Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Aqua(2,2′-diamino-4,4′-bi-1,3-thiazole-κ^2N,N')(iminodiacetato-κ^3O,N,O')chromium(III) chloride monohydrate

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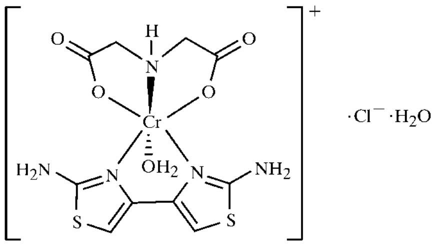
Received 23 October 2003
Accepted 28 January 2004
Online 19 February 2004

Crystals of the title compound, $[Cr(C_4H_5NO_4)(C_6H_6N_4S_2)(H_2O)]Cl\cdot H_2O$, consist of Cr^{III} complex cations, Cl^- counter-ions and lattice water molecules. The complex cation assumes an octahedral coordination geometry, formed by a tridentate iminodiacetate dianion (IDA), a diaminobithiazole (DABT) molecule and a water molecule. The planar DABT group chelates the Cr^{III} ion with normal Cr—N distances [2.0574 (17) and 2.0598 (17) Å], but the DABT molecule is inclined to the coordination plane by a dihedral angle of 17.23 (7)°. In the monodentate carboxylate groups of the IDA ion, the coordinated C—O bonds [1.288 (3) and 1.284 (3) Å] are much longer than the uncoordinated C—O bonds [1.222 (3) and 1.225 (3) Å].

Comment

Metal complexes incorporating 2,2′-diamino-4,4′-bi-1,3-thiazole (DABT) have potential applications in several fields. For example, a Co^{II} complex and an Ni^{II} complex with DABT have been found to be effective inhibitors of DNA synthesis of tumor cells (Waring, 1981; Fisher *et al.*, 1985). As part of a series of structural investigations of metal complexes incorporating DABT, the title Cr^{III} complex, (I), was prepared and its X-ray structure is presented here.

The molecular structure of (I) is shown in Fig. 1. The complex assumes an octahedral coordination geometry, formed by a DABT molecule, an iminodiacetate dianion (IDA) and a coordinated water molecule. The tridentate IDA dianion chelates the Cr^{III} ion in a facial configuration, which is the common mode for IDA ligands in metal complexes (Mootz & Wunderlich, 1980; Subramaniam *et al.*, 1994). Both chelating five-membered rings of the IDA ion display an envelope conformation, with atom N5 in the flap position and lying out of the planes formed by the other four atoms by 0.220 (3) and 0.379 (3) Å. The carboxy groups of the IDA ion coordinate to the Cr^{III} ion in a monodentate manner. The uncoordinated carboxy O atoms are linked to adjacent coordinated water or lattice water molecules *via* hydrogen bonds, as shown in Fig. 1 and Table 2.



(I)

In the carboxy groups, the coordinated C—O distances [1.288 (3) and 1.284 (3) Å] are much longer than the uncoordinated C—O distances [1.222 (3) and 1.225 (3) Å; Table 1]. The differences [0.066 (4) and 0.059 (4) Å] are comparable to that found both in the neutral carboxy group of iminodiacetic acid [0.078 (4) Å; Bernstein, 1979] and in difluoro(propanediaminediacetato)chromium(III) [0.059 (4) Å; Bianchini *et al.*, 1986].

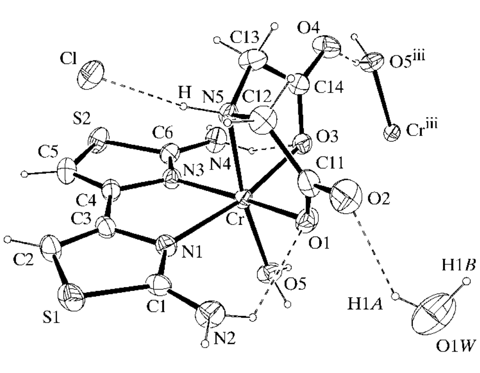


Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. Dashed lines indicate hydrogen bonding. [Symmetry code: (iii) $1 - x, -y, -z$.]

The thiazole rings of the DABT molecule are approximately coplanar, the maximum atomic deviation being 0.0743 (12) Å (atom S2). It is notable that the planar DABT molecule is inclined to the coordination plane defined by atoms O1, O3, N1, N3 and Cr by a dihedral angle of 17.23 (7)°, and hence the Cr^{III} ion lies 0.402 (2) Å out of the DABT mean plane; however, the $Cr—N_{DABT}$ distances are normal. Although no geometrical data for the DABT complex of Cr^{III} are available for comparison, the Cr—N3 [2.0574 (17) Å] and Cr—N1 [2.0598 (17) Å] distances are similar to the average Cr—N distances found in the 2,2′-bipyridine complex of Cr^{III} [2.064 (3) Å; Swaminathan *et al.*, 1988] and the phenanthroline complex of Cr^{III} [2.065 (8) Å; Ohbo *et al.*, 1983]. The C1—N2 [1.319 (3) Å] and C6—N4 [1.331 (3) Å] distances suggest the existence of electron delocalization between the thiazole rings and the amine groups.

DOI: 10.1107/S0108270104002288

Extensive hydrogen-bonding interactions occur in the crystal structure (Table 2). While the amine N atoms of the DABT molecule are intramolecularly hydrogen bonded to the coordinated carboxy O atoms, the Cl^- counter-ion and lattice water molecules are linked to the Cr^{III} complex cation *via* hydrogen bonds (Fig. 1). The Cl^- anion is simultaneously hydrogen bonded to the imine group of the IDA ion, the amine group of the DABT molecule and coordinated water molecules of adjacent complex cations, thus forming the hydrogen-bonded supramolecular structure shown in Fig. 2. The lattice water molecules are also involved in the supramolecular structure *via* hydrogen bonding to the carboxy group of the IDA ion and the amine group of the DABT molecule of neighboring complex cations. Three-centered hydrogen bonds occur in the crystal (Table 2), the sums of the three angles about the H atoms being 354 (for atom H2*B*) and 360° (for atom H4*A*).

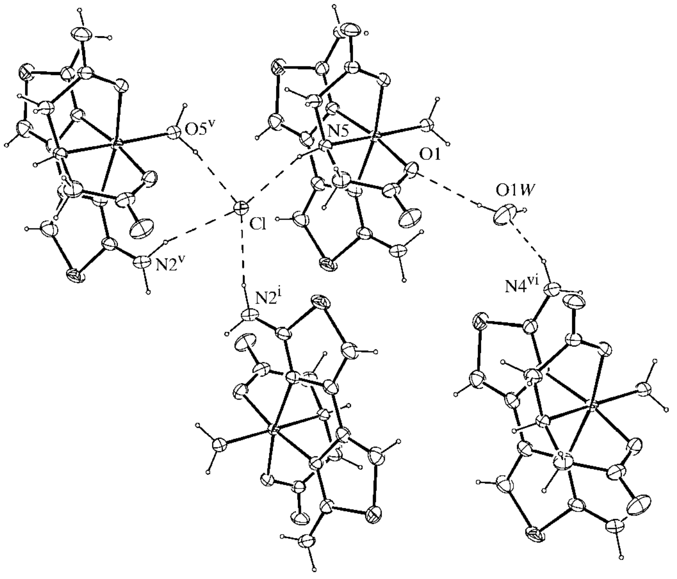


Figure 2
The hydrogen-bonding network between complex cations. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (v) $1 + x, y, z$; (vi) $-1 + x, y, 1 + z$.]

Neighboring parallel DABT planes are separated by 3.716 (7) Å, suggesting van der Waals contacts but not π–π stacking between DABT ligands in the crystal. Two symmetry-related O1*W* water molecules are loosely hydrogen bonded *via* atom H1*B*.

Experimental

Microcrystals of DABT were obtained in the manner reported by Erlenmeyer (1948). An aqueous solution (20 ml) containing DABT (0.1 g, 0.5 mmol) and $CrCl_3\cdot 6H_2O$ (0.13 g, 0.5 mmol) was mixed with another aqueous solution (10 ml) of IDA (0.07 g, 0.5 mmol) and NaOH (0.04 g, 1 mmol). The resulting mixture was refluxed for 3 h and filtered. The filtrate was then cooled to room temperature and filtered once more. Green single crystals of (I) were obtained after 10 d.

Crystal data

$[Cr(C_4H_5NO_4)(C_6H_6N_4S_2)(H_2O)]Cl\cdot H_2O$
$M_r = 452.86$
Triclinic, $P\overline{1}$
$a = 7.9449$ (10) Å
$b = 10.7342$ (11) Å
$c = 10.8835$ (12) Å
$\alpha = 89.0403$ (12)°
$\beta = 69.5740$ (11)°
$\gamma = 82.2042$ (15)°
$V = 861.30$ (17) $Å^3$
$Z = 2$
$D_x = 1.746$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3621 reflections
$\theta = 2.8$–23.0°
$\mu = 1.10$ mm^{-1}
$T = 295$ (2) K
Plate, green
0.41 × 0.32 × 0.13 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.632$, $T_{max} = 0.865$
6761 measured reflections
3069 independent reflections
2862 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 25.2°$
$h = -9 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.084$
$S = 1.04$
3069 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.5018P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e $Å^{-3}$
$\Delta\rho_{min} = -0.50$ e $Å^{-3}$

Table 1
Selected interatomic distances (Å).

Cr—O1	1.9294 (16)	O2—C11	1.222 (3)
Cr—O3	1.9662 (14)	O3—C14	1.284 (3)
Cr—O5	1.9843 (15)	O4—C14	1.225 (3)
Cr—N3	2.0574 (17)	N1—C1	1.339 (3)
Cr—N1	2.0598 (17)	N2—C1	1.319 (3)
Cr—N5	2.0620 (18)	N3—C6	1.325 (3)
O1—C11	1.288 (3)	N4—C6	1.331 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H···Cl	0.93	2.33	3.1634 (19)	149
O1*W*—H1*A*···O2	0.82	2.20	2.891 (4)	142
N2—H2*A*···Cl^{i}	0.91	2.35	3.237 (2)	165
N2—H2*B*···Cl^{ii}	0.95	2.64	3.420 (3)	140
N2—H2*B*···O1	0.95	2.33	2.927 (3)	121
N4—H4*A*···O3	0.89	2.37	3.002 (3)	128
N4—H4*A*···O3^{iii}	0.89	2.31	3.104 (3)	149
N4—H4*B*···O1*W*^{iv}	0.90	2.04	2.882 (4)	157
O5—H5*A*···Cl^{ii}	0.88	2.16	3.0230 (18)	166
O5—H5*B*···O4^{iii}	0.88	1.74	2.607 (3)	168

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

H atoms on C atoms were placed in calculated positions, with C—H distances of 0.97 (methylene) and 0.93 Å (aromatic), and included in the final cycles of refinement in a riding model, with $U_{iso}(H)$ values equal to $1.2U_{eq}$ of the carrier atoms. Other H atoms were located in a difference Fourier map and included in the structure-factor calculations with fixed positional parameters and $U_{iso}(H)$ values of 0.05 $Å^2$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

This project was supported by the Analytical Foundation of Zhejiang University, People's Republic of China.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1675). Services for accessing these data are described at the back of the journal.

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