

## The Crystal Structure of a Cobalt(III) Complex of the Tetradentate Ligand 1,9-Diamino-3,7-dithianonane (ete): *u-cis*[Co(ete)NO<sub>2</sub>Cl]Cl

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**Abstract.** C<sub>7</sub>H<sub>18</sub>Cl<sub>2</sub>CoN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>, *M* = 370.23. Monoclinic, *P*2<sub>1</sub>/*c*, *a* = 8.49 (1), *b* = 7.34 (1), *c* = 23.19 (2) Å, β = 95.7 (1)°, from precession photographs, refined by diffractometer. *Z* = 2, *D<sub>m</sub>*(floatation) = 1.71, *D<sub>c</sub>* = 1.709 g cm<sup>-3</sup>. The cation was formed by treatment of *u-cis*-[Co(ete)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> with dilute hydrochloric acid, and the title compound was recrystallized from a hot methanol-water solution. The crystal structure, refined to *R* = 0.060, shows the chloride ligand *trans* to sulphur; the two sulphur centres have the same chirality, and the six-membered chelate ring has a distorted chair conformation.

**Introduction.** Systematic absences *h*0*l*, *l* odd and 0*k*0, *k* odd gave the space group *P*2<sub>1</sub>/*c*. Data were collected for layers *h*0*l* to *h*7*l* on a Hilger-Watts linear diffractometer (Mo *K*α radiation); of the 3208 observations collected, 2034 independent reflexions had *I* > 3σ. Lorentz and polarization corrections were applied (but no absorption correction) and approximate layer scale factors were obtained by the Wilson-plot method. The positions of the cobalt, sulphur and chlorine atoms were obtained from a sharpened Patterson map, and the remaining non-hydrogen atoms were located from a Fourier synthesis. Refinement was by full-matrix least squares with our adaptation of the *PORFLS* program in the *CRYSTAL 69* system of Powell & Griffiths (1969). Atomic scattering factors were taken from

*International Tables for X-ray Crystallography* (1968). Five cycles of refinement of positional and isotropic thermal parameters and layer scale factors gave *R* = 0.108 (*R* = Σ||*F<sub>o</sub>* - |*F<sub>c</sub>*||/Σ|*F<sub>o</sub>*|), and a further five cycles with anisotropic thermal parameters and the weighting scheme *w* = 1/{1 + [(*F* - *F*<sup>\*</sup>)/*G*<sup>\*</sup>]<sup>2</sup>} with *F*<sup>\*</sup> = 0 and *G*<sup>\*</sup> = 120 converged at *R* = 0.060.† No attempt

† A list of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30167 (14 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

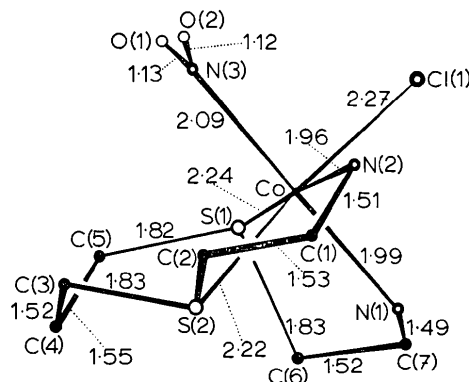


Fig. 1. Bond distances in the [Co(ete)NO<sub>2</sub>Cl]<sup>+</sup> cation (e.s.d. = 0.01 Å).

Table 1. Atomic positions and anisotropic temperature factors ( $\times 10^4$ )

The expression used for the anisotropic temperature factor was  $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Co	-3339 (1)	2648 (1)	3769 (1)	93 (1)	87 (2)	7 (1)	9 (1)	5 (1)	1 (1)
S(1)	-3211 (2)	1287 (3)	2910 (1)	129 (3)	144 (3)	7 (1)	28 (2)	2 (1)	-2 (1)
S(2)	-1202 (2)	1221 (2)	4166 (1)	85 (2)	129 (3)	9 (1)	5 (1)	3 (1)	-4 (1)
Cl(1)	-5629 (2)	4074 (3)	3447 (1)	154 (3)	186 (4)	11 (1)	70 (2)	0 (1)	7 (1)
Cl(2)	3268 (2)	2064 (2)	4968 (1)	102 (2)	127 (3)	11 (1)	9 (2)	8 (1)	1 (1)
O(1)	-2034 (13)	4957 (12)	3021 (4)	406 (21)	209 (20)	40 (2)	-44 (16)	47 (5)	4 (5)
O(2)	-1560 (11)	5811 (12)	3862 (4)	303 (16)	239 (18)	37 (2)	-40 (14)	34 (4)	20 (5)
N(1)	-4625 (7)	523 (8)	3981 (2)	104 (8)	125 (12)	10 (1)	-9 (7)	4 (2)	-3 (2)
N(2)	-3507 (7)	3768 (8)	4527 (2)	110 (8)	122 (12)	8 (1)	4 (7)	5 (2)	-6 (2)
N(3)	-2027 (7)	4853 (7)	3507 (2)	171 (9)	81 (10)	2 (1)	30 (7)	14 (2)	-2 (2)
C(1)	-2362 (9)	3043 (11)	5015 (3)	122 (11)	181 (16)	10 (1)	4 (9)	3 (3)	4 (3)
C(2)	-752 (9)	2749 (11)	4783 (3)	119 (11)	178 (16)	11 (1)	8 (10)	1 (3)	-18 (3)
C(3)	403 (8)	1486 (13)	3704 (4)	76 (9)	278 (20)	15 (2)	5 (11)	14 (3)	-20 (4)
C(4)	59 (10)	227 (14)	3189 (4)	115 (11)	256 (21)	15 (2)	28 (12)	10 (3)	-22 (4)
C(5)	-1217 (10)	910 (13)	2717 (3)	125 (11)	265 (21)	10 (1)	22 (12)	11 (3)	-7 (4)
C(6)	-3845 (10)	-982 (10)	3117 (4)	162 (13)	103 (14)	17 (2)	-16 (10)	3 (4)	-14 (3)
C(7)	-5223 (10)	-628 (12)	3476 (4)	126 (12)	180 (18)	15 (2)	-41 (10)	3 (3)	-10 (4)

was made to locate the hydrogen atoms. Atomic parameters are given in the Table 1. The conformation of the cation and bond lengths are shown in Fig. 1, and bond and torsional angles are given in Table 2.

**Discussion.** There has been some recent interest in the optical and geometrical stereo-selectivity in cobalt(III) complexes of sulphur-nitrogen ligands such as 1,8-diamino-3,6-dithiaoctane (eee) and 1,9-diamino-3,7-

dithianonane (ete) (Worrell & Busch, 1969; Worrell, MacDermott & Busch, 1970). The eee ligand gives only the *s-cis*-[Co(eee)Cl<sub>2</sub>]<sup>+</sup> isomer, whereas ete gives both *trans*-[Co(ete)Cl<sub>2</sub>]<sup>+</sup> and *u-cis*-[Co(ete)Cl<sub>2</sub>]<sup>+</sup>. This is the first crystal structure of an N<sub>2</sub>S<sub>2</sub> complex of this type to be determined, and it was undertaken to give further information for the synthetic and kinetic studies of Hay & Curtis (1971).

The gross structure shows that in the formation of *u-cis*-[Co(ete)NO<sub>2</sub>Cl]<sup>+</sup> from *u-cis*[Co(ete)(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> it is the nitro group *trans* to sulphur, rather than *trans* to nitrogen, which has been replaced, indicating that the *trans*-effect of sulphur is greater than that of nitrogen (Hill, Morallee, Cernivez & Pellizer, 1972).

The sulphur centres may each be either *R* or *S*, and in this cation both have the same chirality. The six-membered ring has a chair conformation, and the two five-membered rings have *gauche* conformations; it therefore corresponds to the chair-*cis*-β-*R,R* isomer of Bosnich, Kneen & Phillip (1969).

The bond lengths in the cation are unremarkable, but the bond and torsional angles within the ring systems indicate a considerable degree of distortion. This can be attributed to the presence of five- and six-membered rings in the ligand and two different types of fusion between them. The C-S-Co angles are quite different in the five- and six-membered rings, with C(2)-S(2)-Co=97.7, C(6)-S(1)-Co=97.5° in the five-membered rings and C(3)-S(2)-Co=109.5, C(5)-S(1)-Co=114.6° in the six-membered ring. The two five-membered rings, each of which has approximate C<sub>2</sub> symmetry, have similar torsion angles, whereas the six-membered ring does not show the expected approximate mirror symmetry. Bond angles of S(1)-C(5)-C(4)=118.7° and C(3)-C(4)-C(5)=115.3° imply distortion of one side of the ring, while S(2)-C(3)-C(4)=107.4° is much nearer to the tetrahedral value. Unsymmetrical distortion of the ring is confirmed by the torsion angles 42.0° for Co-S(1)-C(5)-C(4) and 75.6° for Co-S(2)-C(3)-C(4). This implies a 'flattening' of the six-membered ring on the side adjacent to the *cis*-fused Co-S(1)-C(6)-C(7)-N(1) ring.

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Table 2. Bond angles (e.s.d.=0.2°) and torsion angles in the chelate rings (e.s.d.=0.2°)

Co—S(1)—C(5)	114.6°
Co—S(1)—C(6)	97.5
Co—S(2)—C(2)	97.7
Co—S(2)—C(3)	109.5
Co—N(1)—C(7)	113.7
Co—N(2)—C(1)	115.1
Co—N(3)—O(1)	113.2
Co—N(3)—O(2)	115.7
S(1)—Co—S(2)	92.7
S(1)—Co—N(1)	87.0
S(1)—Co—N(2)	177.8
S(1)—Co—N(3)	90.8
S(1)—Co—C(1)	91.7
S(1)—C(5)—C(4)	118.7
S(1)—C(6)—C(7)	104.6
S(2)—Co—N(1)	88.5
S(2)—Co—N(2)	87.4
S(2)—Co—N(3)	92.8
S(2)—Co—Cl(1)	174.3
S(2)—C(2)—C(1)	103.7
S(2)—C(3)—C(4)	107.5
N(1)—Co—N(2)	90.9
N(1)—Co—N(3)	177.4
N(1)—Co—Cl(1)	88.3
N(1)—C(7)—C(6)	107.8
N(2)—Co—N(3)	91.4
N(2)—Co—Cl(1)	88.0
N(2)—C(1)—C(2)	108.5
N(3)—Co—Cl(1)	90.6
N(3)—O(1)—O(2)	24.6
N(3)—O(2)—O(1)	24.7
C(2)—S(2)—C(3)	106.4
C(3)—C(4)—C(5)	115.3
C(5)—S(1)—C(6)	103.5
O(1)—N(3)—O(2)	130.8
Co—N(2)—C(1)—C(2)	40.2°
N(2)—C(1)—C(2)—S(2)	56.1
C(1)—C(2)—S(2)—Co	45.5
C(1)—C(2)—S(2)—C(3)	158.5
C(2)—S(2)—C(3)—C(4)	179.8
Co—S(2)—C(3)—C(4)	75.6
S(2)—C(3)—C(4)—C(5)	77.3
C(3)—C(4)—C(5)—S(1)	61.2
C(4)—C(5)—S(1)—Co	42.0
C(4)—C(5)—S(1)—C(6)	62.9
C(5)—S(1)—C(6)—C(7)	160.6
Co—S(1)—C(6)—C(7)	43.0
S(1)—C(6)—C(7)—N(1)	59.2
C(6)—C(7)—N(1)—Co	47.1
N(1)—Co—S(1)—C(5)	124.2
N(1)—Co—S(1)—C(6)	15.6
N(2)—Co—S(1)—C(5)	131.1
N(2)—Co—S(1)—C(6)	22.5
N(1)—Co—S(2)—C(2)	111.8
N(1)—Co—S(2)—C(3)	137.7
N(2)—Co—S(2)—C(2)	20.8
N(2)—Co—S(2)—C(3)	131.3