

## Three-Dimensional Structural Investigation of Bis(dimethyldithiocarbamate)nitrosylcobalt: $\text{CoNO}(\text{S}_2\text{CNMe}_2)_2$

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The structure of the title compound has been redetermined by single-crystal X-ray diffraction from three-dimensional data collected by counter methods. The compound crystallizes in the monoclinic space-group  $P2_1/c$  with  $a = 6.408(4)$ ,  $b = 13.514(8)$ ,  $c = 16.821(9)$  Å,  $\beta = 116.66(3)^\circ$ , and  $Z = 4$ . The structure was refined by full-matrix least-squares methods to  $R$  0.035 for 1209 independent reflections. The co-ordination geometry about the cobalt is a tetragonal pyramid with the NO group at the apex. The Co atom is 0.52 Å above the basal plane formed by the four S atoms, and the nitrosyl group is disordered such that the O atom alternately lies above one or the other of the Co-S bonds of the same dithiocarbamate ligand. Co-N is 1.746(7) Å and Co-S (mean) 2.263(4) Å. An improved synthesis of this compound and its solution n.m.r. spectrum are reported.

CURRENT interest in the structures of transition-metal nitrosyls stems from the fact that the NO group may be bound to form either a linear or bent array.<sup>1-9</sup> Additionally, the NO stretching frequencies cover wide ranges:<sup>9</sup> 1950—1550  $\text{cm}^{-1}$ . These experimental data are in sharp contrast to those for carbonyl complexes with which nitrosyls are often compared. It is important to obtain detailed structural information, especially for transition-metal nitrosyls with M-N-O angles less than  $180^\circ$ , in order to understand the circumstances and causes of these unusual properties.

The first compound to be studied which was found to have a strongly bent M-N-O group was bis(dimethyldithiocarbamate)nitrosylcobalt<sup>10</sup> (Co-N-O  $134^\circ$ ). The structure of this compound was obtained from two-dimensional X-ray data for a very small twinned crystal.<sup>10</sup> Apparent difficulty has been encountered in re-preparing this compound and in obtaining suitable single crystals. Moreover, there have been several examples of compounds containing the  $-\text{NO}_2$  group which have been misidentified as nitrosyl complexes.<sup>11,12</sup> Owing to the difficulties encountered in the preparation and analysis

of this compound, there was no compelling evidence that it was indeed a nitrosyl complex. Consequently, the preparation and structural properties have been re-investigated and are here described.

### RESULTS

*Structural Investigation.*—The published fractional coordinates<sup>10</sup> of the Co atom and the dithiocarbamate ligands were the starting point for solution of the structure. Two cycles of full-matrix least-squares refinement assuming isotropic thermal parameters led to  $R$  0.140 and  $R'$  0.207  $\{R' = [\Sigma w(|F_o| - |F_c|)^2 / (\Sigma w|F_o|^2)]^{1/2}\}$  where  $w = 4F_o^2/\sigma^2(F_o^2)$ . The quantity minimized was  $\Sigma w(|F_o| - |F_c|)^2$ . The scattering factors for sulphur, carbon, nitrogen, and oxygen were taken from ref. 13, those for cobalt from ref. 14. The effect of anomalous dispersion was included in  $F_c$ ;<sup>15</sup>  $\Delta f'$  and  $\Delta f''$  for cobalt and sulphur were taken from ref. 16. A difference electron-density map clearly revealed the nitrogen atom position and two possible oxygen atom positions ca. 1.2 Å apart. The refinement was continued after correction of the data for absorption, including an occupancy factor for the oxygen position as one of the least-squares variables;

<sup>1</sup> D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 2345.

<sup>2</sup> D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1282.

<sup>3</sup> C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. (A)*, 1971, 2146.

<sup>4</sup> D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, 1970, **9**, 2760.

<sup>5</sup> C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, 1970, **92**, 4760.

<sup>6</sup> D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1035.

<sup>7</sup> D. M. P. Mingos, W. T. Robinson, and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 1043.

<sup>8</sup> J. M. Waters and K. R. Whittle, *Chem. Comm.*, 1971, 518.

<sup>9</sup> B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, 1966, **7**, 277.

<sup>10</sup> P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 1962, 668.

<sup>11</sup> R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 119.

<sup>12</sup> H. Büttner and R. D. Feltham, *Inorg. Chem.*, in the press.

<sup>13</sup> 'International Tables for X-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1 A.

<sup>14</sup> D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

<sup>15</sup> J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

<sup>16</sup> D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

programs used are listed in ref. 17. Two cycles of isotropic refinement of all atoms converged to  $R$  0.076 and  $R'$  0.102. Anisotropic motion was then assumed for all atoms and two additional cycles of least-squares refinement were carried out. A difference electron-density map revealed the hydrogen atoms of the methyl groups as peaks of 0.3–0.5  $e\text{\AA}^{-3}$ , the largest peaks in the map. All residuals in the vicinity of the NO group were  $<0.25 e\text{\AA}^{-3}$ . Two more cycles of anisotropic refinement with the hydrogen atoms included as fixed contributions<sup>18</sup> resulted in convergence at  $R$  0.035 and  $R'$  0.049 for the 1209 data having  $F_o^2 > 3\sigma(F_o^2)$ .

The final disorder is nearly statistical. The occupancy for position O(1) is 0.46(4). Figure 1 shows that the two

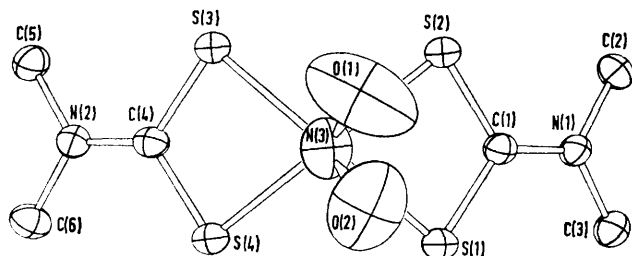


FIGURE 1 Projection of the molecule along the Co–N vector. Both of the half-oxygen atoms of the disordered NO group are shown (this corresponds to Figure 3b of ref. 10)

disordered oxygen atoms are related by a non-crystallographic mirror plane perpendicular to the  $S_4$  plane. Even the thermal motion of the two crystallographically independent half-oxygen atoms maintains this mirror-symmetry relationship. The O(1)  $\cdots$  O(2) distance is only 1.2  $\text{\AA}$ ,

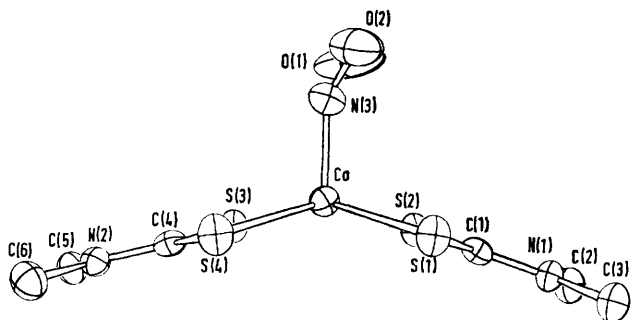


FIGURE 2 Projection of the molecule perpendicular to the Co–N vector. Both of the half-oxygen atoms of the disordered NO group are shown. This corresponds to Figure 3a of ref. 10

and this short distance and the large thermal motion led to some correlation coefficients of the least-squares matrix involving these parameters as large as 0.9.

The thermal behaviour of N(3) appears normal (Figures 1 and 2) and the root-mean-square amplitudes of vibration

\* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

<sup>17</sup> Data reduction, UCFACS, by K. N. Raymond, a modification of PIKOUT, by R. J. Doedens and J. A. Ibers; Fourier summation program, FORDAP, by A. Zalkin; general absorption program, GONO, by W. C. Hamilton; group least-squares refinement, NUCLS, by J. A. Ibers, based on ORFLS, by W. R. Busing and H. A. Levy; ORFFE, by W. R. Busing and H. A. Levy; plotting program, ORTEP, by C. K. Johnson; and weighting analysis, RANGER, by P. W. R. Corfield; all computations were performed on a CDC 6400.

are not abnormally large (Table 1). Moreover, after correction for thermal motion assuming a riding model,<sup>19</sup> the N–O distances are identical within the limits of the determination and are in good agreement with those normally found in metal nitrosyls.<sup>1–9</sup> A final structure-factor calculation

TABLE I  
Root-mean-square amplitudes of vibration<sup>a</sup>

Atom	Minimum	Intermediate	Maximum
Co	0.202(1)	0.215(1)	0.219(1)
S(1)	0.188(2)	0.220(2)	0.269(2)
S(2)	0.184(2)	0.220(2)	0.266(2)
S(3)	0.189(2)	0.217(2)	0.259(2)
S(4)	0.188(2)	0.228(2)	0.272(2)
C(1)	0.178(9)	0.196(9)	0.234(8)
C(2)	0.189(9)	0.250(9)	0.276(8)
C(3)	0.199(9)	0.252(8)	0.262(8)
C(4)	0.180(9)	0.193(9)	0.240(8)
C(5)	0.198(9)	0.240(9)	0.257(9)
C(6)	0.208(9)	0.242(9)	0.273(8)
N(1)	0.187(8)	0.204(7)	0.228(7)
N(2)	0.208(7)	0.210(7)	0.212(7)
N(3)	0.221(9)	0.267(8)	0.306(9)
O(1) <sup>b</sup>	0.23(2)	0.33(3)	0.57(3)
O(2) <sup>b</sup>	0.25(2)	0.36(2)	0.44(3)

<sup>a</sup> Vibration amplitudes are in  $\text{\AA}$ . The figures provide an indication of the direction of the principal axes of vibration.

<sup>b</sup> O(1) and O(2) are the two crystallographically independent half-atoms of the disordered NO group.

on all 1711 data gave  $R$  0.077 and  $R'$  0.054. Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20303 (10 pp., 1 microfiche).<sup>\*</sup> The standard deviation of an observation of unit weight was 1.44 electrons. An analysis of  $w|F|^2$  as a function of indices, intensity and  $\sin \theta/\lambda$  indicated that weak low-angle reflections were slightly overweighted. Final structural parameters are in Table 2.

*Chemical Investigation.*—This compound was first prepared from the reaction between nitric oxide and cobalt(II) in the presence of sodium dimethyldithiocarbamate,<sup>20</sup> and the ethyl analogue has been prepared similarly.<sup>21</sup> Since the yields are low, and nitric oxide is often contaminated with  $\text{NO}_2$ , an alternative method of preparation was sought. Bis(ethylenediamine)nitrosylcobalt diperchlorate,<sup>22</sup> which is readily prepared pure in high yields, proved to be a convenient starting material. In order to establish the purity of the product thus obtained, total elemental analyses, including oxygen, were obtained for all samples. Although some of the oxygen analyses tended to be slightly high, there were no appreciable amounts of  $\text{NO}_2$  impurities present in these samples. The n.m.r. spectra of purified samples showed only a single sharp resonance at  $\delta$  3.35 p.p.m. typical of the dimethyldithiocarbamate ligand.<sup>12</sup> The i.r. spectra of these compounds showed no bands which could be ascribed to the  $\text{NO}_2$  group.

## DISCUSSION

The results of the chemical and spectroscopic investigations have established the purity and identity of this

<sup>18</sup> R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

<sup>19</sup> W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

<sup>20</sup> L. Malatesta, *Gazzetta*, 1940, **70**, 729, 734.

<sup>21</sup> R. L. Carlin, F. Canziani, and W. K. Bratton, *J. Inorg. Nuclear Chem.*, 1964, **28**, 898.

<sup>22</sup> R. D. Feltham and R. S. Nyholm, *Inorg. Chem.*, 1965, **4**, 1334.

compound. Large amounts of another green material also noted by others are often obtained from these reactions, but were removed from the samples used for the structural and spectroscopic investigations.

Our X-ray investigation has verified that the structure previously suggested<sup>10</sup> by use of two-dimensional data

is significantly shorter than a Co-NO<sub>2</sub> distance<sup>23</sup> of 1.92 Å.

It is somewhat disturbing that  $D_m$ , determined by two different techniques on three samples is reproducible, but too high by 0.03 g cm<sup>-3</sup> [1.70(1) vs.  $D_c$  1.67]. If the error were due to the presence of an NO<sub>2</sub><sup>-</sup> complex, then

TABLE 2

Final atomic parameters (all  $\times 10^4$ ) with estimated standard deviations in parentheses<sup>a</sup>

Atom	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Co	-0600.4(14)	2024.1(6)	1288.7(5)	257.0(30)	50.4(5)	41.0(4)	-1.9(10)	48.7(9)	1.0(4)
S(1)	-2560(3)	1707(1)	2100(1)	215(6)	78(1)	41(1)	9(2)	41(2)	2(1)
S(2)	2273(3)	1729(1)	2652(1)	218(5)	74(1)	43(1)	-18(2)	46(2)	-5(1)
S(3)	1395(3)	1593(1)	0510(1)	219(5)	72(1)	40(1)	-10(2)	42(2)	-1(1)
S(4)	-3431(3)	1537(1)	-0029(1)	220(6)	79(1)	45(1)	5(2)	46(2)	-3(1)
C(1)	0116(9)	1534(4)	2975(4)	226(21)	41(4)	42(3)	3(7)	42(7)	-8(3)
C(2)	2812(11)	1124(5)	4479(4)	284(24)	81(5)	35(3)	14(9)	21(7)	4(3)
C(3)	-1468(11)	1080(5)	3988(4)	351(25)	74(5)	48(3)	-2(9)	78(8)	3(3)
C(4)	-1268(9)	1338(4)	-0349(4)	218(20)	40(4)	45(3)	-2(7)	40(7)	7(3)
C(5)	0304(11)	0857(5)	-1360(4)	328(25)	68(5)	45(3)	0(8)	69(8)	-6(3)
C(6)	-3940(11)	0829(5)	-1823(4)	288(25)	68(5)	48(3)	-3(8)	31(8)	-9(3)
N(1)	0463(8)	1284(3)	3781(3)	246(17)	54(3)	34(3)	5(6)	47(5)	4(2)
N(2)	-1597(8)	1040(3)	-1137(3)	266(19)	48(3)	38(3)	-1(6)	45(6)	0(2)
N(3)	-0713(20)	3314(5)	1219(4)	547(31)	55(5)	61(4)	-7(14)	79(9)	-6(3)
O(1) <sup>b</sup>	0415(76)	3875(16)	1555(16)	781(158)	62(12)	186(16)	-38(30)	3(35)	27(11)
O(2) <sup>b</sup>	-1702(70)	3907(12)	1363(16)	1099(172)	76(10)	135(14)	82(28)	222(40)	12(8)

<sup>a</sup>  $x$ ,  $y$ , and  $z$  are in fractional monoclinic co-ordinates. Anisotropic thermal parameters are in the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ . <sup>b</sup> O(1) and O(2) are the two positions for the oxygen of the disordered NO group. The occupancy factor of the O(1) position is 0.46(4).

is correct. Figures 1 and 2 show projections of the molecule corresponding to those of the earlier investigation.<sup>10</sup> Distances and angles are listed in Tables 3 and 4.

TABLE 3

Interatomic distances (Å) with estimated standard deviations in parentheses

Atoms	Distance	Riding model <sup>a</sup>
Co-S(1)	2.265(2)	2.269(2)
Co-S(2)	2.257(2)	2.261(2)
Co-S(3)	2.272(2)	2.275(2)
Co-S(4)	2.259(2)	2.264(2)
Co-N(3)	1.746(7)	1.767(7)
S(1)-C(1)	1.716(6)	
S(2)-C(1)	1.714(6)	
S(3)-C(4)	1.718(6)	
S(4)-C(4)	1.714(6)	
C(1)-N(1)	1.317(7)	
C(4)-N(2)	1.311(7)	
N(1)-C(2)	1.462(7)	1.479(7)
N(1)-C(3)	1.452(8)	1.465(8)
N(2)-C(5)	1.445(8)	1.456(8)
N(2)-C(6)	1.464(7)	1.479(7)
N-O(1) <sup>b</sup>	1.029(24)	1.151(27)
N-O(2) <sup>b</sup>	1.112(22)	1.184(20)

<sup>a</sup> Second atom assumed to ride on the first. <sup>b</sup> O(1) and O(2) are the two crystallographically independent half-oxygen atoms of the disordered NO group.

From the distances and angles it is also apparent] that it is indeed a nitrosyl complex and not a complex of the NO<sub>2</sub><sup>-</sup> anion, since for the latter the O-N-O angle would be *ca.* 120°. The apparent angle between the two half-oxygen atoms of the disordered NO group is only 71(1)°. Moreover, in NO<sub>2</sub><sup>-</sup> complexes the angle between the M-N vector and the normal to the NO<sub>2</sub><sup>-</sup> plane<sup>23</sup> is 90°. The angle involving the Co-N vector and the plane containing the two half-oxygens and N(3) is only 60°. Finally, the Co-N distance of 1.746(7) Å

the sample would have to contain about 50% of this. This possibility has been eliminated by elemental analysis, the spectroscopic investigations, and by the short distance between O(1) and O(2). The previously reported value of  $D_m$  was 1.66 g cm<sup>-3</sup>.<sup>10</sup>

The structure is best described as a tetragonal pyramid with an apical NO ligand and the Co atom 0.52 Å above the weighted least-squares plane passing through the sulphur atoms. (The equation of the plane in monoclinic co-ordinates is  $-13.5y + 0.96z = 2.1$ .) The dithiocarbamate ligands are essentially planar (Figure 2)

TABLE 4

Bond angles (°) with estimated standard deviations in parentheses

Atoms	Angle	Atoms	Angle
S(1)-Co-S(2)	77.02(8)	S(4)-C(4)-N(2)	124.9(4)
S(2)-Co-S(4)	76.83(8)	C(1)-N(1)-C(2)	120.9(5)
S(1)-Co-S(4)	96.73(8)	C(1)-N(1)-C(3)	121.3(5)
S(2)-Co-S(3)	97.23(8)	C(2)-N(1)-C(3)	117.6(5)
Co-S(1)-C(1)	86.2(2)	C(4)-N(2)-C(5)	122.4(5)
Co-S(2)-C(1)	86.4(2)	C(4)-N(2)-C(6)	120.7(5)
Co-S(3)-C(4)	86.2(2)	C(5)-N(2)-C(6)	116.8(5)
Co-S(4)-C(4)	86.7(2)	S(1)-Co-N(3)	102.2(3)
S(1)-C(1)-S(2)	110.3(3)	S(2)-Co-N(3)	103.6(3)
S(3)-C(4)-S(4)	110.3(3)	S(3)-Co-N(3)	103.5(3)
S(1)-C(1)-N(1)	124.8(5)	S(4)-Co-N(3)	103.5(3)
S(2)-C(1)-N(1)	124.8(4)	Co-N(3)-O(1)	134.5(17)
S(3)-C(4)-N(2)	124.8(5)	Co-N(3)-O(2)	135.7(14)

and the dihedral angle between the two ligand planes is 146°. The angle between the Co-N vector and the plane of the four sulphur atoms is 90°. The Co-N

<sup>23</sup> For a recent example of the structure of an NO<sub>2</sub><sup>-</sup> complex of Co<sup>III</sup>, see M. Laing, S. Baines, and P. Sommerville, *Inorg. Chem.*, 1971, 10, 1057.

distance of 1.746(7) Å is slightly shorter than those of 1.82(1)<sup>4</sup> and 1.871(6)<sup>3</sup> found recently for two six-coordinate cobalt complexes having bent nitrosyl groups.

Figures 1 and 2 show that the NO group is oriented in such a way that the two possible oxygen atom positions are above the Co-S bonds of the same dithiocarbamate ligand. The limitation of the disordered oxygen atom to the positions over a single dithiocarbamate ligand is probably due to packing effects. The non-bonded interactions calculated for the two observed disordered positions are normal and virtually identical. However, when hypothetical co-ordinates are derived for the oxygen atoms being above the other dithiocarbamate ligand, then there are intermolecular O...H contacts of 2.4 Å (0.2 Å shorter than the expected van der Waals contact).<sup>24</sup> The barrier to rotation of the NO group about the Co-N vector is probably quite small. The room-temperature n.m.r. spectrum consists of a sharp singlet, whereas a long-lived rotamer should give rise to two methyl resonances.<sup>12</sup> Intramolecular O...S contacts are 3.4 Å and hence not important in determining the NO orientation.

The fact that the half-oxygen atoms lie essentially above the Co-S bond is a striking feature of the structure. The absence of any unusual inter- or intra-molecular steric contacts involving these oxygen positions (*vide supra*) suggests that the observed rotational conformations may be due to electronic effects. Consideration of the co-ordination symmetry about the Co atom leads to a qualitative understanding of the electronic structure of the molecule. Although no symmetry is imposed upon the molecule by the space-group, the effective co-ordination symmetry about the Co atom is  $C_{2v}$ , *mm* with a pseudo-two-fold axis coincident with the Co-N vector. If this axis is defined as the *z* axis of the molecule, then the  $d_{xz}$  and  $d_{yz}$  orbitals of the metal will lie in the mirror planes between the S atoms. Both these orbitals will be filled in either of the two limiting electronic structures suggested for five- and six-co-ordinate complexes with strongly bent M-N-O moieties.\* In addition the  $sp^2$  lone-pair orbital of the nitrogen atom of the NO ligand will be filled. The observed rotational conformations of the NO group minimize the electron-electron repulsions between the filled  $sp^2$  orbital of the NO ligand and the filled  $d_{xz}$  and  $d_{yz}$  orbitals of the metal.

This compound is closely related to the six-co-ordinate cobalt(III) species which have non-linear NO co-ordination.<sup>3,4</sup> It might be expected that the dithiocarbamate complex would also add a sixth ligand in the axial position. However, attempts to form Lewis base adducts of bis(dimethyldithiocarbamate)nitrosylcobalt have not been successful.

\* The known complexes 1-8 may be regarded as NO<sup>-</sup> complexes of a  $d^9$  metal,<sup>4,6,7,25,26</sup> or as complexes of a  $d^8$  metal and NO<sup>+</sup> in which the NO<sup>+</sup> ligand acts as Lewis acid and accepts a pair of electrons from the  $d_{z^2}$  orbital of the metal.<sup>27</sup>

<sup>24</sup> L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 260.

<sup>25</sup> R. D. Feltham, W. Silverthorn, and G. McPherson, *Inorg. Chem.*, 1969, 8, 344.

## EXPERIMENTAL

N.m.r. spectra were obtained by use of a Varian T 60 spectrometer, and i.r. spectra by use of a Perkin-Elmer 337. Cobalt was determined by ethylenediaminetetra-acetic acid titration,<sup>28</sup> and sulphur as barium sulphate. All operations were carried out under nitrogen with deoxygenated solvents; dichloromethane was treated with sodium dithionite and sodium carbonate to remove any chlorine or hydrogen chloride. Bis(ethylenediamine)nitrosylcobalt diperchlorate was prepared as described previously.<sup>22</sup>

*Preparation of the Complex.*—Bis(ethylenediamine)nitrosylcobalt diperchlorate (4.90 g, 12.1 mmol), sodium dimethyldithiocarbamate dihydrate (4.48 g, 25 mmol), and methane (120 ml) were stirred under nitrogen for 2 h. Solvent was carefully removed under vacuum, and deoxygenated water (100 ml) added to the dark brown solid residue to dissolve any salts. This mixture was stirred for 1.5 h, and dichloromethane (100 ml) was then added. The organic layer was separated and stored at -10° overnight. A large amount of brown needles and a few dark green plates were then obtained and were separated mechanically. The brown needles were washed with water; they showed  $\nu(\text{NO})$  at 1630 cm<sup>-1</sup> (Found: C, 21.9; H, 3.8; Co, 17.4; N, 12.6; O, 5.2; S, 38.7. Calc. for C<sub>6</sub>H<sub>12</sub>N<sub>3</sub>CoOS<sub>4</sub>: C, 21.9; H, 3.7; Co, 17.9; N, 12.8; O, 4.9; S, 38.8%). The crystals used for the structural investigation were grown from chloroform by slow evaporation under nitrogen.

*Crystal Data.*—C<sub>6</sub>H<sub>12</sub>CoN<sub>3</sub>OS<sub>4</sub>, Monoclinic,  $M = 329.4$ ,  $a = 6.408(4)$ ,  $b = 13.514(8)$ ,  $c = 16.821(9)$  Å,  $\beta = 116.66(3)^\circ$ ,  $U = 1308.5$  Å<sup>3</sup>,  $D_m = 1.70(1)$ ,  $Z = 4$ ,  $D_c = 1.67$ ,  $F(000) = 676$ . Space-group  $P2_1/c$  from systematic absences:  $h0l$  for  $l \neq 2n$ ,  $0k0$  for  $k \neq 2n$ . Mo- $K_\alpha$  radiation  $\lambda = 0.71069$  Å;  $\mu(\text{Mo-}K_\alpha) = 19.5$ , Temp. = 20° C.

The cell parameters derived from preliminary Weissenberg and precession photographs (taken with Cu- $K_\alpha$  radiation,  $\lambda = 1.5418$  Å) and the pattern of relative intensities agreed with those determined previously,<sup>10</sup> and it was concluded that the material was identical to that studied earlier. There was no evidence of twinning. For data collection a lath-shaped crystal of dimensions *ca.* 0.44 × 0.18 × 0.04 mm was mounted about its long axis, *a*. Precise cell parameters were determined by a least-squares refinement of the setting angles for 12 reflections, with  $2\theta$  values in the range 20–27°, which had been carefully centred on a Picker FACS I four-circle diffractometer. The mosaicity of the crystal was checked by doing  $\omega$  scans on several reflections at a take-off angle of ~0.8°. All reflections had peak-widths at half-height  $\leq 0.1^\circ$ . Data were collected by the  $\theta$ – $2\theta$  scan technique with a scan range from  $2\theta(\text{Mo-}K_{\alpha,1}) - 0.7^\circ$  to  $2\theta(\text{Mo-}K_{\alpha,2}) + 0.7^\circ$  and a scan rate of 1° min<sup>-1</sup> and stationary-crystal-stationary-counter background counts of 10 s at each end of the scan. The apparatus was equipped with a graphite crystal monochromator and fitted with a scintillation counter and pulse-height analyser. During data collection the intensities of three standard reflections were measured every 50 reflections, but showed no systematic changes. The standard deviation of the average intensity of each reflection was <1%. A total of 1711 unique

<sup>26</sup> J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, 1969, 91, 5659.

<sup>27</sup> D. J. Hodgson, N. C. Payne, J. A. McGinety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1968, 90, 4486.

<sup>28</sup> F. J. Welcher, 'The Analytical Uses of Ethylenediamine-tetra-acetic Acid,' Van Nostrand, New York, 1958, p. 230.

reflections having  $2\theta < 45^\circ$  were collected. The data were reduced to  $F^2$  and  $\sigma(F^2)$  by procedures similar to those previously described,<sup>17,29</sup> and were corrected for polarization effects. A value of 0.05 was assigned to  $p$  in the equation for  $\sigma(F^2)$ .<sup>29</sup> Because of the morphology of the data crystal an absorption correction was made,<sup>17</sup> and its

<sup>29</sup> P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

magnitude ranged from 1.16 to 1.39. No correction was made for secondary extinction.

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