Preparation and Magnetic Behaviour of Complex Bromides of Chromium(II)

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Summary The complex bromides $M_2CrBr_4(H_2O)_2$ are paramagnetic ($M=Rb,Cs,NH_4,C_5H_5NH$), but dehydration gives anti-ferromagnetic compounds except for Cs_2CrBr_4 which is ferromagnetic.

ANHYDROUS complex chlorides[1] of chromium(II) of the general formula M_2CrCl_4 form one of the few classes of transition-metal complexes in which ferromagnetism occurs, apparently through magnetic interaction in chloride-bridged

TABLE

Compound[a]	μ_e(B.M.) 295 K	89 K	θ (°)	Reflectance spectra ν_{max} cm^{-1}
$Rb_2CrBr_4(H_2O)_2$[b]	4·88	4·90	0	12,400vb
$Cs_2CrBr_4(H_2O)_2$[b]	4·85	4·91	0	12,400vb
$(NH_4)_2CrBr_4(H_2O)_2$[b]	4·85	4·87	0	12,500vb
$(C_5H_5NH)_2CrBr_4(H_2O)_2$[c]	4·75	4·83	−4	12,850s, 10,100sh
Rb_2CrBr_4	4·19	3·46	86	9100s, 5200m
Cs_2CrBr_4[d]	4·98	7·31		9100s, 5600sh
$(NH_4)_2CrBr_4$	4·17	3·36	95	9600s
$(C_5H_5NH)_2CrBr_4$[e]	4·35	3·70	60	9800s,vb
$((C_2H_5)_4N)_2CrBr_4$	4·58	3·72	80	9800s, 6800w
$(C_5H_5NH)_2CrCl_4$[e]	4·28	3·54	77	11,050s,vb

[a] All compounds are air-sensitive; their analyses are satisfactory. [b] Crystallised from stoicheiometric mixtures of reactants in concentrated hydrobromic acid. [c] Crystallised from hydrated chromium bromide and pyridinium bromide in ethanol. [d] All compounds have spin-forbidden bands at higher frequencies; with Cs_2CrBr_4 unusually prominent bands occur at 18,350 cm^{-1} and 15,600 cm^{-1}. [e] Prepared from the dihydrate by dehydration in vacuum over P_4O_{10} in apparatus which was wholly at 70° (bromide) or 45° (chloride) to prevent condensation of pyridinium halide on colder parts of apparatus.

infinite lattices. Since the nature of the bridging atom[2] is likely to affect the magnitude and sign of the magnetic interaction several new complex bromides of chromium (II) have been synthesised (Table). The anhydrous bromides M_2CrBr_4 were obtained, analogously to the chlorides, by dehydration *in vacuo* at *ca.* 140° of the previously unknown dihydrates $M_2CrBr_4(H_2O)_2$. The bromides were less easily isolated than the chlorides: complex bromides are generally[3] the less stable of the two. The only other known double bromides of chromium(II) are $CsCrBr_3$, Me_4NCrBr_3, and $(C_5H_5NH)_3CrBr_5,2MeCO_2H$, and these were prepared from solutions containing glacial acetic acid and acetyl bromide.[4] No magnetic measurements were carried out. It has been found that, like the chloride dihydrates, the bromide dihydrates are magnetically normal, high-spin chromium(II) compounds,[5] but the anhydrous compounds, M_2CrBr_4, unlike the corresponding chlorides, are antiferromagnetic except for Cs_2CrBr_4, which is ferromagnetic. This has been confirmed by measurements on duplicate preparations. The bromides have reflectance spectra typical[6] of tetragonally distorted octahedral chromium(II); the anhydrous compounds are therefore polymeric.

The new compound $(C_5H_5NH)_2CrCl_4(H_2O)_2$, on dehydration, gives $(C_5H_5NH)_2CrCl_4$ (Table) which, unlike all other chromium(II) chlorides[1] of the same general formula, is antiferromagnetic. Thus the nature of the cation as well as of the bridging atom, and the stoicheiometry, can be important in determining the type of magnetic interaction.

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[1] L. F. Larkworthy and J. K. Trigg, *Chem. Comm.*, 1970, 1221.

[2] R. L. Martin in 'New Pathways in Inorganic Chemistry,' ed. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968, p. 175.

[3] R. Colton and J. H. Canterford, 'Halides of the First Row Transition Metals,' Wiley-Interscience, London, 1969, p. 18.

[4] H. D. Hardt and G. Streit, *Z. anorg. Chem.*, 1970, **373**, 97.

[5] A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *J. Chem. Soc. (A)*, 1965, 3267.

[6] J. P. Fackler and D. G. Holah, *Inorg. Chem.*, 1965, **4**, 1112; A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc. (A)*, 1969, 1339; 2276.