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$[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-}1,4\text{-N}_2\text{C}_6\text{H}_4]$ : A Bimetallic Molecule with  
Antiferromagnetic Coupling between the Uranium Centers

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Antiferromagnetic Coupling Between the Uranium Centers

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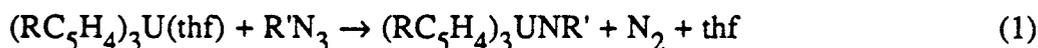
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**Abstract**

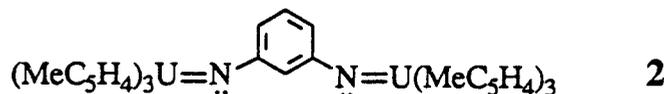
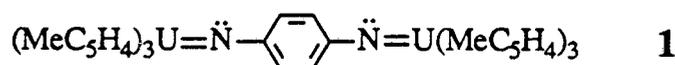
The two bimetallic, pentavalent uranium metallocene compounds,  $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-}1,4\text{-N}_2\text{C}_6\text{H}_4)$  **1** and  $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-}1,3\text{-N}_2\text{C}_6\text{H}_4)$  **2**, have been prepared from  $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$  and 1,4-diazido- and 1,3-diazido-benzene at room temperature, respectively. Magnetic susceptibility studies on these solids from 5-280K show that the spins on **1** antiferromagnetically couple at  $\sim 20\text{K}$  while those on **2** do not couple to 5K. The susceptibility curve for **1** can be fit to a one-dimensional Ising model with a calculated  $J$  of ca.  $19\text{ cm}^{-1}$ . A super-exchange model is postulated to account for these results since the imido-nitrogens of the bridging ligand in **1** are in the 1,4-positions of the benzene ring and they can conjugate, while the bridging ligand in **2** has the imido-nitrogen on the 1,3-positions of the benzene ring and they cannot conjugate.

Antiferromagnetic coupling of electron spins on two or more metal centers that are connected by bridging ligands, referred to as indirect or super-exchange, is a topic of considerable interest in d-transition metal chemistry.<sup>1</sup> In the f-block metals, a few examples of antiferromagnetic exchange coupling have been observed in solid state compounds with extended lattices such as  $\text{UCl}_3$ <sup>2a,b</sup> and  $\text{EuCl}_2$ ,<sup>2c</sup> where the ordering temperatures ( $T_N$ ) are ca. 22K and 1.6K, respectively. Only one example of antiferromagnetic coupling has been observed in a molecular lanthanide system,  $\text{Cp}_4\text{Dy}_2(\mu\text{-Br})_2$ , with  $T_N = 6\text{K}$ , though no coupling was observed in  $\text{Cp}_4\text{Er}_2(\mu\text{-Br})_2$ ,  $\text{Cp}_4\text{Yb}_2(\mu\text{-Br})_2$ <sup>3a-d</sup> or  $[(\text{Me}_5\text{C}_5)_2\text{Yb}]_2(\mu\text{-E})$  where E is O, S, Se, or Te.<sup>3e</sup> In the actinide series no examples of coupling have been documented in molecular systems; the U(IV) compounds  $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2(\mu\text{-E})$ <sup>4a</sup> and  $\{[(\text{Me}_3\text{Si})_2\text{N}]_3\text{U}\}_2(\mu\text{-E})$ <sup>4b</sup> where E is S, Se, or Te and where the U-E-U angles are nearly linear show no coupling to 5K.

A good synthetic route to higher valent uranium compounds, particularly for synthesis of U(V) organoimides, has been discovered recently, as shown in eq. 1.<sup>5</sup>



Extending this reaction to diazidobenzene derivatives gives **1**<sup>6</sup> or **2**.<sup>6</sup> The



bimetallic, pentavalent uranium derivatives of the  $5f^1$  electron configuration show antiferromagnetic coupling in **1** and the lack of coupling in **2**. The plot of  $\chi_M$  vs. T is shown in Figure I for both derivatives and the value of the magnetic moments are listed in Table I for these and related mononuclear organoimides of U(V). The similarity of the

curves for **1** and **2** is obvious from 50-300K as is the difference from 5-50K, the difference being that the spins on the two U(V) centers are antiferromagnetically coupled in **1** with an ordering temperature ( $T_N$ ) of  $\sim 20$ K and the two U(V) centers in **2** behave as independent paramagnets to 5K.<sup>7</sup>

Magnetic susceptibility and electron paramagnetic resonance (EPR) measurements (at  $\sim 4.2$ K) have been carried out on a number of mononuclear, pentavalent uranium compounds of the type  $(\text{MeC}_5\text{H}_4)_3\text{UNR}$ . The magnetic susceptibility curves as a function of temperature are all very similar, Table I, Figure I, but no EPR spectra have been observed. If the symmetry about the  $\text{U}^{5+}$  ion is assumed to be idealized  $C_{3v}$ , then the absence of an EPR spectrum at low temperatures suggests the ground doublet is the degenerate pair,  $\Gamma_5 + \Gamma_6$  ( $C_{3v}$  symmetry) as  $g_{\perp} = 0$  for this pair.<sup>8</sup> With this assignment plus the assumption that only the ground doublet contributes to the magnetic susceptibility at the lowest temperatures, a value of  $g_{\parallel}$  may be obtained from the magnetic susceptibility data.

It is assumed the ground state for **1** is the same as **2** in the absence of electron exchange, and that there is a one-dimensional exchange interaction along the three-fold or z axis for **1**. With the second assumption the exchange interaction in **1** may be treated as an example of the one-dimensional Ising model for an isolated dimer.<sup>1f,9</sup> The Hamiltonian for such a dimer is written as:

$$\mathcal{H} = -2JS_{z1}S_{z2} + g_{\parallel}\mu_B H_z(S_{z1} + S_{z2}). \quad (1)$$

The magnetic susceptibility for this system for a randomly oriented powder (per uranium ion) is<sup>1f</sup>

$$\chi_{\text{ave}} = 1/3 \frac{Ng_{\parallel}^2 \mu_B^2}{2kT} (1 + e^{-J/kT})^{-1} \quad (2)$$

where N is Avogadro's number, k is the Boltzman constant, T the absolute temperature and  $\mu_B$  the Bohr magneton.

The value of  $g_{\parallel} = 2.6$  at low temperatures has been obtained from the magnetic susceptibility data of **2**. The calculated susceptibilities for **1** as a function of temperature for various values of  $J$  are shown in Figure 2. The experimental deviation from the theoretical model at low temperatures is probably due to a small amount of a paramagnetic impurity as different preparations of **1** show differing susceptibilities in this temperature range. Assuming that the impurity is the starting material,  $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ , then ca. 1-2 mol % is sufficient to cause the observed deviations at low temperature. It is concluded that  $J \sim -19 \text{ cm}^{-1}$  and the antiferromagnetic state is lowest in energy.

The observation that the spins on each uranium center of **1** antiferromagnetically couple while those on **2** do not couple to 5K may be rationalized by a super-exchange pathway. The imido-nitrogens in **1** are in the 1,4 positions of the benzene ring and they can form a conjugated ring while those on **2** cannot. It is reasonable to postulate that the spin on each uranium center can communicate across the conjugated ligand in **1** though not in **2**. This may be illustrated by the two resonance structures shown below.



These two resonance structures imply that the two spins communicate by way of the ligand  $\pi$ -system and the electron on each uranium is in a  $\pi$ -symmetry orbital. A spin polarization model can be postulated and this model also rationalizes the observation of antiferromagnetic coupling; <sup>1e.g</sup> we know of no simple way to distinguish between these two physical processes.

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6. (a)  $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-}1,4\text{-N}_2\text{C}_6\text{H}_4]$ , (1). To 0.68 g of  $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$  (1.2 mMol) dissolved in 30 mL of diethyl ether was added 0.10 g of 1,4-diazidobenzene<sup>6c</sup> (0.62 mMol) in 10 mL of diethyl ether. Gas was evolved

immediately, and the color of the solution changed from red to deep purple with formation of a dark precipitate. After stirring for 15 minutes, the volatile material was removed under reduced pressure, leaving a dark solid. This solid was extracted into toluene (60 mL), the purple solution was filtered, and the filtrate was concentrated to 40-45 mL and cooled to  $-20^{\circ}\text{C}$ . Purple-black flakes were isolated by filtration and dried under reduced pressure, yielding 0.19 g of product.

Concentrating the remaining solution to ca. 15 mL and cooling to  $-20^{\circ}\text{C}$  allowed isolation of an additional 0.12 g of product. Total yield was 48% (0.31 g), m.p.  $261\text{-}263^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $30^{\circ}\text{C}$ ): 4.69 (9H,  $\nu_{1/2} = 6$  Hz), -2.46(6H,  $\nu_{1/2} = 23$  Hz), -9.01 (6H,  $\nu_{1/2} = 17$  Hz), 15.11 (4H,  $\nu_{1/2} = 14$  Hz). Anal. Calcd for  $\text{C}_{42}\text{H}_{46}\text{N}_2\text{U}_2$ : C, 47.8; H, 4.40; N, 2.66. Found: C, 48.1; H, 4.54; N, 2.64.

Mass spectrum: 1054, 1055 (calculated relative intensity: observed relative intensity; 100, 100; 47, 36). IR: 1578 w, 1493 m, 1283 m, 1260 m, 1090 w, 1047 w, 1032 m, 928 w, 903 w, 849 m, 833 m, 764 s, 610 m, 592 m, 538  $\text{cm}^{-1}$ . (b)  $[(\text{MeC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-}1,3\text{-N}_2\text{C}_6\text{H}_4]$ , (2). This compound was prepared similarly from  $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$  and 1,3-diazidobenzene<sup>6d</sup> and isolated as brown-red needles from toluene in 37% yield, m.p.  $213\text{-}215^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $59^{\circ}\text{C}$ ): 4.38 (18H,  $\nu_{1/2} = 17$  Hz), -2.27 (12H,  $\nu_{1/2} = 62$  Hz), -9.22 (12H,  $\nu_{1/2} = 55$  Hz), 28.23 (1H,  $\nu_{1/2} = 25$  Hz), -0.46 (1H,  $\nu_{1/2} = 32$  Hz), -6.89 (2H,  $\nu_{1/2} = 32$  Hz).

The NMR was recorded at  $59^{\circ}\text{C}$  because the peak at -0.46 ppm was too broad to be observed at room temperature. Anal. Calcd for  $\text{C}_{42}\text{H}_{46}\text{N}_2\text{U}_2$ : C, 47.8; H, 4.40; N, 2.66. Found: C, 47.5; H, 4.41; N, 2.63. Mass spectrum: 1054 (observed by FAB MS using 18-crown-6 and tetraglyme). IR: 1545 m, 1490 w, 1292 w, 1250 m, 1200 m, 1148 m, 1048 w, 1029 m, 990 m, 861 w, 854 w, 842 m, 797 m, 765 s, 682 m, 604 w, 330  $\text{cm}^{-1}$ . (c) Herring, D.L. J. Org. Chem. **1961**, 26, 3998. (d) Foster, M.O.; Fierz, H.E. J. Chem. Soc. **1907**, 91, 1942.

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**Table I.**  
**Magnetic Susceptibility Values for Uranium(V) Organoimides**

Compound	5-40K		140-280K	
	$\mu_{\text{eff}}^{\text{a}}$	$\theta^{\text{b}}$	$\mu_{\text{eff}}^{\text{a}}$	$\theta^{\text{b}}$
$\text{Cp}_3\text{UNSiMe}_3$	1.19	-0.7	1.83	-82
$(\text{MeC}_5\text{H}_4)_3\text{UNPh}$	1.25	1.03	1.96	-110
2	1.30	-3.95	2.12	-134
1	coupled		2.08	-147

(a) 
$$\chi_{\text{M}}(\text{corr}) = \frac{C}{T-\theta},$$

The effective magnetic moment,  $\mu_{\text{eff}}$ , is calculated as  $\mu_{\text{eff}} = 2.828C^{1/2}$ , where C and  $\theta$ , the Curie and Weiss constants, respectively, are obtained by fitting the magnetic susceptibility data to the equation  $\chi_{\text{M}}(\text{corr}) = C(T-\theta)^{-1}$ . Moments are expressed in Bohr magnetons per U(V). The values reported were determined at 5 kGauss; the values at 40 kG were identical to within 2%. The  $\chi_{\text{M}}(\text{corr})$  values are corrected for container and sample diamagnetism.

(b) in degrees Kelvin.

Figure 1: Experimental magnetic susceptibility data of **1** and **2** as a function of temperature.

Figure 2: Comparison of experimental magnetic susceptibility data with calculated values for **1**. The calculations are with  $g_{II} = 2.6$ . The impurity is assumed to be  $(\text{MeC}_5\text{H}_4)_3\text{U}(\text{thf})$ , and three calculated curves are shown for  $J = -18 \text{ cm}^{-1}$  (no impurity),  $J = -19 \text{ cm}^{-1}$  (1 mole% impurity), and  $J = -20 \text{ cm}^{-1}$  (2 mole% impurity).

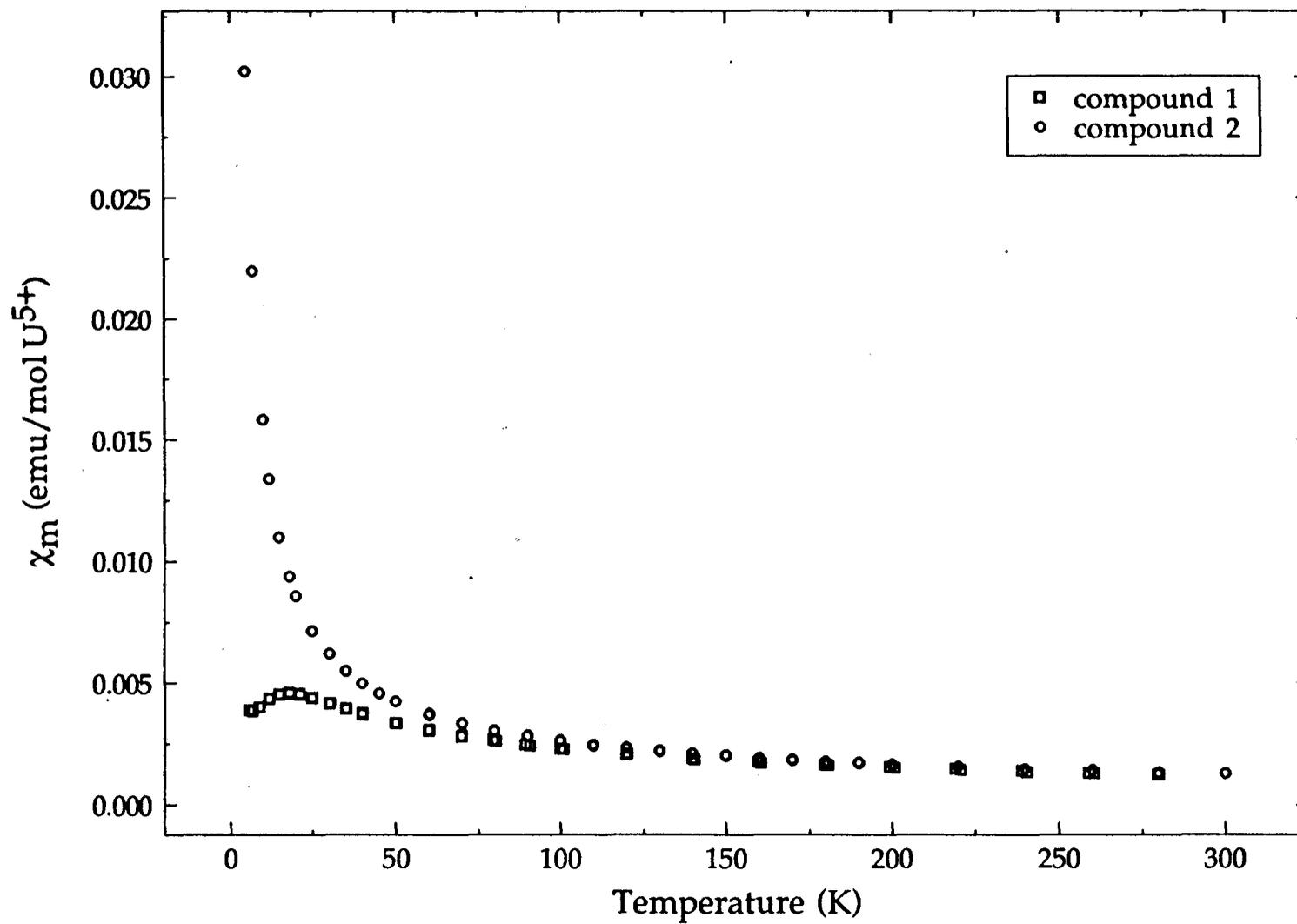


Figure 1

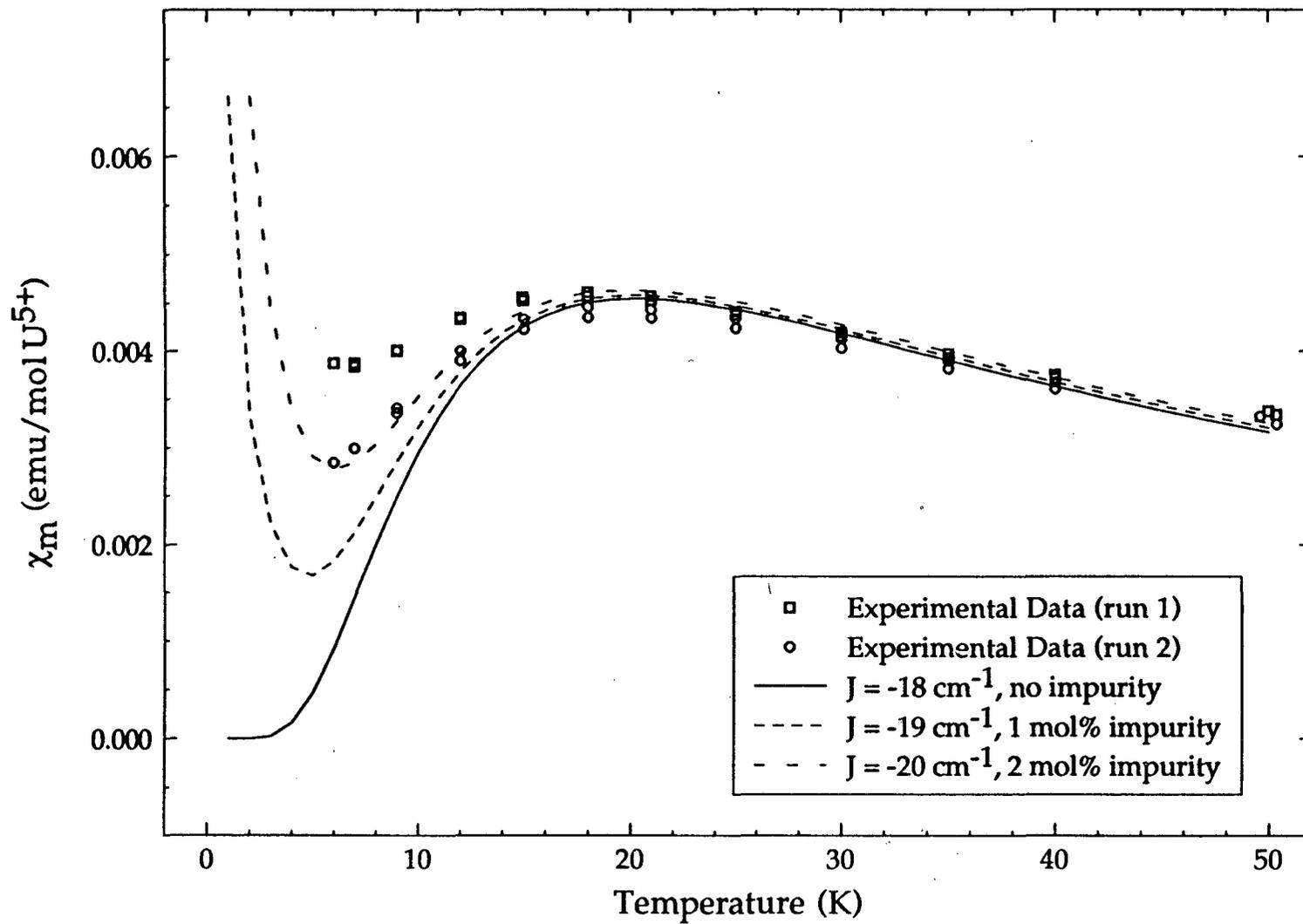


Figure 2

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