

594. Some Magnetically Normal Chromium(II) Salts

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The magnetic properties of several spin-free chromium(II) salts have been investigated between 90 and 330°K. Only the monohydrogen phosphate shows any appreciable variation of magnetic moment with temperature. Measurements of visible spectra in aqueous solution have confirmed previous work. The reaction of an excess of chromium with mineral acid has been found to lead to pure chromium(II) compounds.

COMPARATIVELY little is known of the chemistry of chromium(II), because of the extreme sensitivity of compounds of this oxidation state to aerial oxidation. There are few reports of detailed investigations of even simple hydrated chromium(II) salts. As part of a general study of chromium(II) chemistry, and in order to provide a basis for understanding the complicated magnetic behaviour¹ of certain chromium(II) compounds, paramagnetic susceptibilities of several salts, $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CrBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrI}_2 \cdot 5\text{H}_2\text{O}$, $\text{Cr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, and $\text{CrHPO}_4 \cdot 4\text{H}_2\text{O}$, expected to show magnetically "normal" behaviour, have been determined over the temperature range 90–330°K. Only the sulphate, $\text{CrSO}_4 \cdot 6\text{H}_2\text{O}$, seems hitherto to have been investigated in this way. Lips² has shown it to obey the Curie law, with a magnetic moment of 4.82 B.M. at room temperature. Single-temperature measurements in aqueous solution have given values of 5.0³ and 4.83 B.M.⁴ for the chloride, and 4.83 B.M.⁴ for the sulphate.

Chromium(II) solutions are commonly prepared by three general methods: (i) the electrolytic reduction of chromium(III) solutions; (ii) the reduction of chromium(III) solutions with zinc and mineral acid; and (iii) the solution, in mineral acid, of chromium(II) acetate, previously precipitated from chromium(II) solutions obtained by methods (i) or (ii). However, the compounds listed above, except the monohydrogen phosphate which was prepared by metathesis, were prepared by heating an excess of chromium metal with the appropriate dilute acid. Procedures (i) and (iii) involve more manipulation of air-sensitive solutions than does the use of the metal, and (ii) could lead to contamination with zinc compounds, e.g., zinc phosphate. Since the standard oxidation potentials to the bivalent state for zinc and chromium are similar (–0.763 and –0.91v, respectively⁵), either metal should efficiently reduce chromium(III) ions.

For the Cr(II)/Cr(III) couple, $E_0 = -0.41\text{v}$.⁵ Thus aqueous chromium(II) solutions are thermodynamically unstable to oxidation by hydrogen ions in acid solution. This is apparently why it has been considered that pure chromium(II) salts could not be prepared by dissolving the metal in acids.⁶ Nevertheless, even in acid conditions, and provided that catalysts and complexing agents are absent, oxidation by hydrogen ions is very slow,⁷ and must be even slower in the nearly neutral solutions (pH \approx 5) remaining after the reaction of the acid with the excess of metal is complete. The compounds prepared in this way are analytically pure, and some magnetic data already published in a preliminary form¹ indicate that only traces of chromium(III) impurities can be present. Lux and his collaborators^{8,9} have also recently prepared many pure chromium(II) compounds from the metal, and have shown that the powder photographs⁹ of the hydrated sulphates and fluorides of copper(II) and chromium(II) are very similar.

¹ A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *Proc. Chem. Soc.*, 1963, 281, and unpublished work.

² E. Lips, *Helv. Phys. Acta*, 1934, **7**, 537.

³ D. N. Hume and H. W. Stone, *J. Amer. Chem. Soc.*, 1941, **63**, 1200.

⁴ B. Cabrera and S. P. De Rubies, *Anales Soc. españ. Fis. Quím.*, 1919, **17**, 149.

⁵ W. M. Latimer, "Oxidation Potentials," 2nd edn., Prentice-Hall, New York, 1952.

⁶ H. Remy, "Treatise on Inorganic Chemistry," Elsevier, London, 1956, p. 133.

⁷ J. B. Hunt and J. E. Earley, *J. Amer. Chem. Soc.*, 1960, **82**, 5312; K. D. Kopple, G. F. Svatos, and H. Taube, *Nature*, 1961, **189**, 393; H. W. Stone, *Analyt. Chem.*, 1948, **20**, 747.

⁸ H. Lux and G. Illmann, *Chem. Ber.*, 1958, **91**, 2143.

⁹ H. Lux, L. Eberle, and D. Sarre, *Chem. Ber.*, 1964, **97**, 503.

Absorption Spectra.—The splitting of the ground term 5D ($3d^4$) of the free chromium(II) ion in (a) octahedral and (b) tetragonal fields¹⁰ is given in Figure 1. The few spectral investigations so far reported¹¹⁻¹³ have shown chromium(II) salts in aqueous solution to give a single band near $14,000\text{ cm}^{-1}$, which has been assigned to the expected $^5T_{2g} \leftarrow ^5E_g$ transition (Figures 1 and 2). However, the band is broad and asymmetric, and this has been ascribed to the large tetragonal distortion expected from the orbitally doubly-degenerate E_g ground state. Liehr and Ballhausen¹⁴ have estimated the splitting of the E_g state to be *ca.* 6000 cm^{-1} . From a study of the optical absorption spectra of single crystals of hydrated chromium(II) chloride and sulphate at room temperature and at 77°K , and assuming that $\Delta = 11,700\text{ cm}^{-1}$, Runciman and Syme¹³ obtained a ground-state splitting of 8000 cm^{-1} .

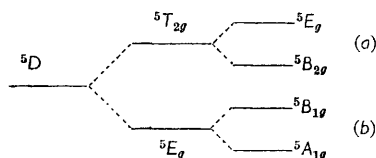


FIGURE 1. Splitting of the free-ion ground term of Cr(II), 5D , in (a) an octahedral field, and (b) a tetragonal field

The earlier work on aqueous solutions has been confirmed. All the soluble salts showed a broad, asymmetric band close to $14,000\text{ cm}^{-1}$, with $\epsilon = 5$. The absorption increased markedly from about $27,000\text{ cm}^{-1}$ into the ultraviolet region, presumably because of charge transfer between the metal and the ligands. Figure 2 shows the spectrum (A) of a

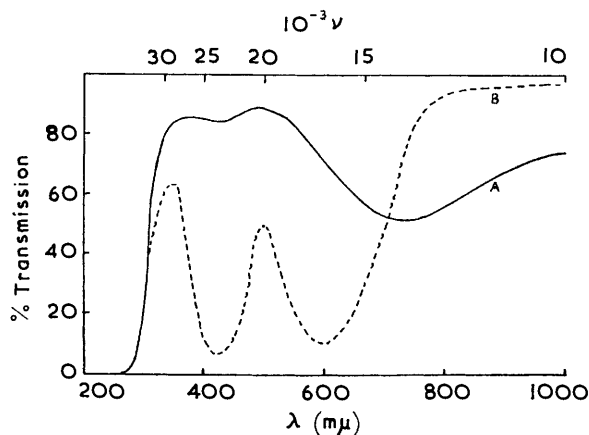


FIGURE 2. Ultraviolet and visible spectra of a 0.062M-aqueous solution of chromium(II) bromide, (A) before oxidation, and (B) after oxidation

0.062M-solution of chromium(II) bromide, and the change (B) after exposure to air for a few minutes. The weak band at $24,100\text{ cm}^{-1}$, superimposed on the low-frequency side of the charge-transfer absorption in the unoxidised solution, apparently arises from a few percent of chromium(III) impurity. Owing to the intense chromium(III) band near $16,700\text{ cm}^{-1}$, a small amount of oxidation can affect the width and position of the chromium(II) band. The nature of the chromium(III) species is not known. Chromium(II) sulphate, once dry, oxidises only slowly in air, and the reflectance spectrum of a freshly prepared sample showed a broad band at $14,000\text{ cm}^{-1}$.

Magnetic Data.—All the compounds, except the phosphate, obeyed the Curie law, with magnetic moments at room temperature close to the spin-only value for four unpaired

¹⁰ B. N. Figgis, *Trans. Faraday Soc.*, 1960, **56**, 1553.

¹¹ O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, 1957, **26**, 1686.

¹² H. L. Schläfer and H. Skoludek, *Z. phys. Chem. (Frankfurt)*, 1957, **11**, 277.

¹³ W. A. Runciman and R. W. G. Syme, *Phil. Mag.*, 1963, **8**, 605.

¹⁴ A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (New York)*, 1958, **3**, 304.

electrons, 4.90 B.M. (Figure 3; the Table). In the first approximation, no orbital contribution to the magnetic moment should arise in octahedral spin-free chromium(II)

Variation of magnetic properties of chromium(II) salts with temperature

| CrSO ₄ ·5H ₂ O | | | | CrCl ₂ ·4H ₂ O | | | |
|--------------------------------------|--------------------------------|----------------------------------|-------------------------|--------------------------------------|--------------------------------|----------------------------------|-------------------------|
| T (°K) | 10 ⁶ χ _A | 10 ⁻² /χ _A | μ _{eff} (B.M.) | T (°K) | 10 ⁶ χ _A | 10 ⁻² /χ _A | μ _{eff} (B.M.) |
| 326.0 | 9151 | 1.093 | 4.91 | 323.8 | 9453 | 1.058 | 4.97 |
| 310.0 | 9622 | 1.039 | 4.91 | 309.8 | 9719 | 1.029 | 4.93 |
| 297.9 | 10,093 | 0.9912 | 4.92 | 297.0 | 10,180 | 0.9827 | 4.94 |
| 274.5 | 10,980 | 0.9100 | 4.93 | 274.5 | 11,050 | 0.9053 | 4.95 |
| 250.0 | 12,080 | 0.8281 | 4.93 | 249.6 | 12,090 | 0.8274 | 4.93 |
| 230.0 | 13,140 | 0.7612 | 4.94 | 228.5 | 13,230 | 0.7559 | 4.94 |
| 207.5 | 14,510 | 0.6892 | 4.93 | 206.1 | 14,710 | 0.6798 | 4.94 |
| 184.5 | 16,450 | 0.6080 | 4.95 | 187.7 | 16,270 | 0.6147 | 4.96 |
| 158.5 | 19,280 | 0.5187 | 4.96 | 164.5 | 18,500 | 0.5405 | 4.95 |
| 132.0 | 23,000 | 0.4348 | 4.95 | 146.5 | 20,740 | 0.4821 | 4.95 |
| 107.7 | 28,560 | 0.3502 | 4.98 | 126.7 | 24,240 | 0.4125 | 4.98 |
| 96.0 | 32,040 | 0.3121 | 4.98 | 108.0 | 28,350 | 0.3528 | 4.97 |
| | | | | 94.0 | 32,680 | 0.3059 | 4.98 |

Diamagnetic correction = -105×10^{-6}

Diamagnetic correction = -99×10^{-6}

| CrBr ₂ ·6H ₂ O | | | | Cr(ClO ₄) ₂ ·6H ₂ O | | | |
|--------------------------------------|--------------------------------|----------------------------------|-------------------------|---|--------------------------------|----------------------------------|-------------------------|
| T (°K) | 10 ⁶ χ _A | 10 ⁻² /χ _A | μ _{eff} (B.M.) | T (°K) | 10 ⁶ χ _A | 10 ⁻² /χ _A | μ _{eff} (B.M.) |
| 324.8 | 9376 | 1.066 | 4.96 | 326.5 | 9392 | 1.065 | 4.97 |
| 309.5 | 9840 | 1.016 | 4.96 | 311.4 | 9820 | 1.018 | 4.96 |
| 291.0 | 10,560 | 0.9469 | 4.98 | 295.3 | 10,420 | 0.9597 | 4.98 |
| 274.0 | 11,060 | 0.9045 | 4.94 | 272.5 | 11,230 | 0.8906 | 4.97 |
| 255.3 | 11,940 | 0.8372 | 4.96 | 248.0 | 12,300 | 0.8130 | 4.96 |
| 229.4 | 13,300 | 0.7519 | 4.96 | 223.0 | 13,610 | 0.7347 | 4.95 |
| 206.5 | 14,750 | 0.6779 | 4.96 | 199.2 | 15,730 | 0.6356 | 5.03 |
| 184.5 | 16,630 | 0.6013 | 4.97 | 172.0 | 18,340 | 0.5452 | 5.04 |
| 159.0 | 19,310 | 0.5178 | 4.98 | 147.0 | 21,260 | 0.4704 | 5.02 |
| 132.0 | 23,400 | 0.4274 | 4.99 | 125.5 | 24,570 | 0.4070 | 4.99 |
| 108.0 | 27,980 | 0.3573 | 4.94 | 108.0 | 28,690 | 0.3486 | 5.00 |
| 96.0 | 31,500 | 0.3175 | 4.94 | 94.5 | 33,040 | 0.3026 | 5.02 |

Diamagnetic correction = -147×10^{-6}

Diamagnetic correction = -142×10^{-6}

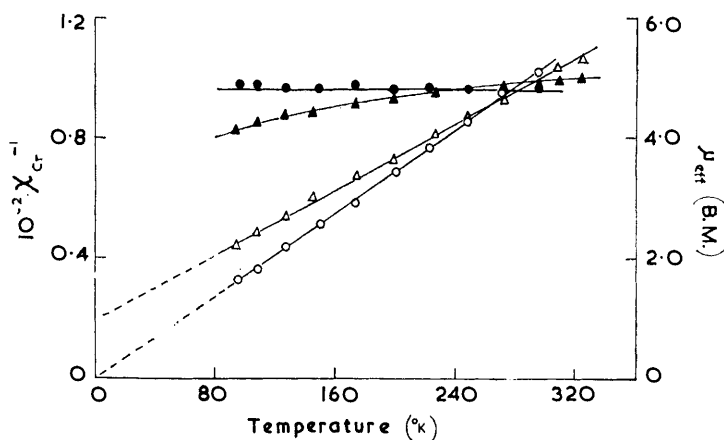


FIGURE 3. Variation, with temperature, of reciprocal of susceptibility, $10^{-2}\chi_{cr}^{-1}$ (○ and △), and magnetic moment, μ_{eff} (● and ▲), of $\text{CrI}_2 \cdot 5\text{H}_2\text{O}$ (circles) and $\text{CrHPO}_4 \cdot 4\text{H}_2\text{O}$ (triangles)

complexes, so that a temperature-independent moment of 4.90 B.M. is expected. However, a second-order effect of spin-orbit coupling should cause a reduction of moment according to the equation

$$\mu_{eff} = \mu_{s.o.} \left(1 - \alpha \frac{\lambda}{\Delta} \right),$$

where the symbols have their usual significance.¹⁵ From the spectral data, the apparent value of Δ is 14,000 cm^{-1} , and if the free-ion value of the spin-orbit coupling constant, $\lambda = 57 \text{ cm}^{-1}$, is taken, then $\mu = 4.86 \text{ B.M.}$, slightly lower than the experimental results. Allowing for temperature-independent paramagnetism of approximately $100 \times 10^{-6} \text{ c.g.s. units}$,¹⁰ this would be increased to 4.88 B.M. Correcting for the tetragonal distortion (*e.g.*, by taking $\Delta = 11,700 \text{ cm}^{-1}$, as used by Runciman and Syme¹³) and for the reduction of λ on complex-formation¹⁶ would have opposite and approximately equal effects on the magnetic results, and would be experimentally undetectable.

From structure determinations, $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$,¹⁷ KCrF_3 ,¹⁸ and the anhydrous halides¹⁹ are known to be tetragonally distorted. Figgis¹⁰ has shown that a tetragonal distortion should lead to temperature-dependence of the magnetic moment. Several of the compounds investigated here, in particular the sulphate and the perchlorate, do show increasing magnetic moments with decreasing temperature, but the change is barely larger than the experimental error. It would be premature to suggest that this verifies Figgis's predictions; any change in magnetic moment would be very small and detectable only at temperatures lower than those used in the present work. It is likely that the reduced magnetic moment of the monohydrogen phosphate is due to slight interaction, perhaps of a superexchange type.

EXPERIMENTAL

Preparation of Salts.—Except in the preparation of the phosphate, an excess of spectroscopically pure chromium pellets, obtained from Johnson Mathey and Co., was heated with the appropriate dilute AnalaR acid until reaction ceased. The excess of metal was then filtered off and the solutions treated as described below. All operations were carried out in a nitrogen atmosphere.

The aqueous solutions of chromium(II) sulphate, chloride, and bromide were concentrated, the compounds precipitated with deoxygenated acetone, filtered off, washed with small amounts of acetone, dried by continuous pumping at room temperature, and sealed in Pyrex tubes. Once dry, the sulphate is reasonably stable to air, but the chloride and bromide are hygroscopic and oxidise readily (Found: Cr, 22.0; SO_4 , 40.3. Calc. for $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$: Cr, 21.8; SO_4 , 40.3%. Found: Cr, 26.7; Cl, 36.4. Calc. for $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$: Cr, 26.7; Cl, 36.4%. Found: Cr, 16.5; Br, 50.7. Calc. for $\text{CrBr}_2 \cdot 6\text{H}_2\text{O}$: Cr, 16.3; Br, 50.0%).

Acetone did not precipitate chromium(II) iodide and perchlorate even from concentrated aqueous solutions. The solid compounds could only be obtained by pumping off all the water from their aqueous solutions. With the iodide, continuous pumping for a few hours at room temperature caused an uneven loss of water of hydration, the crystals changing from blue to greenish-yellow. The crystals were therefore equilibrated overnight with water vapour before sealing off. It was difficult to remove the last traces of water from the perchlorate, and its degree of hydration is uncertain. The solid has not been isolated before. Once the reaction of chromium with dilute perchloric acid⁸ had started, it was necessary to cool the reaction mixture to prevent oxidation by the unreacted acid. The perchlorate was blue when first prepared, but it gradually became green in the sealed tubes, presumably because of internal oxidation-reduction. Both the iodide and the perchlorate are hygroscopic and readily oxidised by air (Found: Cr, 13.1; I, 64.0. Calc. for $\text{CrI}_2 \cdot 5\text{H}_2\text{O}$: Cr, 13.1; I, 64.1%. Found: Cr, 14.7. $\text{Cr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ requires Cr, 14.5%).

The monohydrogen phosphate was precipitated by adding a sulphate solution to a solution of disodium hydrogen phosphate. The dry compound did not change markedly in air (Found: Cr, 23.5; P, 13.7. Calc. for $\text{CrHPO}_4 \cdot 4\text{H}_2\text{O}$: Cr, 23.6; P, 14.1%).

Chromium was determined by direct combustion to Cr_2O_3 , except for the phosphate and perchlorate. In the former, it was estimated volumetrically after oxidation to chromic acid; in the latter, the hydroxide was precipitated first. Chloride and bromide were estimated as

¹⁵ B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," ed. J. Lewis and R. G. Wilkins, Interscience, London, 1960, p. 427.

¹⁶ T. M. Dunn, *J.*, 1959, 623.

¹⁷ K. Ono, *J. Phys. Soc., Japan*, 1959, 12, 1231.

¹⁸ V. Scatturina, L. Corliss, N. Elliott, and J. Hastings, *Acta Cryst.*, 1961, 14, 19.

¹⁹ J. W. Tracy, N. W. Gregory, J. M. Stewart, and E. C. Lingafelter, *Acta Cryst.*, 1962, 15, 460.

the silver halide. Iodide was determined as before.²⁰ Phosphorus and sulphate were estimated as ammonium phosphomolybdate and barium sulphate, respectively.

The thermogravimetric behaviour of $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$ was similar to that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

The infrared spectra showed the expected water absorptions in the 3300- and 1630- cm^{-1} regions. The compound $\text{CrHPO}_4 \cdot 4\text{H}_2\text{O}$ gave the complex absorptions between 850 and 1300 cm^{-1} usual in an acid orthophosphate.²¹

Physical Measurements.—Magnetic measurements were carried out on solid samples sealed in Pyrex tubes.²² Visible spectra were recorded on a Unicam S.P. 500 spectrophotometer. The solutions were protected from oxidation by a tap joined by a graded seal to the 1-cm. silica cell. Infrared spectra were recorded on a Grubb-Parsons GS 2A grating instrument.

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²⁰ A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *Z. anorg. Chem.*, 1964, **334**, 163.

²¹ D. E. C. Corbridge and E. J. Lowe, *J.*, 1954, 493.

²² A. Earnshaw, *Lab. Practice*, 1961, **10**, 294.
