composed of U(5f$_\pi$) and N(2p) atomic orbitals. Each [U(N*t*Bu)$_2$]$^+$ unit forms the molecular orbitals shown in Figure 3 B, and the symmetric combination of the two is shown in Figure 3 C. The U−N bond in one U[(N*t*Bu)$_2$]$^{2+}$ unit has triple-bond character, presenting one σ and two π bonding orbitals.[3] This triple bond breaks into a double bond and a single bond in the dimer complex to form the bridging bond; that is, U1=N4 and U2−N4, U2=N5 and U1−N5, respectively. DFT calculations show that the double bond (2.073 Å) consists of one σ and one π bonding orbitals, whereas the bridging bond at 2.384 Å is a single π bond.

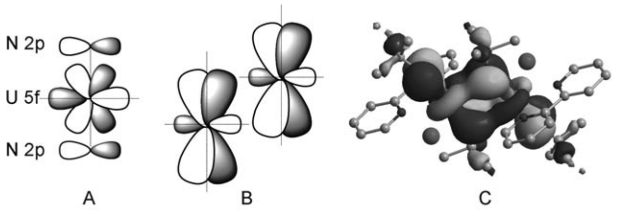
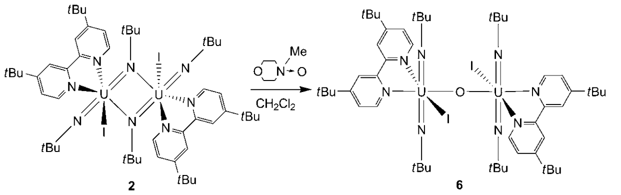


Figure 3. Decomposition of a natural bonding orbital of **5** in atomic and molecular components. A) three atomic orbitals involved in forming the π_u orbital of the U−N bond, B) hybridized fragment orbital forming the U−N bonds, and C) full molecular orbital result of the symmetric combination of the two fragments shown in (B).

The weak coupling between the two units is due not only to the long U−N distance and the interaction between the side lobes, which are smaller, (Figure 3), but also to the fact that 6 of the 12 orbitals consist of antisymmetric combinations, which place a node along the U–N bond. This weak interaction between these orbitals leads to the observed weak magnetic communication between the two uranium centers.

The addition of one equivalent of 4-methylmorpholine *N*-oxide to **2** yields the dinuclear oxo-bridged uranium(VI) complex **6** [Eq. (4)] in reasonable yield. The ^1H NMR spectrum of **6** is consistent with a diamagnetic uranium(VI) complex with asymmetric bpy resonances at $\delta = 7.94$, 8.19, 8.64, 8.72, 11.19, and 11.59 ppm and a singlet at $\delta = 0.21$ ppm that confirms the presence of a *tert*-butyl imido ligand.



2 **6** (4)

The solid-state molecular structure of **6** (see the Supporting Information, Figure S3) features both uranium centers in a pseudo-octahedral geometry. Complex **6** has U–O bonds (average 2.104(9) Å) that are significantly shorter than observed in other uranium(VI) phenolate complexes,[9] and a near linear U-O-U unit (173.3(6)°). The U–O bond in **6** is also significantly longer than U–O(oxo) bonds found in many $[UO_2]^{2+}$ complexes. The uranyl(VI) complex $[UO_2(2,6\text{-}Ph_2C_6H_3O)(thf)_2]$ is representative of many complexes of the $[UO_2]^{2+}$ ion, and features a U–O(oxo) bond of 1.759(14) Å.[9a] Taken together, these structural features suggest that there is some measure of U–O multiple bond character present in the solid state in **6**. Furthermore, the U–N(imido) and U–I bond distances in **6** are similar to other reported *trans*-bis(imido) uranium(VI) complexes.[3]

In conclusion, we have described the synthesis of a new stable pentavalent bis(imido) uranium(V) complex. This finding offers significant impact for the expansion of the small number of uranium complexes with well-defined magnetic coupling and for the formation of new uranium(V) imido architectures. The oxidation of this compound also offers a rich chemistry for the synthesis of new bis(imido) uranium(VI) complexes that are otherwise inaccessible.

Experimental Section

Experimental details for the synthesis of **1**, **2**, and **6**, details of the magnetism studies, and DFT calculations are given in the Supporting Information. CCDC 713660 (**2**) and CCDC 713661 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

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[1] a) “Organoactinide Chemistry: Synthesis and Characterization”: C. J. Burns, M. S. Eisen in *The Chemistry of the Actinide and Transactinide Elements*, *Vol. 1*, 3rd ed. (Eds.: L. R. Morss, N. M. Edelstein, J. Fuger), Springer, Berlin, **2006**; b) C. K. Jørgensen, R. Reisfeld, *J. Electrochem. Soc.* **1983**, *130*, 681–684; c) C. K. Jørgensen, R. Reisfeld, *Struct. Bonding (Berlin)* **1982**, *50*, 121–172.

[2] a) T. W. Hayton, G. Wu, *Inorg. Chem.* **2008**, *47*, 7415–7423; b) T. W. Hayton, G. Wu, *J. Am. Chem. Soc.* **2008**, *130*, 2005–2014; c) L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2006**, *128*, 7152–7153; d) J.-C. Berthet, G. Siffredi, P. Thuery, M. Ephritikhine, *Chem. Commun.* **2006**, 3184–3186; e) F. Burdet, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2006**, *128*, 16512–16513; f) G. Nocton, P. Horeglad, J. Pécaut, M. Mazzanti, *J. Am. Chem. Soc.* **2008**, *130*, 16633–16645.

[3] a) T. W. Hayton, J. M. Boncella, B. L. Scott, P. D. Palmer, E. R. Batista, P. J. Hay, *Science* **2005**, *310*, 1941–1943; b) T. W. Hayton, J. M. Boncella, B. L. Scott, E. R. Batista, P. J. Hay, *J. Am. Chem. Soc.* **2006**, *128*, 10549–10559; c) L. P. Spencer, P. Yang, B. L. Scott, E. R. Batista, J. M. Boncella, *J. Am. Chem. Soc.* **2008**, *130*, 2930–2931; d) L. P. Spencer, R. L. Gdula, T. W. Hayton, B. L. Scott, J. M. Boncella, *Chem. Commun.* **2008**, 4986–4988.

[4] W. J. Evans, *Inorg. Chem.* **2007**, *46*, 3435–3449, and the references therein.

[5] a) P. B. Duval, C. J. Burns, W. E. Buschmann, D. L. Clark, D. E. Morris, B. L. Scott, *Inorg. Chem.* **2001**, *40*, 5491–5496; b) R. C. Schnabel, B. L. Scott, W. H. Smith, C. J. Burns, *J. Organomet. Chem.* **1999**, *591*, 14–23; c) J. G. Brennan, R. A. Andersen, A. Zalkin, *J. Am. Chem. Soc.* **1988**, *110*, 4554–4558.

[6] a) C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2007**, *129*, 11914–11915; b) C. R. Graves, P. Yang, S. A. Kozimor, A. E. Vaughn, D. L. Clark, S. D. Conradson, E. J. Schelter, B. L. Scott, J. D. Thompson, P. J. Hay, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2008**, *130*, 5272–5285; c) J. G. Brennan, R. A. Andersen, *J. Am. Chem. Soc.* **1985**, *107*, 514–516; d) A. Zalkin, J. G. Brennan, R. A. Andersen, *Acta Crystallogr. Sect. C* **1988**, *44*, 1553–1554; e) D. S. J. Arney, C. J. Burns, *J. Am. Chem. Soc.* **1995**, *117*, 9448–9460; f) P. B. Duval, C. J. Burns, W. E. Buschmann, D. L. Clark, D. E. Morris, B. L. Scott, *Inorg. Chem.* **2001**, *40*, 5491–5496; g) I. Castro-Rodriguez, K. Olsen, P. Gantzel, K. Meyer, *J. Am. Chem. Soc.* **2003**, *125*, 4565–4571; h) S. C. Bart, C. Anthon, F. W. Heinemann, E. Bill, N. M. Edelstein, K. Meyer, *J. Am. Chem. Soc.* **2008**, *130*, 12536–12546; i) R. K. Rosen, R. A. Andersen, N. M. Edelstein, *J. Am. Chem. Soc.* **1990**, *112*, 4588–4590.

[7] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**.

[8] G. Zi, L. L. Blosch, L. Jia, R. A. Andersen, *Organometallics* **2005**, *24*, 4602–4612.

[9] a) M. P. Wilkerson, C. J. Burns, D. E. Morris, R. T. Paine, B. L. Scott, *Inorg. Chem.* **2002**, *41*, 3110–3120; b) D. M. Barnhart, C. J. Burns, N. N. Sauer, J. G. Watkin, *Inorg. Chem.* **1995**, *34*, 4079–4084.