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Chromium(II) Double Sulphates

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DOUBLE sulphates of chromium(II) have long been known,¹⁻³ but no investigations of their magnetic or spectral properties have been reported. The blue double sulphates: $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CrSO}_4 \cdot 6\text{H}_2\text{O}$ ($\mu_{\text{eff}} = 4.88$ B.M. at 300°K , $\theta = 0^\circ$); $\text{Na}_2\text{SO}_4 \cdot \text{CrSO}_4 \cdot 2\text{H}_2\text{O}$ ($\mu_{\text{eff}} = 4.89$ B.M., $\theta = 7^\circ$); $\text{K}_2\text{SO}_4 \cdot \text{CrSO}_4 \cdot 3\text{H}_2\text{O}$ ($\mu_{\text{eff}} = 4.80$ B.M., $\theta = 6^\circ$); $\text{Rb}_2\text{SO}_4 \cdot \text{CrSO}_4 \cdot 6\text{H}_2\text{O}$ ($\mu_{\text{eff}} = 4.95$ B.M., $\theta = 0^\circ$); $\text{Cs}_2\text{SO}_4 \cdot \text{CrSO}_4 \cdot 6\text{H}_2\text{O}$ ($\mu_{\text{eff}} = 4.93$ B.M., $\theta = 0^\circ$), have been prepared by the addition of ethanol to concentrated equimolar solutions of the component sulphates.* The second and third compounds were previously said to contain $4\text{H}_2\text{O}^1$ and $6\text{H}_2\text{O}^2$ respectively. The reciprocals of their magnetic susceptibilities decrease linearly with temperature down to liquid-nitrogen temperatures. Effective magnetic moments μ_{eff} at 300°K , and Curie-Weiss constants θ , are given in parenthesis. All magnetic moments are close to the spin-only value for four unpaired electrons of 4.90 B.M. These double sulphates are therefore magnetically dilute, high-spin ($t_{2g}^3 e_g^1$) chromium(II) compounds. Their diffuse reflectance spectra show the broad, asymmetric band near $14,000 \text{ cm}^{-1}$, found in simple, hydrated chromium(II) salts.^{4,5}

The caesium double sulphate loses water to give a violet dihydrate merely by continuous pumping for a few hours at room temperature—the drying process used for the other double sulphates. To obtain the hexahydrate uncontaminated with the dihydrate it is necessary to wash with aqueous

alcohol, alcohol alone causing partial dehydration, and dry for the shortest possible time.

The caesium hexahydrate and $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$ have infrared absorptions typical of ionic sulphate groups (T_d symmetry), but in the infrared spectrum of the violet dihydrate the ν_3 and ν_4 bands of the sulphate groups, which are triply degenerate in the free ion, are well resolved. Thus, the symmetry of the sulphate groups has been reduced to C_{2v} . Such behaviour is characteristic of bidentate chelate or bridging sulphato-groups, but does not distinguish between them.⁶ The dihydrate shows unexpected magnetic behaviour: at 300°K $\mu_{\text{eff}} = 2.8$ B.M., and this moment is almost independent of temperature ($\theta = 10^\circ$). Although few magnetic studies have been carried out, magnetic moments less than 4.9 B.M. have been found in a variety of chromium(II) compounds. In the oxalate,⁷ phosphate,⁴ and ammonium trifluorochromate(II)⁸ weak antiferromagnetic interactions lead to magnetic moments at 300°K a little less than 4.9 B.M. which diminish considerably with decreasing temperature. In the acetate and other carboxylates⁷ strong interactions between chromium atoms in binuclear structures analogous to that of copper(II) acetate lead to magnetic moments of about 1 B.M. which are also temperature-dependent. Thus, antiferromagnetic interactions in an acetate-type structure $[\text{Cr}_2(\text{SO}_4)_4(\text{H}_2\text{O})_2]^{4-}$, sufficiently strong to reduce μ_{eff} to 2.8 B.M., would be expected to cause a marked variation of μ_{eff} with temperature.

* Satisfactory analyses have been obtained for chromium and sulphate.

Magnetic moments of about 3.0 B.M. which are almost independent of temperature have been reported only for spin-paired⁹ complexes, e.g., $[\text{Cr}(\text{bipy})_3]\text{Cl}_2$. From the available evidence the violet dihydrate is a spin-paired compound (t_{2g}^4) although this is surprising since the ligands are SO_4^{2-} and H_2O . If spin-pairing is assumed, the strong, broad absorption at $18,200\text{ cm}^{-1}$ in the reflectance spectrum of the dihydrate can be assigned to a transition from the ${}^3T_{1g}$ ground state to one or more of the group of excited triplet states¹⁰ which are close together in energy.

The violet compound is hygroscopic and air-sensitive and becomes blue in moist nitrogen. Dissolved in water, it gives the spectrum of the aquated chromium(II) ion. By heating at $150\text{--}160^\circ$ an anhydrous, pale blue, high-spin chromium(II) compound is obtained ($\mu_{\text{eff}} = 4.43$ B.M. at 300°K , $\theta = 16^\circ$) which has a broad absorption at $12,800\text{ cm}^{-1}$. This behaviour is restricted to the caesium compound, the rubidium compound, for example, loses water much less readily, and no intermediate violet dihydrate has been obtained.

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