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Note

The preparation, properties and crystal structure of a salt containing the hexabromochromate(III) anion

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Abstract

The hexabromochromate(III) anion, otherwise known only in $Cs_2LiCrBr_6$, has been stabilised in the salt $[4\text{-}BrC_6H_4NH_3]_6[CrBr_6]Br_3\cdot 2CH_3CO_2H$ which forms dark green crystals, space group $P2_1/a$, $a=10.665(4)$, $b=24.650(7)$, $c=11.464(3)$ Å, $\beta=91.81(3)$°. The $[CrBr_6]^{3-}$ anion is sited on a centre of symmetry and shows little departure from octahedral symmetry. The Cr–Br bond distances range from 2.513(1) to 2.521(1) Å, and the Br–Cr–Br angles are 180° or close to 90°. The magnetic behaviour and d–d spectrum are typical of an octahedral chromium(III) complex.

Keywords: Crystal structures; Chromium complexes; Bromide complexes; Salt complexes

1. Introduction

The hexabromochromate(III) anion $[CrBr_6]^{3-}$ has to date been found only in $Cs_2LiCrBr_6$, a member of a series of bromo-elpasolites Cs_2LiMBr_6, where M is Tm, Yb, Lu, Sc, In, V and Cr. To prepare $Cs_2LiCrBr_6$ the residue obtained by taking a solution of CsBr, Li_2CO_3 and CrO_3 in 48% hydrobromic acid carefully to dryness was heated at 250 °C in a stream of hydrogen bromide for 2 days [1]. A second salt of $[CrBr_6]^{3-}$ has been isolated by a different method during attempts to prepare more bromo complexes [2,3] of chromium(II). From chromium(II) bromide and 4-bromoanilinium bromide in glacial acetic acid air-stable, dark green crystals with a reflectance spectrum characteristic of chromium(III) rather than chromium(II) have been isolated, and a single crystal X-ray determination has shown the crystals to be $[4\text{-}BrC_6H_4NH_3]_6[CrBr_6]Br_3\cdot 2CH_3CO_2H$ containing $[CrBr_6]^{3-}$ octahedra. Halide complexes are well known, but the stability and coordination number generally decrease in the order $F > Cl > Br > I$ so that hexabromo complexes of transition elements are uncommon [4], and the stabilisation of $[CrBr_6]^{3-}$ unexpected.

2. Experimental

2.1. Preparation of hexakis(4-bromoanilinium) hexabromochromate(III) tribromide di-acetic acid

Anhydrous chromium(II) bromide (2.0 g, 0.009 mol), prepared by thermal dehydration of $CrBr_2\cdot 6H_2O$ [3], was dissolved in hot glacial acetic acid (150 cm^3) under nitrogen. The light green solution was heated to boiling to extract 4-bromoanilinium bromide (3.0 g, 0.011 mol) on a sintered filter in a Soxhlet-type apparatus. The resulting dark green solution was allowed to cool and the dark green crystals which separated were filtered off, washed with glacial acetic acid (50 cm^3) and dried (oil pump vacuum) for 10 h. The product turned dull green on long exposure to the atmosphere but it has the characteristics of a chromium(III) complex and not the expected chromium(II) complex. *Anal.* Found: C, 25.5; H, 2.95; N, 4.4; Cr, 3.0. Calc. for $C_{40}H_{50}Br_{15}CrN_4O_6$: C, 24.9; H, 2.6; N, 4.4; Cr, 2.7%. The IR spectrum contains bands mainly arising from the cation but a strong band at 1710 cm^{-1} is due to the ν(CO) vibration of the lattice acetic acid and another strong band at 265 cm^{-1} is due to Cr–Br stretching vibrations. The effective magnetic moment is 4.05 at 90 K and 3.87 at 295 K. The complex obeys the Curie–Weiss law

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$[\chi_{Cr}^{-1} \alpha (T+\theta)]$ with $\theta = -11°$. The diamagnetic correction used was 785×10^{-6} c.g.s.u. Reflectance spectrum (cm^{-1}): 12 500br, 17 200br, 25 000br. Analogous procedures from chromium(II) chloride and 4-bromoanilinium chloride produce the ferromagnetic complex $[4\text{-}BrC_6H_4NH_3]_2[CrCl_4]$.

IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer and diffuse reflectance spectra on a Beckman Acta MIV spectrophotometer. Magnetic measurements were determined by the Gouy method.

2.2. X-ray crystal structure analysis

Crystals prepared as above were satisfactory for structure determination and one of approximate dimensions $0.3 \times 0.2 \times 0.2$ mm was sealed under nitrogen in a Lindemann capillary. *Crystal data*: $C_{40}H_{50}Br_{15}CrN_6O_4$, $M_r = 1929.51$, monoclinic, space group $P2_1/a$, $a = 10.665(4)$, $b = 24.650(7)$, $c = 11.464(3)$ Å, $\beta = 91.81(3)°$, $V = 3012(3)$ Å^3, $Z = 2$, $D_c = 2.127$ g cm^{-3}, $F(000) = 1826$, graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), μ(Mo Kα) = 100.8 cm^{-1}).

2.3. Data collection and processing

Cell parameters were determined on an Enraf-Nonius CAD4 diffractometer using 25 accurately centred reflections in the range $13 \leqslant \theta \leqslant 15°$. The intensities of 5122 reflections were measured in the range $1 \leqslant \theta \leqslant 24°$ covering the index range $0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 28$, $-13 \leqslant l \leqslant 13$ which after the usual Lp correction yielded 2623 with $I \geqslant 3\sigma(I)$. An analysis of the standard reflections showed no decay of intensities and an empirical absorption correction was applied using Ψ data which showed strong modulation. Mininum correction 0.400, maximum correction 0.999, average correction 0.805. Examination of the $h0l$ and $0k0$ reflections revealed absences for h odd and k odd leading to space group $P2_1/a$.

2.4. Structure solution and refinement

The original premise was that the structure should contain $CrBr_4$ units with two 4-bromoanilinium cations and an acetic acid molecule. A combination of Patterson methods and the direct methods program [5] showed the presence of a $CrBr_6$ unit sitting on a centre of symmetry together with five other independent Br atoms at another centre of symmetry.

Table 1
Final atomic coordinates for non-hydrogen atoms in $[4\text{-}BrC_6H_4NH_3]_6[CrBr_6]Br_3 \cdot 2CH_3CO_2H$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Br(1)	0.1151(2)	0.28694(9)	0.1883(2)
Br(2)	0.2773(3)	0.2944(1)	0.8797(2)
Br(3)	0.4803(2)	0.19301(8)	0.5511(2)
Br(4)	0.4936(1)	0.49773(7)	0.7176(1)
Br(5)	0.000	0.500	0.000
Br(11)	0.2014(1)	0.55306(6)	0.4991(1)
Br(12)	−0.0879(1)	0.56385(6)	0.6485(1)
Br(13)	0.0893(1)	0.44254(6)	0.6636(1)
Cr	0.000	0.500	0.500
O(1)	0.3297(9)	0.4969(4)	0.0073(8)
O(2)	0.405(1)	0.4227(5)	−0.0737(9)
N(1)	0.296(1)	0.0542(5)	0.1957(9)
N(2)	0.300(1)	0.0518(5)	0.7971(9)
N(3)	0.368(1)	0.4344(5)	0.4903(9)
C(1)	0.344(1)	0.4494(6)	0.007(1)
C(2)	0.294(2)	0.4117(8)	0.096(1)
C(11)	0.256(1)	0.1115(6)	0.190(1)
C(12)	0.318(1)	0.1486(6)	0.255(1)
C(13)	0.277(2)	0.2013(7)	0.251(1)
C(14)	0.175(1)	0.2148(7)	0.184(1)
C(15)	0.113(1)	0.1795(7)	0.118(1)
C(16)	0.153(1)	0.1242(7)	0.118(1)
C(21)	0.293(1)	0.1101(6)	0.820(1)
C(22)	0.389(1)	0.1354(7)	0.876(1)
C(23)	0.386(2)	0.1906(7)	0.896(1)
C(24)	0.280(2)	0.2182(7)	0.859(1)
C(25)	0.185(2)	0.1935(7)	0.801(1)
C(26)	0.190(1)	0.1385(7)	0.778(1)
C(31)	0.398(1)	0.3744(6)	0.501(1)
C(32)	0.505(1)	0.3543(7)	0.464(1)
C(33)	0.531(2)	0.2994(7)	0.482(2)
C(34)	0.449(1)	0.2676(5)	0.530(1)
C(35)	0.343(2)	0.2889(7)	0.567(2)
C(36)	0.317(1)	0.3424(7)	0.553(2)

Table 2
Selected bond lengths (Å) and angles (°) for $[4\text{-}BrC_6H_4NH_3]_6[CrBr_6]Br_3 \cdot 2CH_3CO_2H$ with e.s.d.s in parentheses

Cr–Br(11)	2.515(1)	C(1)–O(1)	1.18(2)
Cr–Br(12)	2.521(1)	C(1)–O(2)	1.32(2)
Cr–Br(13)	2.513(1)	C(1)–C(2)	1.49(2)
Br(11)–Cr–Br(11)	180.00(0)	O(1)–C(1)–O(2)	124(1)
Br(11)–Cr–Br(12)	90.80(4)	O(1)–C(1)–C(2)	125(1)
Br(11)–Cr–Br(13)	89.57(4)	O(2)–C(1)–C(2)	111(1)
Br(12)–Cr–Br(12)	180.00(0)		
Br(12)–Cr–Br(13)	89.34(4)		
Br(13)–Cr–Br(13)	180.00(0)		

Refinement of these heavy atoms caused R to fall to 0.17 and the subsequent Fourier maps revealed the light atoms of the ligands and the acetic acid. Isotropic refinement, including hydrogen atoms in fixed calculated positions converged at $R = 0.118$. Anisotropic refinement, initially Cr and Br only, then for all non-hydrogen atoms finally converged at $R = 0.049$, $R_w = 0.070$ and $S = 1.067$. The weighting scheme [6] used in the final refinement cycles was $w^{-1} = [\sigma(F^2) + (0.048F)^2 + 4.8]$. The positions of the hydrogen atoms were calculated after every refinement cycle and the final difference map showed the highest peak of 0.68 electrons but the hydrogen atom attached to the hydroxyl oxygen atom of the acetic acid was not located. Atomic coordinates are given in Table 1 and selected bond distances and

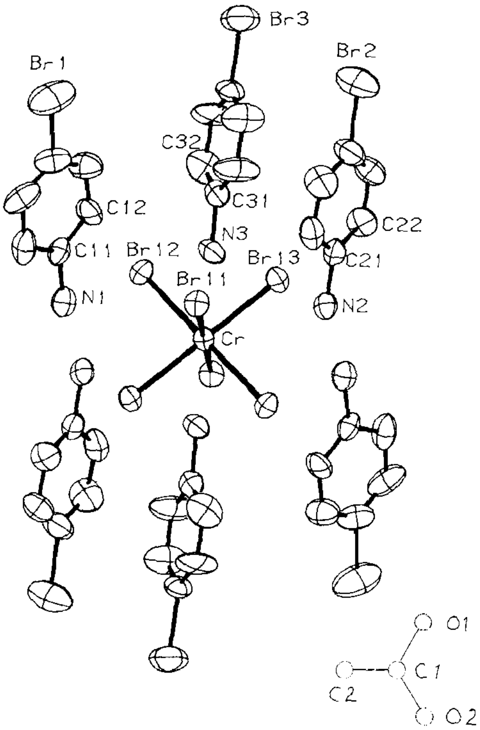

Fig. 1. Molecular structure with atom numbering scheme for [4-$BrC_6H_4NH_3]_6[CrBr_6]Br_3 \cdot 2CH_3CO_2H$. A numbered ball-and-stick drawing is shown for the acetic acid molecules and the ionic bromides Br(4) and Br(5) are not shown.

angles in Table 2. The atom numbering scheme and the structure are illustrated in Fig. 1. All calculations were performed with the Enraf-Nonius Structure Determination Package [7].

3. Results and discussion

The preparation of the chromium(III) complex [4-$BrC_6H_4NH_3]_6[CrBr_6]Br_3 \cdot 2CH_3CO_2H$, described in Section 2, was unexpected because analogous procedures, again under nitrogen, from [4-$BrC_6H_4NH_3$]Cl and chromium(II) chloride gave the chromium(II) complex [4-$BrC_6H_4NH_3]_2[CrCl_4]$. The source of the oxidation is not known. The preparation has, however, provided crystals containing discrete $[CrBr_6]^{3-}$ ions previously reported only in $Cs_2LiCrBr_6$ for which no crystal structure determination was reported.

The $[CrBr_6]^{3-}$ octahedra lie on centres of symmetry and there are three slightly different Cr–Br distances: 2.513(1), 2.515(1) and 2.521(1) Å (Fig. 1). The Br–Cr–Br angles are 180° or close to 90° (89.34(4)–90.80(4)°); consequently, the octahedra are regular as expected for chromium(III) (t_{2g}^3 configuration) but not high-spin chromium(II) ($t_{2g}^3\ e_g^1$ configuration) [2]. The Cr–Br distances are similar to those in $[Cr_2Br_9]^{3-}$ (Cr–terminal Br = 2.417(6) Å and Cr–bridging Br = 2.577(9) Å) [8] and in $CrBr_3$ (2.57 Å, quoted in Ref. [8]); and in *trans*-dibromo(1,4,8,11-tetraazacyclotetradecane)chromium(III) bromide (2.496(1) Å) [9]. The Cr–Br distances are ~0.05 Å less than the sum of the estimated ionic radii (2.575 Å; Cr^{3+}, 0.615, Br^-, 1.96) [10]. The cation-to-anion ratio is 0.314, considerably less than the critical value of 0.414 below which a transformation to a tetrahedral complex might be expected to take place. Also, the Br–Br distances in the coordination sphere are in the range 3.54–3.58 Å ($2 \times r_{Br^-} = 3.92$ Å) suggesting crowding and distortion of the bromide ions around the central metal ion. Fig. 1 shows how six [4-$BrC_6H_4NH_3$] cations surround each $CrBr_6$ group. The stability of this rare group and the overall stability of the compound must be very dependent upon the hydrogen bonding throughout the lattice. The distances between the nitrogen atoms and the nearest bromine atoms of the $CrBr_6$ octahedra indicate weak hydrogen bonds: Br(11) to N(1), N(2), N(3), 3.40–3.50 Å; Br(12) to N(1), N(2), N(3), 3.44–3.55 Å; Br(13) to N(1), N(2), N(3), 3.40–3.63 Å. The lattice acetic acid molecules are extensively hydrogen bonded. The carboxyl hydrogen of the acid was not found crystallographically, but the smaller separation of C(1)–O(1) (1.18 Å) compared with C(1)–O(2) (1.32 Å) indicates that C(1)–O(1) is a double bond and that C(1)–O(2) is a single bond with a hydrogen atom attached to O(2). The IR spectrum has a strong absorption band at 1710 cm^{-1}, too high for an acetate group, which can be assigned to $\nu(C{=}O)$ of a carboxylic acid. The double bond oxygen atom O(1) forms weak hydrogen bonds to two amine cations (O(1)–N(2) = 2.966 Å; O(1)–N(1) = 3.001 Å). Of the three bromide ions per molecule, the unique ion Br(4) sits on a centre of symmetry and is hydrogen bonded to the hydroxyl group O(2) of the acetic acid molecules (O(2)–Br(4) = 3.191 Å). O(2) lies somewhat further from the bromine atom of an amine cation (O(2)–Br(2) = 3.48 Å). The bromide ion Br(4) also has two close contacts with N(3) at 3.29 and 3.30 Å, but distances to N(1) and N(2) are greater than 3.56 Å. The other bromide ions, Br(5), have two symmetrical contacts with N(2) at 3.36 Å and two symmetrical contacts with N(1) at 3.45 Å. Thus the environment around both these bromide ions is sparse and they are only weakly linked to the rest of the structure.

The IR spectrum of the complex contains a strong, broad absorption band at 265 cm^{-1} which is assigned to ν(Cr–Br) stretching vibrations. This is consistent with the assignment [11] of ν(Cr–Cl) vibrations in $[CrCl_6]^{3-}$ to a band at 315 cm^{-1}. The magnetic behaviour and the reflectance spectrum confirm the chromium(III) assignment. Magnetically-dilute chromium(III) complexes have effective magnetic moments near the spin-only value for three unpaired electrons (3.87) as found for this complex (see Section 2). The absorption bands in the diffuse reflectance spectrum at 12 500s (ν_1, 10*Dq*), 17 200m (ν_2) and 26 500s,br (ν_3) cm^{-1} are assigned [12] to the $^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_1), $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ (ν_2),

$^4A_{2g} \rightarrow ^4T_{1g}(P)$ (ν_3) transitions in O_h symmetry. The value of the interelectronic repulsion parameter for $[CrBr_6]^{3-}$ B' (466 cm^{-1}), has been calculated from the secular determinant using the values of ν_1 and ν_2. From this ν_3 is predicted at 27 200 cm^{-1} in reasonable agreement with the experimental value. Krishnamurthy et al. in a footnote to their paper [13] estimate 10*Dq* to be 11 930 cm^{-1} for $[CrBr_6]^{3-}$. The value of B' is much lower than the value for the free ion ($B = 1030$ cm^{-1}) indicating considerable covalent character in the Cr–Br bonds. 10*Dq* for the chloro-elpasolite $Cs_2NaCrCl_6$ has been reported [14] as 12 800 cm^{-1}.

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