metal-organic papers

Barium di-μ-hydroxo-bis[(nitrilotriacetato)-chromium(III)] hexahydrate

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The title compound, $Ba[Cr_2(C_6H_6NO_6)_2(OH)_2]\cdot6H_2O$, is contains two discrete Cr(nta)OH units (nta^{3-} is nitrilotriacetate) in the asymmetric unit, each generating a centrosymmetric dimer with two hydroxo bridges. The ten-coordinate Ba^{2+} cation provides a link between dimeric units. Each Cr^{III} ion is in a distorted octahedral environment and coordinated by two bridging hydroxo O atoms, plus an N atom and three carboxylate O atoms of the nta^{3-} ligand. The important geometrical parameters are Cr—N = 2.0716 (19) and 2.0779 (19) Å, Cr—O = 1.9421 (17)–1.9900 (17) Å, and O—Cr—O = 162.85 (7)–176.90 (7)°.

Comment

The aqueous chemistry of transition metals in the presence of ligands that contain hard donor groups that are likely to be important in natural systems is instructive in many ways. One of the most common amino-polycarboxylic acid tripodal ligands is H_3nta (nitrilotriacetic acid). A search of the Cambridge Structural Database (Version 5.27, August 2006 update; Allen, 2002) revealed only 14 structures of chromium(III) and nta, seven of which are di-μ-hydroxo bridged complexes (Novitchi *et al.*, 2005; Visser *et al.*, 1999; Choi *et al.*, 2003). The present study of the title compound, (I), is part of an ongoing investigation to determine the factors which govern the distortion of the metal–glycinate rings in metal(III) complexes with tripodal ligands (Weakliem & Hoard, 1959; Visser *et al.*, 1997, 1999, 2001, 2005).

(I)
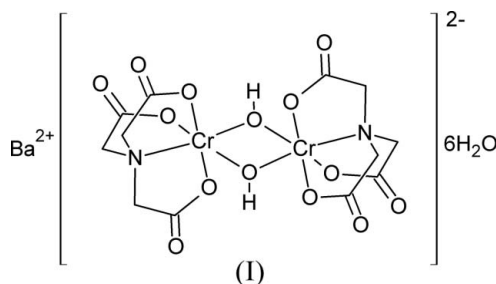
In compound (I), the asymmetric unit contains two crystallographically independent nitrilotriacetate ligands, each bound to a Cr^{III} cation tas units of two different dimeric anions, *A* and *B* (Fig. 1). Each anion lies about a centre of symmetry. The ten-coordinate Ba^{2+} cation provides a link between the two dimeric anions carbonyl O atoms from the nta^{3-} ligands.

The Cr atoms in anions *A* and *B* are surrounded octahedrally (Figs. 2 and 3) by four donor atoms from the nta^{3-} ligands (atoms O2, O4, O6 and N1 for anion *A*, and atoms O8, O10, O12 and N2 for anion *B*) and two bridging OH groups.
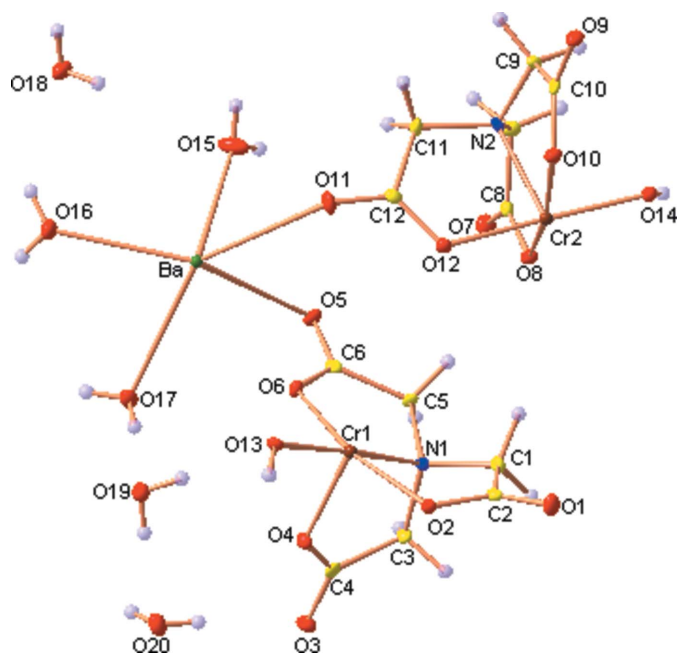
Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
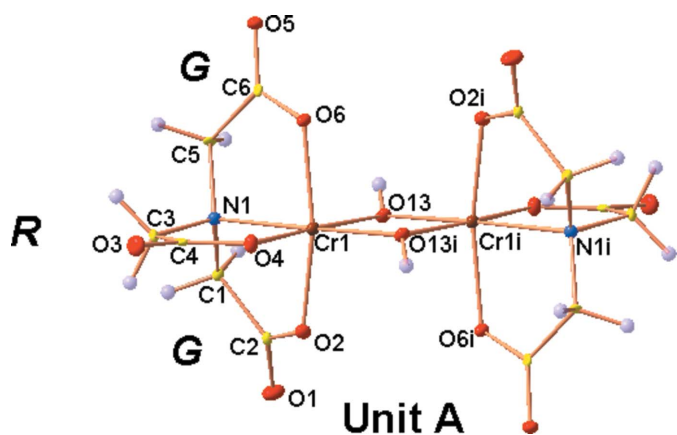

Figure 2
A view of the dimeric anion A formed in (I). Displacement ellipsoids are drawn at the 50% probability level. The chelating rings of the nta^{3-} ligand are labelled R and G after Weakliem & Hoard (1959). [Symmetry code: (i) $-1 - x, 1 - y, -z$.]

All the Cr—N and Cr—O bond distances, including those in the $Cr_2(\mu\text{-OH})_2$ fragments, fall within the expected ranges for this type of complex (Green *et al.*, 1990; Visser *et al.*, 1999; Novitchi *et al.*, 2005). The N—Cr—O and O—Cr—O angles for both A and B indicate that the deviation from octahedral geometry around Cr is significant (Table 1).

Each Ba^{2+} cation interacts with ten O atoms (three from water molecules and seven carboxylate O atoms from four different anions), serving as a link between different layers of A and B anions and generating a polymeric network. The Ba—O distances vary between 2.675 (2) and 3.072 (2) Å. Further links between A and B anions are provided by an extensive network of hydrogen bonds (Table 2).

The deviation from planarity of the glycinate rings formed between the chelating arms of the nta^{3-} ligand and the Cr is
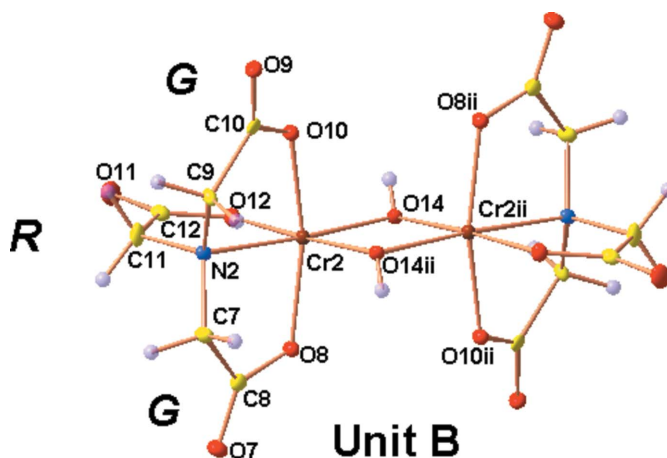

Figure 3
A view of the dimeric anion B formed in (I). Displacement ellipsoids are drawn at the 50% probability level. The chelating rings of the nta^{3-} ligand are labelled R and G after Weakliem & Hoard (1959). [Symmetry code: (ii) $-1 - x, -y, 1 - z$.]

significant. These rings can be designated as one R ring and two G rings, using the classification proposed by Weakliem & Hoard, 1959 (Figs. 2 and 3). An interesting observation is that the G rings in anion B deviate more from planarity than those in anion A (Table 3): the average deviation of N from the G ring CCOO planes is 0.166 Å for anion A, compared with 0.522 Å for anion B. One of the reasons for this observation might be that the Ba^{2+} cations have more contact points with the G rings of anion A than with anion B, thereby preventing the distortion in some way.

Experimental

$Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ (10 g) was dissolved in H_2O (40 ml). Concentrated NH_3 was added dropwise to this solution to precipitate chromium(III) hydroxide. The precipitate was added to a solution containing H$_3$nta (4 g) and heated in a water bath until almost dry. Hot water (30 ml) was added to the reaction solution, after which it was filtered. The pH of the filtrate was adjusted to 5 using NH_4HCO_3. Purple plate-like crystals precipitated after 3 d. The title compound was obtained by recrystallization with excess $BaCl_2$ (yield 64%). IR, $\nu(C=O)$ 1624 cm^{-1}.

Crystal data

$Ba[Cr_2(C_6H_6NO_6)_2(OH)_2]\cdot 3H_2O$	$V = 1174.1\ (3)\ \text{Å}^3$
$M_r = 759.69$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 2.149\ \text{Mg m}^{-3}$
$a = 11.0363\ (13)\ \text{Å}$	Mo $K\alpha$ radiation
$b = 11.0609\ (14)\ \text{Å}$	$\mu = 2.67\ \text{mm}^{-1}$
$c = 11.6223\ (14)\ \text{Å}$	$T = 100\ (2)\ \text{K}$
$\alpha = 66.513\ (5)°$	Plate, purple
$\beta = 65.039\ (6)°$	$0.39 \times 0.14 \times 0.07\ \text{mm}$
$\gamma = 75.568\ (6)°$	

Data collection

Bruker X8 APEXII diffractometer	22175 measured reflections
ω and φ scans	5805 independent reflections
Absorption correction: multi-scan	5427 reflections with $I > 2\sigma(I)$
(*SADABS*; Bruker, 2004)	$R_{int} = 0.038$
$T_{min} = 0.423$, $T_{max} = 0.835$	$\theta_{max} = 28.3°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0217P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.024$	$+ 1.0555P]$
$wR(F^2) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
5805 reflections	$\Delta\rho_{max} = 0.57$ e Å^{-3}
376 parameters	$\Delta\rho_{min} = -0.71$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cr1—O4	1.9421 (17)	Cr2—O14	1.9557 (17)
Cr1—O13	1.9619 (16)	Cr2—O10	1.9581 (17)
Cr1—O13^i	1.9692 (17)	Cr2—O14^{ii}	1.9597 (17)
Cr1—O2	1.9708 (17)	Cr2—O12	1.9690 (16)
Cr1—O6	1.9857 (16)	Cr2—O8	1.9900 (17)
Cr1—N1	2.0716 (19)	Cr2—N2	2.0779 (19)
Cr1—Cr1^i	2.9292 (8)		
O4—Cr1—O13	91.01 (7)	O2—Cr1—N1	81.64 (7)
O4—Cr1—O13^i	174.62 (7)	O6—Cr1—N1	82.68 (7)
O13—Cr1—O13^i	83.66 (7)	O14—Cr2—O10	87.52 (7)
O4—Cr1—O2	93.26 (7)	O14—Cr2—O14^{ii}	83.23 (7)
O13—Cr1—O2	101.03 (7)	O10—Cr2—O14^{ii}	95.28 (7)
O13^i—Cr1—O2	87.12 (7)	O14—Cr2—O12	176.90 (7)
O4—Cr1—O6	92.20 (7)	O10—Cr2—O12	90.82 (7)
O13—Cr1—O6	95.11 (7)	O14^{ii}—Cr2—O12	94.32 (7)
O2—Cr1—O6	162.85 (7)	O14—Cr2—O8	92.60 (7)
O4—Cr1—N1	84.85 (7)	O10—Cr2—O8	164.05 (7)
O13—Cr1—N1	175.21 (8)	O14^{ii}—Cr2—O8	100.57 (7)
O13^i—Cr1—N1	100.51 (7)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O15—H15$A\cdots$O17^{iii}	0.80 (3)	2.18 (3)	2.955 (3)	164 (3)
O15—H15$B\cdots$O20^{iv}	0.76 (3)	2.08 (4)	2.822 (3)	169 (3)
O16—H16$A\cdots$O7^{iii}	0.76 (3)	2.11 (3)	2.820 (3)	155 (3)
O16—H16$B\cdots$O18^v	0.79 (3)	2.56 (3)	3.015 (3)	119 (3)
O16—H16$B\cdots$O18	0.79 (3)	2.26 (3)	2.909 (3)	140 (3)
O16—H16$B\cdots$O18^v	0.79 (3)	2.56 (3)	3.015 (3)	119 (3)
O17—H17$A\cdots$O7^{iii}	0.79 (3)	2.05 (3)	2.835 (3)	172 (3)
O17—H17$B\cdots$O19	0.80 (3)	1.96 (3)	2.759 (3)	175 (3)
O18—H18$A\cdots$O9^{vi}	0.78 (3)	2.05 (4)	2.793 (3)	161 (3)
O18—H18$B\cdots$O8^{vii}	0.81 (3)	2.16 (4)	2.967 (3)	174 (3)
O19—H19$A\cdots$O20	0.79 (3)	2.00 (4)	2.784 (3)	168 (3)
O19—H19$B\cdots$O13	0.82 (3)	2.08 (4)	2.884 (3)	168 (3)
O20—H20$A\cdots$O3^{viii}	0.81 (3)	2.00 (3)	2.807 (3)	171 (3)
O20—H20$B\cdots$O3	0.77 (3)	2.12 (3)	2.887 (3)	172 (3)
O20—H20$B\cdots$O4	0.77 (3)	2.54 (3)	3.110 (3)	132 (3)
O13—H13$\cdots$O12^i	0.71 (3)	2.09 (3)	2.772 (2)	163 (3)
O14—H14$\cdots$O19^{ix}	0.72 (3)	2.01 (3)	2.721 (2)	171 (4)

Symmetry codes: (i) $-x-1, -y+1, -z$; (iii) $-x, -y+1, -z$; (iv) $x, y, z+1$; (v) $-x, -y+2, -z$; (vi) $-x-1, -y+1, -z+1$; (vii) $x, y+1, z$; (viii) $-x, -y+1, -z-1$; (ix) $x, y-1, z+1$.

Table 3
Distances of Cr and N atoms from CCOO planes (Å).

CCOO Plane	Cr distance	N distance
C1/C2/O1/O2	−0.060 (5)	−0.192 (6)
C3/C4/O3/O4	−0.354 (5)	0.188 (6)
C7/C8/O6/O7	0.010 (5)	−0.095 (6)
C9/C10/O8/O9	0.011 (5)	−0.495 (6)

The methylene H atoms were placed in geometrically idealized positions, with C—H = 0.99 Å. H atoms of the bridging hydroxo groups and water molecules were determined from a difference Fourier map and their positional parameters freely refined. For all H atoms, U_{iso}(H) = 1.2U_{eq}(C,O) for methylene and bridging hydroxo H atoms, or 1.5U_{eq}(O) for water H atoms.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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