

Synthesis and Magnetic Characterization of Two Air-Stable Complexes of Chromium(II) with the Squarate Ion

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Air-stable chromium(II) compounds are normally characterized by having dimeric or polymeric structures and low solubilities. We have prepared two chromium(II) squarates that represent no exception to that rule.

Our interest in the compounds originates from the fact that chromium(II) sulfate pentahydrate reacts with *N,N'*-bis(pyridylmethyl)amine forming a dinuclear chromium(III) complex with the sulfate ion as a bidentate bridging ligand.¹ In consequence we wanted to find out whether this method of inserting a suitable bridging ligand in chromium(III) complexes by starting from an appropriate chromium(II) compound was of general utility. The squarate ion was expected to be a potential bridging ligand but chromium(II) squarate had never been described.

West and Niu² were the first to synthesize a series of isomorphous compounds of the general formula $\text{Me(II)C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$, where Me = Mg, Mn, Fe, Co or Ni. They proposed a chain structure with the squarate ion acting as a bridging chelate ligand. Later, Gerstein and Habenschuss³ suggested a three-dimensional structure based on an X-ray investigation of a twinned crystal of the nickel compound. They found that all four squarate oxygen atoms were involved in the bridging of four different nickel atoms (Fig. 1a). Robl and Weiss⁴ have accomplished the X-ray structure analysis of $\text{CuC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$. They found a chain structure with the squarate ion acting as a bridging non-chelating ligand (Fig. 1b). The chains are

interlinked by common water molecules coordinated to metal atoms in different chains, and weak bonds between metal atoms in one chain and squarate oxygen atoms in another. Finally, Weiss *et al.*⁵ have synthesized an isomorphous series of squarates of the general formula $\text{Me(II)C}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$ where Me = Mn, Fe, Co, Ni or

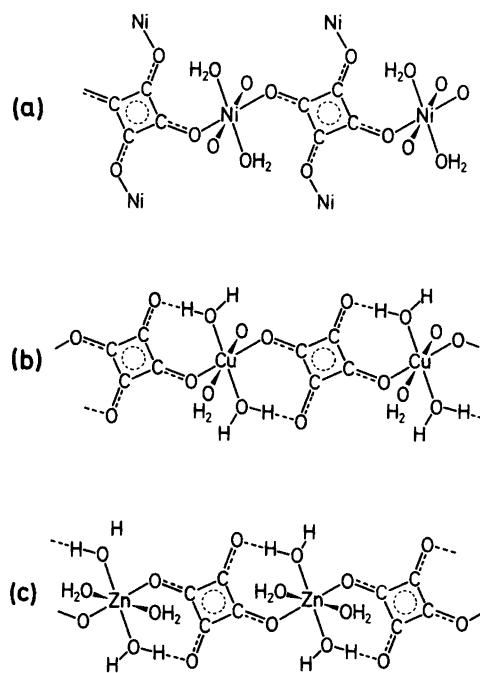


Fig. 1. Structures of different types of metal squarates.

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Zn. By X-ray structure determination of the zinc compound they have proven an open-chain structure (Fig. 1c) with chains that are interlinked by hydrogen bonding.

Weiss *et al.*⁵ found that the dihydrates were formed at high temperatures and the tetrahydrates at low temperatures. With that in mind we were able to synthesize two different chromium(II) squarates with 2 and 4 mol of water per mol of chromium, respectively. The compounds had different powder diagrams and different reactivity towards acids and bases. Neither of them is isomorphous with the compounds described above. They may, however, have polymeric structures similar to those described above, with the squarate ion acting as a bridging non-chelate ligand.

Experimental

Reagents and analyses. Chromium(II) sulfate pentahydrate was prepared by standard methods.⁶ Squaric acid, 3,4-dihydroxy-3-cyclobutene-1,2-dione, was bought from Fluka AG, Buchs, Switzerland. The chromium analyses were performed on a Perkin-Elmer 403 atomic absorption spectrophotometer. The carbon and hydrogen analyses were carried out by standard methods. The oxidation state of chromium was confirmed by titration with Ce(IV).

Preparations. a. *Chromium(II) squarate dihydrate*, $\text{CrC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$. Squaric acid (0.500 g ~ 4.38 mmol) was dissolved in boiling water (7.5 ml). The solution was filtered, and crushed chromium(II) sulfate pentahydrate (1.000 g ~ 4.20 mmol) was added. An apple-green compound started to separate immediately. After 15 min the precipitate was filtered off and carefully washed with boiling water and with ethanol. Yield: 0.50 g (60%). Anal. $\text{CrC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$: Cr, C, H.

b. *Chromium(II) squarate tetrahydrate*, $\text{CrC}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$. Squaric acid (0.100 g ~ 0.88 mmol) was dissolved at room temperature in water (10 ml). The solution was cooled below 10° and crushed chromium(II) sulfate pentahydrate (0.21 g ~ 0.88 mmol) was added. The precipitation of a lime-coloured compound started immediately. The compound was filtered off after 15 min, and washed with ice-water and with ethanol. Yield: 0.083 g (40%). Anal. $\text{CrC}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$: Cr, C, H.

Physical measurements. The magnetic susceptibilities of powdered samples were measured by the Faraday method in the temperature range 2–300 K at a field strength of 1.3 T. The magnetic field strength was calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$.⁷ A more detailed description of the equipment has been published elsewhere.⁸ The X-ray powder photographs were obtained on a camera of the Guinier type with $\text{CuK}\alpha$ radiation. Silicon was used as internal standard (cf. Table 1).

Chemical reactions

$\text{CrC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ when suspended in hydrochloric acid (1 M) showed only sparse signs of reaction, even after 24 h. $\text{CrC}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$, however, immediately formed a blue-green solution from which a grey-blue precipitate had separated the next day. This compound was identified by means of analyses and X-ray powder photographs as the dinuclear complex $[(\text{H}_2\text{O})_2\text{Cr}(\text{C}_4\text{O}_4)_2(\text{OH})_2\text{Cr}(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, investigated by West and Niu,² and by Chesick and Doany.⁹ The dihydrate reacted with sodium hydroxide (1 M) to form a black-brown precipitate that was transformed to a green insoluble solid, presumably chromium(III) hydroxide, after some time. Under the same circumstances the tetrahydrate formed the hydroxide immediately. Both squarates reacted with *N,N*-bis(pyridylmethyl)amine to form dinuclear chromium(III) complexes with the squarate ion acting as a bridging as well as a terminal ligand.¹⁰

Table 1. Lattice spacings (Å) calculated from Guinier diffraction patterns.

$\text{CrC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$	6.60 w	5.61 m	4.91 w	4.31 s	3.96 m	3.50 w	3.20 w
	3.09 m	2.81 m	2.74 m				
$\text{CrC}_4\text{O}_4 \cdot 4\text{H}_2\text{O}$	7.24 w	4.82 s	4.02 m	3.63 w	3.51 w	3.11 w	2.69 w

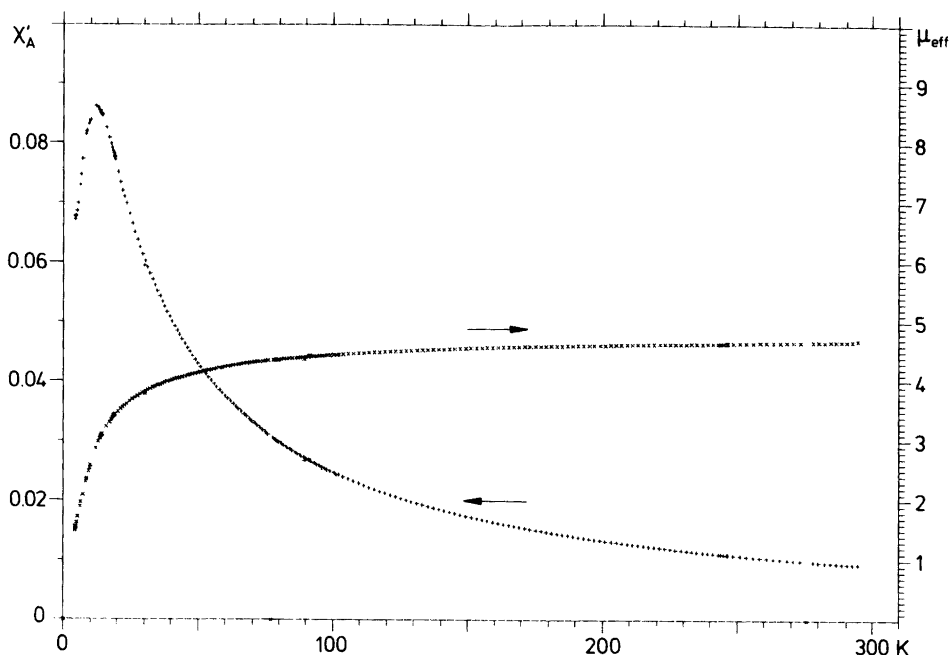


Fig. 2. Magnetic susceptibilities (left scale, in cgs units) and calculated effective moments (right scale, in Bohr magnetons) of $\text{CrC}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Magnetic properties

For both compounds the variation of the susceptibilities as a function of temperature resembles the behaviour predicted for antiferromagnetically coupled dimeric units, each with $S = 2$. The dihydrate exhibits a maximum of $\chi'_A = 8.627 \cdot 10^{-2}$ cgsu at 11.93 K (cf. Fig. 2), and the tetrahydrate a maximum of $\chi'_A = 1.353 \cdot 10^{-1}$ cgsu at 7.89 K. In both cases, the calculated effective magnetic moments approach 4.8 BM at 300 K and appear 0 BM at 0 K. The magnetic moments at room temperature are as expected for weakly coupled high spin d^4 systems in symmetries low enough to quench orbital contributions to the moments. Fittings of the entire data sets⁸ show that simple Heisenberg Hamiltonians applied to dimeric units with $S = 2$ do not account for the observations within the uncertainties of our measurements. The best fits (calculated variance per degree of freedom was 80) give singlet-triplet separations of $3.61(2) \text{ cm}^{-1}$ and $2.37(2) \text{ cm}^{-1}$ for the dihydrate and tetrahydrate, respectively. The deviations from the predictions of such a simple model are probably due to extended interactions in one or more dimensions.

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