Crystal Structure of Tris(dithiocarbamato)cobalt(III)

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The crystal structure of the title compound has been determined by direct methods from *X*-ray diffractometer data and refined by full-matrix least-squares to *R* 0.050 for 3 448 observed reflections. Crystals are monoclinic, space group $P2_1/a$, a = 16.300(2), b = 10.056(2), c = 7.095(1) Å, β = 101.00(2)°, Z = 4. Co–S distances range from 2.258(1) to 2.292(1) Å, and C–N 1.316(6) to 1.325(5) Å

PREVIOUS attempts to delineate any changes in the geometry of the S_2CN conjugated fragment of the symmetrically co-ordinated disubstituted dithiocarbamate ligand, MCS_2NR_2, have shown with one possible exception that variations, if any, must be small and of the order of 0.02 Å or less, the C–S distances being *ca.* 1.72 Å and C–N *ca.* 1.33 Å.[1-4] The exception is the unsubstituted ligand (R = H): a structure determination of $[Ni(CS_2{\cdot}NH_2)_2]$ showed mean C–N 1.37_5 Å.[5]

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[1] P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 1460.

[2] J. M. Martin, P. W. G. Newman, B. W. Robinson, and A. H. White, *J.C.S. Dalton*, 1972, 2233.

[3] P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 2239.

[4] P. W. G. Newman, C. L. Raston, and A. H. White, *J.C.S. Dalton*, 1973, 2332.

[5] G. F. Gasparri, M. Nardelli, and A. Villa, *Acta Cryst.*, 1967, **23**, 384.

However, the use of film data and the non-location of hydrogen atoms suggested that little confidence could be placed in the differences exhibited by that result compared to the others. The present structure determination was undertaken to re-examine the situation of the unsubstituted ligand; the cobalt(III) derivative was chosen for study because it provides three independent measurements of the C–N distance and preliminary examination showed the existence of a quite extensive data set. We now report the results of this structural study.

EXPERIMENTAL

The complex was prepared by conventional means and recrystallized from ethanol. A prismatic crystal 0.10 × 0.12 × 0.15 mm was used for the *X*-ray study.

Unit-cell calibration was carried out by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 20° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 60°$ was gathered by a conventional 2θ—θ scan yielding 4 387 independent reflections, of which 3 448 with $I > \sigma(I)$ were used in the structure solution and refinement; a few reflections at high *h* were lost in the latter stages of data collection owing to a machine failure. No absorption correction was applied.

TABLE 1

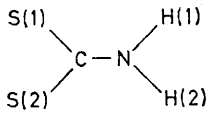
Atomic fractional cell (for Co,S × 10^5; for C,N × 10^4; H × 10^3) and thermal parameters (for Co,S × 10^4; others, × 10^3 Å^2), with least squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	39 655(2)	20 682(4)	30 295(5)	228(2)	246(2)	251(2)	20(1)	32(1)	19(1)
Ligand (1)									
S(1)	46 251(5)	01 616(8)	2 534(1)	253(3)	306(4)	354(4)	57(3)	3(3)	−3(3)
S(2)	30 117(5)	09 761(8)	0 765(1)	252(3)	378(4)	324(4)	48(3)	2(3)	−32(3)
C	3 774(2)	−0 206(3)	0 848(4)	28(1)	29(1)	31(1)	−2(1)	7(1)	0(1)
N	3 704(2)	−1 289(3)	−0 224(5)	34(2)	45(2	53(2)	3(1)	5(1)	−20(1)
H(1)	412(2)	−176(4)	−023(5)	34(10					
H(2)	333(3)	−134(5)	−116(7)	67(15)					
Ligand (2)									
S(1)	34 613(5)	12 962(8)	5 587(1)	336(4)	355(4)	336(4)	12(3)	106(3)	55(3)
S(2)	306 42(5)	36 960(8)	3 563(1)	334(4)	331(4)	365(4)	100(3)	38(3)	0(3)
C	2 862(2)	2 688(3)	5 363(5)	28(1)	46(2)	32(1)	2(1)	6(1)	5(1)
N	2 324(3)	2 979(5)	6 468(6)	64(2)	79(3)	63(3)	26(2)	38(2)	11(2)
H(1)	225(3)	245(5)	712(7)	57(16)					
H(2)	196(3)	369(6)	612(8)	101(20)					
Ligand (3)									
S(1)	51 228(5)	29 999(8)	4 853(1)	321(4)	368(4)	301(4)	−49(3)	19(3)	21(3)
S(2)	45 467(5)	32 440(8)	0 861(1)	378(4)	339(4)	294(4)	−25(3)	58(3)	55(3)
C	5 306(2)	3 670(3)	2 788(5)	34(2)	25(1)	38(2)	0(1)	9(1)	0(1)
N	5 977(2)	4 372(3)	2 628(6)	50(2)	47(2)	46(2)	−21(2)	8(2)	4(2)
H(1)	627(3)	457(4)	365(6)	61(14)					
H(2)	604(3)	468(4)	170(6)	51(13)					

Crystal Data.—$C_3H_6CoN_3S_6$, $M = 335.4$, Monoclinic, $a = 16.300(2)$, $b = 10.056(2)$, $c = 7.095(1)$ Å, $\beta = 101.00(2)°$, $U = 1\,141.6(4)$ Å^3, $D_m = 1.94(1)$, $Z = 4$, $D_c = 1.96$ g cm^{-3}, $F(000) = 672$. Mo-K_α radiation (monochromatic), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) $= 24.4$ cm^{-1}. $P2_1/a$ (C^5_{2h}, No. 14). Neutral atom scattering factors,[6] those for cobalt and sulphur being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[7]

Structure Solution and Refinement.—The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$, hydrogen atoms being refined isotropically.[8] Refinement converged at R 0.050 and R' 0.046 [$R' = (\Sigma w||F_o|^2 - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$, a weighting scheme of the form $w = [\sigma^2(F_o) + 3 \times 10^{-4}(F_o)^2]^{-1}$ being found appropriate.

Structure amplitudes are listed in Supplementary Publication No. SUP 21447 (16 pp., 1 microfiche).* Final atom parameters are listed in Table 1. Computation was carried out on the local CDC 6200 machine, using a local variant of the '*X*-Ray '72' program system.[9] Ligand numbering is as above, the atom number being preceded where necessary by the ligand number (1—3); S(1) and H(1) are on the same side of the ligand, S(*i*l) form a contiguous upper triangle of the CoS_6 pseudo-D_3 core and S(*i*2) a lower triangle.



DISCUSSION

As expected, the lattice is comprised of discrete molecules with the usual general configuration of three planar ligands, each coplanar with the cobalt and

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[6] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

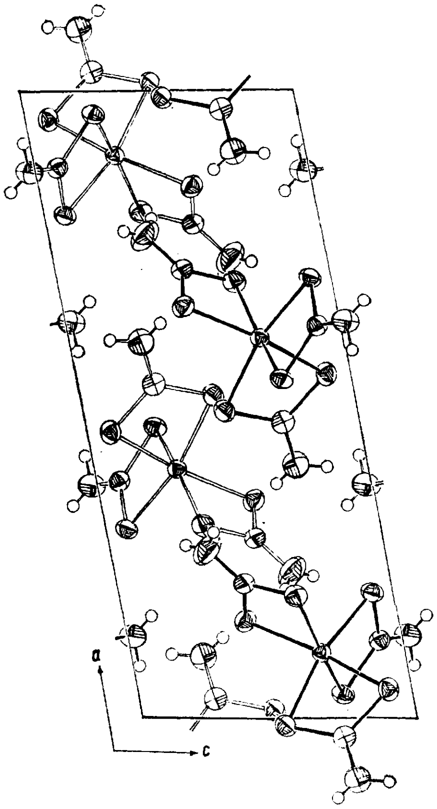
[7] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] '*X*-Ray System, June 1972,' Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A.

arranged about it in the form of a D_3 three-bladed propeller (Figure).

The geometry of the $CoS_6C_3N_3$ part of the molecule is as expected and, in general, resembles that of $[Co(CS_2{\cdot}NEt_2)_3]$;[10] both structures have been determined accurately. In the CoS_6 core, in the present structure, the mean Co–S distance is significantly larger than that observed in the diethyl derivative (2.275, *cf.* 2.258 Å);[10,11] this difference is consistent with the observation previously suggested by the structures of the nickel analogues (and related derivatives) on the basis of less accurate data,[1-5] that the metal–sulphur distance is a function of the crystal-field properties of the disubstituted ligand, and may change by as much as 0.03 Å by replacing a ligand of strong crystal field, *e.g.* $[CS_2{\cdot}NPr^i_2]^-$, to one of weak field, *e.g.* $[CS_2{\cdot}NH_2]^-$. An alternative reason for the observation in both series, however, may lie at least partly in the differences in the thermal motion of the two structural types, that in the unsubstituted derivative being less than in the less strongly hydrogen-bonded diethyl derivative. In the present case, an interesting systematic distortion is imposed on the CoS_6 core, lowering the symmetry slightly from D_3 to approximately C_3; in each ligand the Co–S(2) is significantly longer than the Co–S(1) distance. This



Unit-cell contents projected down *b*, showing 50% thermal ellipsoids

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

(*a*) Intraligand geometries

	(1)	(2)	(3)	< >
Co–S(1)	2.258(1)	2.267(1)	2.276(1)	2.265
Co–S(2)	2.292(1)	2.279(1)	2.285(1)	2.285
Co–S(1)–C	86.9(1)	86.1(1)	86.3(1)	86.4
Co–S(2)–C	85.3(1)	85.4(1)	85.5(1)	85.4
S(1)–Co–S(2)	76.32(3)	76.67(3)	76.38(3)	76.45
S(1)–C	1.691(3)	1.696(4)	1.690(3)	1.692
S(2)–C	1.713(3)	1.711(4)	1.714(3)	1.712
S(1)–C–S(2)	111.4(2)	111.7(2)	111.8(2)	111.6
S(1)–C–N	123.9(2)	124.4(3)	124.8(3)	124.4
S(2)–C–N	124.7(2)	123.9(3)	123.2(3)	123.9
C–N	1.321(5)	1.316(6)	1.326(5)	1.321
N–H(1)	0.83(4)	0.73(5)	0.81(4)	0.80
N–H(2)	0.82(4)	0.93(6)	0.75(5)	
C–N–H(1)	120(2)	116(4)	114(3)	118
C–N–H(2)	119(3)	118(4)	123(3)	
H(1)–N–H(2)	116(4)	123(5)	121(4)	120
S(1) · · · S(2)	2.811(1)	2.820(1)	2.819(1)	2.817

(*b*) CoS_6 core angles

S(11)–Co–S(21)	95.16(3)	S(11)–Co–S(22)	167.65(4)
S(21)–Co–S(31)	94.23(3)	S(21)–Co–S(32)	167.56(3)
S(31)–Co–S(11)	94.04(3)	S(31)–Co–S(12)	166.85(4)
S(12)–Co–S(22)	95.05(3)	S(12)–Co–S(21)	95.52(3)
S(22)–Co–S(32)	95.94(4)	S(22)–Co–S(31)	95.77(3)
S(32)–Co–S(12)	95.09(3)	S(32)–Co–S(11)	93.65(3)

(*c*) Intermolecular S · · · H contacts (<3.05 Å) and associated angles

S(21) · · · H(22$^{\text{I}}$)(N(2$^{\text{I}}$))	2.91(6) (3.363(4))
S(22) · · · H(12$^{\text{II}}$)(N(I$^{\text{II}}$))	2.56(4) (3.766(5))
S(22) · · · H(31$^{\text{III}}$)(N(3$^{\text{III}}$))	2.70(4) (3.451(4))
S(32) · · · H(32$^{\text{IV}}$)(N(3$^{\text{IV}}$)	2.81(4) (3.435(4))
S(32) · · · H(11$^{\text{V}}$)(N(1$^{\text{V}}$))	2.74(4) (3.610(4))
S(12) · · · H(21$^{\text{VI}}$)(N(2$^{\text{VI}}$))	3.03(5) (3.643(5))
S(21) · · · H(22$^{\text{I}}$)–N(2$^{\text{I}}$)	153(5)
S(22) · · · H(12$^{\text{II}}$)–N(I$^{\text{II}}$)	167(5)
S(22) · · · H(31$^{\text{III}}$)–N(3$^{\text{III}}$)	154(4)
S(32) · · · H(32$^{\text{IV}}$)–N(3$^{\text{IV}}$)	142(4)
S(32) · · · H(11$^{\text{V}}$)–N(I$^{\text{V}}$)	171(3)
S(12) · · · H(21$^{\text{IV}}$)–N(2$^{\text{VI}}$)	143(4)

Transformations of the asymmetric unit:

I $\frac{1}{2} - x, y - \frac{1}{2}, \bar{z}$ II $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$
III $1 - x, y - \frac{1}{2}, 1 - \bar{z}$ IV $1 - x, 1 - y, \bar{z}$
V $1 - x, \bar{y}, \bar{z}$ VI $x, y, 1 + z$

TABLE 3

Least-squares planes in the form $pX + qY + rZ = s$; the orthogonal Å frame is defined by $X = ax + cz\cos\beta$, $Y = by$, $Z = cz \sin \beta°$; σ Å is the standard deviation of the atoms defining the plane. Atomic deviations Δ are given in Å. All planes are defined by the S_2NC entity

Plane	(1)	(2)	(3)
10^4p	5 261	6 034	5 392
10^4q	4 994	4 701	−8.285
10^4r	−6 884	6 442	−1 512
s	2.649	6.058	1.129
σ	0.007	0.007	0.016
χ^2	15.6	11.4	52.6
Deviations :			
S(1)	−0.003	0.003	0.007
S(2)	−0.003	0.003	0.007
C	0.011	−0.010	−0.024
N	−0.004	0.004	0.010
H(1)	0.11	−0.08	−0.08
H(2)	0.16	−0.14	−0.02
Co	0.12	−0.08	0.09

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[10] S. Merlino, *Acta Cryst.*, 1968, **B24**, 1441.

[11] T. Brennan and I. Bernal, *J. Phys. Chem.*, 1969, **73**, 443.

phenomenon is paralleled by the observation that the long Co–S(2) distances correlate with short C–S(2) distances and *vice versa*; in addition angle Co–S(2)–C is always less than the corresponding Co–S(1)–C. These observations are typical of situations in which asymmetric bidentate dithiocarbamate ligands are found. In this case, the probable source of the asymmetry lies in interactions with hydrogen atoms from adjacent molecules; it will be noted (Table 2) that sulphur atoms S(*i*2) are considerably more included in these interactions than S(*i*1), and the interaction with S(2) in each ligand is considerably greater than that of S(1) as evidenced by the shortness and number of the S $\cdots$ H contacts. There is evidence of a small but consistent trigonal pyramidal distortion about each nitrogen atom (Table 3); this might arise also from hydrogen-bonding effects leading to an sp^3 orbital contribution to the nitrogen bonding. In view of the difficulty of providing an appropriate scattering model for the hydrogen atoms, however, this observation must be taken *cum grano salis* also. The mean C–S distance of 1.70_2 is shorter than those recently observed generally in a variety of accurate diethyldithiocarbamate structures which tend to lie in the 1.71—1.73 Å range and this effect must be considered real, since thermal correction should tend to enhance the difference. The C–N distance (mean 1.32_1) is similar to that observed in the diethyldithiocarbamate ligand, possibly even marginally shorter. This suggests that the previous estimates of the C–N distance in the structure of $[Ni(CS_2{\cdot}NH_2)_2]$ are too great, the probable reason lying in the biassing of the nitrogen atom position towards the hydrogen atoms which were not included in the model.

[5/526 *Received*, 17*th March*, 1975]