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cis-Dinitrito(1,4,8,11-tetraazacyclotetradecane-κ^4N)chromium(III) nitrite

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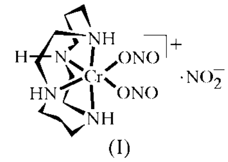
In the title compound, $[Cr(ONO)_2(cyclam)]NO_2$ (cyclam is 1,4,8,11-tetraazacyclotetradecane, $C_{10}H_{24}N_2$), the complex cation is located on a twofold symmetry axis. The central Cr atom has a distorted octahedral coordination, involving two Cr—O bonds, with the monodentate nitrite O atoms adopting a *cis* configuration, and four Cr—N bonds. The mean Cr—N and Cr—O distances are 2.0895 (14) and 1.9698 (14) Å.

Comment

The nitrite ion is a versatile ligand that can bind transition metal ions in a number of coordination modes, giving rise to mononuclear, dinuclear and polynuclear complexes. This ion can thus act as a monodendate, chelating or bridging–bidentate ligand type (Hitchman & Rowbottom, 1982). In principle, three types of ligand binding modes are possible for mononuclear Cr^{III} complexes, namely the nitro ($Cr—NO_2$), monodentate (nitrite-*O*) or chelating (nitrite-*O*,*O*′) binding modes. Furthermore, the cyclam (1,4,8,11-tetraazacyclotetradecane) ligand is a moderately flexible structure, which can adopt both planar (*trans*) and folded (*cis*) configurations (Poon & Pun, 1980). There are five configurational *trans* isomers for the cyclam ligand, which differ in the chirality of the *sec*-NH centers. The *trans*-V configuration can fold to form the *cis*-V isomer. The 14-membered cyclam ligand and its derivatives are involved in diverse fields, such as catalysis, enzyme mimicry, pharmacology and extraction of metal cations (Meyer, Dahaoui-Gindrey *et al.*, 1998, and references therein). We have previously described spectroscopic and ligand-field properties on the basis of emission, far-IR and electronic spectroscopy of the *cis*-$[Cr^{III}X_2(cyclam)]^{n+}$ system (*X* = en/2, pn/2, NH_3, F^-, Cl^-, Br^-, NCS^-, N_3^-, ONO^-, ONO_2^- and $ox^{2-}/2$; en, pn and ox are 1,2-ethanediamine, 1,3-propanediamine and oxalate, respectively; Choi, 2000*a*,*b*; Choi, Hong & Park, 2002; Choi *et al.*, 2004). The electronic absorption and vibrational spectra can be used diagnostically to identify the geometric isomers of chromium(III) complexes (Poon & Pun, 1980; Choi, Hong & Park, 2002). However, assignments based on spectral properties are not always conclusive (Stearns & Armstrong, 1992).

An X-ray crystallographic analysis of the title chromium(III) complex, (I), with the 14-membered macrocyclic cyclam ligand and two nitrite groups was undertaken in order to confirm the type of linkage involved and to verify structural assignment made on the basis of spectroscopic measurements.



(I)

Selected bond lengths and angles for (I) are listed in Table 1. A perspective drawing of the structure, together with the atomic labeling scheme, is shown in Fig. 1.

The complex cation is located on a twofold symmetry axis. The coordinated nitrite anions are each bound to the Cr atom *via* only one O atom. The cyclam ligand is folded along the N2···N2*A* direction, with four N atoms coordinating to the Cr atom; the two nitrite ligands coordinate to the Cr atom in a *cis* configuration. However, the non-bonded nitrite O atoms are located *trans* to the Cr atom, in a monodentate nitrite coordination. The fold angle (95.09°) in the cyclam unit is slightly different from the corresponding angles (98.55, 94.51 and 92.8°) in $[Cr(ox)(cyclam)]ClO_4$, *cis*-$[Cr(N_3)_2(cyclam)]ClO_4$ and *cis*-$[CrCl_2(cyclam)]Cl$, respectively (Forsellini *et al.*, 1986; Meyer, Bendix *et al.*, 1998; Choi *et al.*, 2004).

The crystal structure of the title compound contains a (cyclam)dinitritochromium(III) monocation and a nitrite anion in a 1:1 molecular ratio, so (I) can be formulated as *cis*-$[Cr(ONO)_2(cyclam)]NO_2$. This structure is in agreement with the elemental analysis. The Cr1—O1 bond length is 1.9698 (14) Å, which is comparable to the distances of 1.972 and 1.952 Å found in the $[Cr(dpt)(glygly)]^+$ [dpt is bis(3-aminopropyl)amine and glygly is glycylglycinate] and $[Cr(edma)_2]^+$ (edma is ethylenediaminemonoacetate)

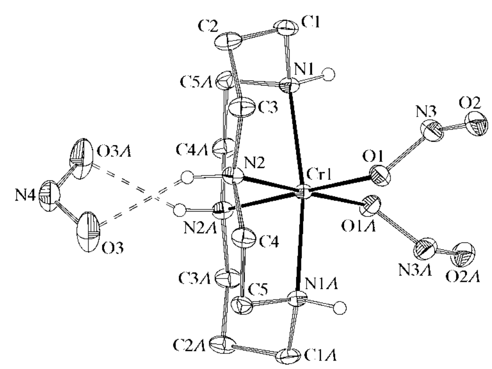


Figure 1
A view of (I), with displacement ellipsoids shown at the 30% probability level. For clarity, H atoms are not shown, except those bonded to N atoms. [Symmetry code: (*A*) $1-x$, y, $\frac{1}{2}-z$.]

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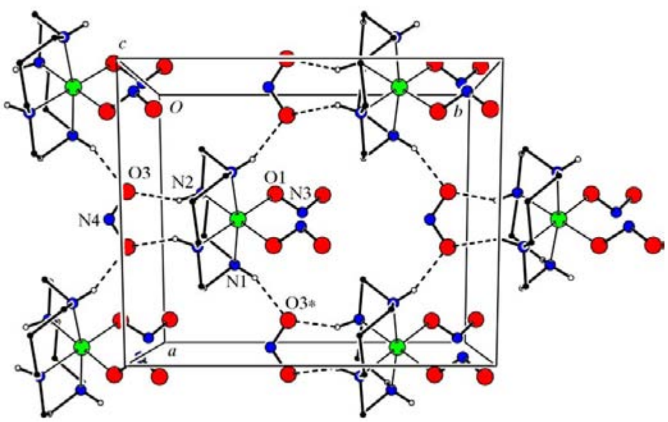

Figure 2
A view of part of the two-dimensional hydrogen-bonded network in (I). [Symmetry code: (*) $\frac{1}{2}+x, \frac{1}{2}+y, z$.]

moieties, respectively (Choi *et al.*, 1995; Choi, Suzuki, Subhan *et al.*, 2002). In (I), the Cr—N bond lengths of the CrN_4 moiety lie in the range 2.0874 (16)–2.0916 (15) Å, and the O1—Cr1—O1*A* angle is 94.03 (9)°. The Cr—N bond lengths of the secondary amine are also comparable to the Cr—N distances of the amine groups in the *trans*-$[Cr(Me_2tn)_2Br_2]^+$ and $[Cr_2(\mu\text{-}OH)_2(nta)_2]^{2-}$ complexes (2.054–2.089 Å; Me_2tn is 2,2-dimethyl-1,3-propanediamine and nta is nitrilotriacetate; Choi, Suzuki & Kaizaki, 2002; Choi *et al.*, 2003). The O1—N3 bond length is 1.317 (2) Å, while the O2—N3 bond length is 1.212 (2) Å. The (CrO)N—O bond length is shorter than the (Cr)O—N(O) bond length and is consistent with the length of a localized double bond (DeLeo *et al.*, 2000). However, this situation contrasts with that for the $[Cr(NH_3)_5(ONO)]Cl_2$ complex, in which the two N—O distances [1.190 (4) and 1.191 (4) Å] are essentially equal (Nordin, 1978). The Cr—O—N and O—N—O bond angles are 118.99 (11) and 114.19 (16)°, respectively. The N1—Cr1—N1^{i} angle is 169.77 (9)°, while the O1^{i}—Cr1—N2 angle is 179.19 (6)° [symmetry code: (i) $1-x, y, \frac{1}{2}-z$].

As is usually observed, the five-membered chelate rings adopt a *gauche* configuration and the six-membered rings adopt chair conformations. The mean bond angles in the five- and six-membered chelate rings around the Cr^{III} atom are 82.94 (6) and 90.14 (6)°, respectively.

Hydrogen bonds between secondary NH groups and nitrite anions (as detailed in Table 2 and shown in Fig. 2) help to stabilize the crystal structure and generate a two-dimensional network.

Experimental

The free ligand cyclam was purchased from Stream Chemicals and used as provided. All chemicals were of reagent grade and were used without further purification. Compound (I) was synthesized according to the method of Ferguson & Tobe (1970). Recrystallization from an ethanol–water solution gave bright-orange crystals suitable for crystallographic analysis. Analysis found: C 30.12, H 5.98, N 24.53%; calculated for $C_{10}H_{24}CrN_7O_6$: C 30.77, H 6.19, N 25.12%.

Crystal data

$[Cr(C_{10}H_{24}N_2)(NO_2)_2]NO_2$
$M_r = 390.36$
Monoclinic, $C2/c$
$a = 9.878$ (2) Å
$b = 11.813$ (2) Å
$c = 14.837$ (3) Å
$\beta = 104.69$ (3)°
$V = 1674.7$ (6) Å^3
$Z = 4$
$D_x = 1.548$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 930 reflections
$\theta = 2.7$–28.3°
$\mu = 0.73$ mm^{-1}
$T = 293$ (2) K
Block, orange
0.5 × 0.3 × 0.3 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1999)
$T_{min} = 0.770$, $T_{max} = 0.804$
5231 measured reflections
1977 independent reflections
1771 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$
$\theta_{max} = 28.3°$
$h = -11 \rightarrow 12$
$k = -12 \rightarrow 15$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.103$
$S = 1.06$
1977 reflections
110 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2 + 1.3864P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.79$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cr1—O1	1.9698 (14)	Cr1—N1	2.0916 (15)
Cr1—N2	2.0874 (16)		
O1^{i}—Cr1—O1	94.03 (9)	N2^{i}—Cr1—N1^{i}	90.14 (6)
O1^{i}—Cr1—N2	179.19 (6)	N1^{i}—Cr1—N1	169.77 (9)
O1—Cr1—N2	85.44 (7)	N3—O1—Cr1	118.99 (11)
N2—Cr1—N2^{i}	95.09 (9)	C1—N1—Cr1	119.26 (12)
O1^{i}—Cr1—N1^{i}	97.68 (6)	C5^{i}—N1—Cr1	109.14 (10)
O1—Cr1—N1^{i}	89.31 (6)	C3—N2—Cr1	116.20 (12)
N2—Cr1—N1^{i}	82.94 (6)	C4—N2—Cr1	106.19 (11)

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3^{i}	0.91	2.03	2.890 (3)	158
N2—H2···O3	0.91	2.12	2.949 (3)	151

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$.

H atoms were placed geometrically, with N—H distances of 0.91 Å and C—H distances of 0.97 Å, and treated as riding.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1172). Services for accessing these data are described at the back of the journal.

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