Molecular magnet based on the $Fe^{II,III}$ complex with squaric acid

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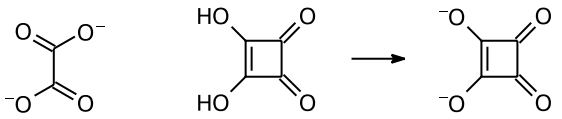
The reaction of Fe^{II} and Fe^{III} salts with tetrabutylammonium squarate in an aqueous solution gives rise to a new molecular magnet (T_c = 8.6 K).

Key words: molecular magnet, iron complexes, squaric acid.

Vigorous research has been undertaken lately to find compounds capable of magnetic ordering, *i.e.*, molecular magnets.[1] This study is an attempt at obtaining such compounds based on transition metal complexes with the squaric acid anion (Sq), which commonly functions as a bridging ligand.[2—6] The Sq anion contains four electron-donating atoms and thus resembles the oxalate anion (Ox), whose tris-chelate complexes have formed the basis for a family of molecular magnets.[7—10] However, unlike Ox, Sq does not tend to form chelates with metal ions of the first transition row, because of substantially larger distances between adjacent oxygen atoms (~2.6—2.7 Å for Ox and ~3.2—3.3 Å for Sq). Only few examples of chelation by the Sq anion are known for metals with large ion radii (like Pb and Ce).[11]



Indeed, our attempts to synthesize heterometallic *3d* metal complexes with Sq in the same way as oxalate complexes were unsuccessful. Nevertheless, the formation of a $Fe^{II,III}$ compound was detected under conditions similar to those used in the heterometallic oxalate syntheses. This product was identified as $[N(n\text{-}C_4H_9)_4]_2[Fe^{II}Fe^{III}(C_4O_4)_3(HC_4O_4)]\cdot 7H_2O$ (**1**) relying on the reproducible data of elemental analysis. Since H_2Sq is a fairly strong acid (pK_1 = 1.2, pK_2 = 3.5),[12] compound **1** contains water molecules rather than hydroxy groups. Furthermore, the composition of the solid phase of **1** did not change upon variation of the initial Fe/Sq ratio, which implies that this is an individual compound. Note that the synthesis of **1** requires the simultaneous presence, in the reaction mixture, of iron ions in different oxidation states and the tetrabutylammonium squarate, because the reaction of either Fe^{II} or Fe^{III} alone with $[N(n\text{-}C_4H_9)_4]_2Sq$ affords the known $Fe(C_4O_4)\cdot 2H_2O$ and $Fe(C_4O_4)(OH)\cdot 3H_2O$ complexes, respectively.[13,14] Compound **1** has a characteristic IR spectrum (Fig. 1). The presence of the tetrabutylammonium cation is confirmed by the ν(C—H) bands in the region of 2870—2970 cm^{-1}, and the presence of water molecules is validated by a broad band at about 3300—3600 cm^{-1}. Repeated attempts to grow a high-quality single crystal by recrystallizing **1** from CH_2Cl_2 or MeCN or by interdiffusion of aqueous solutions of iron salts and $[N(n\text{-}C_4H_9)_4]_2Sq$ in agar or silicate gels failed; this precluded structure determination. A powder X-ray diffraction pattern attests that **1** is a crystalline compound. It contains no peaks typical of the known Fe^{II} or Fe^{III} compounds with squaric acid, $Fe(C_4O_4)\cdot 2H_2O$ or $Fe(C_4O_4)(OH)\cdot 3H_2O$, which were prepared by known procedures[14] and used for comparison.

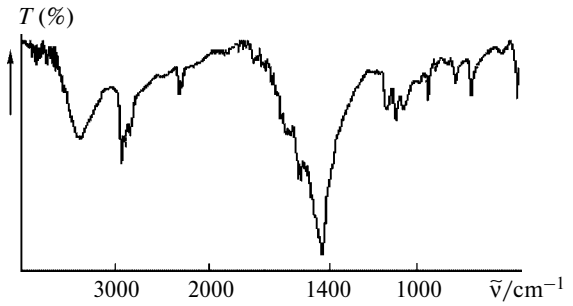


Fig. 1. IR spectrum of compound **1**.

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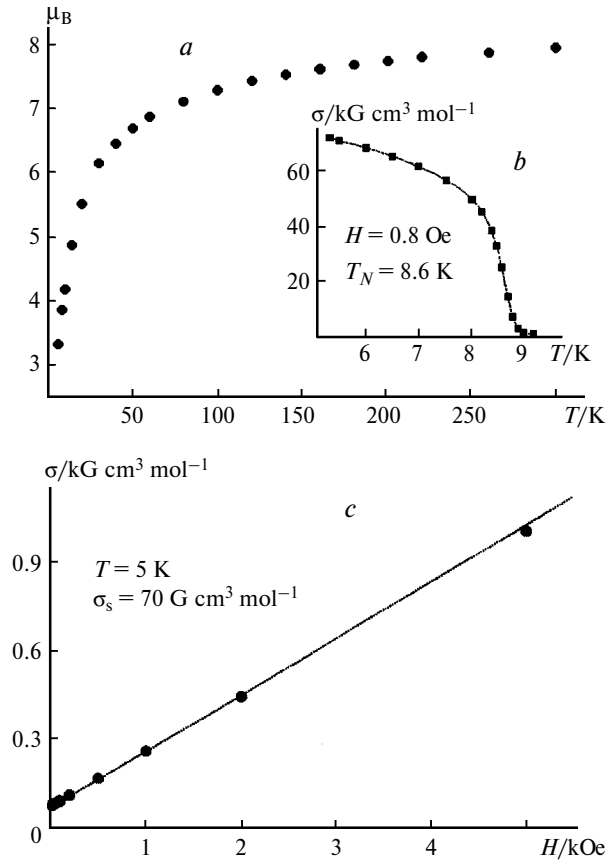

Fig. 2. Magnetic properties of compound **1**: (*a*) temperature dependence of the effective magnetic moment; (*b*) temperature dependence of magnetization; (*c*) field dependence of magnetization at $T = 5$ K.

Study of the magnetic properties showed that the effective magnetic moment of compound **1** at room temperature is 7.9 μ_B, which is close to the theoretical value, 7.68 μ_B, for noncoupled Fe^{III} ($S = 5/2$) and Fe^{II} ($S = 2$) spins. As temperature decreases, μ_{eff} decreases (Fig. 2), indicating the predominance of antiferromagnetic exchange interactions. Below 10 K, complex **1** undergoes a magnetic phase transition into a magnetically ordered state. The ordering temperature ($T_N = 8.6$ K) was determined as the extremum of $\partial\sigma/\partial T$ for the $\sigma(T)$ curve measured in a low field (0.8 Oe). Below T_N, the magnetization isotherms obey the equation $\sigma(H) = \sigma_s + \chi H$, where σ_s = 70 G cm^3 mol^{-1} at $T = 5$ K. These results imply that at $T_N < 8.6$ K, the substance passes to an antiferromagnetic state with a weak ferromagnetism. We also confirmed the published data[14] stating that in the case of $Fe(C_4O_4) \cdot 2H_2O$ and $Fe(C_4O_4)(OH) \cdot 3H_2O$, the cooperative magnetic ordering effects are not manifested down to 2 K.

Experimental

The IR spectra were recorded using a Bruker Vector 22 spectrometer in the 400—4000 cm^{-1} range for samples pressed as pellets with KBr. The magnetic susceptibilities of the obtained phases in the 2—300 K temperature range were measured using a Quantum Design MPMS-5S SQUID magnetometer.

Synthesis of tris(squarato)hydrosquaratodiferrate(II,III)bistetrabutylammonium heptahydrate, $[N(n\text{-}C_4H_9)_4]_2[Fe^{II}Fe^{III}(C_4O_4)_3(HC_4O_4)] \cdot 7H_2O$. A solution of $H_2C_4O_4$ (171 mg, 1.5 mmol) in 5 mL of water was neutralized at ~20 °C with a 40% aqueous solution of $N(n\text{-}C_4H_9)_4OH$ to pH 7 (acidity was controlled using a Calimatic 756 pH-meter). A solution containing $FeCl_3 \cdot 6H_2O$ (135 mg, 0.5 mmol) and $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (196 mg, 0.5 mmol) in 5 mL of water was added to the obtained solution of $[N(C_4H_9)_4]_2C_4O_4$. The mixture immediately turned dark violet. After 3 h, the finely dispersed dark violet precipitate was filtered off, washed with cold water, and dried in air. Yield 235 mg (53%). Found (%): Fe, 9.6; C, 49.3; N, 2.6; H, 7.1. $Fe_2C_{48}H_{87}O_{23}N_2$. Calculated (%): Fe, 9.5; C, 49.2; N, 2.4; H, 7.5.

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