Crystal and Molecular Structure of a Complex Bromide containing Planar Diaquadibromochromium(II) Units †

Mark F. C. Ladd, Leslie F. Larkworthy,* Gordon A. Leonard, David C. Povey, and Santokh S. Tandon
The Joseph Kenyon Laboratory, Department of Chemistry, University of Surrey, Guildford GU2 5XH

A single-crystal *X*-ray analysis has shown that the magnetically dilute complex $[Hpy]_2[CrBr_4{\cdot}2H_2O]$, where Hpy is the pyridinium cation, contains discrete *trans*-planar $CrBr_2(OH_2)_2$ units and bromide ions instead of the expected distorted octahedral anions, *trans*-$[CrBr_4(OH_2)_2]^{2-}$. The bromide ions are held by strong hydrogen bonds to the pyridinium cations.

From their *X*-ray powder patterns it was shown[1] that the chromium(II) complexes $M_2[CrX_4(OH_2)_2]$, where M = Cs, Rb, or NH_4 and X = Cl or Br, are isomorphous with the corresponding copper(II) complexes. The latter contain *trans*-octahedral anions $[CuX_4(OH_2)_2]^{2-}$, with two short and two long metal–halide bonds, so in the absence of single-crystal investigations similar structures were assumed for the chromium(II) dihydrates. The dihydrate with M = pyridinium (Hpy) and X = Br is slightly different in colour from the other dihydrates and is not isomorphous with them, but like them it is magnetically dilute and was believed[1] to contain analogous anions. However, the present investigation shows that two Cr–Br distances are so long (4.91 Å) that the solid must be considered to contain the neutral *trans*-planar $CrBr_2(OH_2)_2$ units and ionic bromide.

Experimental

Preparation of Pyridinium Diaquatetrabromochromate(II).— Anhydrous chromium(II) bromide[1] (0.85 g) was dissolved in hot glacial acetic acid (40 cm^3) under nitrogen. To the hot solution was added a solution of pyridinium bromide (1.28 g) in glacial acetic acid (10 cm^3). The pale yellowish green solution obtained was allowed to cool slowly. The yellowish green crystals which separated were filtered off, washed with acetic acid, and dried in vacuum for several hours. Pale green, very air-sensitive needles suitable for *X*-ray investigation were obtained on recrystallisation from glacial acetic acid. In spite of the use of anhydrous chromium(II) bromide the product was a dihydrate (Found: C, 21.2; H, 2.4; Br, 56.2; Cr, 9.1; N, 4.8. Calc. for $[C_5H_5NH]_2[CrBr_4{\cdot}2H_2O]$: C, 21.1; H, 2.8; Br, 56.3; Cr, 9.15; N, 4.9%). The glacial acetic acid is probably the source of the water since it was not dried before use. The dihydrate was earlier[1] prepared from $CrBr_2{\cdot}6H_2O$ and pyridinium bromide in ethanol.

All operations were carried out under nitrogen or in vacuum in glass apparatus, sometimes using an inert-atmosphere box and recirculatory gas-purification system manufactured by Faircrest Engineering Ltd., Croydon.

Determination of the Structure.—For the *X*-ray investigation single crystals (0.5 × 0.1 × 0.1 mm) of the chromium(II) complex were sealed into Lindemann capillaries under nitrogen. The unit-cell dimensions were determined by least-squares refinement of a set of 25 reflections [$(\sin\theta)/\lambda \leqslant 0.45$].

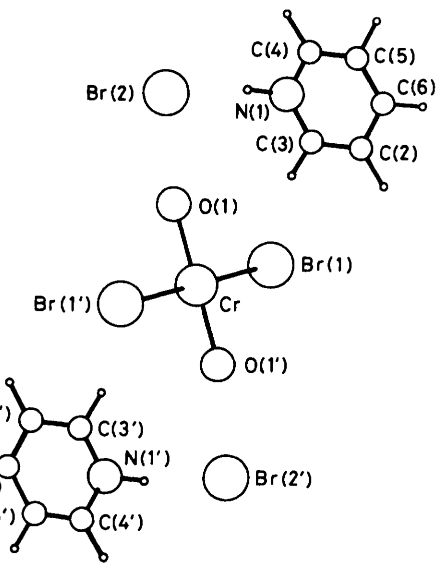

Figure. Representation of $[CrBr_2(OH_2)_2]{\cdot}2[Hpy]Br$

Crystal data. $C_{10}H_{16}Br_4CrN_2O_2$, $M_r = 567.9$, triclinic, $a = 8.560(2)$, $b = 12.745(4)$, $c = 4.239(5)$ Å, $\alpha = 91.46(1)$, $\beta = 90.81(1)$, $\gamma = 74.15(2)^\circ$, $U = 447.7(4)$ Å^3, space group $P\bar{1}$, $Z = 1$, $D_c = 2.12$ g cm^{-3}, $F(000) = 270$, graphite-monochromated, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 95.29 cm^{-1}.

The intensity data were collected on an Enraf–Nonius CAD4 four-circle diffractometer in a θ–2θ scan mode. 1 267 Unique reflections were measured [$(\sin\theta)/\lambda \leqslant 0.57$] of which 1 168 were considered to be observed [$I \geqslant 2.58\sigma(I)$]. The data were corrected for Lorentz and polarisation effects. An empirical absorption correction[2] was applied. A reference reflection measured every 30 min of exposed *X*-ray time showed no significant change in intensity. The crystals are of the triclinic system and an examination of the *E* statistics indicated the space group to be $P\bar{1}$.

Examination of a three-dimensional Patterson synthesis revealed the positions in the unit cell of the chromium atom and one of the bromine atoms. Using these as a basis for the solution of the structure, further F_0 Fourier maps revealed the positions of all the other non-hydrogen atoms.

---

† *Supplementary data available* (No. SUP 56026, 3 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Final atomic parameters for non-hydrogen atoms in $[CrBr_2(OH_2)_2]\cdot2[Hpy]Br$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cr	0.500	0.000	0.000
Br(1)	0.287 0(1)	−0.005 23(9)	0.419 3(3)
Br(2)	0.382 2(2)	0.358 71(9)	0.520 0(3)
N(1)	0.729(1)	0.330(1)	0.117(3)
C(2)	0.953(2)	0.192(1)	−0.008(6)
C(3)	0.809(2)	0.226(1)	0.123(4)
C(4)	0.788(2)	0.404(1)	−0.025(4)
C(5)	0.926(2)	0.372(1)	−0.152(4)
O(1)	0.578(1)	−0.166 1(6)	−0.007(2)
C(6)	0.011(2)	0.271(2)	−0.160(5)

Assigning anisotropic thermal parameters to all atoms and coupling this with three cycles of anisotropic refinement reduced *R* to 0.073. The positions of the hydrogen atoms were calculated geometrically and when a Hughes weighting scheme was applied [$w = 1.0$ for $K < F$ or $w = (K/F)^2$, $K = 169.0$] *R* was reduced to a final value of 0.065.

Final atomic parameters are shown in Table 1, relevant bond lengths and angles in Table 2. The Figure shows a representation of the molecule.

All computations were carried out using the Enraf–Nonius SPD-plus package of programs and a DEC PDP 11/23 computer.

Discussion

The chromium atom lies on a centre of symmetry. The $CrBr_2(OH_2)_2$ units are consequently strictly *trans*-planar. The Cr–OH_2 and Cr–Br(1) distances (2.04 and 2.60 Å) are short enough for these entities to be considered bonded. The Cr–Br(2) distances, however, are almost 5.0 Å, and the Br(2) atoms are displaced laterally from the axis through chromium perpendicular to the $CrBr_2(OH_2)_2$ plane along which they should lie if bonded (Figure). They are therefore ionic. This is confirmed by comparison with the structure [3] of the guanidinium salt $[C(NH_2)_3]_2[CrBr_4(CH_3CO_2H)_2]$, the only tetrabromochromate(II) for which detailed structural data are available. The *trans* anions contain acetic acid molecules bonded by carbonyl oxygen (Cr–O 2.06 Å), and there are two short (2.64 Å) and two long (2.84 Å) Cr–Br bonds {*cf.* $M_2[CuBr_4(OH_2)_2]$ above}. The first two distances are comparable to the Cr–O and Cr–Br(1) distances in the pyridinium compound, but the last is much shorter than the Cr–Br(2) separation. A Br(2)–H(1) distance of 2.34 Å is indicative of a strong hydrogen bond between the pyridinium cation and Br(2). This, with the other packing requirements of the pyridinium cation compared with the spherical cations in $M_2[(Cu\text{ or }Cr)Br_4(OH_2)_2]$, has apparently led to the unexpected molecular structure.

Table 2. Bond lengths (Å) and angles (°) for $[CrBr_2(OH_2)_2]\cdot2[Hpy]Br$ with e.s.d.s in parentheses

Cr–Br(1)	2.579(1)	
Cr–O(1)	2.038(2)	
Br(1)–Cr–O(1)		90.05(6)
Br(1′)–Cr–O(1)		89.95(6)
N(1)–C(3)	1.321(8)	
N(1)–C(4)	1.337(7)	
C(3)–N(1)–C(4)		122.2(4)
C(2)–C(3)	1.317(9)	
N(1)–C(3)–C(2)		119.8(5)
C(2)–C(6)	1.409(9)	
C(3)–C(2)–C(6)		116.8(5)
C(4)–C(5)	1.265(8)	
N(1)–C(4)–C(5)		118.6(5)
C(5)–C(6)	1.295(8)	
C(4)–C(5)–C(6)		122.9(2)

References

1 M. A. Babar, L. F. Larkworthy, and A. Yavari, *J. Chem. Soc., Dalton Trans.*, 1981, 27.

2 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

3 M. A. Babar, M. F. C. Ladd, L. F. Larkworthy, G. A. Leonard, and D. C. Povey, *J. Crystallogr. Spectrosc. Res.*, 1983, **13**, 325.

Received 5th March 1984; Paper 4/369