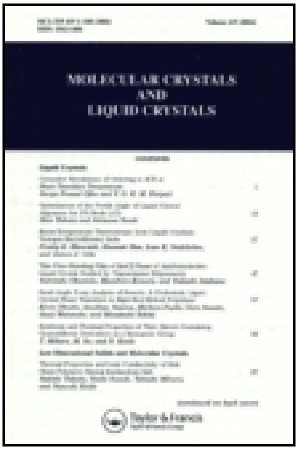

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Multifunctional Coordination Compounds: Design and Properties

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Multifunctional Coordination Compounds: Design and Properties

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Cleverly designed molecular building blocks provide chemists with the tools of a powerful molecular-scale construction set. They enable them to engineer materials having a predictable order and useful solid-state properties. Hence, it is in the realm of supramolecular chemistry to follow a strategy for synthesizing materials which combine a selected set of properties, for instance from the areas of magnetism, photophysics and electronics. As a successful approach, host/guest solids which are based on extended anionic, homo- and bimetallic oxalato-bridged transition-metal compounds with two-and three-dimensional connectivities have been investigated. In this report, a brief review is given on the structural aspects of this class of compounds followed by a presentation of a thermal and magnetic study for two distinct, heterometallic oxalato-bridged layer compounds.

Keywords: crystal engineering; supramolecular compounds; molecular magnetism; heat capacity measurements

INTRODUCTION

Interest in functional materials based on molecular crystals persists, owing to the potential for manipulating solid-state properties by systematic variation of the molecular structures as well as of the stoichiometries and properties of the molecular components. However, up to now, the crystal engineering of molecular materials has been frustrated by the absence of reliable and general structural paradigms that are needed for systematic design of crystal lattices with predictable structure and desirable functions. Therefore, learning how to create large supramolecular units, and the elucidation of rules mediating their macroscopic organization into multifunctional materials, will offer a fascinating prospect for technology [1-4].

In particular, the present work focuses on the transition-metal oxalate system, its fascinating structural versatility and its potential as a multifunctional material which lies mainly in the areas of molecule-based magnetism and photophysics. Starting with a brief discussion about the structural aspects of this supramolecular coordination compounds, we will further present some new magnetic and thermal studies for two distinct, heterometallic oxalato-bridged layer compounds.

CRYSTAL ENGINEERING

Our laboratory has already reported on the synthesis and structure determination of coordination solids based on transition-metal oxalates, which typically behave as host/guest compounds with different lattice dimensionalities[5-8]. Thereby, the idea of a reasonable strategy looks simple: mix metal ions with a preference for a particular coordination geometry with bridging ligand-systems, and under the right conditions - and it is important to control both the kinetics and thermodynamics of the assembly process - a crystalline network will nucleate and grow. Clearly, the strategy relies on the robustness of some coordination subunits and of the supramolecular motif as a whole. In the actual case of this report, the molecular subunits are chiral anionic, tris-chelated transition-metal oxalato complexes $[M^{z+}(ox)_3]^{(6-z)-}$, ox $= C_2O_4^{2-}$. Now, if such building blocks of different chirality are alternately linked, a layered honeycomb motif will result. In contrast, an assembling of building blocks of the same chiral configuration will lead to a three-dimensional framework structure.

Although the topological rules give an understanding of the different structural possibilities, the synthetic chemists still need to find the optimal reaction and crystallization conditions for each specific compound. In case of these tris-chelated transition-metal oxalato complexes, the discrimination between the formation and crystallization either of a 2D or a 3D framework structure relies on the choice of the templating counterion. Evidently, the template cation determines the crystal chemistry. Thus, cationic, tris-chelated transition-metal diimine complexes, $[M(bpy)_3]^{2+/3+}$ act as templates for the formation and crystallization of the 3D host/guest assembly[7], whereas $[XR_4]^+$ (X=N, P; R=phenyl, n-propyl, n-butyl, n-pentyl) cations initiate the growth of 2D layer structures (see Fig. 1)[8].

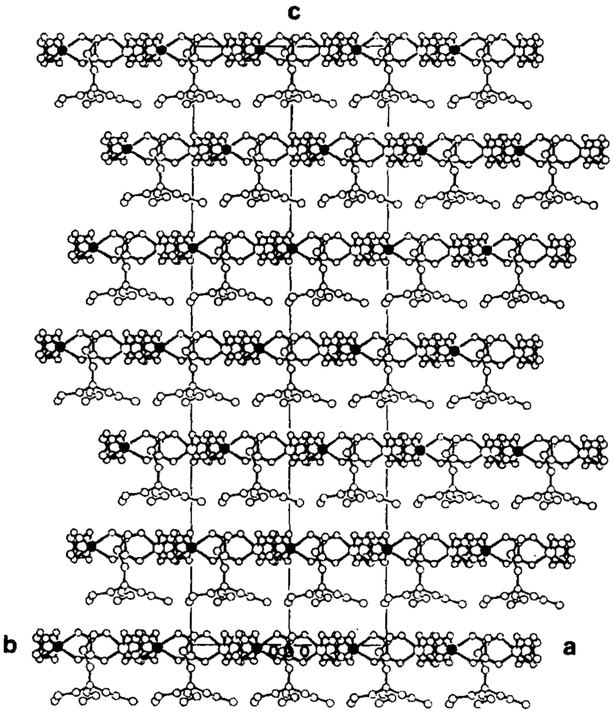

FIGURE 1 [110] projection of $\{[N(n\text{-}C_3H_7)_4][Mn^{II}Cr^{III}(ox)_3]\}_n$. Black atoms indicate Mn positions.

THERMAL AND MAGNETIC STUDIES

For both, 2D and 3D oxalate-bridged network compounds, different magnetic phases have been described in the literature[5-16]. In the following, we will concentrate our discussion on the layer-type compounds, which express a large variety in their molecular-based magnetic behavior. As a matter of fact, within the series $\{[N(n\text{-}C_4H_9)_4][M^{II}Cr^{III}(ox)_3]\}_n$, M^{II}=Mn, Fe, Co, Ni, Cu, which has been shown to be structurally two-dimensional (2D)[5], ferromagnetic phase transitions have been determined at temperatures below 15 K[9]. On the contrary, the compounds $\{[N(n\text{-}C_4H_9)_4][M^{II}Fe^{III}(ox)_3]\}_n$, M^{II}=Fe, Ni, behave as ferrimagnets at temperatures below 43 K and 28 K respectively[10]. The mixed valency compounds $\{[XR_4][Fe^{II}Fe^{III}(ox)_3]\}_n$, X=N, P; R=n-propyl, n-butyl, phenyl) exhibit ferrimagnetism with an unprecedented anomalous negative magnetization in the tetrabutylammonium derivative[11]. Moreover, a further type with a mixed-valency network stoichiometry, $\{[N(n\text{-}C_4H_9)_4][Cr^{II}Cr^{III}(ox)_3]\}_n$ shows only short-range antiferromagnetic correlations but no long-range ordering above the experimental temperature limit of 2 K[12]. Finally, $\{[N(n\text{-}C_4H_9)_4][Mn^{II}Fe^{III}(ox)_3]\}_n$ is an example revealing an antiferromagnetic transition around 50 K[13,14].

However, up to now, some controversy in the literature appears concerning the actual magnetic dimensionality of these 2D compounds and how the structural disorder can affect it. Up to now, there are neither calorimetric studies nor frequency dependent magnetic measurements discussed. The combined use of such independent techniques can help to gain a deeper insight into the magnetic behavior of these systems. In particular, the compounds $\{[P(Ph)_4][M^{II}Cr^{III}(ox)_3]\}_n$, M^{II}=Mn, Fe, have therefore been investigated by a combination of these techniques and some results and conclusions are presented herein.

In a sequel, we shall discuss now the corresponding Mn^{II} and Fe^{II} compounds separately. Fig. 2 shows the heat capacity (C_p) of the heterometallic 2D compound $\{[P(Ph)_4][Mn^{II}Cr^{III}(ox)_3]\}_n$ from 3 to 30 K. A clear lambda peak appears at T_c = 5.8 K indicating the establishment of long-range magnetic ordering.

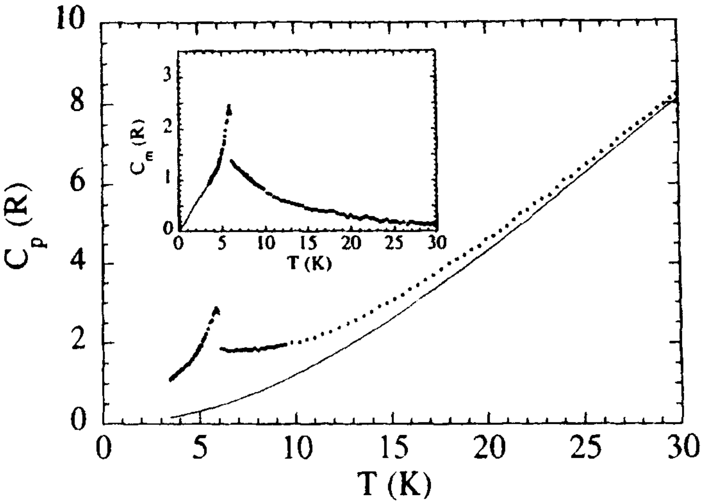

FIGURE 2 Heat capacity of $\{[P(Ph)_4][Mn^{II}Cr^{III}(ox)_3]\}_n$ and estimated lattice contribution (continous line). The inset shows the magnetic contribution to the heat capacity and the spin-waves extrapolation (continous line).

This result is in agreement with a sharp peak observed in the in-phase component (χ') of the ac-susceptibility (T_m=5.6 K), which is accompanied with a strong out-of-phase component. At 1.8 K the magnetization, M, saturates at low applied fields at nearly the expected value for a parallel alignment of the spins (see Fig. 3, lines are guide to the eye). These values agree with previous magnetic measurements[5,13]. According to the crystallographic structure, the intra-plane magnetic interaction through the oxalato bridges is expected to be the strongest. Long-range magnetic ordering can only be due to either the influence of a small interplane interaction or to a small anisotropy.

Since no 2D theoretical magnetic models with alternating 5/2 and 3/2 spins are available, and due to the low spin anisotropy of the Mn^{II} and Cr^{III}

ions, we have analyzed the χ' data using high temperature series in the classical Heisenberg approximation with a mean spin S and J as free parameters. The best fit in the range 15 K < T < 250 K is for the honeycomb model and gives S = 2.06(1) K and J/K = 0.87(1). This value of $S * (S_{Cr}+S_{Mn})/2$ is consistent as a mean value for $S_{Cr} = 3/2$ and $S_{Mn} = 5/2$, and J is in agreement with the expected Mn(II)-ox-Cr(III) interaction[9].

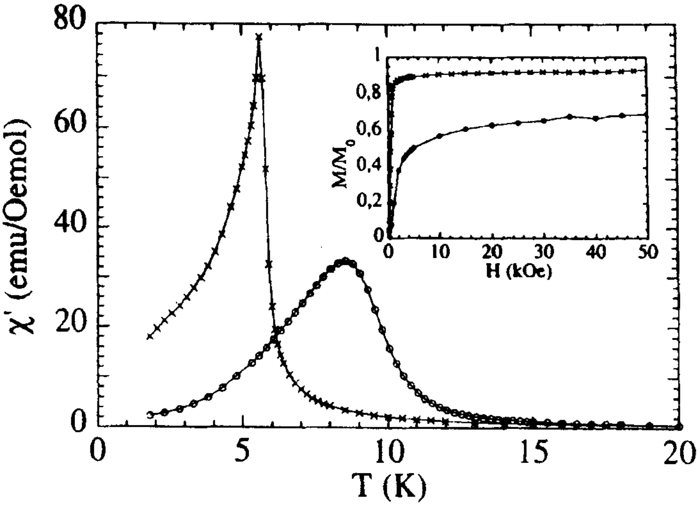

FIGURE 3 χ' versus temperature of polycrystalline $\{[P(Ph)_4][Mn^{II}Cr^{III}(ox)_3]\}_n$ (x) and $\{[P(Ph)_4][Fe^{II}Cr^{III}(ox)_3]\}_n$ (o). The inset shows magnetization versus field, at 1.8 K, scaled to the saturation value of each one $M_0=2*(S_1+S_2)\mu_B$.

The magnetic heat capacity contribution, C_m, can be evaluated by subtracting the lattice contribution, C_L, from C_p. Using the first term from the high temperature series expansion for the Heisenberg honeycomb model we have estimated C_m and calculated C_L for $T > 3\ T_c$. C_L has been extrapolated down in temperature (continous line in Fig. 2) and the magnetic contribution deduced after the subtraction is shown in the inset of Fig. 2. The estimated entropy content, ΔS, after the extrapolation of the experimental data to the expected spin-wave contribution for 2D ferromagnets, is 2.8 R which represents almost 90 % of the theoretical 3.18 R. It indicates that all the magnetic ions contribute to the magnetic ordering. These results strongly support a dimensionality of two for the magnetic system where the magnetic ordering could be triggered by the small anisotropy of the metallic ions.

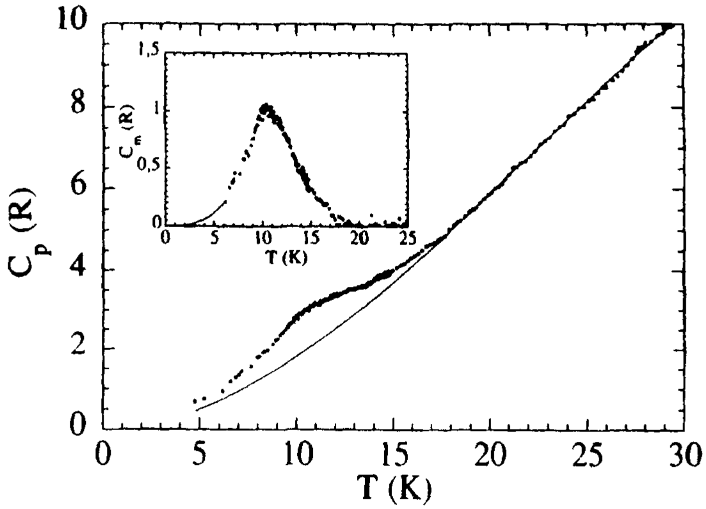

FIGURE 4 Heat capacity of $\{[P(Ph)_4][Fe^{II}Cr^{III}(ox)_3]\}_n$ and estimated lattice contribution (continous line). The inset shows the magnetic contribution to the heat capacity and the spin-waves extrapolation (continous line).

On the other hand, $\{[P(Ph)_4][Fe^{II}Cr^{III}(ox)_3]\}_n$ exhibits a small rounded anomaly in C_p with a maximum at T_m=10.4 K (see Fig. 4), showing no clear evidence of long range magnetic ordering. This behavior is also evident in the magnetic measurements where a broad peak (T_m=8.5 K) is observed in χ' and M(H) at 1.8 K approaches saturation very slowly, representing at 50 kOe only 70 % of the saturation value (see Fig. 3). The shape of the anomaly detected by C_p and its position (at higher temperature than the corresponding anomaly in χ') suggest a spin-glass-like state and ΔS is only 0.69 R which corresponds only to 23 % of the theoretical expected value for a magnetic ordering, 3 R. Additionally, a frequency dependence of the χ' is detected in the range 1-1'000 Hz. The displacement of the maximum of χ', T_m, with frequency can be evaluated as $\Delta T_m/T_m\,\Delta(\log\omega)=0.0085(1)$ which is a typical value for spin glasses.

The observed behavior of $\{[P(Ph)_4][Fe^{II}Cr^{III}(ox)_3]\}_n$ points to the presence of magnetic disorder. Although these systems are crystalline, some amount of structural disorder has been detected in several compounds of the family. Now, recent neutron diffraction experiments on the analogous $\{[N(n\text{-}C_4H_9)_4][Fe^{II}Cr^{III}(ox)_3]\}_n$ compound[15] show asymmetric Bragg peaks which preclude the existence of a true spin-glass. A likely possibility for the low-temperature magnetic state of $\{[P(Ph)_4][Fe^{II}Cr^{III}(ox)_3]\}_n$ is that of asperomagnetism due to the presence of random anisotropy in a system with ferromagnetic interactions. This anisotropy disorder effect is, in principal, not detectable in the case of the Mn^{II} derivative due to the higher isotropic character of that ion, thus showing a ferromagnetic behavior below 6 K.

Acknowledgments

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