

Crystal structure of the molecular ferromagnet $\text{NBu}_4[\text{MnCr}(\text{C}_2\text{O}_4)_3]$ ($\text{Bu} = n\text{-C}_4\text{H}_9$)

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An x-ray study of a single crystal of the composition $\text{NBu}_4[\text{MnCr}(\text{C}_2\text{O}_4)_3]$ reveals a layered structure with an ordered distribution of Mn^{2+} and Cr^{3+} ions. The ferromagnetic system which arises here is a quasi-2D system in terms of the nature of its exchange interactions. According to data on the orientation dependence of the magnetization in an external field, the magnetic moments of Mn^{2+} and Cr^{3+} are directed along the c axis of the crystal.

Molecular magnetic materials, which are new on the scene, exhibit some unusual magnetic properties, which have not been studied extensively.

Most of the molecular magnetic materials produced so far have been constructed on the basis of 1D chains of spins with a ferromagnetic or ferrimagnetic order, coupled with each other by a weak interchain interaction.¹⁻³ A group of Japanese researchers recently produced a family of new metal-complex ferromagnets with the general formula $\text{NBu}_4[\text{M}(\text{C}_2\text{O}_4)_3]$, where $\text{M} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$; NBu_4^+ is the ammonium tetra(n -butyl) ion, and $\text{C}_2\text{O}_4^{2-}$ is the oxalate ion.⁴ Working from a comparative evaluation of the parameters of the superexchange interaction in an $\text{M}^{2+} - (\text{O}_2\text{C}_2\text{O}_2)^{2-} - \text{Cr}^{3+}$ chain, Tamaki *et al.*⁴ suggested that these new compounds are 3D ferromagnets in terms of the nature of their exchange interactions. A valid test of this suggestion requires comparing the results of superstructure and magnetic measurements on single crystals of these compounds. (The study in Ref. 4, like all other reported studies of molecular magnetic materials, was carried out with powders.)

In this letter we are reporting an x-ray study of the structure of a single crystal of the compound $\text{NBu}_4[\text{MnCr}(\text{C}_2\text{O}_4)_3]$. It is our hope that structural studies will shed light on the role played by the large organic cation NBu_4 in shaping the structure and on the reasons for the structural ordering of the magnetic Mn^{2+} and Cr^{3+} ions which is required for interactions with a parallel orientation of magnetic moments.⁵ We also measured the magnetization as a function of the applied magnetic field for various orientations of the crystal with respect to this applied field.

The $\text{NBu}_4[\text{MnCr}(\text{C}_2\text{O}_4)_3]$ single crystals were grown by slow diffusion of aqueous

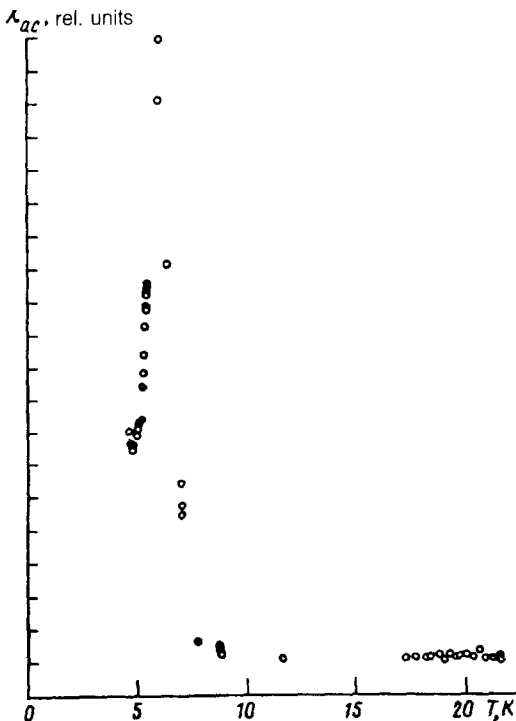


FIG. 1. Dynamic magnetic susceptibility χ_{ac} versus the temperature.

solutions of a mixture of NBu_4Br with $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]3\text{H}_2\text{O}$ and MnCl_2 in an H -shaped tube in an argon atmosphere for two weeks.

Using a set of selected single crystals with typical dimensions of 0.3–0.5 mm, we measured the temperature dependence $\chi_{ac}(T)$ ($\nu = 111$ Hz, $h_{\text{max}} = 10^{-5}$ T) (Fig. 1). The maximum of the magnetic susceptibility at 6 K corresponds to the temperature of the transition to a ferromagnetic state, in agreement with the data of Ref. 4, obtained on a polycrystalline sample.

The x-ray structural analysis was carried out on a single crystal with the shape of a truncated regular pyramid (the side of the triangle at the base of the pyramid was 0.45 mm long, and the height of the pyramid was 0.2 mm). For these measurements we used a KM-4 automatic four-circle diffractometer with monochromatized $\text{Mo } K\alpha$ radiation.

The molecular structure was deciphered and refined in the space group $R3c$ with the help of the AREN x-ray software package. The lattice constants of the hexagonal lattice are $a = b = 9.414(5)$ Å and $c = 53.662(6)$ Å, with $V = 4125$ Å³ and $d_{\text{cal}} = 1.485$ g/cm³. In the experiment, measurements were made of 570 independent reflections with $I > 3\sigma$, $\sin \theta/\lambda < 0.595$ Å⁻¹. The carbon atoms of the cation were disordered; we did not succeed in determining their positions accurately.

Figure 2 is a 3D image of the arrangement of atoms in the cell. For simplicity the

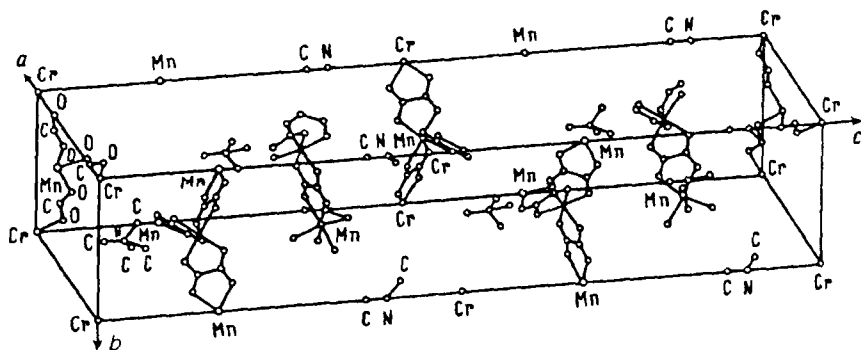


FIG. 2. Three-dimensional image of the arrangement of atoms in the cell. For clarity, some of the atoms are not shown; it is not possible to select a better viewpoint.

NBu_4^+ cation is represented by a nitrogen atom and the four carbon atoms bound to it. The metal ions are on threefold axes and are in a distorted octahedral neighborhood made up of the oxygen ions of oxalate groups $(\text{C}_2\text{O}_4)^{2-}$. Each ion of a given species is bound by $(\text{C}_2\text{O}_4)^{2-}$ groups to three ions of a different species and forms a layer in the form of a hexagonal network, in a manner similar to that modeled in one version of the structure in Ref. 4.

The nitrogen atoms of the NBu_4^+ cations are also on threefold axes, forming a plane above a network of the nearest anion layer at a distance of 3.32 Å. One of the butyl groups near a threefold axis (the c axis) penetrates a void in a neighboring $[\text{MnCr}(\text{C}_2\text{O}_4)_3]_{200}$; the three others are directed toward Mn^{2+} ions of the opposite layer. This configuration apparently creates a difference between the Mn^{2+} and Cr^{3+} sites and promotes an ordered arrangement of these ions in the crystal. The Cr–O distances are 1.97(2) and 2.03(2) Å, and the Mn–O distances are 2.14(2) and 2.15(2) Å. Each metal ion of a given species in an anion layer has only a single nearest neighbor: an ion of another species in a layer below or above the given layer, at a distance of 8.95 Å.

By virtue of the structural order of the magnetic ions, a ferromagnetic order of the spins thus becomes possible thanks to $\text{Mn}^{2+} - (\text{O}_2\text{C}_2\text{O}_2) - \text{Cr}^{3+}$ interactions within a layer and a weak interplanar $\text{Mn}^{2+} - \text{Cr}^{3+}$ exchange at a distance ~ 9 Å. It might be possible to strengthen this exchange and to achieve the corresponding increase expected in T_c by bringing the layers of metal ions closer together, by (for example) reducing the length of the organic “tail” of the cation by replacing one C_4H_9 butyl group by shorter groups, C_3H_7 or C_2H_5 . It can be concluded that this magnetic system is a quasi-2D system in terms of the nature of its exchange interactions. A positive sign of the direct or indirect exchange in the $d^5 - d^3$ pair is predicted by the semiempirical Goodenough-Kanamori rules⁵ and is in agreement with experimental data.⁶

Measurements of the magnetization as a function of the external magnetic field, $M(H)$, were carried out on an identical single crystal at 4.5 K on a PARC M4500 vibration magnetometer for two orientations of the external field: along the c axis of

the crystal and perpendicular to it. It turns out that in the orientation $\mathbf{H} \parallel \mathbf{c}$ saturation is reached in fields as low as ~ 0.05 T, while in the orientation $\mathbf{H} \perp \mathbf{c}$ the $M(H)$ curve is still far from saturation in a field $H=1$ T. According to the data of Ref. 5, the saturation field in a polycrystalline sample is ~ 3 T. The magnetic moments of Mn and Cr are probably aligned along the \mathbf{c} axis of the crystal (it is an Ising ferromagnet), but this conclusion requires further testing.

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