

**[CrBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>][CrBr<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>], a new chromium(III) complex****Ludwig Stork, Xiaohui Liu, Boniface P. T. Fokwa and Richard Dronskowski\***

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Green single crystals of *trans*-tetraamminedibromidochromium(III) *trans*-diamminetetraabromidochromate(III), [CrBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>][CrBr<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>], are found to contain two symmetry-independent sixfold coordinated Cr<sup>III</sup> cations on centres of inversion. The structure is composed of octahedral *trans*-[CrBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> cations and octahedral *trans*-[CrBr<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>−</sup> anions, and adopts a distorted CsCl-type lattice. The cations and anions are linked by N—H⋯Br interactions. This is the first example in which both ions are mixed ammine–bromide Cr<sup>III</sup> complexes.

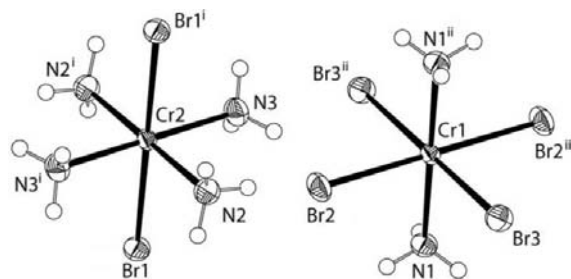
**Comment**

There is ongoing interest in chromium(III) complexes owing to the importance of chromium in catalytic processes and its magnetic and optical properties. The often observed sixfold coordination of Cr<sup>III</sup> with an essentially octahedral ligand arrangement is due to the high stability of the *d*<sup>3</sup> configuration. In particular, ammonia complexes are the most numerous Cr<sup>III</sup> derivatives and the most extensively studied, including the pure ammine [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, for example, [Cr(NH<sub>3</sub>)<sub>6</sub>][CuCl<sub>5</sub>] (Ohba *et al.*, 1995), and the mixed ammine–acid types, [CrA<sub>*x*</sub>(NH<sub>3</sub>)<sub>6−*x*</sub>]<sup>(3−*x*)<sup>+</sup></sup> (*x* = 0–6), for example, *trans*-[CrCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]I (Brencic *et al.*, 1985) and Hg<sub>6</sub>As<sub>4</sub>[CrBr<sub>6</sub>]Br (Olenov *et al.*, 2003).

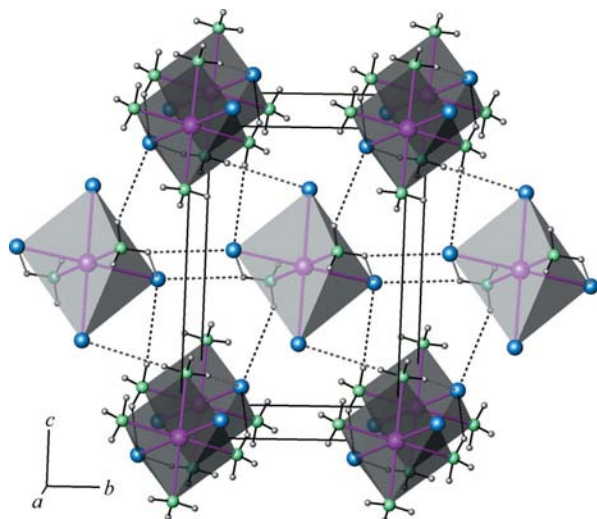
The synthesis and crystal structure of the title compound *trans*-tetraamminedibromidochromium(III) *trans*-diamminetetraabromidochromate(III), [CrBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>][CrBr<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>], are the result of exploratory investigations of mixed ammine–acido Cr<sup>III</sup> complexes. Although the *trans*-[CrBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> cation was first mentioned (but without a crystal structure report) more than three decades ago (Glerup & Schäffer, 1976), the *trans*-[CrBr<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>−</sup> anion is observed here for the first time. To the best of our knowledge, the occurrence of Cr<sup>III</sup> as part of both a complex cation and a complex anion in one compound is extremely rare. The only cases are [Cr(NH<sub>3</sub>)<sub>6</sub>]-[Cr(CN)<sub>6</sub>] (Nielsen *et al.*, 1986) and [Cr(NH<sub>3</sub>)<sub>6</sub>][CrF<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> (Göbbels & Meyer, 2000). [Cr(NH<sub>3</sub>)<sub>6</sub>][Cr-

(CN)<sub>6</sub>] was crystallized from [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and [Cr(CN)<sub>6</sub>]<sup>3−</sup> in aqueous solution under mild conditions. However, when these ammonia and cyanide complexes are present in aqueous solution, the formation of mixed ammine–acido complexes will not occur. [Cr(NH<sub>3</sub>)<sub>6</sub>][CrF<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>, on the other hand, was obtained by the reaction of elemental Cr, B and NH<sub>4</sub>F at 573 K, resulting in the mixed ammine–acido anion [CrF<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>−</sup>. For the synthesis of the title compound, an alternative non-aqueous route was used, using Cr<sub>2</sub>(NCN)<sub>3</sub> as a starting material together with NH<sub>4</sub>Br, and this provides a stable and ‘naked’ Cr<sup>3+</sup> cation. Thus, the structurally stable compound [CrBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>][CrBr<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>] is achieved as a function of the synthetic route. The title compound can be also considered as the first real mixed ammine–acido Cr<sup>III</sup> cation–anion compound, namely, [CrA<sub>*x*</sub>(NH<sub>3</sub>)<sub>6−*x*</sub>][CrB<sub>*y*</sub>(NH<sub>3</sub>)<sub>6−*y*</sub>] (*x/y* = 1–5, *x* + *y* = 6).

The title compound crystallizes in the centrosymmetric triclinic space group *P* $\bar{1}$ . The two symmetry-independent Cr<sup>III</sup> centres from the [CrBr<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> cation and the [CrBr<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>−</sup> anion are positioned on the 1*g* and 1*d* inversion centres, respectively, while N and Br are on general positions. In the complex anion, the Cr<sup>III</sup> centre (Cr1) is bonded to two apical NH<sub>3</sub> groups and four equatorial Br<sup>−</sup> ions (Fig. 1). In the complex cation, the Cr<sup>III</sup> centre (Cr2) is surrounded by four equatorial NH<sub>3</sub> groups and two apical Br<sup>−</sup> ions. The coordinations of the Cr<sup>III</sup> centres deviate from regular octahedral symmetry due to the different Cr–N and Cr–Br bond lengths. Comparison of the two complex ions shows that the Cr–N bond lengths are quite similar and that the equatorial Cr–Br bonds are slightly longer than the axial ones (Table 1). A rigid-body correction of both octahedral entities according to the procedure of Schomaker & Trueblood (1968) is possible and yields, for the Cr1-based complex anion, rather small bond increases of 0.007 Å for Cr–Br and 0.005 Å for Cr–N (*R* = 0.043). For the Cr2-based complex cation, the increases are likewise small, namely *ca* 0.005–0.006 Å for both bond types (*R* = 0.066). Based on the bond angles around the Cr<sup>III</sup> centres, both octahedral entities are very close to *D*<sub>4h</sub> symmetry, although there is no crystallographically imposed symmetry. The highly stable *d*<sup>3</sup> electron configuration at both metal centres favours the formation of *trans* complexes for both the cation and anion. With four identical ligands in the equatorial

**Figure 1**

The structure of the title compound, showing the coordination around the two independent Cr<sup>III</sup> ions. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + 1, -y, -z$ .]

**Figure 2**

A view of the crystal packing along the *a* axis, showing a distorted CsCl-type lattice. The  $[\text{CrBr}_2(\text{NH}_3)_4]^+$  cations are shown as darker octahedra (top and bottom) and the  $[\text{CrBr}_4(\text{NH}_3)_2]^-$  anions as lighter octahedra (centre). Dashed lines indicate  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bonds.

plane for each, there is no electronic reason for any distortion from  $D_{4h}$  symmetry.

The crystal structure can be considered a typical ionic one, with a distorted CsCl motif (Fig. 2). It is quite common for the CsCl structure to be adopted when both ions are similar in size, and this is also found for  $[\text{Cr}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  (Nielsen *et al.*, 1986). The elongation of the *b* axis ( $b/a = 1.15$ ) is caused by the nonregular octahedral ions, with  $[\text{CrBr}_2(\text{NH}_3)_4]^+$  a lengthened and  $[\text{CrBr}_4(\text{NH}_3)_2]^-$  a flattened octahedron.

Besides the dominating Coulombic attractions, neighbouring  $\text{Cr}^{\text{III}}$  complex ions are also connected to each other *via* numerous weak  $\text{N}-\text{H}\cdots\text{Br}$  hydrogen bonds between ionic species to form a three-dimensional network (Table 2). These are likely to be responsible for the fact that the  $c/a$  ratio is 1.67, such that the cations and anions are not able to approach each other more closely.

## Experimental

Single crystals of  $[\text{CrBr}_2(\text{NH}_3)_4][\text{CrBr}_4(\text{NH}_3)_2]$  were synthesized *via* a typical solid-state reaction. A mixture of  $\text{Cr}_2(\text{NCN})_3$  and  $\text{NH}_4\text{Br}$  (1:10 molar ratio, 1.0 g total weight) was sealed in a silica tube, annealed at 723 K for a week and furnace-cooled. The synthesized products were a mixture of green  $[\text{CrBr}_2(\text{NH}_3)_4][\text{CrBr}_4(\text{NH}_3)_2]$  crystals and a black powder of undetermined composition. The crystals used for analysis were selected manually on the basis of colour and morphology. Attempts to synthesize the compound from a mixture of  $\text{CrBr}_3$  and  $\text{NH}_4\text{Br}$  were unsuccessful.

### Crystal data

$[\text{CrBr}_2(\text{NH}_3)_4][\text{CrBr}_4(\text{NH}_3)_2]$

$M_r = 685.66$

Triclinic,  $P\bar{1}$

$a = 5.9697$  (5) Å

$b = 6.8410$  (5) Å

$c = 9.9092$  (8) Å

$\alpha = 86.184$  (2)°

$\beta = 87.300$  (2)°

$\gamma = 84.293$  (2)°

$V = 401.45$  (6) Å<sup>3</sup>

$Z = 1$

Mo  $K\alpha$  radiation

$\mu = 16.26$  mm<sup>-1</sup>

$T = 293$  K

$0.08 \times 0.07 \times 0.05$  mm

**Table 1**

Selected bond lengths (Å).

Cr1—Br2	2.5047 (4)	Cr2—Br1	2.4736 (4)
Cr1—Br3	2.5100 (4)	Cr2—N2	2.090 (3)
Cr1—N1	2.073 (3)	Cr2—N3	2.084 (3)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H11 $\cdots$ Br2 <sup>i</sup>	0.83 (4)	2.88 (4)	3.617 (3)	149 (4)
N1—H12 $\cdots$ Br1 <sup>ii</sup>	0.83 (3)	2.80 (4)	3.520 (3)	147 (5)
N1—H13 $\cdots$ Br2 <sup>iii</sup>	0.88 (4)	2.81 (4)	3.573 (3)	146 (4)
N2—H21 $\cdots$ Br1 <sup>ii</sup>	0.86 (5)	2.88 (5)	3.623 (3)	146 (4)
N2—H22 $\cdots$ Br3 <sup>iii</sup>	0.87 (4)	2.78 (4)	3.578 (3)	153 (5)
N3—H31 $\cdots$ Br1 <sup>ii</sup>	0.85 (4)	2.78 (4)	3.533 (3)	148 (5)
N3—H32 $\cdots$ Br2 <sup>iv</sup>	0.88 (4)	2.76 (3)	3.594 (3)	159 (4)

Symmetry codes: (i)  $x+1, y, z$ ; (ii)  $-x+1, -y+1, -z+1$ ; (iii)  $-x+1, -y+1, -z$ ; (iv)  $x, y, z+1$ .

### Data collection

Bruker SMART CCD area-detector diffractometer	4174 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1992 independent reflections
$T_{\min} = 0.283$ , $T_{\max} = 0.443$	1764 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.061$	$\Delta\rho_{\max} = 0.55$ e Å <sup>-3</sup>
$S = 1.06$	$\Delta\rho_{\min} = -1.05$ e Å <sup>-3</sup>
1992 reflections	
97 parameters	
15 restraints	

All H atoms were located by difference Fourier synthesis and refined as riding atoms, with  $\text{N}-\text{H} = 0.87$  (3) Å and  $\text{H}\cdots\text{H} = 1.39$  (2) Å (using DFIX), and with free but identical  $U_{\text{iso}}(\text{H})$  values for all H atoms bonded to the same N atom (using EADP).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3202). Services for accessing these data are described at the back of the journal.

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