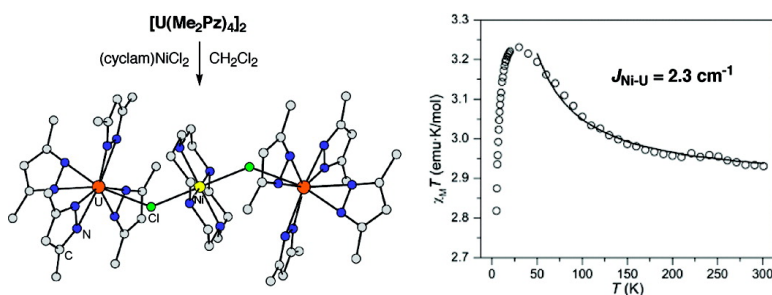Communication

Magnetic Exchange Coupling in Chloride-Bridged 5f−3d Heterometallic Complexes Generated via Insertion into a Uranium(IV) Dimethylpyrazolate Dimer

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Magnetic Exchange Coupling in Chloride-Bridged 5f−3d Heterometallic Complexes Generated via Insertion into a Uranium(IV) Dimethylpyrazolate Dimer

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The observation of slow magnetic relaxation in certain high-spin molecules has sparked a search for new systems capable of supporting higher relaxation barriers.[1] Recently, a number of such "single-molecule magnets" have been discovered in which lanthanide ions contribute substantially or entirely to the magnetic anisotropy responsible for the relaxation barrier.[2] Unfortunately, high spin ground states that are well-isolated in energy are difficult to achieve in species of this type, because the contracted 4f orbitals of lanthanide ions have little overlap with bridging ligand orbitals, leading to magnetic exchange constants of only a few wavenumbers at best.[3] In contrast, the 5f orbitals of actinide ions can exhibit an increased radial extension relative to the core electron density,[4] potentially enabling stronger magnetic coupling via superexchange. To date, however, there are only a few cases of actinide-containing molecules for which the presence of magnetic exchange coupling has been established.[5] This is due in part to difficulties with interpreting the magnetic susceptibility data, but also to the dearth of approaches for generating multinuclear 5f−3d assemblies.[6] Herein, we present a new strategy for synthesizing halide-bridged 5f−3d clusters, and demonstrate weak ferromagnetic coupling within a linear $U^{IV}-Cl-Ni^{II}-Cl-U^{IV}$ species.

The homoleptic dimer complex $[U(Me_2Pz)_4]_2$ ($Me_2Pz^- = 3,5$-dimethylpyrazolate) was obtained from a reaction of UCl_4 with KMe_2Pz in THF. Its formation proceeds under mild conditions, in stark contrast to the more demanding synthetic procedures required for generating homoleptic lanthanide pyrazolates.[7] Depending on reaction conditions, two additional products were observed: a THF adduct, $(Me_2Pz)_4U(THF)$, and a salt of the pentapyrazolate uranium-(IV) complex, $K[U(Me_2Pz)_5]\cdot THF$. Despite the propensity of uranium(IV) for binding THF,[8] the dimer can be isolated in high yield by repeated extractions into toluene. The pentapyrazolate byproduct is insoluble in toluene, and its yield was minimized by adjusting the reaction stoichiometry to precisely four equivalents of unsolvated KMe_2Pz per equivalent of UCl_4.

Green needle-shaped crystals of $[U(Me_2Pz)_4]_2\cdot0.5PhMe$ formed upon cooling a saturated toluene solution of the dimer, and X-ray analysis revealed the structure depicted at the top of Figure 1. Here, considering each pyrazolate ligand as a single entity, the U^{IV} centers adopt a trigonal bipyramidal coordination geometry. Two of the ligands, one equatorial and one axial, form asymmetric bridges, with the latter exhibiting the more elongated U−N bonds of 2.616-(7) and 2.719(7) Å. To our knowledge, this is the first example of a homoleptic pyrazolate complex of an actinide element. Related dimeric structures in which each metal center bears just two terminal pyrazolate ligands have been observed, for example, in $[Ln({}^tBu_2Pz)_3]_2$ (Ln = La, Nd, Yb, Lu).[9] In contrast to the tetravalent uranium ions, the trivalent lanthanide ions exhibit a coordination geometry intermediate between square planar and tetrahedral, with cases of both symmetric and asymmetric pyrazolate bridging modes arising.
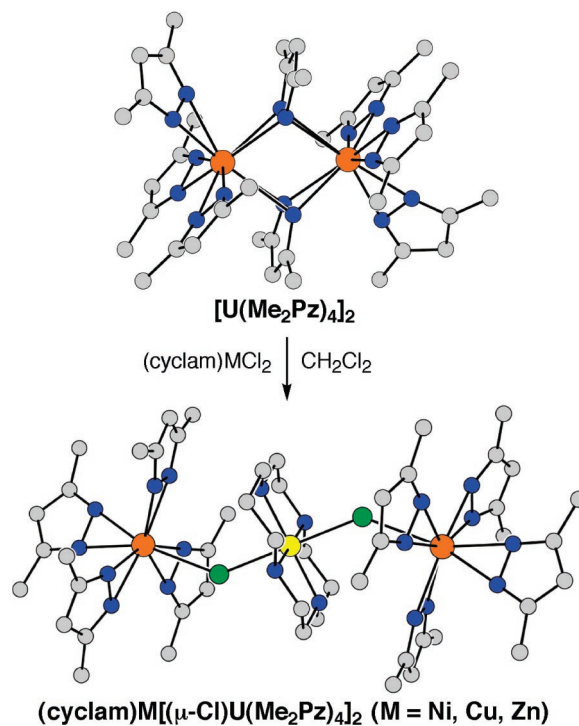

Figure 1. Insertion of $(cyclam)MCl_2$ complexes into the uranium(IV) 3,5-dimethylpyrazolate dimer to give linear, chloride-bridged clusters. Orange, yellow, green, gray, and blue spheres represent U, M, Cl, C, and N atoms, respectively; H atoms are omitted for clarity. The trinuclear clusters reside upon inversion centers within the crystal structures. Selected interatomic distances (Å) and angles (deg) for $[U(Me_2Pz)_4]_2$: mean $U-N_{terminal}$ 2.37(3), $U-N_{bridging}$ 2.489(7)−2.719(7), U···U 3.9485(5), mean U−N−U 99.1(7), $U-N_{bridging}-C$ 116.5(6)−119.8(5), 140.9(6)−144.2(6), and for $(cyclam)M[(\mu-Cl)U(Me_2Pz)_4]_2$ with M = Ni, Cu, Zn, respectively: U−Cl 2.838(2), 2.785(2), 2.822(2), mean U−N 2.39(1), 2.40(1), 2.40(2), M−Cl 2.564(2), 2.774(2), 2.680(2), mean M−N 2.061(2), 2.020(3), 2.085-(3), U···M 5.0687(8), 5.1822(6), 5.1419(5), U−Cl−M 139.47(9), 137.61-(7), 138.31(6).

Bases are capable of cleaving the uranium(IV) dimer via displacement of the axial bridging pyrazolate ligands. For example, reaction with THF yields the pseudo trigonal bipyramidal complex $(Me_2Pz)_4U(THF)$, wherein THF occupies an axial coordination site (see Figure S6 in the Supporting Information). More interestingly, the dimer can be cleaved via insertion of a terminal chloride ligand of a transition metal complex. In particular, reactions with $(cyclam)MCl_2$ (M = Ni, Cu, Zn; cyclam = 1,4,8,11-tetraazacyclotetradecane) in dichloromethane generate the trinuclear species $(cyclam)M-[(\mu-Cl)U(Me_2Pz)_4]_2$. Note that this is consistent with the established halophilicity of uranium(IV),[10] and that, fortunately, in these cases, complete chloride abstraction does not occur. Although there are examples of molecular compounds with halide ligands bridging between uranium(IV) and alkali metal cations,[11] to our knowledge
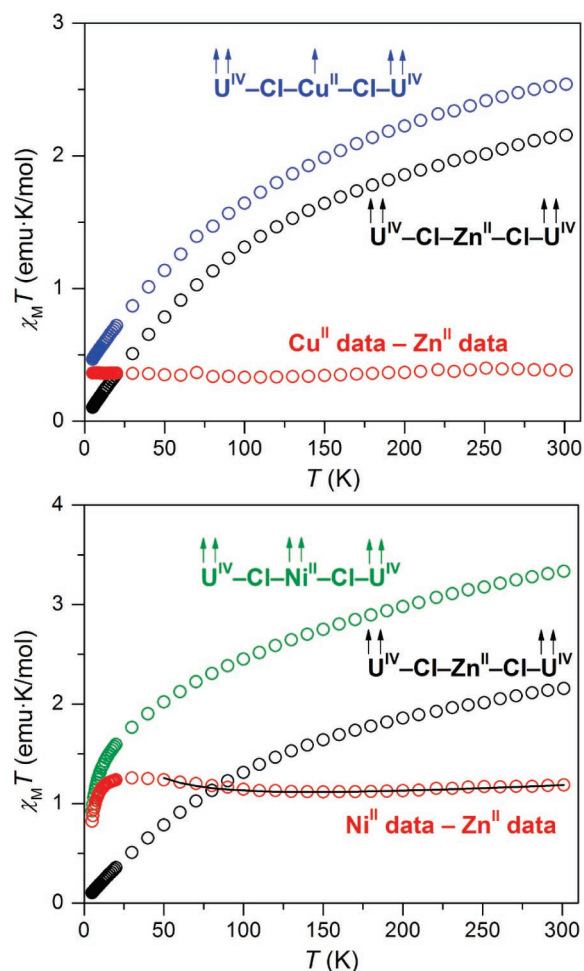
Figure 2. Variable temperature magnetic data for the linear clusters (cyclam)M[(μ-Cl)U(Me₂Pz)₄]₂ (M = Ni (green), Cu (blue), Zn (black)).[12] The data sets shown in red were obtained upon subtracting the Zn data from the Cu data (upper) and Ni data (lower). The solid line represents a fit to the latter data, as discussed in the text.

these are the first examples of halide-bridged species involving uranium(IV) and transition metal ions.

Cooling saturated solutions of the products afforded a set of isostructural crystals, featuring the intended linear, chloride-bridged clusters (see Figure 1, lower). Here, a U(Me₂Pz)₄ unit is appended to each of the trans chloride ligands of a central (cyclam)MCl₂ complex. In comparing the three structures, the most obvious difference lies in the variation of the M^{II}—Cl distances, with a Jahn—Teller distortion leading to a significantly longer Cu^{II}—Cl separation. Importantly, the U—Cl—M angle and U^{IV} coordination environment show little variation as M changes. Thus, the species containing the diamagnetic Zn^{II} ion can be used as a reasonable model in accounting for the U^{IV} contributions to the magnetism of the other clusters. Note that such an approach is necessitated by the lack of a suitable theoretical construct for predicting the temperature dependence of the magnetic moments of the constituent actinide ions. This method has been employed previously in probing exchange coupling in bridged uranium(IV)—transition metal complexes[5b−f] and is commonly applied in evaluating compounds containing lanthanide ions with unquenched orbital angular momentum.[3c]

Variable-temperature magnetic susceptibility data were measured for all three trinuclear complexes (see Figure 2). The data for the ZnU₂ cluster exhibit a steady drop in $\chi_M T$ as the temperature is lowered, decreasing from 2.16 emu·K/mol at 298 K to 0.10 emu·

K/mol at 5 K.[12] This behavior is typical of 5f² U^{IV} complexes, and the reduction in moment at lower temperatures is consistent with a poorly isolated singlet ground state arising from crystal field effects.[13] For the CuU₂ cluster, the data show a nearly identical temperature dependence, but with increased $\chi_M T$ values. By subtracting the ZnU₂ data from the CuU₂ data, the individual U^{IV} contributions are removed, leaving the magnetism of the central $S = \frac{1}{2}$ Cu^{II} ion, together with any vestiges of magnetic exchange coupling. The subtracted data, shown in red, reveal a moment that is essentially invariant with temperature, affording a mean value of $\chi_M T = 0.36(2)$ emu·K/mol ($\mu_{eff} = 1.70(4)$ μ_B). The results are consistent with a Cu^{II} ion in the absence of any magnetic exchange coupling, albeit with a moment that is slightly below the usual value for a pseudooctahedral complex. For comparison, (cyclam)CuCl₂ was observed to display a mean value of $\chi_M T = 0.43(1)$ emu·K/mol ($\mu_{eff} = 1.84(1)$ μ_B).[14] The slight difference may be associated with the change in ligand field arising upon attachment of a U^{IV} center to each chloride ligand, and perhaps with the presence of a small amount of diamagnetic impurity. The sole unpaired electron of the Cu^{II} center of the CuU₂ cluster resides in the d$_{x^2−y^2}$ orbital, which has δ symmetry with respect to the Cu—Cl bonds. Thus, the lack of exchange coupling can be explained as arising from the orthogonality of the Cu^{II} spin orbital with σ- and π-type orbitals of the chloride bridges. The complete invariance of the subtracted data affirms that the ZnU₂ cluster serves well in partitioning out the magnetism of the U^{IV} centers.

As shown at the bottom of Figure 2, the $\chi_M T$ data for the NiU₂ cluster display a quite different temperature dependence. Subtracting the ZnU₂ data affords a $\chi_M T$ value of 1.19 emu·K/mol at 298 K, consistent with the presence of an $S = 1$ Ni^{II} ion having $g = 2.18$. Below 100 K, the subtracted data increases, achieving a maximum of 1.26 emu·K/mol at 30 K. This rise in moment is not expected for an isolated Ni^{II} center and indicates the presence of ferromagnetic exchange interactions. To assess the strength of the exchange coupling, a simple spin-only model was adopted. A temperature-invariant contribution of $\chi_M T = 1.00$ emu·K/mol for each U^{IV} center was added back into the subtracted data (see Figure S2, Supporting Information). Utilizing MAGFIT 3.1[15] and a spin Hamiltonian of the form $\hat{H} = -2\hat{J}_{Ni}\cdot(\hat{S}_{U(1)} + \hat{S}_{U(2)}) + g\mu_B \mathbf{S}\cdot\mathbf{B}$, the data above 40 K were then fit to give the parameters $J = 2.3$ cm^{-1}, $g = 1.86$, and TIP $= 8.25 \times 10^{-4}$ emu/mol. To our knowledge, this represents the first estimate of a 5f−3d coupling constant within a molecular complex. Note, however, that the treatment provides only a lower bound for J. The actual J value is likely substantially higher, since we have not accounted for the gradual loss of spin on the U^{IV} centers with decreasing temperature.

The drop in $\chi_M T$ for the subtracted data below 30 K stems in part from this loss of U^{IV} spin, but probably also from a zero-field splitting contribution to the ground state. Indeed, variable-field magnetization data collected at low temperatures reveal large separations between isofield lines (see Figure S3, Supporting Information), as typically associated with a significant axial zero-field splitting. Despite this large anisotropy, ac magnetic susceptibility measurements carried out at temperatures down to 1.8 K with switching frequencies of up to 1500 Hz showed no out-of-phase signal attributable to single-molecule magnet behavior.

Density functional theory calculations were performed on a [(Me₂Pz)₄UCl]$^-$ fragment of the NiU₂ cluster to determine the symmetry of 5f orbitals involved in magnetic exchange. Assuming the z-axis is oriented along the U−Cl bond, the spin-containing orbitals are 5f$_{xyz}$ and 5f$_{z(x^2−y^2)}$ (see Figure 3). Importantly, both of these orbitals exhibit δ symmetry with respect to the U−Cl bond, such that they are rigorously orthogonal to the Ni^{II} 3d$_{z^2}$ spin feeding
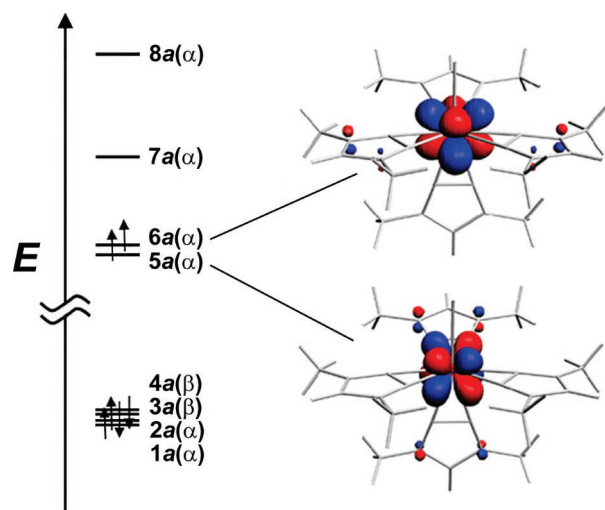
Figure 3. Frontier energy level diagram and depictions of the spin-containing molecular orbitals, as calculated for $[(Me_2Pz)_4UCl]^-$ using density functional theory. The Me_2Pz^- ligands are shown as skeletal representations, and the U−Cl axis is oriented vertically.

through σ-type Cl^- orbitals. Thus, the observed ferromagnetic coupling is consistent with a simple superexchange mechanism.

The foregoing results disclose a potentially generalizable means of assembling 5f−3d clusters, and demonstrate weak ferromagnetic coupling between U^{IV} and Ni^{II} through a chloride bridge. Future investigations will focus on utilizing this synthetic approach to achieve higher-nuclearity clusters, as well as to enhance exchange coupling via introduction of either bromide or iodide bridges, or lower-valent uranium centers. We note that each of these directions presents significant synthetic difficulties[16] and that the utilization of actinide elements in generating high-anisotropy single-molecule magnets therefore remains a daunting challenge.

Supporting Information Available: Complete experimental and computational details. X-ray crystallographic files. This material is available free of charge via the Internet at http://pubs.acs.org.

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