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trans-Bis(isothiocyanato)bis(ethylenediamine)cobalt(III) Thiocyanate

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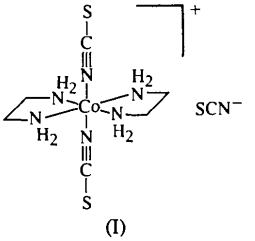
Abstract

Two independent cations are present in the asymmetric unit of [Co(NCS)$_2$(C$_2$H$_8$N$_2$)$_2$]SCN, one lying on an inversion center and the other on a twofold axis that bisects each ethylenediamine ligand. The centrosymmetric cation has Co—N(ethylenediamine) bond lengths of 1.953 (1) and 1.954 (1) Å, and a Co—NCS bond length of 1.901 (1) Å. The twofold cation has Co—N(ethylenediamine) bond lengths 1.945 (1) and 1.947 (1) Å, and a Co—NCS length of 1.896 (1) Å. In both cases, the isothiocyanato ligands coordinate slightly non-linearly, forming an angle of 175.9 (1)° in the centrosymmetric case and 163.8 (1)° in the twofold symmetric case.

Comment

The title compound, (I), was formed in an attempt to convert [(en)$_2$Co(O$_2$),(NH$_2$)Co(en)$_2$]I$_3$ (en = ethylenediamine) (Thewalt, 1970) into its thiocyanate salt by heating it at 343 K in an aqueous solution of KSCN. The dark red crystals which formed upon slow cooling were subjected to crystal structure analysis in order to ascertain their identity.



(I)

The title cobalt complex has the expected octahedral structure but contains, unexpectedly, two independent cations with different site symmetries, namely 2 and $\bar{1}$. The twofold axis of the cation with symmetry 2 (containing atom Co1) passes through the central C—C bonds of both ethylenediamine ligands. Although it is not required by symmetry, the two ethylenediamine ligands of this cation have a λ conformation, with positive N—C—C—N torsion angles. The ethylenediamine ligands of the $\bar{1}$ symmetry cation (containing atom Co2) have λ,δ conformations as required by symmetry. Co—N(en) distances in the two

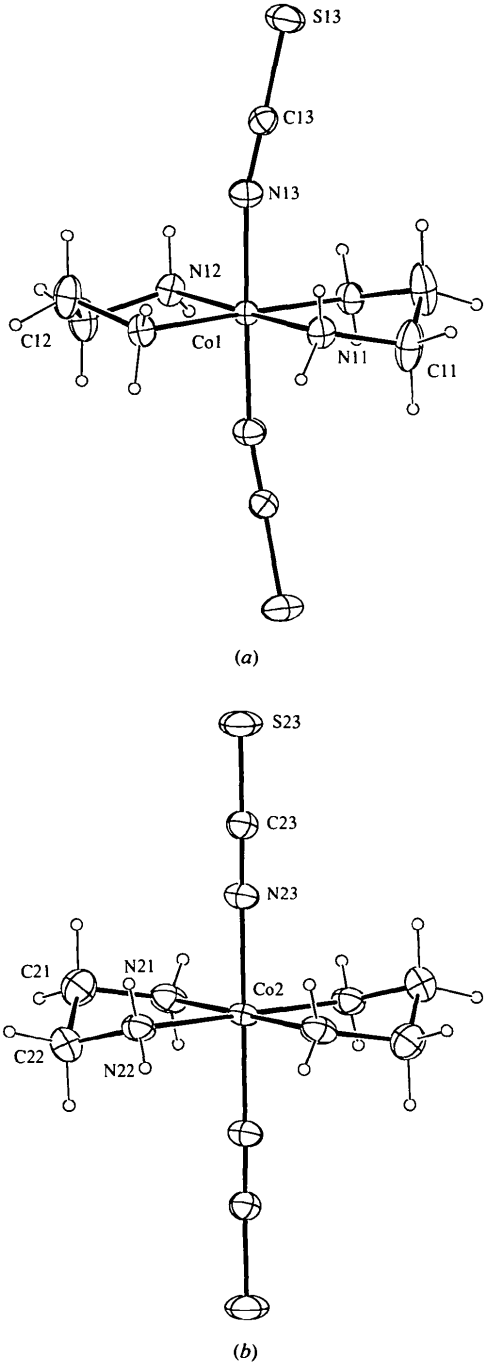


Fig. 1. Representation of the numbering scheme for the title compound with displacement ellipsoids drawn at the 40% probability level for the two independent cations. H atoms are drawn with arbitrary radii.

cations range from 1.945 (1) to 1.954 (1) Å, which are comparable to values of 1.936 (4)–1.954 (4) Å in *cis*-$[Co(en)_2(NCS)_2]SCN$ (Schubert, Zimmer-Gasser, Dash & Chaudhury, 1981), 1.948 (6) and 2.052 (5) Å in *trans*-$[Co(dmen)_2(NCS)_2]ClO_4$ (dmen = dimethylethylenediamine) (Eminger, Fallab, Zehnder & Dobler, 1992) and 1.953 (8)–1.973 (7) Å in *trans*-$[Co(en)_2(NCS)(S_2O_3)].H_2O$ (Tang, Kastner, Cooper, Kanaskie & Monoski, 1993). The Co—NCS distances of the title compound are comparable to lengths of 1.906 (4) and 1.914 (4) Å in *cis*-$[Co(en)_2(NCS)_2]SCN$, 1.875 (5) Å in *trans*-$[Co(dmen)_2(NCS)_2]ClO_4$, and 1.938 (8) and 1.941 (7) Å in *trans*-$[Co(en)_2(NCS)(S_2O_3)].H_2O$. The NCS ligands coordinate slightly non-linearly, as is also noted in the Co—N—CS angles of 165.2 (4) and 173.4 (4)° in *cis*-$[Co(en)_2(NCS)_2]SCN$, 170.1 (6)° in *cis*-$[Co(en)_2(NCS)(S_2O_3)].H_2O$ (Tang, Kastner, Cooper, Kanaskie & Monoski, 1993), and 171.7 (6) and 172.1 (6)° in *trans*-$[Co(en)_2(NCS)(S_2O_3)].H_2O$.

Refined C—H distances range from 0.95 (2) to 1.06 (2) Å, while N—H distances range from 0.79 (2) to 0.94 (2) Å. Isotropic B values for the H atoms range from 2.2 (4) to 4.0 (5) Å^2 for those bonded to N and from 3.4 (4) to 5.9 (6) Å^2 for those bonded to C. All H atoms attached to N atoms are involved in N—H···N or N—H···S contacts to thiocyanate and all but two of the eight involve the SCN^- ion, the other two involving atom S13 of the twofold symmetric cation. The contacts are neither extremely short [shortest N···N distance is 2.975 (2) and shortest N···S distance is 3.443 (2) Å] nor linear [N—H···X angles are in the range 132 (2)–170 (2)°], but are clearly important in determining the unusual packing of the ions.

The occurrence of $Z = 8$ with moieties of both $\bar{1}$ and 2 symmetries is clearly a very rare structural type. $Z = 8$ is common for space group $C2/c$, occurring in 43.5% of the structures in that space group in the tabulation of Brock & Dunitz (1994). Both $Z = 4$ with symmetry $\bar{1}$ and $Z = 4$ with symmetry 2 are also relatively common in space group $C2/c$ according to the compilation of structural classes by Chernikova, Belŏskii & Zorkii (1991) for homomolecular organic crystals, with abundances of 9.4 and 34.3%, respectively. That compilation also lists two examples of $Z = 8$ with two molecules of $\bar{1}$ symmetry and two examples of $Z = 8$ with two molecules of symmetry 2, but no examples of one $\bar{1}$ and one 2. The hydrogen bonds in the title structure apparently stabilize this anomalous structural type.

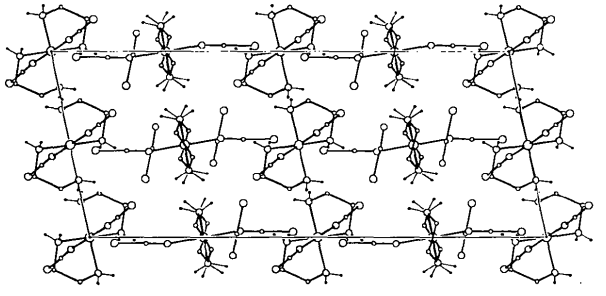


Fig. 2. Projection of the title structure down the symmetry axis, with the c axis horizontal.

Experimental

Crystals of the title compound were obtained by evaporation from H_2O.

Crystal data

$[Co(NCS)_2(C_2H_8N_2)_2]SCN$
$M_r = 353.38$
Monoclinic
$C2/c$
$a = 9.8472$ (5) Å
$b = 12.2385$ (6) Å
$c = 23.5157$ (10) Å
$\beta = 101.292$ (4)°
$V = 2779.1$ (7) Å^3
$Z = 8$
$D_x = 1.689$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–12°
$\mu = 1.66$ mm^{-1}
$T = 302$ K
Irregular fragment
0.40 × 0.30 × 0.25 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.884$, $T_{max} = 0.998$
4410 measured reflections
4038 independent reflections
3439 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.013$
$\theta_{max} = 30°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 17$
$l = -33 \rightarrow 32$
3 standard reflections
frequency: 166.7 min
intensity decay: < 1%

Refinement

Refinement on F
$R = 0.024$
$wR = 0.032$
$S = 1.677$
3439 reflections
229 parameters
All H-atom parameters refined
$w = 4F_o/[\sigma^2(I) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.14$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Co1	0	0.07800 (2)	1/4	1.334 (4)
Co2	1/2	0	0	1.753 (5)
S13	0.02990 (5)	0.12630 (4)	0.44770 (2)	3.089 (9)
S23	0.32890 (6)	−0.31104 (4)	−0.10666 (2)	3.65 (1)
S5	0.31550 (4)	0.09491 (4)	0.14802 (2)	3.020 (8)
N11	0.1369 (1)	0.1934 (1)	0.25182 (6)	2.01 (2)
N12	−0.1351 (1)	−0.0378 (1)	0.25038 (6)	1.92 (2)
N13	0.0340 (1)	0.0800 (1)	0.33220 (6)	2.21 (2)
N21	0.6915 (1)	−0.0383 (1)	−0.00232 (6)	2.62 (3)
N22	0.5231 (2)	−0.0871 (1)	0.07080 (6)	2.44 (3)
N23	0.4371 (1)	−0.1258 (1)	−0.04493 (6)	2.34 (2)

N5	0.5974 (2)	0.0634 (1)	0.19421 (7)	3.28 (3)
C11	0.0636 (2)	0.2977 (1)	0.2376 (1)	3.70 (4)
C12	−0.0750 (2)	−0.1416 (1)	0.23520 (9)	2.83 (3)
C13	0.0310 (2)	0.1001 (1)	0.38010 (6)	2.01 (3)
C21	0.7362 (2)	−0.1260 (2)	0.04070 (9)	3.52 (4)
C22	0.6729 (2)	−0.1042 (2)	0.09261 (8)	3.25 (4)
C23	0.3915 (2)	−0.2019 (1)	−0.07106 (7)	2.26 (3)
C5	0.4812 (2)	0.0783 (1)	0.17651 (6)	2.16 (3)

Table 2. *Selected geometric parameters* (Å, °)

Co1—N11	1.947 (1)	Co2—N21	1.954 (1)
Co1—N12	1.945 (1)	Co2—N22	1.953 (1)
Co1—N13	1.896 (1)	Co2—N23	1.901 (1)
N11—Co1—N11^{i}	87.01 (5)	N21—Co2—N22	86.61 (6)
N11—Co1—N12	178.49 (5)	N21—Co2—N23	90.08 (6)
N11—Co1—N12^{i}	93.28 (5)	S13—C13—N13	178.6 (1)
N12—Co1—N12^{i}	86.48 (5)	S23—C23—N23	178.6 (1)
N13—Co1—N13^{i}	178.54 (6)	S5—C5—N5	176.7 (2)
N11—Co1—N11^{i}—C11^{i}	−12.7 (1)	N22—Co2—N21—C21	11.5 (1)
Co1—N11—C11—C11^{i}	35.6 (2)	Co2—N21—C21—C22	−37.0 (2)
N11—C11—C11^{i}—N11^{i}	−47.1 (2)	N21—C21—C22—N22	51.1 (2)
Co1—N12—C12—C12^{i}	39.3 (2)	C21—C22—N22—Co2	−40.6 (2)
N12—C12—C12^{i}—N12^{i}	−51.5 (2)	C22—N22—Co2—N21	16.6 (1)
N12—Co1—N12^{i}—C12^{i}	−14.3 (1)		

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

The space group was determined by systematic absences (*hkl* with $h + k$ odd, *h0l* with *l* odd) and successful refinement of a centrosymmetric model.

Programs used include *SDP* (Frenz, 1978), *ORTEP* (Johnson, 1965) and *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Brock, C. P. & Dunitz, J. D. (1994). *Chem. Mater.* **6**, 1118–1127.
Chernikova, N. Yu., Belōskii, V. K. & Zorkii, P. M. (1991). *J. Struct. Chem.* **31**, 661–666.
Eminger, R., Fallab, S., Zehnder, M. & Dobler, M. (1992). *Helv. Chim. Acta*, **75**, 1245–1250.
Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1978). *MULTAN*78. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Schubert, U., Zimmer-Gasser, B., Dash, K. C. & Chaudhury, G. R. (1981). *Cryst. Struct. Commun.* **10**, 251–254.
Tang, K., Kastner, M. E., Cooper, J. N., Kanaskie, M. & Monoski, A. (1993). *Acta Cryst.* C**49**, 1265–1267.
Thewalt, U. (1970). *Z. Naturforsch. Teil B*, **25**, 569–571.

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Guanidinium *β-cis*-(Carbonato-*O*,*O*′)-(*N*,*N*′-ethylenediaminediacetato-*N*,*N*′,*O*,*O*″)-cobaltate(III)

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Abstract

The title compound {aminomethanamidinium Λ-*uns-cis*-(*R*,*R*)-carbonato(*N*,*N*′-ethylenediaminediacetato)cobaltate(III), [C(NH$_2$)$_3$][Co(C$_6$H$_{10}$N$_2$O$_4$)(CO$_3$)]} crystallizes in the space group $P2_1/c$. The guanidinium cations and amino groups on the edda ligand form a complex network of eight to ten hydrogen bonds to both the coordinated and uncoordinated O atoms of the edda carboxylate groups and the carbonate ligands of neighbouring chelate anions. The hydrogen bonding between the guanidinium cations and carbonate ligands neither resembles that in guanidinium bicarbonate nor that between arginine and bound carbonate in ferrilactoferrin, an iron-binding protein which contains a carbonate ligand on the Fe^{3+} ion. Bond lengths and angles in the Co^{III} coordination sphere are not significantly different from those of other Co^{III} carbonate complexes or other Co^{III} edda complexes.

Comment

The structure determination of the title compound, (I), was carried out in order to compare the mode of interaction between the guanidinium cation and the carbonate ligand of the Co atom with that between guanidinium and the free bicarbonate anion (Baldwin, Denner, Egan & Markwell, 1986), as well as that