metal-organic papers

Caesium bis[*N*-(carbamoylmethyl)imino-diacetato]chromate(III) dihydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.080
Data-to-parameter ratio = 17.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $Cs[Cr(C_6H_8N_2O_5)_2]\cdot 2H_2O$, important geometric parameters are Cr—N = 2.090 (2) and 2.096 (2) Å, Cr—O = 1.950 (2), 1.953 (2), 1.957 (2) and 1.962 (2) Å, O—Cr—O = 179.00 (11) and 179.18 (10)°, and N—Cr—N = 179.33 (9)°.

Comment

N-(Carbamoylmethyl)iminodiacetic acid [H_2ADA or $H_2NCOCH_2N(CH_2CO_2H)_2$] is widely used in biological buffers. Several solution studies have been reported since Swarzenbach and co-workers first investigated the chelation of ADA with different divalent metal ions (Swarzenbach *et al.*, 1955; Lance & Nakon, 1981; Nepal & Dubey, 1987).

In contrast, solid-state studies of ADA complexes are very limited. Two different research groups have reported on the structure of a vanadium(V) oxo–monoperoxo complex (Sivak *et al.*, 1996; Colpas *et al.*, 1996). Since then, four structures of mixed-ligand complexes of metal ions M^{II} with ADA (*M* = Cu, Ni or Co) have been reported, in which ADA acts as a tetradentate ligand (Bugella-Altamirano *et al.*, 1999; Bugella-Altamirano *et al.*, 2000*a*,*b*). Only one structure in which ADA acts as a tridentate ligand has been reported to date, to the best of our knowledge (Bugella-Altamirano *et al.*, 2002). No structural reports of metal(III) complexes with ADA are available in the literature [Cambridge Structural Database (CSD), Version 5.26, February 2005 update; Allen, 2002]. The present study of the title compound, (I), is part of an ongoing investigation to determine which factors govern the distortion of the metal glycinate rings in metal(III) complexes with tripod-type ligands (Weakliem & Hoard, 1959; Visser *et al.*, 1997, 1999, 2001).

(I)
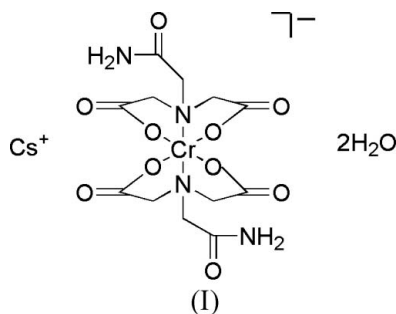
The Cr atom in (I) is octahedrally surrounded (Fig. 1, Table 1) by four O atoms (O1, O3, O6 and O8) and two N ligands (N1 and N3). The Cr—O bonding distances vary between 1.949 (2) and 1.961 (2) Å, while the Cr—N bond lengths are 2.090 (2) and 2.096 (2) Å. All Cr—N and Cr—O

N atom to be lifted somewhat when the ligand is bonded in tridentate mode. This seems to be the case if the comparison with $Cs_2[Cr_2(NTA)_2(\mu-OH)_2]\cdot4H_2O$ is made, where deviations of up to 0.705 (6) Å from the CCOO planes were observed (Visser *et al.*, 1999).

The $Cs^I\cdots O$ interatomic distances vary between 2.988 (4) and 3.398 (2) Å. The geometry of this arrangement is in the form of a twisted dodecahedron. These interactions serve to link four adjacent molecules. Furthermore, each molecule is linked to seven adjacent molecules by weak hydrogen-bonding interactions (Table 2).

Lastly, it is of interest to report on the IR spectrum of this complex. Previous workers observed overlapping of $\nu(COO^-)$ and the amide bands in the 1600–1700 cm^{-1} region (Bugella-Altamirano *et al.*, 2000a). This overlap gives rise to the broad band observed at 1615 cm^{-1} for the title complex. The band at 1681 cm^{-1} is attributed to $\nu(C{=}O)$ of the primary amide, which is the same as that found for the free ligand, thereby confirming that the opened 'arm' of ADA in this case is indeed the glycinamido arm.
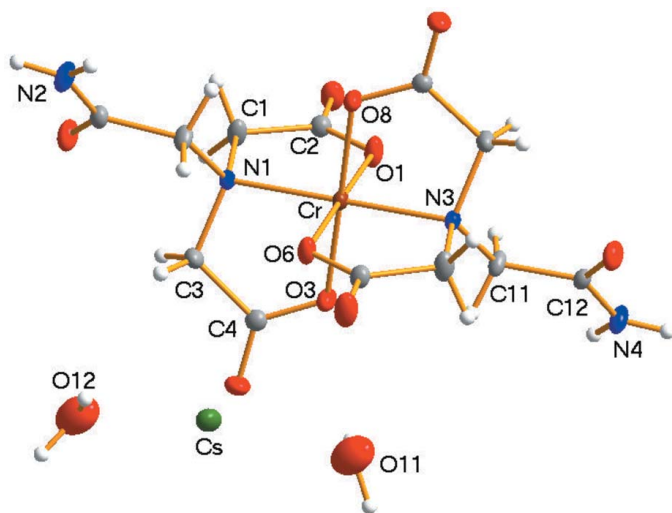

Figure 1
The structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

bonding distances fall within the expected ranges for this type of complex (Green *et al.*, 1990; Visser *et al.*, 1999). The rest of the N—C, C—C and C—O bond distances are considered normal and correlate well with those found in H_2ADA (Bugella-Altamirano *et al.*, 2000a).

The deviation around Cr from octahedral geometry is significant. The N—Cr—O bond angles are the most distorted, with values varying between 82.90 (9) and 97.51 (9)°. The O—Cr—O angles vary between 88.57 (10) and 90.82 (10)°, while the *trans*-O—Cr—O and N—Cr—N bond angles are 179.00 (11), 179.21 (10) and 179.31 (10)°.

The strain in complexes like these is usually described by the deviation from planarity of the acetate rings (Weakliem & Hoard, 1959). According to that work, the sum of the endocyclic angles of planar acetate rings should be 538.4°, and any deviation from this implies non-planarity of the rings. The sums of the endocyclic angles of the rings in the title complex vary between 531.9 and 540.7°, a maximum deviation of *ca* 7°. This is less than that found for $Cs_2[Cr_2(NTA)_2(\mu-OH)_2]\cdot4H_2O$ (NTA is nitrilotriacetic acid), where deviations of up to 12° were observed in some of the acetate rings (Visser *et al.*, 1999).

Least-squares calculations further illustrate the deviation from planarity of the acetate rings (Table 3). The N and Cr atoms are displaced on opposite sides of the CCOO plane for all the rings except one, with distances of Cr and N from the planes varying between 0.494 (6) and 0.010 (5) Å.

The primary reason for the non-planarity of such rings is presumed to be the angular strain of the coordinated N atom of the tripod ligand, in this case ADA (Visser *et al.*, 1999). When bonded in tetradentate mode, the N atom is at the intersection of three five-membered chelate rings with two common members, Cr and N. Each ring attempts to impose its own stereochemical requirements on the N atom, which is also constrained to approximately tetrahedral geometry. The resulting compromise structure contains not only angle and bond-length abnormalities, but also significant distortions of the N tetrahedra. One would expect the angular strain on the

Experimental

$Cr_2(SO_4)_3\cdot K_2SO_4\cdot24H_2O$ (5.252 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 ADA (2 g) and heated in a water bath until almost dry. Hot water (30 ml) was added to the reaction solution, which was then filtered. Orange crystals precipitated after 2 d. The title compound was obtained by recrystallization with excess CsCl (yield 3.53 g, 77%). IR: $\nu(NH_2$ and COO^- overlapped) 1615 cm^{-1}, $\nu(C{=}O)$ 1681 cm^{-1}; UV–Vis (H_2O): λ_{max} 501, 355 nm.

Crystal data

$Cs[Cr(C_6H_8N_2O_5)_2]\cdot2H_2O$	$D_x = 2.053$ Mg m^{-3}
$M_r = 597.23$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 813
$a = 9.1471$ (11) Å	reflections
$b = 12.1267$ (14) Å	$\theta = 2.7$–$26.9°$
$c = 17.475$ (2) Å	$\mu = 2.52$ mm^{-1}
$\beta = 94.516$ (2)°	$T = 293$ (2) K
$V = 1932.4$ (4) Å^3	Rhombic prism, orange
$Z = 4$	$0.23 \times 0.22 \times 0.18$ mm

Data collection

Bruker SMART CCD 1K area-detector diffractometer	4773 independent reflections
	3882 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.024$
Absorption correction: multi-scan	$\theta_{max} = 28.3°$
(*SADABS*; Bruker, 1998)	$h = -11 \rightarrow 12$
$T_{min} = 0.595$, $T_{max} = 0.660$	$k = -7 \rightarrow 16$
12675 measured reflections	$l = -23 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$+ 2.6041P]$
$wR(F^2) = 0.080$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4773 reflections	$\Delta\rho_{max} = 1.38$ e Å^{-3}
267 parameters	$\Delta\rho_{min} = -0.97$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cr—O1	1.950 (2)	Cr—O8	1.962 (2)
Cr—O6	1.953 (2)	Cr—N3	2.090 (2)
Cr—O3	1.957 (2)	Cr—N1	2.096 (2)
O1—Cr—O6	179.00 (11)	O3—Cr—N1	82.88 (9)
O1—Cr—O3	90.40 (11)	O8—Cr—N1	96.62 (9)
O6—Cr—O3	88.60 (10)	N3—Cr—N1	179.33 (9)
O1—Cr—O8	90.20 (11)	C5—N1—C3	112.3 (2)
O6—Cr—O8	90.80 (10)	C5—N1—C1	112.8 (2)
O3—Cr—O8	179.18 (10)	C3—N1—C1	111.9 (3)
O1—Cr—N3	95.68 (9)	C5—N1—Cr	108.03 (17)
O6—Cr—N3	84.37 (9)	C3—N1—Cr	105.40 (17)
O3—Cr—N3	97.52 (9)	C1—N1—Cr	105.82 (17)
O8—Cr—N3	82.98 (9)	C11—N3—Cr	108.34 (17)
O1—Cr—N1	84.84 (9)	C9—N3—Cr	104.71 (17)
O6—Cr—N1	95.10 (9)	C7—N3—Cr	106.99 (17)

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12B···O5[i]	0.92	2.14	2.936 (5)	145
O12—H12A···O7[ii]	0.90	2.03	2.927 (5)	171
O11—H11D···O5[iii]	0.92	2.02	2.911 (5)	162
O11—H11C···O3	0.90	2.53	3.087 (5)	120
O11—H11C···O4	0.90	2.50	3.136 (5)	128
N4—H4B···O9[iv]	0.86	2.11	2.955 (4)	167
N4—H4A···O7[v]	0.86	2.30	3.099 (4)	154
N2—H2B···O4[vi]	0.86	2.24	3.073 (4)	162
N2—H2A···O2[vii]	0.86	2.29	3.111 (3)	159

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x, -y, -z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x + 1, y, z$; (vi) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x - 1, y, z$.

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

CCOO plane	Distance to Cr	Distance to N
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)

Methylene and amine H atoms were placed in geometrically idealized positions (N—H = 0.86 Å and C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms. Aqua H atoms were located in a difference Fourier map and then refined isotropically. The minimum and maximum residual electron density are located within 2.0 Å of the Cr atom, indicating no physical meaning.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Berndt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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