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Stereochemistry and Crystal Structure of a Cobalt(III) Sulphito Complex: *trans*-Sulphiteisothiocyanate-bis(ethylenediamine)cobalt(III) Dihydrate

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The crystal structure of $\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$ has been determined from three-dimensional X-ray data and refined by the full-matrix least-squares method to a residual of 0.078. The compound crystallizes in the monoclinic system, space group $P2_1/c$ with four molecules in the unit cell of dimensions $a = 9.13 \pm 0.02$, $b = 6.59 \pm 0.02$, $c = 22.88 \pm 0.06$ Å, $\beta = 95.5 \pm 0.5^\circ$. The coordination around the metal atom is octahedral, the sulphito group being bonded through sulphur to the metal and in *trans* configuration. The Co-N(NCS) distance is not significantly different from the Co-N(en) distances. Some important dimensions are: Co-S, 2.203 ± 0.006 Å; mean Co-N(en), 1.962 ± 0.010 Å; mean S-O, 1.485 ± 0.012 Å; mean O-S-O, $110.3 \pm 0.7^\circ$; Co-N(NCS), 1.974 ± 0.018 Å.

Introduction

Recently, the infrared and visible absorption spectra of a series of sulphito-bis(ethylenediamine)cobalt(III) complexes were measured by Baldwin (1961). These spectra, together with measurements of conductivity in aqueous solution and a study of chemical reactions, were interpreted by Baldwin in terms of possible structures for these complexes. For $\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$ it was postulated that the sulphito group is bonded through sulphur, the bond possibly involving $d\pi-d\pi$ bonding, and that the compound had the *cis* configuration. Kinetic studies of sulphito complexes of Co^{III} have also been made recently, indicating that the sulphito group has a marked *trans* labilizing effect (Tewari, Gaver, Wilcox & Wilmarth, 1967).

We undertook the structure determination of this compound in order to establish whether the postulated structure was correct, and, if so, to compare the dimensions of the sulphito group coordinated to Co^{III} , with the dimensions found for this group in $\text{PdSO}_3(\text{NH}_3)_3$ (Spinnler & Becka, 1967). Furthermore, we considered that a comparison between the different Co-N distances in this compound would be of interest

in relation to the kinetics of reaction of sulphito complexes. In an earlier communication (Baggio & Becka, 1967) we described the main features of the structure as obtained from least-squares refinement with individual isotropic temperature factors. In this paper we give the details of the structure and structure determination with individual anisotropic temperature factors for Co, the atoms of SO_3 , and the atoms of NCS.

Experimental

Preparation

$\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$ was prepared by the method reported by Baldwin (1961), and crystals suitable for X-ray studies were obtained by recrystallization. The chemical and physical properties of the sample were in good agreement with those reported previously. Chemical analysis of a sample gave the following percentage composition for C, N and H: C, 17.37; N, 19.21; H, 5.75, the theoretical composition being: C, 16.59; N, 19.83; H, 5.66.

Crystal data

Name of substance: *trans*-sulphiteisothiocyanate-bis(ethylenediamine)cobalt(III) dihydrate. Chemical formulae: structural, $\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$; alpha-

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betized, $C_5H_{20}O_5N_5S_2Co$. Formula weight: 353.25. Crystal system: monoclinic. Cell dimensions: $a=9.13 \pm 0.02$, $b=6.59 \pm 0.22$, $c=22.88 \pm 0.06$ Å, $\beta=95.5 \pm 0.5^\circ$, at $25 \pm 1^\circ C$. Cell volume = 1372 Å³. Measured density, $D_m=1.71$ g.cm⁻³ (by flotation). $Z=4$; calculated density, $D_x=1.71$. Types of X-rays used for cell dimensions determination, Fe-filtered Co radiation with $\lambda_{Co} K\alpha_1=1.78892$ Å and $\lambda_{Co} K\alpha_2=1.79278$ Å; for intensity measurements, Zr-filtered Mo radiation. Linear absorption coefficient, for Co $K\alpha$, $\mu=75$ cm⁻¹ for Mo $K\alpha$, $\mu=18.5$ cm⁻¹. Space group $P2_1/c$ (no. 14), uniquely determined.

The cell dimensions and their standard deviations were determined by the method of Main & Woolfson (1963) from zero level Weissenberg photographs.

Collection and reduction of intensity data

Intensity data were collected on two single crystals. Crystal I had dimensions $0.7 \times 0.08 \times 0.08$ mm, the longest dimension being along the b axis; crystal II had nearly spherical shape, with a mean diameter of 0.2 mm. Crystal I was mounted along the b axis and crystal II along the a axis. Levels $h0l$ to $h7l$ were recorded with crystal I, and levels $0kl$ to $1kl$ with crystal II, by the equi-inclination Weissenberg technique. Level $hk0$ was recorded with crystal I on a precession camera. Thus, a total of 1397 reflexions with non-zero intensity were obtained; of these, 1148 were independent. There was no reflexion of observable intensity at $\sin \theta/\lambda > 0.70$ Å⁻¹. Reflexions $10\bar{2}$ and 010 were not included in the refinements because they were interfered with by the beam stop. We explored $\sim 70\%$ of the reflexion sphere of $\sin \theta/\lambda=0.60$ Å⁻¹, $\sim 60\%$ of the independent reflexions within the explored region were of measurable intensity.

Measurements were made with a microdensitometer on mechanically integrated spots. The ratio of maximum to minimum measured intensity was: 1.000:1. Lorentz and polarization corrections were applied. Assuming that crystal II absorbs as a sphere of 0.2 mm diameter, and that crystal I absorbs as a cylinder of 0.08 mm diameter, for Mo $K\alpha$ radiation, the absorption correction is independent of $\sin \theta$ within 1% in any given layer. Therefore, we made no absorption correction to the data. Reflexions from individual layer lines were put on the same intensity scale by use of the method of Hamilton, Rollett & Sparks (1965), in order to compute the initial Patterson and Fourier synthesis. The experimental uncertainty in the F_o was estimated from the difference in intensity of equivalent reflexions measured on different layer lines, the discrepancy index being $R(F_o)=6\%$.

Solution and refinement of structure

The positions of the Co, S, N, O and C(NCS) atoms were obtained from a three-dimensional Patterson synthesis. The light atoms appeared in the same positions in a three-dimensional Fourier synthesis computed

with phases calculated with the heavy atoms. The discrepancy factor obtained calculating structure factors with these positions and estimated isotropic temperature factors for each atom was $R=32\%$. A least-squares refinement with use of the block-diagonal approximation and isotropic temperature factors was started with these atomic positions. The function minimized in the least-squares refinement is $R' = \sum w(|F_o| - |KF_c|)^2$.

After several cycles of refinement the R index dropped to 20%, but the oxygen atoms of the water molecules and the two C atoms of one of the ethylenediamine groups had relatively high temperature factors, of the order of 7 Å². A three-dimensional difference-Fourier synthesis was computed at this stage, with structure factors calculated excluding these atoms. The largest positive peaks in the resulting map were very broad and appeared near to the previously estimated positions for these atoms. The refinement was continued with all the atoms except hydrogens, using a full-matrix program and individual isotropic temperature factors and individual scale factors for each layer line. After three cycles the R index was reduced to 10.7% for the independent non-zero reflexions, reflexions with a $[\omega(|F_o| - |F_c|)^2]^{1/2}$ value greater than three times the average value of this quantity having been excluded from the refinement. Finally, four cycles of a full-matrix least-squares refinement were computed with isotropic temperature factors for the atoms of the ethylenediamine group and for the oxygen atoms of the water molecules, and anisotropic temperature factors for the other nonhydrogen atoms. For these last cycles we also included equivalent reflexions, and rejected some of the reflexions from the least-squares calculation following the same criteria as before. The final discrepancy factor for the reflexions included in the refinement is $R=7.8\%$ ($R=7.5\%$ for just the independent reflexions). Each sequence of refinement was ended when all parameter shifts were smaller than one fifth of the corresponding standard deviations. The weighting scheme chosen was $\omega = [1 - \exp(-100 \cdot \sin \theta/\lambda)]^2 / (10.0 - 0.39F_o + 0.007F_o^2)$. This gave a fairly constant average value of ωd^2 in ranges of $\sin \theta$ and F_o . Changes of 30% in all the parameters of the weighting scheme produced no significant variation in either parameters or estimated standard deviations (e.s.d.). Atomic scattering factors used throughout the refinement were those given by Ibers (1962) for neutral C, N and O, and those of Cromer & Waber (1965) for Co and S. No anomalous dispersion correction was applied at any stage of the refinement. As a final check on the correctness of the structure we computed a difference-Fourier synthesis with the structure factors calculated in the last cycle of refinement. The resulting electron density map showed no peak exceeding ± 0.6 e.Å⁻³.

In Table 1 the final parameters and their e.s.d.'s are given and in Table 2 the F_o and F_c values computed with these parameters.

The following programs were used and are gratefully acknowledged:

1. O.S.Mills. General Fourier Synthesis (Mercury).
2. J.S.Rollett. Structure Factor and Least-Squares (Mercury).
3. A.Zalkin & B.Foxman. General Fourier Synthesis, Fordap (IBM 360).
4. C.T.Prewitt, B.Foxman & L.Becka. Full-Matrix Least-Squares, SFLS5 (IBM 360).
5. D.P.Shoemaker. Crystallographic Bond Distance, Bond Angle and Dihedral Angle Computer Program, Distan (IBM 360).
6. D.P.Shoemaker & S.R.Srivastava. Anisotropic Temperature Factor Interpreting Program, Vibell (IBM 360).
7. M.E.Pippy & F.R.Ahmed. Mean Plane Calculation (IBM 360).

Discussion and description of the structure

Molecular structure

Table 3 gives the molecular dimensions, and Fig. 1 shows the molecular structure of $\text{Co(en)}_2\text{SO}_3\text{NCS}$. Table 4 contains the equations of mean planes and the

deviations of relevant atoms from these planes. The coordination around the cobalt atom is almost perfectly octahedral, the maximum deviation from the octahedral angle being 4.6° for the $\text{N}(1)\text{-Co-N}(4)$ angle. The geometry of the isothiocyanate group is practically the same as found in other coordination compounds in which it also coordinates through nitrogen (Hazell, 1963). The $\text{Co-N}(5)\text{-C}(5)$ angle (170.7°) is also similar to that found in these complexes. The infrared spectrum of the crystal has absorption maxima that can be assigned to the C-N and C-S stretching modes of NCS at 2120 and 790 cm^{-1} respectively, frequencies that are also observed in other nitrogen bonded isothiocyanate complexes (Lewis, Nyholm & Smith, 1961).

The mean value of the Co-N(en) distances is 1.962 ± 0.010 , the same as the value of 1.96 ± 0.02 found in $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ by Barnet, Craven, Freeman, Kine & Ibers (1966). The $\text{Co-N}(5)$ distance is $1.974 \pm 0.0184 \text{ \AA}$; and the angle between the $\text{Co-N}(5)$ bond and the N-C-S group is about 171° , whereas in the compound $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{NO}_3)_2$ this angle is 136° and the Co-N(NCS) bond length is 2.15 \AA (Malinovskii, Samus & Belov). Since the Co-N-C(NCS) angle is very different in these two compounds, it is not pos-

Table 1. Final parameters

Standard deviations, given in parentheses, are in units of the last decimal place. For numbering of the atoms see Fig. 1.

(a) Fractional coordinates and isotropic temperature factors*.

	X	Y	Z	$B(\text{\AA})^2$
Co	0.2078 (2)	-0.0216 (2)	0.1176 (1)	0.90*
S(1)	0.3873 (5)	-0.5541 (5)	0.2454 (2)	2.62*
S(2)	0.1411 (4)	0.2224 (5)	0.0549 (2)	1.51*
O(1)	-0.0187 (10)	0.2108 (14)	0.0364 (4)	1.87*
O(2)	0.2260 (11)	0.2003 (16)	0.0029 (4)	2.32*
O(3)	0.1780 (13)	0.4177 (14)	0.0853 (5)	2.99*
O(4)	0.2528 (15)	-0.0256 (24)	0.3069 (6)	5.88 (32)
O(5)	0.2406 (13)	-0.0467 (19)	0.4299 (5)	3.88 (25)
N(1)	0.4001 (15)	0.1125 (20)	0.1330 (6)	2.68 (26)
N(2)	0.0184 (13)	-0.1631 (16)	0.1016 (5)	1.53 (20)
N(3)	0.2992 (14)	-0.1768 (18)	0.0576 (5)	2.27 (24)
N(4)	0.1173 (14)	0.1244 (18)	0.1791 (5)	1.98 (25)
N(5)	0.2711 (15)	-0.2309 (18)	0.1768 (6)	2.94*
C(1)	0.4999 (19)	0.0462 (27)	0.0904 (8)	3.08 (34)
C(2)	-0.0763 (26)	-0.1091 (36)	0.1474 (10)	5.68 (53)
C(3)	0.4644 (19)	-0.1757 (26)	0.0720 (8)	2.97 (33)
C(4)	-0.0263 (24)	0.0520 (36)	0.1867 (10)	5.63 (50)
C(5)	0.3221 (15)	0.3638 (19)	0.2057 (5)	1.39*

* Equivalent isotropic temperature factors calculated with the expression

$$B(\text{equivalent}) = \left(\frac{4}{3}\right) [B_{11} \cdot a^2 + B_{22} \cdot b^2 + B_{33} \cdot c^2 + 2 \cdot B_{13} \cdot a \cdot c \cdot \cos \beta]$$

have been derived for the atoms with anisotropic thermal parameters (Hamilton, 1959).

(b) Anisotropic thermal parameters in $\text{\AA}^2 (\times 10^4)$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	124 (9)	115 (14)	100 (8)	-19 (9)	-19 (6)	-5 (8)
S(1)	473 (26)	214 (21)	279 (20)	51 (18)	-111 (19)	70 (17)
S(2)	254 (20)	146 (19)	160 (19)	12 (16)	-55 (16)	41 (15)
O(1)	196 (53)	208 (50)	277 (54)	39 (46)	-135 (44)	-13 (44)
O(2)	314 (59)	366 (58)	214 (53)	-11 (53)	89 (46)	100 (48)
O(3)	560 (72)	132 (52)	408 (64)	-69 (47)	-168 (55)	16 (50)
N(5)	560 (94)	159 (62)	414 (87)	21 (63)	113 (72)	126 (62)
C(5)	280 (79)	179 (65)	50 (60)	-96 (62)	-85 (62)	-51 (57)

2.07 Å, respectively, the corresponding Ni-N-C angles being 165° and about 180°, and (2) the Ni-N distances of bonds involving nitrogen atoms of amino or of

ethylenediamino groups is also about 2.10 Å (see Table of Ni-N distances in a paper by Nardelli, Gasparri, Musatti & Manfredotti, 1966). Thus, it might

Table 3. *Interatomic distances (Å) and angles (°) in Co(en)₂SO₃NCS*

Estimated standard deviations, shown in parentheses are in units of the last decimal place.

Co—S(2)	2.203 (6)	S(2)—Co—N(1)	88.6 (5)
Co—N(1)	1.968 (17)	S(2)—Co—N(2)	92.4 (5)
Co—N(2)	1.969 (14)	S(2)—Co—N(3)	92.0 (5)
Co—N(3)	1.961 (15)	S(2)—Co—N(4)	90.0 (5)
Co—N(4)	1.952 (16)	S(2)—Co—N(5)	177.5 (5)
Co—N(5)	1.974 (18)	Co—N(1)—C(1)	110.3 (1.0)
N(1)—C(1)	1.463 (34)	Co—N(2)—C(2)	108.6 (1.5)
N(2)—C(2)	1.464 (40)	Co—N(3)—C(3)	109.0 (1.0)
N(3)—C(3)	1.513 (34)	Co—N(4)—C(4)	112.4 (1.5)
N(4)—C(4)	1.421 (48)	Co—N(5)—C(5)	170.7 (1.0)
S(1)—C(5)	1.629 (18)	N(5)—C(5)—S(1)	177.5 (1.2)
S(2)—O(1)	1.482 (15)	O(1)—S(2)—O(2)	109.9 (9)
S(2)—O(2)	1.487 (15)	O(1)—S(2)—O(3)	110.6 (9)
S(2)—O(3)	1.487 (15)	O(2)—S(2)—O(3)	110.3 (9)
C(1)—C(3)	1.549 (39)	N(1)—Co—N(2)	177.8 (6)
C(2)—C(4)	1.438 (54)	N(1)—Co—N(3)	85.9 (7)
N(5)—C(5)	1.174 (29)	N(1)—Co—N(4)	94.6 (7)
O(1)—O(2)	2.430 (22)	N(1)—Co—N(5)	89.6 (7)
O(2)—O(3)	2.441 (22)	N(2)—Co—N(3)	92.7 (6)
O(1)—O(3)	2.441 (22)	N(2)—Co—N(4)	86.8 (6)
O(3)—N(1)	2.989 (25)	N(2)—Co—N(5)	89.5 (7)
O(3)—N(4)	2.980 (25)	N(3)—Co—N(4)	177.8 (6)
O(2)—N(3)	2.836 (25)	N(3)—Co—N(5)	89.7 (7)
S(2)—O (mean)	1.485 (12)	N(4)—Co—N(5)	88.3 (7)
Co—N(en) (mean)	1.962 (10)	N(2)—C(2)—C(4)	116.9 (2.0)
O—S(2)—O (mean)	110.3 (7)	N(4)—C(4)—C(2)	114.4 (2.0)
		N(3)—C(3)—C(1)	104.0 (1.7)
		N(1)—C(1)—C(3)	109.6 (9)

* All distances uncorrected for thermal motion.

Table 4. *Equations of least-squares planes and deviations (Å) from these planes*, together with e.s.d.'s of these deviations in parentheses*

Coefficients are direction cosines relative to orthogonal axes. X, Y and Z are also orthogonal coordinates, in Å†.

Equation of plane	Atom	Deviation
$(-0.8426)X + (-0.4817)Y + (-0.2410)Z - (-1.9687) = 0$	Co	0.0105 (18)
	S(2)	-0.0226 (37)
	N(5)	-0.0258 (125)
	N(3)	0.0185 (125)
	N(4)	0.0194 (133)
$(0.4360)X + (-0.5345)Y + (-0.7240)Z - (-1.1518) = 0$	Co	0.0036 (20)
	S(2)	-0.0276 (41)
	N(5)	-0.0312 (132)
	N(1)	0.0281 (135)
	N(2)	0.0271 (119)
$(-0.2348)X + (0.7050)Y + (-0.6692)Z - (-2.2973) = 0$	Co	0.0197 (18)
	N(3)	-0.0137 (117)
	N(4)	-0.0137 (117)
	N(1)	0.0038 (134)
	N(2)	0.0039 (112)
	*C(1)	0.1092 (180)
	*C(2)	-0.2167 (233)
	*C(3)	-0.5747 (176)
	*C(4)	-0.1542 (232)
$(-0.1872)X + (0.7500)Y + (-0.6343)Z - (0.5630) = 0$	O(1)	0.0
	O(2)	0.0
	O(3)	0.0
	*S(2)	0.4755 (39)

* Asterisk indicates atom not included in the plane calculation.

† Orthogonal coordinates in ångströms are obtained by transforming the fractional coordinates with the matrix $(a, 0, b \cos \beta / 0, b, 0/0, 0, c \sin \beta)$, the orthogonal axes being parallel to **a**, **b** and **c***

be expected that if there is no structural *trans* effect associated with the kinetic *trans* labilizing effect of the SO_3 group (Tewari, Gaver, Wilcox & Wilmarth, 1967), the length of the Co–N(NCS) and Co–N(en) bonds should also be nearly equal in the compound *trans* $\text{Co(en)}_2\text{SO}_3\text{NCS}$. Furthermore, since the octahedral covalent radius of Ni^{II} is 0.17 Å larger than that of Co^{III} (Pauling, 1960), the difference between chemically equivalent Ni–N and Co–N bond lengths should also be about 0.17 Å. Thus, within the accuracy of the present structure determinations, it can be concluded that the Co–N(NCS) bond in $\text{Co(en)}_2\text{SO}_3\text{NCS}$ is of the same nature as the Ni–N(NCS) bonds of the Ni^{II} compounds quoted above, and that there is no evidence of a structural *trans* effect.

The bond distances and angles of the ethylenediamine groups have relatively large e.s.d.'s. The carbon atoms of one of these groups, C(2) and C(4), have high temperature factors, and bond angles that are more than three e.s.d.'s. apart from the expected tetrahedral angle. Furthermore, this group does not adopt the usual *gauche* conformation. A possible explanation for these odd features is that the geometry found for this group is affected by disorder.

In order to test this hypothesis of disorder we examined two difference Fourier syntheses using F_o 's calculated including atoms C(2) and C(4) for one of the maps, and F_o 's calculated without these atoms for the other map. The electron density observed around the

positions of atoms C(2) and C(4) does not give a clear indication of the existence of disorder. Thus we did not consider it worth while to refine a molecular model which takes into account this possibility of disorder.

The other angles and distances of the ethylenediamine groups are within two e.s.d.'s. of their expected values.

The sulphito group is coordinated through the sulphur atom to the metal, with a Co–S(2) distance (2.203 Å) which is somewhat shorter than the sum of covalent radii (2.26 Å) calculated taking a radius of 1.22 Å Co^{III} (Barnet, Craven, Freeman, Kine & Ibers, 1966) and a radius of 1.04 Å for tetrahedral sulphur (Pauling, 1960). These features are in agreement with the bonding proposed by Baldwin (1961), but this sulphito compound has the *trans* configuration instead of the *cis* configuration which Baldwin (1961) assumed to be more likely on the basis of an analysis of the infrared spectra. The plane passing through the oxygen atoms of the sulphito group is almost perpendicular to the Co–S(2) vector and the three S(2)–O distances and angles do not differ significantly from each other, so that the sulphito group can be considered as maintaining its C_{3v} symmetry. The mean of the S(2)–O distances and the mean of the O–S(2)–O angles of the sulphito group, 1.485 Å and 110.3° respectively, are nearly the same as found in $\text{SO}_3\text{Pd}(\text{NH}_3)_3$, where the corresponding values are 1.488 Å (not corrected for libration) and 109.5° (Spinnler & Becka, 1967). The dimensions of the ionic sulphito group in $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ are 1.525 ± 0.006 Å for the mean of the S–O distances and $104.8 \pm 0.4^\circ$ for the mean of the O–S–O angles. These values show that there is a significant difference between the dimensions of the coordinated sulphito group and the ionic sulphite. The shortening of the S–O distance, and the opening of the O–S–O angle in the coordinated sulphito group is in keeping with the explanation given for the same effect in the discussion of the structure of $\text{PdSO}_3(\text{NH}_3)_3$ (Spinnler & Becka, 1967). Also the S–O stretching frequencies: 1099, 1089, and 1079 cm^{-1} , determined from the infrared spectrum, are appropriately larger than those assigned to these modes in SO_3Na_2 , 925 and 966 cm^{-1} (Simon & Waldmann, 1955). The fact that three stretching modes are active in the infrared spectra of the solid, instead of the two expected by the nearly perfect C_{3v} symmetry of the group can be attributed to intermolecular forces or to interactions between the oxygen atoms of SO_3 and the amino groups of ethylenediamine. Distances between oxygen atoms of the SO_3 group have a mean value of 2.44 Å, a value that is practically identical to that found in $\text{PdSO}_3(\text{NH}_3)_3$, in $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, and in a number of sulphates. That fact that the O---O distances of the SO_3 groups are practically the same in the various sulphites, indicates that the variation in the O–S–O angles can be explained by a predominant effect of non-bonded repulsions, as discussed by McDonald & Cruickshank (1967) when analysing tetrahedral distortions in sulphates.

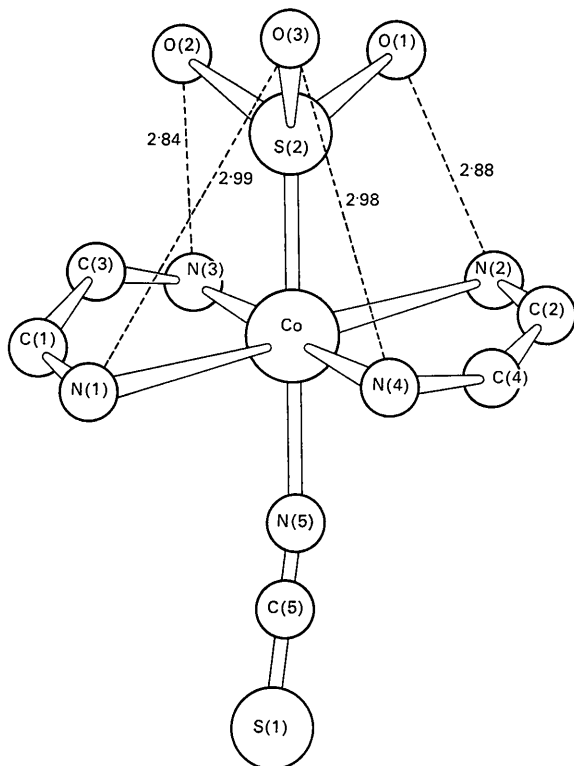


Fig. 1. A view of the molecule $\text{Co(en)}_2\text{SO}_3\text{NCS}$.

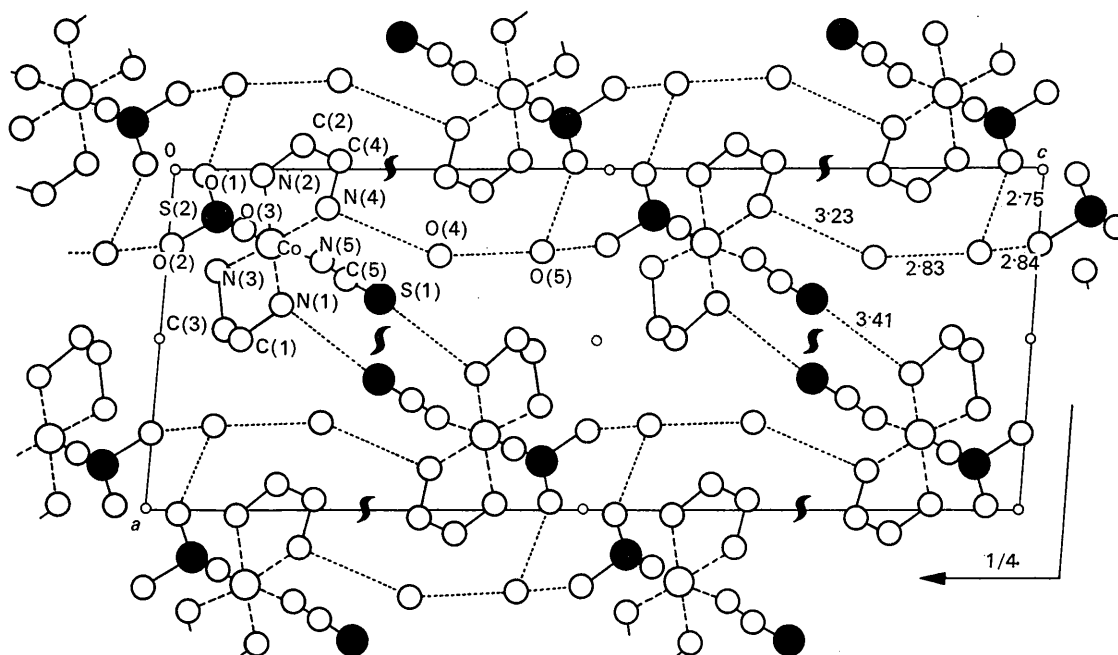


Fig. 2. Projection down the b axis of the unit cell of $\text{Co(en)}_2\text{SO}_3\text{NCS}\cdot 2\text{H}_2\text{O}$.

Crystal packing

In Table 5 and Fig. 2 the shortest intermolecular distances are shown. The $\text{S}(1')\cdots\text{N}(1)$ distance 3.41 \AA is consistent with the mean value of 3.40 \AA suggested by Wallwork (1962) for a $\text{S}\cdots\text{H}\cdots\text{N}$ bond, and fulfils the angular criterion for hydrogen bonding (Fuller, 1959) [$\angle\text{S}(1')\text{---N}(1)\text{---C}(2) = 108^\circ$, $\angle\text{S}(1')\text{---N}(1)\text{---Co} = 115^\circ$].

Table 5. Intermolecular contacts

Atom of reference molecule	Atom in neighbouring molecule	Distance (\AA)
O(4)	O(5)	2.83 (3)
O(4)	N(4)	3.23 (2)
O(5)	O(2) ($x, \frac{1}{2}-y, \frac{1}{2}+z$)	2.84 (2)
	O(1) ($-x, \frac{1}{2}+y, \frac{1}{2}-z$)	2.75 (2)
N(1)	S(1) ($-x, \frac{1}{2}+y, \frac{1}{2}-z$)	3.41 (2)

Apparently the molecules are held together in the crystal by hydrogen bonds involving the water molecules, and by hydrogen bonds between sulphur atoms of SCN and an amino group of another molecule. These bonds would involve each molecule in a three-dimensional bonding network and would account for the low solubility of the crystals in non-polar solvents.

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