# **124.** *The Crystal Structure of Nitroso(dimethyldithiocarbonato)cobalt* $[Co(NO)\{S_2C{\cdot}N(CH_3)_2\}_2]$.

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The structure of $[Co(NO)\{S_2CN(CH_3)_2\}_2]$ has been derived from a study of the [010] and [100] projections; the [100] projection could be solved only by the use of statistical relationships between the signs of the structure factors.

The co-ordination round the cobalt atom is that of a rectangular-based pyramid, with the nitric oxide molecule at the apex and the four sulphur atoms at the corners of the base: the cobalt atom is 0·54 Å above the basal plane.

The dithiocarbamate ligands are planar, the C–N bond being essentially a double bond. The N–O bond is inclined at 139° to the pyramidal axis, and the nitric oxide group appears to form an unsymmetrical π-complex with the cobalt atom. A full three-dimensional analysis has proved to be impracticable.

THERE are several complex molecules in which a central atom is surrounded by five atoms at the apices of a trigonal bipyramid, *e.g.*, phosphorus pentachloride [1] and trimethylantimony dibromide,[2] but the alternative tetragonal pyramidal arrangement is uncommon, and has not been reported in any transition-metal complex. From the theoretical work of Daudel and Bucher [3] it seemed possible that the square pyramidal arrangement might occur in the compound $[Co(NO)\{S_2C{\cdot}N(CH_3)_2\}_2]$, and we have therefore determined its structure; it is that of a rectangular-based pyramid, with the nitric oxide at the apex. A preliminary note on the results has been published.[4]

## EXPERIMENTAL

The compound was prepared by Dr. L. M. Venanzi, using Malatesta's method,[5] and recrystallised twice by slow evaporation of a chloroform solution (Found: C, 22·1; H, 3·6; N, 12·2; S, 38·0. Calc. for $C_6H_{12}CoN_3OS_4$: C, 21·9; H, 3·7; N, 12·8; S, 38·9%).

The crystals are monoclinic prisms elongated along [100]. They are opaque even when only 0·01 mm. thick, and are highly reflecting, like metallic mirrors. Very thin crystals are yellow-brown, and are pleochroic (yellow-green, yellow-brown). Most of the crystals are twinned on the (001) plane.

*Crystal Data.*—$C_6H_{12}CoN_3OS_4$, $M = 339{\cdot}4$, monoclinic; $a = 6{\cdot}49 \pm 0{\cdot}02$, $b = 13{\cdot}51 \pm 0{\cdot}04$, $c = 16{\cdot}95 \pm 0{\cdot}05$ Å, $\beta = 116{\cdot}5°$; $U = 1330$ Å$^3$, $D_m = 1{\cdot}66_3$ (by flotation), $Z = 4$, $D_c = 1{\cdot}69_5$, $F(000) = 672$ (662·6 after allowance for anomalous dispersion). Space group $P2_1/c$ ($C_{2h}^5$, No. 14). Co-$K_\alpha$ radiation ($\lambda = 1{\cdot}790$ Å), single crystal rotation and Weissenberg photographs about *a*- and *b*-axes.

The intensities of the reflections of the (0*kl*) and (*h*0*l*) zones were measured by visual comparison with a standard scale, and multiplied by the usual Lorentz and polarisation factors. Since the maximum dimension of the crystals used was only 0·02 mm., and the linear absorption coefficient is 114 cm.$^{-1}$, absorption corrections were small and were ignored. The structure factors *F* were put on the absolute scale, and the mean Debye temperature factor for the molecule determined by Wilson's method [6] for each projection. Because of the difficulty of finding untwinned crystals, a full three-dimensional analysis was impracticable.

*The* [100] *projection.* Patterson and sharpened Patterson functions were calculated for the 198 observed terms, but gave no indication of the positions even of the cobalt atoms.

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[1] Brockway and Beach, *J. Amer. Chem. Soc.*, 1938, **60**, 1836; Braune and Pinnow, *Z. phys. Chem.*, 1937, **35**, 739; Skinner and Sutton, *Trans. Faraday Soc.*, 1940, **36**, 668.

[2] Wells, *Z. Krist.*, 1938, **99**, 367.

[3] Daudel and Bucher, *J. Chim. phys.*, 1952, **42**, 6.

[4] Alderman and Owston, *Nature*, 1956, **178**, 1071.

[5] Malatesta, *Gazzetta*, 1940, **70**, 734.

[6] Wilson, *Nature*, 1942, **150**, 152.

After the structure had been solved it was seen that the molecular symmetry causes vectors involving the sulphur atoms to overlap and dominate the Patterson map, obscuring the cobalt–cobalt vectors (Fig. 1).

We therefore calculated the unitary structure factors $|U|_{hkl} = (F^2_{hkl}/\sum f^2_{hkl})^{\frac{1}{2}}$ and used them in all the inequality expressions listed by de Wolff and Bouman [7] in an attempt to determine

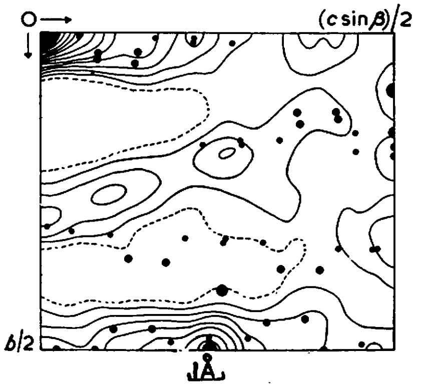

FIG. 1. Patterson projection $P(VW)$. The vectors marked were derived from the final structure. The filled-in circles have the following significations, in order of decreasing size: 2Co–Co; Co–Co, 2S–S; Co–S; S–S.

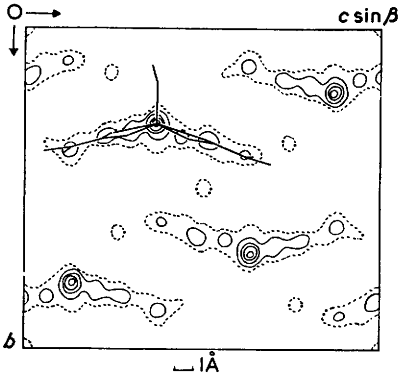

FIG. 2. Fourier projection down the *a*-axis, using only the 72 terms whose signs were derived from the sign-relations. The structure finally derived is shown in outline.

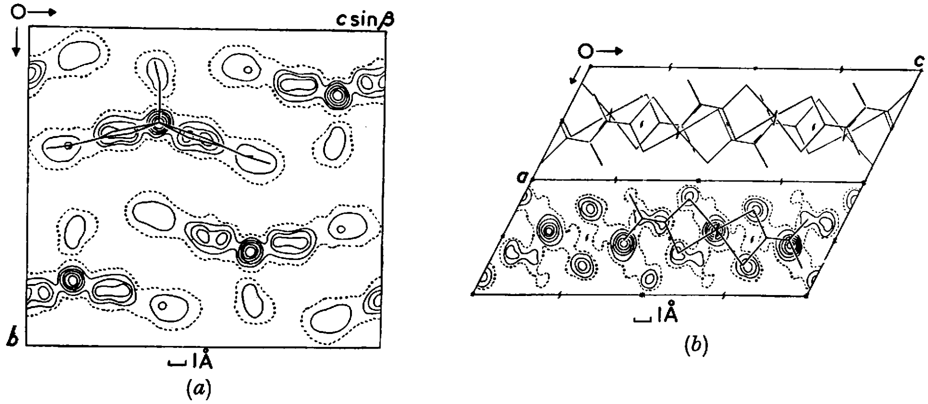

FIG. 3. Fourier projections: (*a*) Down the *a*-axis: contours at intervals of 2 e.Å$^{-2}$, with the 2 e.Å$^{-2}$ contour dotted. (*b*) Down the *b*-axis: contours at intervals of 5 e.Å$^{-2}$, with the 2·5 e.Å$^{-2}$ contour dotted. Only one molecule is superposed on the contour map, the degree of overlap from other molecules being shown in the upper cell.

the signs of the structure factors. No results were obtained, however, mainly because none of the unitary structure factors was outstandingly large, and only four were greater than 0·5.

The problem was finally solved by the use of sign relations.[8] If $s_1$, $s_2$, and $s_3$ are the signs of three reflections related so that $(h_1 + h_2 - h_3) = (k_1 + k_2 - k_3) = (l_1 + l_2 - l_3) = 0$, the probability that the triple product $s_1s_2s_3$ is positive is $P_+ = \frac{1}{2} + \frac{1}{2}\tanh [K|U_1U_2U_3|]$; the constant $K$ is given by the expression $[\sum_j N_j^3/F^3(000)][F^2(000)/\sum_j N_j^2]^3$, where $N_j$ is the atomic number of the atom j. This equation applies strictly only when none of the atoms overlap in projection, and underestimates $P_+$ when there is overlap.

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[7] de Wolff and Bouman, *Acta Cryst.*, 1954, **7**, 328.

[8] Cochran, *Acta Cryst.*, 1952, **5**, 65.

For this structure $K = 17{\cdot}5$, and the triple products for which $|U_1U_2U_3|$ is 0·018 or more have at least a 2 : 1 probability of being positive ($P_+ \geqslant 0{\cdot}65$). These triple products were therefore selected, and when they were all assumed to be positive a unique solution giving the signs of 55 *hk*0 reflections was obtained; the subsequent analysis showed that only four of these signs were incorrect. These 55 reflections, together with a further 17 also found by the sign-relation method, were used in calculating a Fourier map (Fig. 2), from which a satisfactory trial structure was derived.

The discrepancy factor $R$ for this trial structure was 0·32, and after refinement of the atomic co-ordinates and isotropic temperature factors by a combination of least-squares and difference-Fourier methods it fell to 0·18. The parameters of the heavy atoms were refined first, and the positions of the light atoms were then derived from the partial difference map. When using the least-squares method, the principal off-diagonal terms were included to allow for the overlapping of atoms. The use of anisotropic temperature factors further reduced the value of $R$ to 0·122; the maximum residual electron density in the difference-Fourier at this stage was 1·8 e.Å$^{-2}$.

TABLE 1.

Final atomic co-ordinates and anisotropic temperature factors.*

| | $x/a$ | $y/b$ | $z/c$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{23}$ | $\beta_{31}$ |
|---|---|---|---|---|---|---|---|---|
| Co | −0·0796 | 0·2028 | 0·1289 | 0·03000 | 0·00482 | 0·00372 | 0·00013 | 0·00981 |
| S(1) | −0·2549 | 0·1694 | 0·2102 | 0·02990 | 0·00809 | 0·00431 | 0·00044 | 0·01436 |
| S(2) | 0·2377 | 0·1715 | 0·2656 | 0·03575 | 0·00846 | 0·00844 | −0·00064 | 0·01185 |
| S(3) | 0·1350 | 0·1586 | 0·0487 | 0·04462 | 0·00712 | 0·00292 | 0·00022 | 0·01376 |
| S(4) | −0·3457 | 0·1527 | −0·0037 | 0·02861 | 0·00826 | 0·00229 | −0·00015 | 0·00276 |
| C(1) | −0·014 | 0·153 | 0·294 | 0·0915 | 0·0065 | 0·0022 | −0·0030 | 0·0358 |
| C(4) | −0·140 | 0·135 | −0·039 | 0·0637 | 0·0067 | 0·0003 | −0·0011 | 0·0142 |
| N(1) | 0·013 | 0·130 | 0·367 | −0·0018 | 0·0086 | 0·0057 | −0·0007 | −0·0021 |
| N(2) | −0·171 | 0·102 | −0·113 | 0·0474 | 0·0141 | 0·0046 | 0·0055 | −0·0015 |
| N(3) | −0·126 | 0·327 | 0·129 | 0·0631 | 0·0066 | 0·0048 | 0·0059 | −0·0126 |
| O | 0·002 | 0·386 | 0·142 | 0·1191 | 0·0074 | 0·0232 | 0·0014 | 0·0982 |
| CH$_3$(2) | 0·254 | 0·116 | 0·448 | 0·0546 | 0·0193 | 0·0092 | 0·0027 | 0·0204 |
| CH$_3$(3) | −0·176 | 0·113 | 0·390 | 0·0881 | 0·0183 | 0·0096 | 0·0034 | 0·0133 |
| CH$_3$(5) | 0·016 | 0·100 | −0·135 | 0·0368 | 0·0179 | 0·0123 | −0·0090 | 0·0296 |
| CH$_3$(6) | −0·381 | 0·076 | −0·187 | 0·1290 | 0·0193 | 0·0138 | −0·0090 | 0·0272 |

* The expression used was $\exp - [h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + hl\beta_{31}]$.

TABLE 2.

Bond lengths (Å) and bond angles.

| Bond | | Angle | | Angle | |
|---|---|---|---|---|---|
| Co–S(1) | 2·19 | S(1)–Co–N(3) | 94° | S(1)–C(1)–S(2) | 112° |
| Co–S(1) | 2·35 | S(2)–Co–N(3) | 105 | S(1)–C(1)–N(1) | 126 |
| Co–S(3) | 2·42 | S(3)–Co–N(3) | 113 | S(2)–C(1)–N(1) | 123 |
| Co–S(4) | 2·24 | S(4)–Co–N(3) | 104 | | |
| | | | | S(3)–C(4)–S(4) | 109 |
| Co–N(3) | $1{\cdot}7_0$ | S(1)–Co–S(2) | 79 | S(3)–C(4)–N(2) | 124 |
| N(3)–O | 1·1 | S(2)–Co–S(3) | 92 | S(4)–C(4)–N(2) | 127 |
| | | S(3)–Co–S(4) | 75 | | |
| S(1)–C(1) | $1{\cdot}5_9$ | S(4)–Co–S(1) | 101 | C(1)–N(1)–CH$_3$(2) | 124 |
| S(2)–C(1) | $1{\cdot}9_1$ | | | C(1)–N(1)–CH$_3$(3) | 124 |
| C(1)–N(1) | 1·2 | Co–S(1)–C(1) | 91 | CH$_3$(1)–N(1)–CH$_3$(2) | 120 |
| N(1)–CH$_3$(2) | 1·6 | Co–S(2)–C(1) | 79 | | |
| N(1)–CH$_3$(3) | 1·5 | | | C(4)–N(2)–CH$_3$(5) | 129 |
| | | Co–S(3)–C(4) | 84 | C(4)–N(2)–CH$_3$(6) | 112 |
| S(3)–C(4) | $1{\cdot}7_7$ | Co–S(4)–C(4) | 91 | CH$_3$(5)–N(2)–CH$_3$(6) | 111 |
| S(4)–C(4) | $1{\cdot}7_1$ | | | | |
| C(4)–N(2) | 1·3 | Co–N(3)–O * | 127 | | |
| N(2)–CH$_3$(5) | 1·4 | | | | |
| N(2)–CH$_3$(6) | 1·4 | | | | |

* The angle between the N–O bond and the pyramid axis is
(*a*) 139° from the co-ordinates in Table 1,
(*b*) 140° from the *y* and *z* co-ordinates if N–O = 1·08 (triple bond-length), or 134° if N–O = 1·18 (double bond-length); the e.s.d. of these angles is 2·5°.

### TABLE 3.

Observed and calculated structure factors.

(a) [100] *Projection.*

| $l$ | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 00$l$ | |
| 2 | <8 | −4 |
| 4 | 36 | −44 |
| 6 | 5 | 12 |
| 8 | 82 | 80 |
| 10 | <11 | −4 |
| 12 | 50 | −62 |
| 14 | 15 | 21 |
| 16 | 24 | 22 |
| | 01$l$ | |
| 1 | 61 | 67 |
| 2 | 63 | −47 |
| 3 | 17 | 21 |
| 4 | 4 | 6 |
| 5 | 42 | 44 |
| 6 | 37 | 35 |
| 7 | 20 | 19 |
| 8 | 18 | −18 |
| 9 | <12 | 4 |
| 10 | 19 | −15 |
| 11 | <12 | 2 |
| 12 | 15 | 14 |
| 13 | 8 | −9 |
| 14 | 39 | 41 |
| 15 | 16 | 12 |
| 16 | 12 | −6 |
| | 02$l$ | |
| 0 | 144 | −152 |
| 1 | 103 | −102 |
| 2 | 17 | 16 |
| 3 | 16 | 16 |
| 4 | 11 | −10 |
| 5 | 82 | −82 |
| 6 | 8 | 6 |
| 7 | 17 | 16 |
| 8 | 46 | −43 |
| 9 | <12 | −5 |

| | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 02$l$ | |
| 10 | <12 | 7 |
| 11 | <12 | −5 |
| 12 | 26 | 28 |
| 13 | 41 | 41 |
| 14 | 14 | −15 |
| 15 | 8 | 9 |
| 16 | 11 | −11 |
| | 03$l$ | |
| 1 | 102 | −98 |
| 2 | 137 | 141 |
| 3 | 56 | −59 |
| 4 | 7 | 3 |
| 5 | 37 | −37 |
| 6 | 44 | −45 |
| 7 | 28 | −28 |
| 8 | <11 | 3 |
| 9 | 5 | −5 |
| 10 | 31 | 35 |
| 11 | 9 | 5 |
| 12 | 7 | 5 |
| 13 | 13 | 15 |
| 14 | 20 | −16 |
| 15 | 10 | −26 |
| 16 | <10 | 3 |
| | 04$l$ | |
| 0 | 214 | −228 |
| 1 | 159 | 158 |
| 2 | 35 | −34 |
| 3 | 12 | −14 |
| 4 | 30 | −24 |
| 5 | 6 | 5 |
| 6 | <11 | −7 |
| 7 | 20 | −17 |
| 8 | <12 | −4 |
| 9 | 26 | 23 |
| 10 | 9 | −5 |

| | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 04$l$ | |
| 11 | 12 | 15 |
| 12 | 8 | 13 |
| 13 | 38 | −36 |
| 14 | <12 | −5 |
| 15 | 8 | −9 |
| 16 | <10 | −3 |
| | 05$l$ | |
| 1 | 64 | 59 |
| 2 | 21 | 13 |
| 3 | 35 | −28 |
| 4 | 7 | −2 |
| 5 | 25 | −27 |
| 6 | 15 | 16 |
| 7 | 25 | 23 |
| 8 | 3 | 8 |
| 9 | 8 | 6 |
| 10 | 14 | −14 |
| 11 | 18 | −18 |
| 12 | 5 | −6 |
| 13 | 13 | −11 |
| 14 | 20 | −22 |
| 15 | 22 | 21 |
| 16 | <9 | −3 |
| | 06$l$ | |
| 0 | 110 | 107 |
| 1 | 46 | −38 |
| 2 | 6 | −4 |
| 3 | 14 | −14 |
| 4 | 73 | 74 |
| 5 | 37 | 35 |
| 6 | 8 | −4 |
| 7 | 22 | 21 |
| 8 | 14 | 13 |
| 9 | 32 | −31 |
| 10 | <13 | 0 |
| 11 | 11 | −10 |

| $l$ | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 06$l$ | |
| 12 | 16 | −16 |
| 13 | 8 | 6 |
| 14 | 15 | 17 |
| 15 | <10 | −1 |
| | 07$l$ | |
| 1 | <11 | 0 |
| 2 | 70 | −68 |
| 3 | 82 | 87 |
| 4 | 17 | −16 |
| 5 | 46 | 46 |
| 6 | 13 | 12 |
| 7 | 22 | −20 |
| 8 | <12 | −7 |
| 9 | 19 | −16 |
| 10 | 15 | −17 |
| 11 | 20 | 19 |
| 12 | <12 | −1 |
| 13 | 9 | 6 |
| 14 | 25 | 27 |
| 15 | <9 | −3 |
| | 08$l$ | |
| 0 | 34 | −29 |
| 1 | 31 | −31 |
| 2 | 34 | 37 |
| 3 | 28 | 32 |
| 4 | 3 | 3 |
| 5 | 37 | −44 |
| 6 | 7 | 11 |
| 7 | 15 | −15 |
| 8 | 17 | −18 |
| 9 | 19 | 18 |
| 10 | <12 | 3 |
| 11 | <12 | 2 |
| 12 | 7 | 12 |
| 13 | 8 | 9 |
| 14 | 8 | −7 |

| $l$ | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 09$l$ | |
| 1 | 21 | −23 |
| 2 | 31 | 31 |
| 3 | 27 | −27 |
| 4 | <12 | −5 |
| 5 | 19 | −24 |
| 6 | 19 | −23 |
| 7 | 11 | 12 |
| 8 | <12 | 3 |
| 9 | 13 | 11 |
| 10 | 22 | 20 |
| 11 | 10 | −11 |
| 12 | <11 | 3 |
| 13 | <10 | 2 |
| | 010$l$ | |
| 0 | 7 | −4 |
| 1 | 17 | 20 |
| 2 | 15 | −17 |
| 3 | 24 | −23 |
| 4 | 54 | −56 |
| 5 | 29 | 31 |
| 6 | <13 | −6 |
| 7 | <12 | 6 |
| 8 | 22 | 21 |
| 9 | <12 | −2 |
| 10 | 7 | −5 |
| 11 | <11 | −1 |
| 12 | 9 | −6 |
| | 011$l$ | |
| 1 | <13 | −3 |
| 2 | 10 | −12 |
| 3 | 16 | −15 |
| 4 | 16 | 14 |
| 5 | <12 | −3 |
| 6 | 23 | 26 |

| | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 011$l$ | |
| 7 | <12 | −4 |
| 8 | <12 | 3 |
| 9 | <11 | 0 |
| 10 | 10 | −12 |
| 11 | <9 | 1 |
| | 012$l$ | |
| 0 | 10 | 10 |
| 1 | <12 | −3 |
| 2 | 9 | −7 |
| 3 | <12 | 4 |
| 4 | 32 | 35 |
| 5 | <12 | 2 |
| 6 | <11 | −6 |
| 7 | <11 | 5 |
| 8 | 14 | −11 |
| 9 | 7 | −5 |
| 10 | <9 | 2 |
| | 013$l$ | |
| 1 | 10 | 10 |
| 2 | <11 | 3 |
| 3 | 15 | 17 |
| 4 | <11 | −2 |
| 5 | 8 | 10 |
| 6 | 14 | −15 |
| 7 | <10 | −2 |
| 8 | <9 | −2 |
| | 014$l$ | |
| 0 | <11 | 2 |
| 1 | <10 | −1 |
| 2 | 9 | 12 |
| 3 | 10 | 9 |
| 4 | <10 | −4 |
| 5 | 18 | −18 |

(b) [010] *Projection.*

| $l$ | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 00$l$ | |
| 2 | <5 | −4 |
| 4 | 41 | −44 |
| 6 | 6 | 12 |
| 8 | 98 | 80 |
| 10 | <8 | −4 |
| 12 | 73 | −62 |
| 14 | 26 | 21 |
| 16 | 34 | 22 |
| | 10$l$ | |
| 0 | 210 | 213 |
| 2 | 33 | 14 |
| 4 | 167 | −193 |
| 6 | 23 | −15 |
| 8 | 12 | −7 |
| 10 | 9 | −7 |
| 12 | 83 | −77 |
| 14 | 7 | −6 |

| | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 10$l$ | |
| −2 | 50 | −29 |
| −4 | 78 | −84 |
| −6 | 42 | −26 |
| −8 | 116 | 103 |
| −10 | 96 | −89 |
| −12 | 50 | −41 |
| −14 | 14 | −14 |
| −16 | <8 | −9 |
| | 20$l$ | |
| 0 | 38 | −37 |
| 2 | 48 | 40 |
| 4 | 164 | −143 |
| 6 | 31 | −25 |
| 8 | 20 | 11 |
| 10 | 15 | 8 |
| 12 | 15 | −9 |

| | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 20$l$ | |
| −2 | 21 | −22 |
| −4 | 77 | −77 |
| −6 | 155 | 148 |
| −8 | 49 | 42 |
| −10 | 54 | −45 |
| −12 | 33 | −19 |
| −14 | 14 | −9 |
| −16 | 22 | −22 |
| −18 | 43 | −50 |
| | 30$l$ | |
| 0 | 30 | 22 |
| 2 | 23 | 19 |
| 4 | 8 | 15 |
| 6 | 40 | −38 |
| 8 | 45 | 39 |
| 10 | 32 | 25 |

| $l$ | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 30$l$ | |
| −2 | 31 | −29 |
| −4 | 20 | −16 |
| −6 | 218 | 219 |
| −8 | 17 | 14 |
| −10 | 29 | 35 |
| −12 | <9 | 5 |
| −14 | 72 | 64 |
| −16 | <8 | −5 |
| −18 | 34 | −27 |
| | 40$l$ | |
| 0 | <9 | 12 |
| 2 | 18 | −16 |
| 4 | 14 | 7 |
| 6 | 35 | −38 |
| −2 | 152 | −122 |
| −4 | <8 | −1 |

| | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 40$l$ | |
| −6 | 41 | 21 |
| −8 | <8 | −5 |
| −10 | 38 | −25 |
| −12 | 18 | −5 |
| −14 | 65 | 59 |
| −16 | 25 | −22 |
| −18 | 23 | −14 |
| | 50$l$ | |
| 0 | <9 | −4 |
| 2 | 30 | 22 |
| 4 | <7 | −2 |
| −2 | 55 | −54 |
| −4 | <9 | 2 |
| −6 | 25 | −25 |
| −8 | 18 | 14 |
| −10 | 45 | −48 |

| | $\|F_o\|$ | $F_c$ |
|---|---|---|
| | 50$l$ | |
| −12 | 35 | 35 |
| −14 | 31 | 22 |
| −16 | <7 | −1 |
| | 60$l$ | |
| 0 | <7 | −6 |
| −2 | <8 | 17 |
| −4 | <8 | −9 |
| −6 | 24 | 20 |
| −8 | <8 | −4 |
| −10 | 24 | −11 |
| −12 | 45 | 31 |
| −14 | 14 | 6 |
| | 70$l$ | |
| −6 | <6 | 11 |
| −8 | 25 | −29 |
| −10 | <6 | 1 |

The scattering factors were taken from the tables of Viervoll and Ögrim;[9] the values tabulated for fluorine were used for the methyl groups, and the values for cobalt were corrected for anomalous dispersion.[10]

*The* [010] *projection.* The positions of the heavier atoms were found from the Patterson map calculated for the 90 observed terms, and the refinement was begun in the same way as that of the [100] projection. The overlapping of atoms from different molecules prevented systematic refinement of the positions of the light atoms, and a structure was therefore obtained by taking the $z$ co-ordinates from the [100] projection and finding the $x$ co-ordinates which best fitted the [010] electron-density maps. After refinement of the positions and thermal parameters of the heavy atoms the parameters from the two projections were reconciled, and

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[9] Viervoll and Ögrim, *Acta Cryst.*, 1949, **2**, 279.

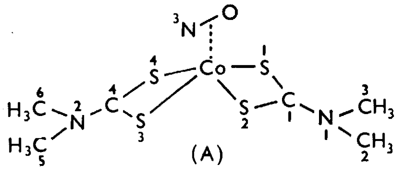
[10] James, " The Optical Principles of the Diffraction of X-Rays," Bell, London, 1948, p. 608.

three cycles of anisotropic least-squares refinement were calculated, leading to the results in Table 1. The weighting factors used were $\sqrt{w} = 45/(45 + F^2_{\text{obs.}})$, and only the diagonal terms of the matrix were used. The observed and calculated structure factors are appended as Table 3; the final values for the discrepancy factor $R$ were 0·086 for the [100] and 0·156 for the [010] projections, including the unobserved reflections for which the following criteria were adopted: $|F_{\text{calc.}}| < |F_{\text{min.}}|$, $\Delta F = 0$; $|F_{\text{calc.}}| > |F_{\text{min.}}|$, $\Delta F = F_{\text{min.}} - F_{\text{calc.}}$, where $F_{\text{min.}}$ is the minimum observable structure factor.

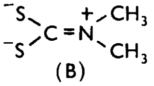
The standard deviations for the $y$ and $z$ co-ordinates were calculated from formulæ of the type $[\sum w(\Delta F)^2]/[(n - v)\sum w(\partial F/\partial y)^2]$, where $n$ is the number of observations and $v$ is the number of variable parameters, and are 0·002 Å for Co, 0·005 Å for S, and 0·015 Å for the other atoms. There is no satisfactory method of estimating the standard deviations of the $x$ co-ordinates in the [010] projection; they will certainly be larger, especially for the lighter atoms.

## RESULTS AND DISCUSSION

The bond lengths and angles are listed in Table 2, the atoms being numbered as in (A). The co-ordination round the cobalt atom is that of a rectangular-based pyramid, with the cobalt atom on the pyramidal axis 0·54 Å above the plane of the four sulphur atoms. It thus differs from the tetragonal pyramidal configuration found in several compounds of $Sb^{3+}$ and in bromine pentafluoride, where the central atom lies below the basal plane;[11,12] this is no doubt because the $s^2$ lone pair of electrons which is present in $Sb^{3+}$ and $Br^{5+}$ is absent in $Co^{2+}$ or $Co^+$.



(A)



(B)

The Co–S, S–C, and N–$CH_3$ distances are all normal for single bonds within the limits of error, and the N–C distance is close to that for a double bond. The $S_2C{\cdot}N(CH_3)_2$ ligands are planar, showing that the polar structure (B) is one of the principal resonance forms, in agreement with infrared evidence.[13] The cobalt atom is coplanar with each dithiocarbamate group.

The Co–N bond-length is close to the metal–nitrogen distances found in other nitric oxide complexes of cobalt and iron [14] and is shorter than the expected single-bond distance. The point of intersection of the axis of the co-ordination pyramid and the N–O bond is not well-defined because of the uncertainty in the $x$ co-ordinates of the light atoms; it is approximately at the mid-point of the N–O bond, rather than at the nitrogen atom. The angle between the N–O bond and the pyramidal axis, 134—140°, is much more accurately known, since it can be found from the $y$ and $z$ co-ordinates, by assuming the N–O bond to have a bond-order between 2 and 3 (see footnote, Table 2). Other examples of nitric oxide complexes in which the metal–N–O angle differs from 180°, though by a smaller amount, are two ruthenium complexes [15] where the angles are 150° and 153°, and Roussin's red salt and black ester,[14] where the angles vary between 160° and 175°; in these compounds the metal–NO bonding appears to be solely through the nitrogen atom.

The atomic positions indicate that the metal electrons and the $\pi$-electrons of the N–O multiple bond interact, and that the compound is a $\pi$-complex. Unlike the symmetrical

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[11] Grdenić and Šćavničar, *Proc. Chem. Soc.*, 1960, 147.

[12] Burbank and Bensey, *J. Chem. Phys.*, 1957, **27**, 982.

[13] Chatt, Duncanson, and Venanzi, *Suomen Kem.*, 1956, *B*, **29**, 75.

[14] Lewis, *Sci. Progr.*, 1959, **47**, 506; Johansson and Lipscomb, *Acta Cryst.*, 1958, **11**, 594; Thomas, Robertson, and Cox, *ibid.*, 1958, **11**, 599.

[15] Bokii and Parpiyev, *Kristallografiya*, 1957, **2**, 691; Parpiyev and Porai-Koshits, *Kristallografiya*, 1959, **4**, 30.

bonds in ethylene π-complexes,[16] the Co–(NO) bond is unsymmetrical because of the difference of electronegativity between nitrogen and oxygen.

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[16] Alderman, Owston, and Rowe, *Acta Cryst.*, 1960, **13**, 149.