Crystal and Molecular Structures of the Antiferromagnetic Linear Chain Halide-bridged Complexes $[CrX_2(MeCN)_2]$ (X = Cl or Br)†

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Single-crystal *X*-ray analysis has shown that the acetonitrile complex $[CrBr_2(MeCN)_2]$ is a bromide-bridged linear polymer in which the metal atom is in distorted octahedral co-ordination, with metal–ligand bond distances Cr–N 2.066(4), Cr–Br, two at 2.545(0) and two at 2.976(1) Å. The Cr . . . Cr separation is 4.054(4) Å. The complexes $[CrBr_2(MeCN)_2]$ and $[CrCl_2(MeCN)_2]$ are isomorphous, and both are antiferromagnetic ($J \approx -1.5$ cm^{-1}, $g = 2.0$).

The complexes of acetonitrile with bivalent chromium, $[CrX_2(MeCN)_2]$ (X = Cl, Br, or I), were first reported by Holah and Fackler.[1] From comparisons of reflectance spectra of $[CrX_2(py)_2]$ (py = pyridine) and $[CrX_2(MeCN)_2]$ (X = Cl or Br) the environment of Cr^{II} in the latter was considered to be distorted octahedral, with four halides and two MeCN groups bonded to the metal ion, *i.e.* bridging halide is present. However, elsewhere[2] $[CrCl_2(MeCN)_2]$ is listed as a distorted tetrahedral complex. In this paper single-crystal investigations which confirm the proposed polymeric structure, and magnetic investigations which show $[CrX_2(MeCN)_2]$ (X = Cl or Br) to be weakly antiferromagnetic, are described.

Experimental

Preparation of Bis(acetonitrile)dichlorochromium(II).—Microcrystalline samples of the compound, suitable for magnetic susceptibility studies, were obtained by adding an excess of acetonitrile (h.p.l.c. grade) directly with stirring to anhydrous chromium(II) chloride prepared by thermal dehydration of $CrCl_2{\cdot}4H_2O$. The pale blue suspension which formed was stirred and warmed for 15 min to ensure complete reaction. It was then filtered and the blue solid obtained washed with acetonitrile and dried under vacuum. The reflectance spectrum [13 200 and 9 600 (sh) cm^{-1}] is as reported[1] (Found: C, 23.2; H, 3.0; Cl, 35.6; Cr 24.2; N, 13.3. $C_4H_6Cl_2CrN_2$ requires C, 23.4; H, 2.95; Cl, 34.6; Cr, 25.4; N, 13.7%). Crystals for single-crystal *X*-ray studies were obtained by adding ethanol dropwise to the warm suspension in acetonitrile while stirring until the solid just dissolved. The solution was then left to cool slowly and pale blue needles formed.

Preparation of Bis(acetonitrile)dibromochromium(II).—The bromide was prepared by the above procedure. Pale blue-green needles crystallised from the acetonitrile–ethanol solution. The reflectance spectrum [13 200 and 9 800 (sh) cm^{-1}] is as before[1] (Found: C, 15.5; H, 2.1; Br, 54.5; Cr, 17.4; N, 8.9. $C_4H_6Br_2CrN_2$ requires C, 16.35; H, 2.1; Br, 54.35; Cr, 17.7; N, 9.5%).

Attempts to prepare $[CrI_2(MeCN)_2]$ by the above method gave blue crystals that very readily lost acetonitrile leaving brown anhydrous chromium(II) iodide. Washing the solid with acetonitrile restored the blue colour. Holah and Fackler[1] reported that the blue crystals obtained by recrystallising $CrI_2{\cdot}6H_2O$ from acetonitrile are very sensitive to trace amounts of oxygen. It may be that ligand loss affected their product too. They produced an apparently more stable iodide $[CrI_2(MeCN)_2]$ by reduction of CrI_3 in MeCN with Zn–Hg which is also very sensitive to oxygen.

The i.r. spectra of the chloride and bromide are very similar above 400 cm^{-1}, and contain absorptions due to the CN stretching vibrations of MeCN at 2 310w and 2 300s cm^{-1}. The far-i.r. spectra (500—200 cm^{-1}) of the complexes gave the following bands: $[CrCl_2(MeCN)_2]$, 420m, 410m, 350(sh), 320vs,vbr [ν(Cr–N) and ν(Cr–Cl)], and 220m; $[CrBr_2(MeCN)_2]$, 420m, 410m, 340m [ν(Cr–N)], 285(sh), 270vs [ν(Cr–Br)], and 250(sh) cm^{-1}.

All preparations and measurements, including the placing of crystals in Lindemann capillaries for *X*-ray studies, were carried out under nitrogen.

Determination of the Structure.—Both $[CrBr_2(MeCN)_2]$ and $[CrCl_2(MeCN)_2]$ separate from solution as twinned needle crystals, making intensity data collection in the *X*-ray studies difficult. Fortunately, a crystal of the bromide was found in which one twin was more in the nature of a satellite fragment rotationally displaced around one axis. Consequently, it was just possible to collect data from the other twin which gave a much stronger diffraction pattern without overlap of reflections. No equivalent reflections were measured but the crystal symmetry and approximate unit-cell dimensions for the two compounds were obtained from oscillation and Weissenberg photographs. Accurate unit-cell dimensions were obtained by least-squares refinement of 25 reflections on an Enraf-Nonius CAD 4 diffractometer [$17 < \theta < 20°$]

Intensity data for $[CrBr_2(MeCN)_2]$ were collected at ambient temperature with Mo-K_α radiation out to a limit of $\theta < 24°$ in a ω—2θ scan mode on a needle crystal of 0.3 mm linear dimension. Magnetic susceptibility studies were carried out with a variable-temperature Gouy balance supplied by Newport Instruments Ltd., from room temperature to liquid-nitrogen temperature. The field was calibrated with $Hg[Co(NCS)_4]$ and $[Ni(en)_3]S_2O_3$ (en = ethylenediamine) and the temperature with $CuSO_4{\cdot}5H_2O$ as described by Earnshaw.[3]

Crystal data. $[CrCl_2(MeCN)_2]$, $M_r = 205.02$, monoclinic, $a = 7.6$, $b = 13.5$, $c = 3.8$ Å, $\beta = 92°$, space group $P2_1/a$ (determined from photographs using Cu-K_α radiation, $\lambda = 1.542$ Å).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

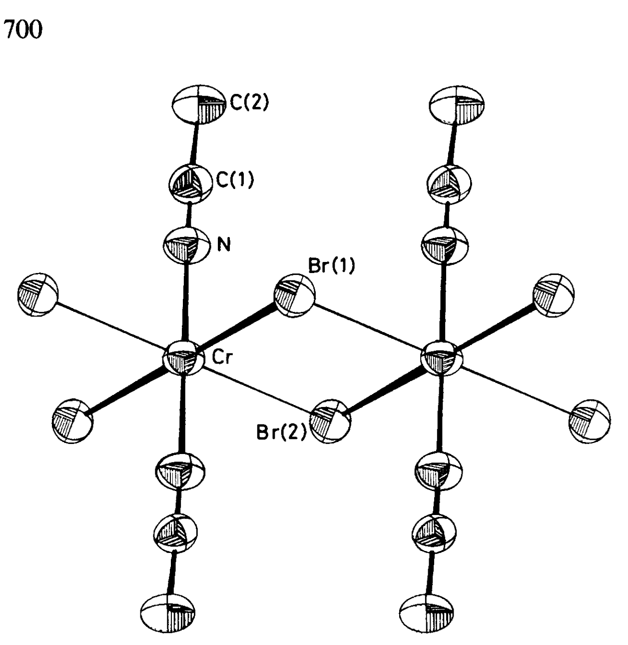

Figure. Atom numbering scheme and representation of the bromide-bridged structure of $[CrBr_2(MeCN)_2]$

Table 1. Variation of molar susceptibilities (χ_A) and effective magnetic moments (μ_{eff}) with absolute temperature

$[CrCl_2(MeCN)_2]^a$			$[CrBr_2(MeCN)_2]^b$		
T/K	$10^6\chi_A/$ c.g.s.u.	$\mu_{eff.}$	T/K	$10^6\chi_A/$ c.g.s.u.	$\mu_{eff.}$
295.5	9 710	4.79	295.2	9 688	4.78
263.0	10 750	4.76	263.0	10 820	4.77
230.0	12 210	4.74	230.0	12 110	4.72
198.6	14 110	4.73	197.9	14 070	4.72
166.9	16 420	4.68			
136.0	19 650	4.62	136.8	19 830	4.66
104.0	24 340	4.50	104.0	24 610	4.52
91.5	27 250	4.46	89.9	27 810	4.47

[a] Diamagnetic correction 91 × 10^{-6} c.g.s.u. (S.I. = c.g.s.u. × $4\pi/10^6$) calculated from Pascal's constants;[3] Curie–Weiss law taken as $\chi_A{}^{-1} \propto (T + \theta)$, $\theta = 20$ K; $J = -1.7$ cm^{-1}, $g = 2.02$. [b] Diamagnetic correction 112 × 10^{-6} c.g.s.u; $\theta = 20$ K; $J = -1.5$ cm^{-1}, $g = 2.01$.

Table 2. Final atomic parameters for the atoms in $[CrBr_2(MeCN)_2]$ with e.s.d.s. in parentheses

Atom	x	y	z
Br	0.121 69(5)	0.113 60(3)	0.432 47(9)
Cr	0	0	0
N	0.218 5(5)	−0.077 2(3)	0.015(1)
C(1)	0.339 7(6)	−0.117 5(3)	0.034(1)
C(2)	0.495 4(6)	−0.168 0(4)	0.067(1)

Table 3. Bond distances (Å) and angles (°) for $[CrBr_2(MeCN)_2]$ with e.s.d.s in parentheses

Cr–Br(1)	2.545(0)	Cr–N–C(1)	177.4(4)
Cr–Br(2)	2.976(1)	N–C(1)–C(2)	178.4(5)
Cr–N	2.066(4)	Br(1)–Cr–N	90.8(1)
Cr · · · Cr†	4.054(4)	Br(1)–Cr–Br(2)	85.82(5)
N–C(1)	1.129(6)	N–Cr–Br(2)	89.21(5)
C(1)–C(2)	1.444(7)		

† Symmetry code: $x, y, 1 + z$

$[CrBr_2(MeCN)_2]$, $M_r = 293.92$, monoclinic, $a = 8.072(1)$, $b = 13.938(2)$, $c = 4.054(4)$ Å, $\beta = 91.15(2)°$, $U = 456.10$ Å^3, space group $P2_1/a$, $Z = 2$, $D_c = 2.14$ g cm^{-3}, $F(000) = 276$, graphite-monochromated Mo-K_α radiation ($\lambda = 0.710 69$ Å), μ (Mo-K_α) = 95.3 cm^{-1}.

The crystal data limits were $1 \leqslant \theta \leqslant 28°$, $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 18$, and $-5 \leqslant l \leqslant 5$. The minimum absorption correction was 0.449 and the maximum 1.320. The extinction was negligible. Of the 1 096 unique reflections measured [$(\sin\theta)/\lambda \leqslant 0.57$], 891 [$I \geqslant 2.58\sigma(I)$] were used in the structure determination. After normal data reduction procedures the bromine and chromium atoms were located by the Patterson heavy-atom method and the other atoms found from Fourier difference maps. Hydrogen atoms were included in idealised positions. Isotropic refinement converged at $R = 0.152$ and was then followed by an absorption correction by a method due to Walker and Stuart[4] which reduced R' to 0.073. Full-matrix anisotropic refinement of all the atoms converged at $R = 0.037$, $R' = 0.051$, estimated standard deviation (e.s.d.) of unit weight = 1.25 using a weighting scheme of the type $w^{-1} = [\sigma(I)^2 + (0.07F^2)^2]^{\frac{1}{2}}$.

Final atomic parameters are given in Table 2, bond distances and angles in Table 3. A diagram of the molecule is shown in the Figure.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

The bromide-bridged structure of $[CrBr_2(MeCN)_2]$ is shown in the Figure. The bridges are unsymmetrical, Cr–Br(1) 2.545(0) and Cr–Br(2) 2.976(1) Å. The short Cr–Br bonds are of similar length to those (2.60 Å) in the *trans*-planar units $CrBr_2(OH_2)_2$ of $[Hpy]_2[CrBr_4{\cdot}2H_2O]$.[5] The Cr–N bonds are of normal length so that the structure could be considered as composed of planar $[CrBr_2(MeCN)_2]$ units linked by long *trans*-Cr–Br bonds of 2.976 Å to neighbouring units.

Holah and Fackler[1] have reported that *X*-ray powder patterns show $[CrBr_2(MeCN)_2]$ and $[CrCl_2(MeCN)_2]$ not to be isomorphous. However, our single-crystal data (Experimental Section) show that they are. Thus a distorted tetrahedral structure for $[CrCl_2(MeCN)_2]$ is ruled out.

Earlier, magnetic moments of 4.81 and 4.85 at room temperature were obtained[1] for the chloride and bromide respectively. These values are as expected for magnetically dilute, high-spin chromium(II) ($3d^4$ configuration, $\mu_{s.o.} = 4.90$) and they have been confirmed (Table 1). However, the moments decrease as the temperature is lowered, and the magnetic behaviour of each complex can be satisfactorily reproduced by substitution of the values of J and g given in Table 1 in Smith and Friedberg's[6] expression for antiferromagnetic interaction in a linear chain complex. Effects other than magnetic exchange are not expected to produce any significant variation of magnetic moment with temperature over the range investigated.[7,8]

The J values indicate similar weak interaction in both complexes. The Cr · · · Cr separation in the chloride is less (3.84 Å, calculated from the unit-cell dimensions) than in the bromide (4.05 Å), and the bridging distances would be expected to be smaller thus favouring direct interaction and superexchange. However, the more polarisable, less electronegative bromide can permit easier transmission of magnetic interaction and the net effect is apparently similar in the two complexes.

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