Ferromagnetic Monoalkylammonium Tetrabromochromates(II)

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Summary The complex bromides of chromium(II), $[MeNH_3]_2[CrBr_4]$ and $[EtNH_3]_2[CrBr_4]$, are ferromagnetic.

RECENT studies have shown that a new series of tetrachlorochromates(II), *i.e.* $[RNH_3]_2[CrCl_4]$, where R = Me[1,2]

Et,[1,2] C_8H_{15}[1] and $C_{10}H_{21}$[1]; and $[enH_2][CrCl_4]$, $[dienH_3][CrCl_4]Cl$, and $[trienH_4][CrCl_4]Cl_2$ (where [2] en, dien, and trien are, respectively, ethylenediamine, diethylenetriamine, and triethylenetetra-amine) have the same unusual ferromagnetic properties and optical spectra as the alkali metal tetrachlorochromates(II).[3–6]. Previously, only $Cs_2[CrBr_4]$ among the known[7] alkali metal and other tetrabromochromates(II) exhibited similar behaviour. The caesium salt was obtained as a powder by thermal dehydration of the corresponding dihydrate. We have now prepared the new tetrabromochromates(II), $[MeNH_3]_2[CrBr_4]$ and $[EtNH_3]_2[CrBr_4]$, by the more convenient method of crystallisation from solutions in glacial acetic acid of stoicheiometric amounts of chromium(II) bromide and the amine hydrobromide. These greenish-yellow complexes were prepared and handled in a nitrogen atmosphere because they are very air-sensitive.

The effective magnetic moments of the compounds were found to be well above the values (4·8—4·9 B.M.) commonly exhibited[7] by magnetically dilute, high-spin chromium(II) compounds at room temperature, and they increased greatly as the temperature was reduced (Table). Extrapolation of the upper linear portion of the plots of reciprocal susceptibility against absolute temperature gave large positive intercepts on the temperature axis characteristic of ferromagnetic interaction.

TABLE

	Temp./K	μ_{eff}/B.M.	θ[a]/°	J[b]/cm^{-1}	g
$[MeNH_3]_2[CrBr_4]$	295	6·27	−100	11·6	1·98
	90	16·3			
$[EtNH_3]_2[CrBr_4]$	295	5·94	− 87	10·0	1·94
	90	13·1			

[a] Curie–Weiss law expressed as $\chi_A^{-1} \propto (T + \theta)$. [b] Nearest-neighbour exchange integral.

The powder reflectance spectra of both complexes contained two narrow, unusually intense, spin-forbidden bands near 18,500 and 15,500 cm^{-1}, assigned to quintet–triplet transitions. These would be expected to lose their intensity through ferromagnetic ordering on cooling to 4·2 K as occurs[1,6] with bands at almost identical frequencies in the spectra of the tetrachlorochromates(II). Cooling to liquid nitrogen temperature, the limit of our equipment, reduced the intensity slightly. The very broad absorption near 10,500 cm^{-1}, asymmetric to lower frequency, and characteristic of tetragonally distorted hexacoordinate chromium(II), can be assigned to overlapping transitions: $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{2g}$, and ^5E_g. The magnetic behaviour and spectra suggest that the anions are polymerized.

X-Ray powder diffraction data show that $[EtNH_3]_2[CrBr_4]$ and $[EtNH_3]_2[CuBr_4]$ are isomorphous. The structure of the latter has not been reported, but it, and therefore the chromium(II) compound also, would be expected to contain square-planar $[MBr_4]^{2-}$ units held in a two-dimensional network by two long bonds to neighbouring anions. This type of structure is present[8] in $[EtNH_3]_2[CuCl_4]$ and related copper(II) complex chlorides which are also isomorphous with the corresponding chromium(II) compounds.[2] In these structures the networks are well separated by intervening alkylammonium cations.

The magnetic data for the two tetrabromochromates(II) can be satisfactorily replicated over the temperature range investigated by substitution of the J and g values, given in the Table, in the high-temperature series-expansion expression[9] for a sheet ferromagnet. The values of J (and θ) for $[MeNH_2]_2[CrBr_4]$ are larger than any so far deduced[2–4] for the tetrachlorochromates(II). This suggests that bromide can permit the transmission of stronger coupling effects than chloride.

(*Received, 17th December* 1976; *Com.* 1371.)

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