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Curie Temperatures of some Tetrabromochromates(II)

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Tetrabromochromates(II) of the type $[NRH_3]_2[CrBr_4]$ have effective magnetic moments [1] well above the spin-only value of 4.90 B.M. for high-spin chromium(II) which increase markedly as the temperature is lowered, *e.g.* for R = CH_3, μ_{eff} = 6.27 B.M. at 295 K and 16.3 B.M. at 90 K. The complexes obey the Curie-Weiss law above *ca.* 150 K with large positive intercepts (~90°) on the temperature axis indicative of ferromagnetic behaviour. However, the Curie temperatures T_c could not be observed because they lie below the limit (~85 K) of the measurements which were carried out by the Gouy method. The Faraday method is more suitable for investigations of ferromagnetic substances, and magnetic measurements by this method in the temperature range 2 to 70 K have now confirmed the ferromagnetic behaviour. The atom susceptibility χ was determined at three or more field strengths at each temperature, and as the temperature was lowered the bromides developed field dependence between 50 and 60 K: for example, for $[NPr^nH_3]_2[CrBr_4]$ at 41.0 K, χ_1 =14.8, χ_2 =8.46, χ_3 = 6.00, and χ_5 = 4.00 c.g.s. units; and at 5.3 K, χ_1 = 22.1, χ_2 = 12.55, and χ_3 =8.57 c.g.s. units, where the subscripts represent the electromagnet current I (amperes).

The apparatus (see Experimental) did not permit the independent variation of magnetic field H and field gradient ∂H/∂x, and only their product was obtained from the calibration. Since H was not known, the product χI was taken to be approximately proportional to the magnetisation χH (or M), and at 5.3 K, this product increased by only a few percent from 25.1 to 25.6 as the current increased from 2 to 3 amps so that these complexes can be considered to be saturated in the field corresponding to the 3 amp current. To determine the Curie temperature χ_3 was plotted against temperature and extrapolated to T = 0 to give $(\chi_3)_O$, the ratio $(\chi_3)_T/(\chi_3)_O$ was then calculated, taken to be equal to the reduced magnetisation M(T)/M(O), and plotted against temperature. Extrapolation to zero $(\chi_3)_T/(\chi_3)_O$ then gave the Curie temperature. An example is given in Fig. 1. No single crystal data are available but the ferromagnetic bromides are believed to contain layers of bridged $[CrBr_4]^{2-}$ units well separated by the alkylammonium ions like the analogous chlorides which are also ferromagnetic [2, 3].

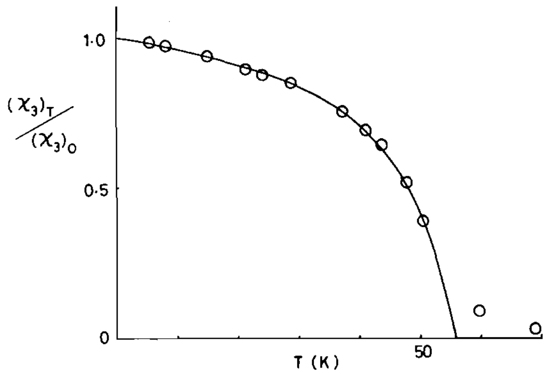

Fig. 1. Determination of Curie temperature of $[NPr^nH_3]_2[CrBr]_4$.

TABLE I. Curie Temperatures (T_c).

Compound	T_c/K
$[NMeH_3]_2[CrBr_4]$	59
$[NPr^nH_3]_2[CrBr_4]$	57
$[N(n\text{-}C_{12}H_{25})H_3]_2[CrBr_4]$	58
$[dienH_3][CrCl_4]Cl$	38

The Curie temperatures (Table I) are similar to those [2] of $[NMeH_3]_2[CrCl_4]$, 58 K, and $[NEtH_3][CrCl_4]$, 55 K. Since analysis of the magnetic behaviour above the Curie point in terms of a high temperature series expansion for a sheet ferromagnet gives slightly larger values of coupling constants for the bromides [1] (~11 cm^{-1}) than for the corresponding chlorides [2, 3] (~9 cm^{-1}), the bromides might have been expected to have higher Curie temperatures. The interlayer spacing would be expected to increase with alkylammonium chain length but this does not affect T_c significantly.

The chlorochromate(II) $[dienH_3][CrCl_4]Cl$, in which dien is diethylenetriamine, contains [4] layers of bridged $[CrCl_4]^{2-}$ units separated by the cations and chloride ions. Its Curie point has been found to be 38 K (Table I).

Experimental

The complexes were prepared as before [1]. The main components of the Faraday apparatus were a Sartorius vacuum microbalance which was mounted above an Oxford Instruments sample entry chamber connected to a CF 200 continuous flow helium cryostat. The magnetic field was provided by a water-cooled Newport 4″ electromagnet equipped with Faraday pole pieces, and the product $H\partial H/\partial X$ was determined by calibration with $Hg[Co(NCS)_4]$. The readings of the DTC 2 temperature controller were checked by calibration with $(NH_4)_2SO_4 \cdot MnSO_4 \cdot 6H_2O$. The samples were placed in 2 mm inside diameter buckets machined from 10 mm lengths of 4 mm diameter teflon rod. The lids were machined to a tight push fit and with a ring to which the terylene suspension was attached. A pin-hole was drilled through the lid so that it would not come off during evacuation of the cryostat. The air-sensitive samples were loaded in a nitrogen box.

References

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