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Structure and Magnetic Characteristics of an Oxalate-Bridged U(IV)−Mn(II) Three-Dimensional Network

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The construction of extended solids from molecular building blocks may afford materials with controlled and tunable properties. Our interest in this field concerns molecule-based magnetic materials. In such materials a three-dimensional structure, in which each paramagnetic molecular subunit has interactions with its neighbors, is a prerequisite for magnetic order to occur at higher temperatures.[1−4]

The search for magnets with large coercive fields (hard magnets) makes the f-block ions desirable paramagnetic elements because of their large and anisotropic magnetic moments. In solid-state chemistry lanthanides and actinides are already used for the design of such materials.[5−9] Since the discovery of ferromagnetic coupling in Cu(II)−Gd(III) complexes,[10] molecular compounds of the 4f elements have been intensively studied.[11−17] In contrast, not much is known about the magnetic properties of molecular compounds involving 5f ions, although for these ions the f electrons are recognized to be less shielded than they are for the lanthanide ions. Consequently, interesting magnetic behaviors should be anticipated for compounds in which a paramagnetic 5f ion is in interaction with another spin carrier. In this report we describe a compound involving the 5f^5 U(IV) and 3d^5 Mn(II) ions.

One of the challenges for a chemist in this field of research is to control the topology in order to obtain interactions between spin carriers in all three directions of space. The high coordination number usually exhibited by the actinide ions is promising with respect to the construction of extended structures. Several ligands have been involved in the construction of extended structures where two paramagnetic ions are interacting. Among them, the oxalate anion is one of the most versatile. The assembling of two metal ions by means of oxalate bridges most often leads to a two-dimensional honeycomb-like structure.[18−23] Examples of 3D polymers involving this ligand could be obtained only in the presence of a chiral cation.[23−27] Surprisingly, all examples reported so far are based on trisoxalato transition metal building blocks, whereas tetrafunctional synthons, with tetrahedrally arranged linkers, are well-known to assemble in diamond-like networks.[28] We now report that the partial substitution of potassium in $K_4U(C_2O_4)_4$ by Mn(II) ions spontaneously affords a three-dimensional network.

The reaction of the tetraoxalato uranate compound, $K_4U(C_2O_4)_4$, with Mn(II) in H_2O leads to well-shaped single crystals of $K_2MnU(C_2O_4)_4\cdot 9H_2O$ suitable for X-ray diffraction analysis.[29] As a result of the reaction, an U(IV) ion is linked to four Mn(II) ions via each of its oxalate ligands, as shown in Figure 1. The coordination sphere of the Mn(II) ion also consists of four oxalate−U linkages. Hence, every metal ion is linked four times by oxalate bridges to the other metal ion. In this architecture the Mn(II) sites are surrounded by eight oxygen atoms. This comparatively high coordination number of 8 for Mn(II), though unusual, has already been observed in other compounds.[30,31] The U(IV) ion is 9-coordinate, with four oxalate ligands and one H_2O molecule. The resulting 3D network shows a diamond-like topology, and the charge neutrality of the compound is provided

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[⊥] This paper is dedicated to the memory of Prof. O. Kahn who passed away suddenly on December 8, 1999.

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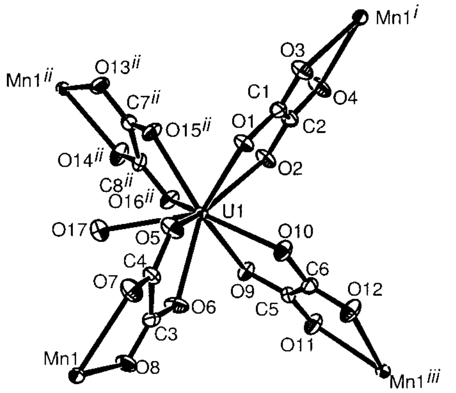

Figure 1. View of the coordination sphere of U(IV) within $K_2MnU(C_2O_4)_4 \cdot 9H_2O$. Selected bond lengths and distances (Å): U−O, 2.375(4)−2.456(4); U−O(17), 2.542(5); Mn−O, 2.283(4)−2.416(4); U−Mn, 6.102(3)−6.193(3).

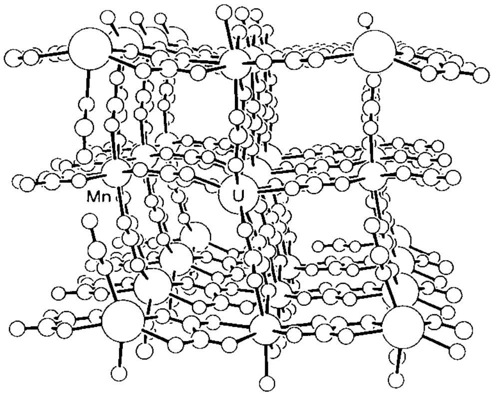

Figure 2. View of the $\{U(ox)_4Mn\}^{2-}$ network shown in the [010] projection. K^+ and H_2O are omitted for clarity.

by K^+ cations. Each potassium cation interacts with four H_2O molecules and four O atoms of two $M(C_2O_4)_4$ units, giving rise to {K−Mn} and {K−U} chains. A view of the network is shown in Figure 2, pointing out the square-shaped channels running along the *b* direction.

The magnetic susceptibility of a polycrystalline sample of $K_2MnU(C_2O_4)_4 \cdot 7H_2O$[32] was investigated in the temperature range 2−300 K, with an applied field of 1 kOe. The resulting $\chi_M T$ versus T plot (χ_M stands for the molar magnetic susceptibility and T for the temperature) is reported in Figure S1 (see Supporting Information). The magnetic properties of most mononuclear U(IV) compounds are characterized by a temperature-independent paramagnetism resulting from the coupling between a nonmagnetic ground state at the first order and low-lying excited states through the Zeeman perturbation. The magnetic susceptibility usually increases as T is lowered, and it tends to a temperature-independent value as T approaches absolute zero.[33,34] The product of the magnetic susceptibility with temperature, $\chi_M T$, is expected to decrease monotonically down to zero as T is lowered to a very low temperature. In the present case, the magnetic properties can be interpreted as the sum of the U(IV) and Mn(II) contributions. At room temperature $\chi_M T$ is equal to 5.19 cm^3 K mol^{-1}. As T is lowered, $\chi_M T$ slowly decreases to reach 4.2 cm^3 K mol^{-1} at 2 K. The high-temperature value of $\chi_M T$ is consistent with the presence of Mn(II) and U(IV). For the latter ion, values on the order of 1 cm^3 K mol^{-1} at room temperature are usually observed in molecular compounds.[33,34] At 2 K the value of $\chi_M T$ is 4.2 cm^3 K mol^{-1}, close to what is expected for the contribution of Mn(II) only. The field dependence of the magnetization of $K_2MnU(C_2O_4)_4 \cdot 7H_2O$ was recorded at 2 K. The experimental data agree almost perfectly with the theoretical behavior for Mn(II) calculated with the Brillouin function for a $^5/_2$ spin (inset of Figure S1), which confirms that the local ground state of the U(IV) site should be nonmagnetic.

The use of a tetrafunctionalized supramolecular synthon like $\{U(C_2O_4)_4\}^{4-}$ appears to be a valuable approach for the construction of 3D networks of paramagnetic units. However, in the reported compound the magnetic coupling is too weak to become apparent. A modification of either the spin carrier or the bridging ligand surrounding the U(IV) ion might enhance these interactions.

Experimental section

$K_4U(C_2O_4)_4$ is synthesized in situ from $U(C_2O_4)_2 \cdot 6H_2O$ (0.2 g, 0.4 mmol) and potassium oxalate (0.15 g, 0.8 mmol) in 12 mL of water at 80 °C.[35] To the hot, green solution, $Mn(ClO_4)_2 \cdot 6H_2O$ (0.15 g, 0.4 mmol) dissolved in 2 mL of water is added. The reaction mixture is allowed to cool, and ethanol is added by slow diffusion. After 3 days green crystals were obtained that were manually separated from precipitated white manganese oxalate and light-green uranium oxalate. Anal. Calcd for $C_8O_{16}K_2MnU \cdot 7H_2O$: C, 11.31; H, 1.66; K, 9.20; Mn, 6.47; U, 28.02. Found: C, 12.16; H, 1.62; K, 9.32; Mn, 6.58; U, 28.24. IR (KBr, cm^{-1}): ν = 3467 (s), 1654 (s), 1455 (m),1440 (m), 1303 (m), 907 (w), 800 (m), 485 (m).

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Supporting Information Available: Experimental $\chi_M T$ vs T and field dependence of the magnetization for $K_2MnU(C_2O_4)_4 \cdot 7H_2O$. Listings of crystal data, atomic coordinates, and bond distances and angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Crystal structure analysis: $C_8H_{18}O_{25}K_2MnU$; M = 885.39 g mol^{-1}; monoclinic, space group $P2_1$ (no. 4); a = 11.360(6) Å, b = 8.9614(17) Å, c = 11.405(9) Å, β = 97.22(9)°, V = 1151.8(11) Å^3; ρ_{cal} = 2.521 g cm^{-3} for Z = 2. Cell dimensions and orientation matrix for data collection were obtained at 273 K from least-squares refinement with 11.956 ≥ θ ≥ 9.323. A green crystal was measured on an Enraf−Nonius CAD-4 diffractometer (Mo Kα radiation, λ = 0.710 73 Å) by using θ−2θ scan (2θ_{max} = 30°), F(000) = 820. From a total of 3695 reflections measured, 3537 were independent reflections and 3410 reflections were observed with $F^2 > 2\sigma(F^2)$. After a semiempirical ψ-scan[36] absorption correction (T_{min} = 0.769 727; T_{max} = 0.998 630; μ(Mo Kα) = 8.045 mm^{-1}). From the systematic extinctions, the possible space groups are $P2_1$ or $P2_1/m$. All attempts with the centrosymmetric space group $P2_1/m$ lead to strong disorder, giving rise to aberrant results. The noncentrosymmetric space group $P2_1$ was then used. The structure solution was found by direct methods with SHELXS-86 [37] and refined with SHELXL-97 [38] by least squares against F_o^2; 334 parameters. The crystal structure was solved in both $P2_1$ and $P2_1/m$; however, best results were obtained with the $P2_1$ space group. The refinement of variables with anisotropic thermal parameters, with all reflections, gave R = 0.0219 and wR = 0.0548 and a residual electron density of 1.40 (0.87 from U1) and −1.87 (1.50 from O2).

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