Acta Crystallographica Section C
Crystal Structure
Communications
ISSN 0108-2701

Bis(ethylenediamine-*N*,*N*′)(pyrimidine-2-carboxylato-*N*^{1},*O*)cobalt(III) bis(trifluoromethanesulfonate) dihydrate

Snježana Antolić, Biserka Kojić-Prodić and Jasna Lovrić

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(ethylenediamine-*N*,*N*′)(pyrimidine-2-carboxylato-*N*^{1},*O*)cobalt(III) bis(trifluoromethanesulfonate) dihydrate

Snježana Antolić,[a] Biserka Kojić-Prodić[a]* and Jasna Lovrić[b]

[a]Laboratory for Chemical and Biological Crystallography, Rudjer Bošković Institute, POB 1016, 10001 Zagreb, Croatia, and [b]Faculty of Medicine, University of Zagreb, Šalata 3 b, 10000 Zagreb, Croatia
Correspondence e-mail: kojic@rudjer.irb.hr

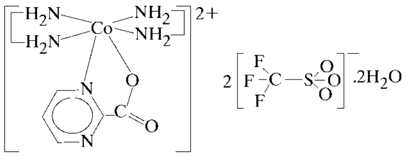
Received 20 December 1999
Accepted 10 January 2000

Data validation number: IUC0000014

In the title compound, the coordination geometry of the Co^{III} atom is only slightly distorted from regular octahedral, and the racemic nature of the material was confirmed by X-ray structure analysis.

Comment

Studies of electron-transfer reactions between two metal centres, where 2,2′-bipyrimidine (bpm) or its ring-substituted analogues would serve as a chelating bridging ligand, included a preparation of $[Co(en)_2(bpm)](CF_3SO_3)_3$ complex (en = ethylenediamine) (Dixon *et al.*, 1981) and its chloride analogue. Hovewer, under unpredictable circumstances we ended up with the title compound. Most likely, the relatively high impurity of the bpm batch (Lancaster Syntheses Ltd) used for the preparation without purification is responsible for such a result. In order to understand unusual 'reaction path', the products obtained were characterized by X-ray structure analysis. The analysis revealed bis(ethylenediamine)(pyrimidin-2-ylcarboxylato)cobalt(III) bis(trifluoromethanesulfonate) dihydrate, (I), and its chloride analogue.



(I)

As 2,2′-bipyrimidine was not coordinated to the metal atom, the analysis of the commercial chemical was undertaken. It revealed the presence of pyrimidine-2-carboxylic acid which has been of higher preference to be coordinated *via* mixed O,N-donated ligands than *N,N* of bpm. Due to the low quality of the data collected for bis(ethylenediamine)(pyrimidine-2-carboxylato)cobalt(III) chloride 1.5-hydrate, (II), the detailed description of crystal and molecular structure will be given only for bis(ethylenediamine)(pyrimidin-2-ylcarboxylato)cobalt(III) bis(trifluoromethanesulfonate) dihydrate, (I).

The solved structures revealed the same cation structure with ethylenediamine as a bidentate ligands. Cobalt is in a 3+ oxidation state and two ethylenediamine ligands and pyrimidinyl-2-carboxylato ligand (which was supposed to be bpm) built an octahedral environment. Tris-bidentate ligands in the complexes might introduce certain degree of octahedral distortion. However, the title complex reveals minor octahedral distortion. In the structures with different ligands electron-donating ability of nitrogen varies, thus Co—N bond lengths might be different. Here, five Co—N bonds with mean value 1.952 (2) Å are all nearly equal. The bite angle values range from 83.84 (7) to 86.60 (8)°. Other bonding angles do not deviate significantly from 90° (<2°). In the synthesis of (II), optically pure, Δ absolute configuration was obtained whereas in (I), the racemate appeared. Chirality of these complexes can be deduced from the space-group symmetry. Three-dimensional hydrogen-bond network involves: (a) N—H···O between ethylenediamine ligands and trifluoromethanesulfonates in the [111] direction; (*b*) N—H···N between ethylenediamine ligands and N atoms of pyrimidine-2-carboxylato ligand; (*c*) O—H···O between crystalline water molecules and crystalline water molecules towards trifluoromethanesulfonate anions.

Experimental

Crystals of both compounds were grown by slow evaporation from ethanol and acetone mixtures affording acceptable crystallographic samples. The crystals obtained were used for intensity data collection. In order to minimize crystal decay, the data for (I) were collected at low temperature (100 K), while the data for (II) were collected at room temperature.

Crystal data

$[Co(C_5H_3N_2O_2)(C_2H_8N_2)_2](CF_3O_3S)_2 \cdot 2H_2O$
$M_r = 636.42$
Triclinic, $P\bar{1}$
$a = 6.4976$ (4) Å
$b = 12.729$ (1) Å
$c = 14.741$ (1) Å
$\alpha = 73.40$ (1)°
$\beta = 81.98$ (1)°
$\gamma = 74.61$ (1)°
$V = 1123.8$ (2) Å^3
$Z = 2$
$D_x = 1.881$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 20$–24°
$\mu = 1.062$ mm^{-1}
$T = 100$ (2) K
Prismatic, orange
0.28 × 0.28 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*PLATON*97; Spek, 1997*a*)
$T_{min} = 0.817$, $T_{max} = 0.899$
7328 measured reflections
6780 independent reflections
4867 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 30.40°$
$h = 0 \rightarrow 9$
$k = -17 \rightarrow 18$
$l = -20 \rightarrow 20$
3 standard reflections every 87 reflections frequency: 180 min intensity decay: 0.7%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0370$
$wR(F^2) = 0.0989$
$S = 0.949$
6780 reflections
417 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0450P)^2 + 1.1493P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 0.63$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O7	1.915 (2)	C8—C9	1.514 (3)
Co1—N4	1.940 (2)	C9—O8	1.232 (3)
Co1—N1	1.956 (2)	C9—O7	1.284 (3)
Co1—N2	1.957 (2)	S1—O3	1.441 (2)
Co1—N3	1.959 (2)	S1—O2	1.444 (2)
Co1—N5	1.962 (2)	S1—O1	1.454 (2)
N1—C1	1.490 (3)	S1—C10	1.830 (3)
C1—C2	1.508 (3)	C10—F1	1.332 (3)
C2—N2	1.497 (3)	C10—F2	1.333 (3)
N3—C3	1.487 (3)	C10—F3	1.336 (3)
C3—C4	1.511 (3)	S2—O5	1.439 (2)
C4—N4	1.489 (3)	S2—O4	1.438 (2)
N5—C8	1.348 (3)	S2—O6	1.460 (2)
N5—C5	1.346 (3)	S2—C11	1.823 (3)
C5—C6	1.386 (3)	C11—F6	1.324 (3)
C6—C7	1.379 (3)	C11—F5	1.329 (3)
C7—N6	1.346 (3)	C11—F4	1.326 (3)
N6—C8	1.321 (3)		
O7—Co1—N4	86.59 (8)	N6—C8—C9	119.36 (19)
O7—Co1—N1	90.64 (8)	N5—C8—C9	114.41 (18)
N4—Co1—N1	92.61 (9)	O8—C9—O7	125.8 (2)
O7—Co1—N2	176.19 (8)	O8—C9—C8	120.35 (19)
N4—Co1—N2	91.78 (9)	O7—C9—C8	113.84 (19)
N1—Co1—N2	85.99 (8)	C9—O7—Co1	116.12 (14)
O7—Co1—N3	91.79 (8)	O3—S1—O2	115.01 (11)
N4—Co1—N3	86.60 (8)	O3—S1—O1	115.96 (11)
N1—Co1—N3	177.40 (9)	O2—S1—O1	113.37 (10)
N2—Co1—N3	91.55 (9)	O3—S1—C10	103.14 (12)
O7—Co1—N5	83.84 (7)	O2—S1—C10	104.42 (11)
N4—Co1—N5	169.61 (8)	O1—S1—C10	102.72 (11)
N1—Co1—N5	91.54 (8)	F1—C10—F2	108.5 (2)
N2—Co1—N5	98.01 (8)	F1—C10—F3	108.04 (19)
N3—Co1—N5	89.65 (8)	F2—C10—F3	107.9 (2)
C1—N1—Co1	108.62 (15)	F1—C10—S1	111.00 (17)
N1—C1—C2	106.43 (19)	F2—C10—S1	111.12 (16)
N2—C2—C1	106.77 (18)	F3—C10—S1	110.11 (18)
C2—N2—Co1	109.38 (14)	O5—S2—O4	115.46 (13)
C3—N3—Co1	109.36 (14)	O5—S2—O6	113.88 (11)
N3—C3—C4	106.73 (19)	O4—S2—O6	113.86 (11)
N4—C4—C3	107.56 (19)	O5—S2—C11	104.53 (12)
C4—N4—Co1	108.50 (15)	O4—S2—C11	104.78 (13)
C8—N5—C5	117.03 (19)	O6—S2—C11	102.44 (11)
C8—N5—Co1	111.64 (15)	F6—C11—F5	109.0 (3)
C5—N5—Co1	131.26 (16)	F6—C11—F4	108.0 (2)
N5—C5—C6	120.4 (2)	F5—C11—F4	107.2 (2)
C7—C6—C5	118.0 (2)	F6—C11—S2	110.02 (18)
N6—C7—C6	122.0 (2)	F5—C11—S2	110.44 (19)
C8—N6—C7	116.3 (2)	F4—C11—S2	112.11 (19)
N6—C8—N5	126.2 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11N···O6^{i}	0.85	2.15	2.991 (3)	174 (3)
N1—H12N···O3	0.86	2.22	3.019 (2)	155 (3)
N2—H21N···O6^{ii}	0.88	2.27	3.044 (3)	147 (2)
N2—H22N···O1^{iii}	0.94	2.12	3.025 (3)	162 (3)
N3—H31N···N6^{iv}	0.88	2.26	3.129 (3)	167 (3)
N3—H32N···O8^{v}	0.84	2.15	2.987 (3)	172 (3)
N4—H41N···O2^{iii}	0.89	2.10	2.921 (3)	152 (3)
N4—H42N···O1^{vi}	0.89	2.06	2.928 (3)	164 (4)
O9—H91···O5	0.91	2.13	3.042 (3)	175 (4)
O9—H92···O10^{vii}	0.86	1.96	2.798 (4)	166 (4)
O10—H101···O5	0.85	2.15	2.908 (3)	149 (4)
O10—H102···O9^{viii}	0.81	1.98	2.754 (2)	161 (5)

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

H atoms were located from a different synthesis and refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXL*97 (Sheldrick, 1997*b*).

References

Dixon, N. E., Jackson, W. G., Lancaster, M. J., Lawrence, G. A. & Sargeson, A. M. (1981). *Inorg. Chem.* **20**, 470–476.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.

Sheldrick, G. M. (1997*a*). *SHELXL*97. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXS*97. University of Göttingen, Germany.

Spek, A. L. (1997*a*). *PLATON*. Version of 1997. University of Utrecht, The Netherlands.

Spek, A. L. (1997*b*). *HELENA*. Utrecht University, The Netherlands.

e52 Snježana Antolić *et al.* • $[Co(C_5H_3N_2O_2)(C_2H_8N_2)_2](CF_3O_3S)_2 \cdot 2H_2O$ *Acta Cryst.* (2000). C**56**, e51–e52