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The Crystal and Molecular Structure of Biacetylbis(mercaptoethylimine)nickel(II)

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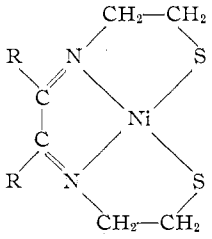
Received June 1, 1965

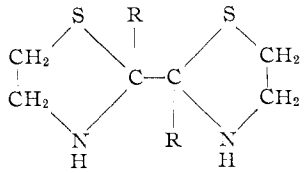
The crystal and molecular structure of biacetylbis(mercaptoethylimine)nickel(II) has been established by a single crystal three-dimensional X-ray study. The complex forms orthorhombic crystals in the space group $Pna2_1$ with four molecules in a unit cell of dimensions $a = 16.50$, $b = 8.93$, and $c = 7.29$ Å. The molecule was found to be a tetracoordinated nickel complex which deviates significantly from planarity.

Square-planar complexes are formed by metal ions with a d^8 configuration, *e.g.*, nickel(II) and platinum(II), and the magnetic properties and ligand field splittings of these complexes have been used to confirm their stereochemistry. X-Ray crystallographic studies have shown, however, that in a number of presumably square-planar complexes, the donor atoms and the metal ion do not lie on one plane and that the angle formed by the metal ion and two neighboring bonding atoms differs significantly from 90°. It is only recently that conclusive evidence has been obtained for the existence of a square-planar complex of nickel(II); the crystal structure determination of the nickel(II) chelate of the dianion of maleonitriledithiol has shown that the complex is square-planar.[2] Since then a number of nickel(II) chelates, formed with ligands containing one or more sulfur donor atoms, have been reported to be square-planar. One such compound, biacetylbis(mercaptoethylimine)nickel(II) (I), was prepared by Thompson and Busch by the reaction of biacetyl with 2-aminoethanethiol in an ethanol solution in the presence of nickel acetate.[3] The complex was diamagnetic and showed a ligand field transition that is consistent with that predicted for *cis*-planar nickel(II) complexes. On this evidence it was postulated that compound I is square-planar.[3] Moreover, the nickel(II) ion was assumed to act as a template in the formation of the square-planar complex since, in the absence of nickel acetate, the reaction of biacetyl and 2-aminoethanethiol resulted in the formation of a thiazolidine (III). In a related study it was found that, in general, thiazolidines, *e.g.*, IV, could be induced to undergo a rearrangement reaction in the presence of transition metal ions, *e.g.*, nickel(II), zinc(II), and cadmium(II), to compound II, but the rearrangement of the thiazolidine III to the nickel chelate I did not take place to any appreciable extent.[4,5] It is of importance therefore to establish the structure of this nickel chelate.

Thompson and Busch have subsequently reported that the nickel chelate I, which has three fused five-membered chelate rings, probably has a trapezoidal



I, R = CH_3
II, R = H



III, R = CH_3
IV, R = H

structure rather than a square-planar structure and that it can form a compound with four fused rings by undergoing ring closure at the two sulfur donor atoms with α,α'-dibromo-*o*-xylene.[6] Steric effects that are involved in this important type of ring closure can be best understood if the structure of the nickel chelate I is known.

Experimental

Biacetylbis(mercaptoethylimine)nickel(II) was prepared by the reaction of 2-aminoethanethiol and biacetyl in the presence of nickel acetate in an ethanol solution.[3] The nickel(II) complex was obtained in the form of dark green needles which were found to be orthorhombic. The cell dimensions obtained from oscillation and Weissenberg photographs with Cu Kα radiation (λ 1.542 Å.) are: $a = 16.50 \pm 0.02$ Å., $b = 8.93 \pm 0.02$ Å., $c = 7.29 \pm 0.02$ Å. The systematic absence of the $0kl$ reflections with $(k + l)$ odd and $h0l$ with h odd characterize the space group as $Pna2_1$ or $Pnam$. The density of the crystals, determined by flotation, was found to be 1.64 g./ml., and calculation of the molecular weight (265 observed, 261 theoretical) showed the presence of four molecules in the unit cell.

The structure was deduced from intensities collected from two needles, the largest dimension of which was 0.13 mm. No correction was made for absorption ($\mu = 57.3$ cm.$^{-1}$). The intensities of the diffracted spectra were obtained by means of the multiple-film technique from equi-inclination Weissenberg photographs. Reflections from the zeroth through fourth levels around [*b*] and [*c*] were recorded with unfiltered Cu K radiation and estimated visually with a calibrated scale; 895 independent reflections were obtained. Lorentz and polarization corrections were applied in the normal manner and values of $|F_o|$ averaged for the common reflections.

Structure Determination

From the great strength of the 002 reflection it was clear that the molecular plane must be, at least approximately, normal to the *c* axis. If the space group is Pnam the molecule must possess a mirror plane which must coincide with the molecular plane, and alternate layers up [*c*] must have identical intensity distributions.

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(2) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *J. Am. Chem. Soc.*, **84**, 3596 (1962).

(3) M. C. Thompson and D. H. Busch, *ibid.*, **86**, 213 (1964).

(4) H. Jadamus, Q. Fernando, and H. Freiser, *Inorg. Chem.*, **3**, 928 (1964).

(5) H. Jadamus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, **86**, 3056 (1964).

(6) M. C. Thompson and D. H. Busch, *ibid.*, **86**, 3651 (1964).

The *hk*0, *hk*2, and *hk*4 layers were indeed very similar, but a careful search showed some significant discrepancies. The space group was, therefore, taken to be the noncentrosymmetric $Pna2_1$, and refinement has confirmed that the molecule departs from strict planarity.

The structure was solved in projection down [*c*]. The nickel atom in the asymmetric unit was located from a Patterson synthesis and the coordinates were used to phase the structure factors. A Fourier synthesis yielded approximate positions for all the remaining atoms, except hydrogen atoms which were ignored throughout. The coordinates were refined by successive Fourier and difference syntheses until *R* had dropped to 14.8% for the 161 *hk*0 reflections.

The *z* coordinates were estimated from the known *x* and *y* coordinates and a molecular model, and refinement with all 895 reflections was commenced by differential Fourier synthesis. The positional parameters refined smoothly until *R* was 30.1%. It was then evident that the molecular motion was highly anisotropic, the direction of maximum motion being approximately along [*c*]. Accordingly anisotropic thermal parameters of the form

$$\exp -[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}2hk + B_{23}2kl + B_{13}2hl]$$

were introduced, and refinement continued until *R* had fallen to its final value of 17.9%. The scattering factors were taken from the International Tables, with the nickel figures corrected for the real part of the dispersion.

Results and Discussion

The final coordinates are shown in Table I, and the thermal factors in Table II. Table III shows the observed and calculated structure factors. Bond lengths and angles are given in Tables IV and V. All standard deviations are given as units in the last place. The bond lengths involving the nickel atom and the labeling of the atoms are shown in Figure 1.

TABLE I

ATOM COORDINATES (Å.)

Atom	*X*	*Y*	*Z*[a]
Ni	1.197 (5)	0.563 (6)	1.738 (7)
S_1	3.034 (9)	1.708 (10)	1.872 (14)
S_2	−0.155 (10)	2.227 (11)	1.651 (14)
N_1	−0.244 (21)	−0.604 (25)	1.683 (23)
N_2	2.175 (26)	−1.010 (26)	1.765 (30)
C_1	4.114 (35)	0.289 (57)	2.275 (51)
C_2	3.672 (36)	−0.953 (35)	1.981 (45)
C_3	−1.606 (39)	−0.157 (79)	1.773 (48)
C_4	−1.737 (33)	1.340 (42)	1.554 (44)
C_5	1.448 (30)	−2.136 (34)	1.765 (32)
C_6	0.028 (32)	−1.900 (35)	1.721 (38)
C_7	2.052 (48)	−3.508 (67)	1.967 (69)
C_8	−1.021 (50)	−2.919 (48)	1.842 (64)

[a] Since not all the *z* parameters are independent, the errors quoted for these parameters in the above table are applicable to the calculation of molecular parameters.

The mean value of the Ni–S distance (2.157 Å.) agrees well with the value (2.156 Å.) obtained by Eisenberg and Ibers.[7] The mean value of the Ni–N distance (1.85 Å.) agrees with values found in other diamagnetic nickel(II) complexes.[8] In the rest of the molecule bonds adopt the expected values,[9] although the standard deviations are rather high.

TABLE II

ANISOTROPIC THERMAL FACTORS (Å.²)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
Ni	2.84	2.38	7.89	−0.07	−0.15	−0.04
S_1	3.02	2.47	9.79	−0.72	−0.28	0.34
S_2	3.96	2.30	10.18	0.76	−0.19	−0.15
N_1	2.55	2.45	5.12	−0.20	−0.09	−0.24
N_2	2.90	1.93	7.34	−0.05	0.12	−1.54
C_1	1.05	2.86	7.88	−0.30	0.28	0.18
C_2	3.72	3.80	8.69	0.60	−0.08	0.07
C_3	5.11	5.62	8.03	−1.73	−0.81	0.12
C_4	3.37	2.11	6.06	0.26	−0.83	0.15
C_5	2.99	5.27	5.89	−0.90	−0.97	0.27
C_6	3.58	1.73	7.40	−0.28	−1.90	0.57
C_7	5.58	4.88	10.29	0.62	0.61	1.21
C_8	7.19	3.25	10.18	−2.29	−0.02	−1.79

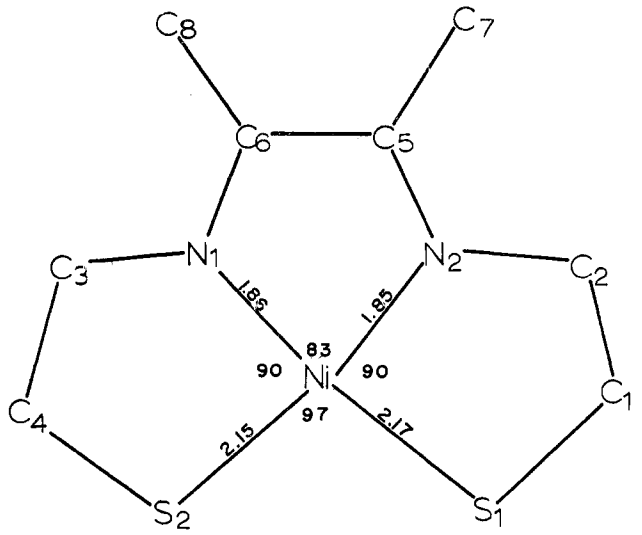

Figure 1.—Bond lengths and bond angles in biacetylbis(mercaptoethylimine)nickel(II).

The N–Ni–S angles are both equal to 90°, within experimental error. The N–Ni–N angle is appreciably less than 90°, the S–Ni–S angle is appreciably greater than 90°, and, to a first approximation, the four atoms coordinated to the nickel atom form a trapezium as predicted by Thompson and Busch.[6] However, the four donor atoms and the nickel atom are not coplanar. The S–Ni–N angles are 173° with a standard deviation of less than 1°. The distortion from planarity is not great although it is highly significant and is tetrahedral rather than square-pyramidal: N_1 and S_1 lie on one side of the nickel atom and N_2 and S_2 on the other.

The best least-squares plane was calculated through all thirteen atoms and, apart from the deviation mentioned above, it was evident that a number of significant deviations occurred in other parts of the molecule. Least-squares planes were calculated through

(7) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).
(8) J. M. Stewart and E. C. Lingafelter, *Acta Cryst.*, **12**, 842 (1959).
(9) "Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

Table III

Observed and Calculated Structure Factors on an Absolute Scale

h k l	$F_{obs.}$	$F_{calc.}$
0 0 2	279.6	312.1
0 0 4	134.2	120.1
0 0 6	53.1	37.0
0 0 8	16.2	9.5
0 1 1	36.4	49.3
0 1 3	25.8	28.0
0 1 5	12.2	11.2
0 1 7	4.6	2.9
0 2 0	22.2	24.7
0 2 2	11.7	20.7
0 2 4	3.5	10.3
0 3 1	25.4	21.1
0 3 3	3.2	8.9
0 3 5	3.1	1.8
0 3 9	1.4	.5
0 4 0	29.6	24.6
0 4 2	15.0	18.6
0 4 4	7.8	9.6
0 5 1	60.4	52.4
0 5 3	32.1	29.5
0 6 0	58.9	45.4
0 6 2	35.7	38.1
0 6 4	20.7	22.7
0 7 1	27.2	23.9
0 7 3	11.4	18.9
0 8 0	30.1	20.8
0 8 2	17.0	17.6
0 8 4	9.4	10.5
0 9 1	5.5	3.0
0 9 3	3.3	5.2
0 10 0	18.4	11.9
0 10 2	10.3	10.3
0 10 4	4.9	6.7
0 11 1	20.1	20.8
1 1 0	103.8	138.4
1 1 1	61.1	72.2
1 1 2	75.6	100.2
1 1 3	31.8	34.9
1 1 4	56.1	46.5
1 1 5	9.5	11.1
1 1 6	20.0	17.0
1 1 7	4.6	2.6
1 1 8	7.5	5.1
1 2 0	39.9	29.0
1 2 1	55.3	53.0
1 2 2	19.0	21.8
1 2 3	27.8	27.4
1 2 4	9.4	10.6
1 2 5	12.4	9.8
1 2 6	3.0	3.8
1 2 7	4.8	2.1
1 3 0	13.5	9.1
1 3 1	32.8	26.0
1 3 2	8.4	7.7
1 3 3	17.9	17.9
1 3 4	4.1	4.5
1 3 5	8.2	9.5
1 4 0	30.8	9.4
1 4 1	21.6	15.4
1 4 2	10.8	6.3
1 4 3	15.3	12.1
1 4 4	3.3	4.6
1 4 5	10.2	6.3
1 4 7	4.8	2.2
1 5 1	14.4	12.1
1 5 2	3.2	4.1
1 5 3	3.4	9.0
1 5 4	3.0	3.2
1 6 0	58.0	46.9
1 6 1	24.0	17.8
1 6 2	31.7	36.5
1 6 3	13.2	11.9
1 6 4	16.0	17.9
1 7 0	60.5	40.1
1 7 1	27.7	24.9
1 7 2	34.5	33.2
1 7 3	14.6	16.9
1 7 4	17.8	19.5
1 8 0	4.6	2.6
1 8 1	8.0	9.5
1 8 3	3.3	7.0
1 9 0	17.1	12.1
1 9 1	9.3	6.5
1 9 2	10.0	9.9
1 9 3	4.6	4.2
1 9 4	5.3	5.4
1 10 0	15.4	10.8
1 10 1	21.3	16.9
1 10 2	10.7	9.6
1 10 3	11.2	11.6
1 10 4	5.7	6.4
1 11 0	9.5	6.0
1 11 1	17.2	5.6
2 0 0	123.9	117.4
2 0 1	93.7	113.9
2 0 2	92.7	95.6
2 0 3	68.1	63.0
2 0 4	62.7	51.7
2 0 5	29.5	25.3
2 0 6	22.5	20.7
2 0 7	10.9	8.1
2 0 8	7.4	6.3
2 1 0	7.9	7.6
2 1 1	9.2	8.9
2 1 2	6.7	9.5
2 1 3	4.8	13.2
2 1 4	7.3	7.4
2 1 7	5.2	2.8
2 2 0	23.8	24.1
2 2 1	11.8	9.3
2 2 2	4.2	9.9
2 2 3	8.1	8.1
2 2 4	4.2	3.2
2 2 5	4.9	4.5
2 2 6	4.8	3.8
2 3 0	40.7	21.9
2 3 1	13.7	13.8
2 3 2	25.3	20.6
2 3 3	12.0	13.3
2 3 4	16.8	14.1
2 3 5	8.6	8.6
2 3 6	11.1	6.6
2 3 7	4.7	3.7
2 3 8	3.8	2.3
2 4 0	53.3	42.0
2 4 1	18.7	15.0
2 4 2	29.5	33.7
2 4 3	6.6	8.6
2 4 4	16.4	18.2
2 4 6	6.3	6.8
2 4 8	5.4	1.7
2 5 0	49.5	36.2
2 5 1	39.7	37.3
2 5 2	27.3	29.0
2 5 3	26.5	26.5
2 5 4	15.6	15.7
2 6 0	72.6	55.3
2 6 1	38.5	31.0
2 6 2	39.7	44.3
2 6 3	20.5	20.4
2 6 4	20.2	23.6
2 7 0	62.1	43.6
2 7 1	34.6	38.2
2 7 2	34.7	35.6
2 7 3	17.4	21.9
2 7 4	16.9	19.9
2 8 0	4.6	6.6
2 8 1	28.2	25.1
2 8 2	4.7	4.6
2 8 3	13.7	17.0
2 9 0	31.6	24.1
2 9 1	20.3	20.7
2 9 2	17.2	19.8
2 9 3	10.3	15.3
2 9 4	9.6	11.0
2 10	36.0	27.4
2 10 1	4.6	6.8
2 10 2	23.0	22.5
2 10 4	8.5	12.4
2 11 0	10.7	5.4
3 1 0	6.3	2.3
3 1 1	12.0	17.4
3 1 3	24.6	23.4
3 1 4	2.4	4.0
3 1 5	15.8	13.9
3 1 7	8.2	5.1
3 2 0	29.7	25.7
3 2 1	23.0	26.6
3 2 2	21.8	21.6
3 2 3	9.1	13.5
3 2 4	15.4	12.7
3 2 6	7.6	5.2
3 2 8	2.5	1.6
3 3 0	61.7	48.4
3 3 1	13.3	14.1
3 3 2	33.6	36.0
3 3 3	14.7	13.1
3 3 4	16.4	17.0
3 3 5	8.4	6.7
3 3 6	6.6	5.8
3 3 7	3.3	1.9
3 4 0	119.5	87.8
3 4 1	43.9	38.8
3 4 2	68.6	70.0
3 4 3	21.3	23.4
3 4 4	36.9	37.4
3 4 5	9.4	9.6
3 4 6	18.0	14.3
3 4 7	3.2	2.6
3 5 0	33.8	23.2
3 5 1	26.3	22.5
3 5 2	18.1	18.5
3 5 3	12.6	13.9
3 5 4	7.5	9.8
3 6 0	23.8	15.2
3 6 1	32.3	27.4
3 6 2	15.0	16.4
3 6 3	14.2	18.2
3 6 4	10.6	13.1
3 7 0	18.5	12.6
3 7 1	32.0	28.8
3 7 2	10.5	11.2
3 7 3	19.3	19.7
3 7 4	5.9	7.9
3 8 0	5.7	8.4
3 8 1	7.0	6.4
3 8 3	7.6	4.7
3 9 0	4.4	2.0
3 9 1	20.1	15.2
3 9 3	11.1	10.7
3 10 0	13.7	11.4
3 10 2	9.4	9.3
3 10 3	3.0	3.1
3 10 4	4.0	5.3
3 11 0	10.3	9.7
4 0 0	8.5	16.8
4 0 1	27.1	27.0
4 0 2	4.6	7.3
4 0 4	2.4	1.7
4 0 5	4.6	6.1
4 1 0	13.6	21.7
4 1 1	20.5	26.3
4 1 2	7.8	14.9
4 1 3	9.6	12.3
4 1 4	3.4	6.7
4 2 0	50.7	40.0
4 2 1	64.3	68.4
4 2 2	32.3	34.7
4 2 3	39.5	39.4
4 2 4	17.5	20.0
4 2 5	19.3	15.3
4 2 6	7.6	7.4
4 2 7	7.4	3.9
4 3 0	124.5	105.5
4 3 1	36.2	39.0
4 3 2	74.1	80.7
4 3 3	26.6	28.9
4 3 4	31.5	40.2
4 3 5	15.4	14.6
4 3 6	19.6	14.8
4 3 7	5.1	5.1
4 3 8	5.8	4.2
4 4 0	59.1	50.8
4 4 1	11.6	5.5
4 4 2	28.7	36.8
4 4 3	3.4	3.6
4 4 4	13.3	15.8
4 4 8	3.9	1.4
4 5 0	52.9	37.2
4 5 1	24.1	19.0
4 5 2	30.4	30.3
4 5 3	6.5	8.9
4 5 4	16.1	16.7
4 6 0	25.2	22.9
4 6 1	39.7	40.7
4 6 2	14.6	19.6
4 6 3	25.9	26.9
4 6 4	7.6	11.8
4 7 1	29.0	28.1
4 7 3	18.1	21.9
4 7 4	3.1	4.1
4 8 0	14.1	11.0
4 8 1	12.7	8.1
4 8 2	6.5	8.5
4 8 4	3.1	3.4
4 9 1	25.8	23.1
4 9 3	12.5	14.3
4 10 0	15.8	10.9
4 10 1	18.1	16.3
4 10 2	7.6	8.2
4 10 3	6.2	11.4
4 11 0	14.5	12.8
5 1 0	30.3	21.8
5 1 1	51.1	54.8
5 1 2	18.5	19.7
5 1 3	23.0	27.0
5 1 4	12.8	12.4
5 1 5	8.0	7.8
5 1 6	5.7	5.3
5 2 0	19.5	23.0
5 2 1	39.7	41.3
5 2 2	15.3	19.7
5 2 3	21.5	23.8
5 2 4	12.0	12.5
5 2 5	11.5	10.3
5 2 6	7.3	6.0
5 2 7	4.6	3.9
5 2 8	2.4	2.3
5 3 0	65.9	48.9
5 3 1	20.5	25.7
5 3 2	37.0	38.0
5 3 3	13.5	14.6
5 3 4	18.7	19.7
5 3 5	7.6	5.2
5 3 6	7.7	7.6
5 4 0	80.7	73.5
5 4 1	53.4	52.7
5 4 2	49.4	56.6
5 4 3	33.8	34.4
5 4 4	27.7	28.0
5 4 5	17.4	15.7
5 4 6	12.2	10.1
5 4 7	5.6	5.3
5 5 0	33.6	27.6
5 5 1	22.2	16.1
5 5 2	19.7	22.6
5 5 3	11.0	11.1
5 5 4	10.4	12.6
5 6 0	18.8	11.0
5 6 2	7.8	8.1
5 6 3	2.5	5.7
5 6 4	3.1	3.2
5 7 1	14.8	8.9
5 7 3	7.5	6.8
5 8 0	8.0	7.7
5 8 2	4.6	6.0
5 9 0	9.9	9.6
5 9 1	13.8	15.8
5 9 2	5.9	8.0
5 9 3	9.2	10.8
5 9 4	3.9	4.6
5 10 0	8.1	3.8
5 10 2	5.7	4.5
5 10 3	4.5	4.2
5 11 0	12.3	10.7
6 0 0	34.3	21.6
6 0 1	16.1	15.5
6 0 2	11.2	17.1
6 0 3	8.4	9.8
6 0 4	5.6	8.1
6 0 5	4.8	4.2
6 0 6	3.6	2.1
6 1 0	55.0	50.5
6 1 1	31.7	35.2
6 1 2	29.4	37.3
6 1 3	13.0	19.6
6 1 4	14.5	17.5
6 1 6	4.7	6.1
6 2 0	110.0	101.0
6 2 1	11.9	12.4
6 2 2	59.9	73.7
6 2 3	8.0	8.5
6 2 4	31.6	32.3
6 2 5	4.2	4.2
6 2 6	11.1	9.5
6 2 8	3.2	1.8
6 3 0	56.1	42.4
6 3 1	99.1	99.3
6 3 2	26.4	33.3
6 3 3	52.9	60.3
6 3 4	15.4	17.6
6 3 5	29.1	25.6
6 3 6	5.9	7.0
6 3 7	9.3	8.5
6 3 8	2.3	2.2
6 4 0	21.2	22.2
6 4 2	14.4	19.6
6 4 4	8.5	11.9
6 5 0	11.1	8.2
6 5 1	23.0	17.8
6 5 2	4.7	5.8
6 5 3	11.0	13.6
6 6 1	13.7	14.6
6 6 3	5.9	9.5
6 6 4	3.1	4.8
6 7 0	21.8	18.5
6 7 1	19.8	18.8
6 7 2	11.8	14.6
6 7 3	9.8	11.4
6 7 4	6.1	7.1
6 8 0	24.8	17.6
6 8 1	22.9	22.1
6 8 2	13.7	14.5
6 8 3	10.8	14.4
6 8 4	6.1	8.1
6 9 0	19.4	14.2
6 9 1	12.5	9.0
6 9 2	9.8	11.5
6 9 3	8.3	10.4
6 9 4	5.3	6.1
6 10 0	13.5	10.4
6 10 2	8.3	8.9
7 1 0	53.5	49.9
7 1 1	9.6	6.3
7 1 2	31.0	38.3
7 1 3	5.3	7.8
7 1 4	17.4	18.8
7 1 6	7.5	6.3
7 2 0	38.6	29.2
7 2 1	58.3	56.3
7 2 2	18.1	23.7
7 2 3	31.6	37.0
7 2 4	9.6	13.1
7 2 5	16.5	17.4
7 2 6	3.1	5.1
7 2 7	6.9	6.3
7 3 0	31.9	21.1
7 3 1	30.7	36.3
7 3 2	15.7	17.3
7 3 3	14.6	20.0
7 3 4	9.6	9.9
7 3 5	4.8	6.5
7 3 6	5.4	4.2
7 3 8	2.2	1.3
7 4 0	43.5	31.1
7 4 1	36.6	29.3
7 4 2	17.5	23.6
7 4 3	19.5	21.4
7 4 4	6.6	10.7
7 4 5	10.8	11.4
7 4 7	4.9	4.6
7 5 0	22.1	14.1
7 5 1	25.3	24.8
7 5 2	11.1	10.9
7 5 3	14.6	17.4
7 5 4	5.2	5.2
7 6 0	6.2	5.0
7 6 1	32.5	29.7
7 6 2	4.5	5.3
7 6 3	16.0	19.4
7 6 4	3.1	4.4
7 7 0	25.0	18.2
7 7 2	13.6	14.7
7 7 4	7.8	7.9
7 8 0	7.1	5.8
7 9 0	18.7	16.8
7 9 2	10.8	14.4
7 9 4	6.5	8.9
7 10 0	11.0	9.2
7 10 1	17.4	13.2
7 10 2	5.0	7.1
7 10 3	7.2	8.7
8 0 0	4.9	1.2
8 0 1	50.8	39.0
8 0 2	8.7	6.4
8 0 3	22.7	24.6
8 0 4	10.3	9.4
8 0 5	8.9	11.0
8 0 6	5.0	6.1
8 1 0	5.2	2.7
8 1 1	33.3	30.0
8 1 3	16.0	21.9
8 1 5	5.8	11.7
8 2 0	27.2	16.3
8 2 1	5.1	3.7
8 2 2	17.8	21.6
8 2 3	2.5	2.9
8 2 4	11.5	17.3
8 2 6	5.4	7.6
8 2 8	2.8	1.9
8 3 0	9.6	6.8
8 3 1	66.8	58.4
8 3 2	7.1	6.2
8 3 3	31.3	39.8
8 3 4	4.0	4.4
8 3 5	16.2	19.0
8 3 7	6.4	6.5
8 4 0	19.1	13.3
8 4 1	7.2	9.2
8 4 2	8.4	9.3
8 4 3	3.5	8.4
8 4 4	3.2	3.4
8 5 0	27.2	24.4
8 5 1	9.4	5.2
8 5 2	16.6	19.5
8 5 3	7.4	7.3
8 5 4	8.7	10.0
8 6 0	23.3	18.5
8 6 1	33.1	31.0
8 6 2	11.1	14.9
8 6 3	17.1	20.9
8 6 4	4.1	7.9
8 7 1	23.2	21.9
8 7 2	11.2	3.5
8 7 3	13.2	16.5
8 8 0	50.9	48.1
8 8 4	17.2	21.2
8 9 1	26.6	34.0
8 10 1	12.3	11.2
9 1 0	25.5	3.5
9 1 1	37.8	32.8
9 1 2	3.2	3.5
9 1 3	20.8	24.8
9 1 4	4.2	2.5
9 1 5	8.3	12.9
9 1 7	4.9	4.6
9 2 0	51.5	35.9
9 2 1	45.3	39.6
9 2 2	28.9	30.0
9 2 3	21.9	25.6
9 2 4	14.1	17.4
9 2 5	8.2	11.7
9 2 6	6.3	7.0
9 2 7	4.8	4.1
9 2 8	2.7	1.9
9 3 0	13.0	8.3
9 3 1	12.2	14.6
9 3 2	7.7	6.9
9 3 4	4.0	4.3
9 4 0	10.1	5.4
9 4 1	10.3	8.8
9 4 2	8.5	9.3
9 4 3	5.2	7.1
9 4 4	6.1	8.7
9 4 5	3.4	4.4
9 4 6	3.9	4.3
9 4 7	2.5	2.0
9 6 0	25.9	19.0
9 6 1	26.8	26.1
9 6 2	15.9	16.4
9 6 3	13.9	18.1
9 6 4	8.7	10.2
9 7 0	26.0	19.1
9 7 1	31.5	32.0
9 7 2	13.0	15.5
9 7 3	16.7	22.2
9 7 4	6.4	8.2
9 8 1	24.7	10.6
9 8 3	3.7	7.5
9 9 0	10.4	6.6
9 9 1	14.7	14.0
9 9 2	4.2	6.0
9 9 3	15.7	10.3
9 10 0	10.3	8.1
10 0 0	62.1	44.3
10 0 1	78.9	64.3
10 0 2	37.6	38.1
10 0 3	38.8	44.0
10 0 4	16.7	23.2
10 0 5	17.3	21.3
10 0 6	6.8	9.6
10 0 7	9.6	7.5
10 1 0	77.3	62.3
10 1 1	25.9	22.7
10 1 2	43.5	48.6
10 1 3	10.5	14.2
10 1 4	19.3	24.2
10 1 6	8.0	7.9
10 2 0	52.4	43.1
10 2 1	5.1	3.7
10 2 2	28.1	32.2
10 2 3	3.3	2.5
10 2 4	11.3	14.0
10 2 6	2.9	3.7
10 2 7	2.9	1.1
10 3 0	37.8	24.5
10 3 1	27.2	23.7
10 3 2	19.4	19.9
10 3 3	11.5	13.2
10 3 4	11.6	11.1
10 3 5	4.8	4.1
10 3 6	5.4	4.6
10 4 0	27.6	21.6
10 4 1	26.8	26.4
10 4 2	19.3	19.0
10 4 3	13.4	16.9
10 4 4	9.1	12.3
10 4 5	5.9	7.3
10 4 6	5.0	5.4
10 4 7	2.2	2.3
10 5 0	27.0	21.1
10 5 1	11.9	14.3
10 5 3	6.0	10.0
10 5 4	8.6	10.0
10 6 0	9.2	7.1
10 6 1	19.5	17.6
10 6 2	4.7	5.6
10 6 3	11.5	13.6
10 8 0	8.6	5.6
10 8 1	17.0	23.7
10 8 2	4.0	4.9
10 8 3	15.3	16.7
10 9 0	11.7	8.6
10 9 2	5.4	7.6
10 9 3	9.0	7.7
11 1 0	29.9	23.8
11 1 1	49.0	49.4
11 1 2	19.4	19.2
11 1 3	27.2	29.9
11 1 4	9.6	10.6
11 1 5	11.9	12.3
11 1 6	4.3	4.2
11 1 7	6.0	4.2
11 2 0	27.6	22.8
11 2 1	28.4	23.6
11 2 2	17.3	17.8
11 2 3	13.3	15.5
11 2 4	9.2	8.9
11 2 5	6.4	6.8
11 2 6	4.8	3.2
11 2 7	2.7	2.1
11 3 0	16.8	15.0
11 3 1	18.7	15.3
11 3 2	10.4	12.1
11 3 3	9.1	10.0
11 3 4	3.7	6.3
11 3 5	4.7	4.4
11 4 0	35.9	29.4
11 4 1	4.0	7.9
11 4 2	22.6	23.1
11 4 4	10.8	11.5
11 4 6	6.0	3.8
11 5 0	29.0	25.6
11 5 1	8.0	5.0
11 5 2	16.9	21.0
11 5 3	5.2	5.0
11 5 4	8.9	11.8
11 6 0	19.2	13.9
11 6 2	10.5	10.5
11 6 4	4.6	4.4
11 7 0	19.0	14.5
11 7 1	18.2	19.3
11 7 2	10.3	12.3
11 7 3	12.3	13.8
11 7 4	5.9	7.6
11 9 0	10.6	9.0
11 9 1	11.1	10.8
11 9 2	4.7	7.4
11 9 3	2.4	7.4
12 0 0	74.1	54.2
12 0 1	36.2	33.0
12 0 2	40.6	42.5
12 0 3	21.3	23.7
12 0 4	21.1	21.6
12 0 5	9.5	12.7
12 0 6	9.3	8.2
12 0 7	5.9	5.2
12 1 0	8.4	4.5
12 1 1	29.3	24.7
12 1 2	5.3	7.3
12 1 3	16.1	14.7
12 1 4	3.1	7.0
12 1 5	4.5	5.2
12 2 0	5.9	5.5
12 2 1	35.0	28.9
12 2 2	4.3	7.5
12 2 3	19.2	20.4
12 2 4	2.5	6.3
12 2 5	11.1	10.5
12 2 7	4.3	3.9
12 3 0	6.5	4.0
12 3 1	22.8	18.0
12 3 2	4.7	3.9
12 3 3	12.0	12.7
12 3 4	2.8	2.7
12 3 5	7.2	6.3
12 4 0	49.2	36.0
12 4 2	25.8	28.3
12 4 4	11.8	14.1
12 4 6	4.8	4.8
12 5 0	27.7	23.7
12 5 1	18.7	19.3
12 5 2	15.3	19.2
12 5 3	8.7	10.5
12 5 4	7.5	10.1
12 6 0	23.4	19.2
12 6 1	27.4	29.0
12 6 2	13.2	16.6
12 6 3	14.1	19.2
12 6 4	7.8	10.5
12 7 0	11.9	10.0
12 7 2	5.7	8.0
12 8 0	13.2	10.3
12 8 1	6.1	8.0
12 8 2	8.4	8.8
12 9 0	12.8	13.5
13 1 0	37.2	24.4
13 1 1	21.3	16.3
13 1 2	22.2	20.1
13 1 3	16.4	15.1
13 1 4	11.4	11.6
13 1 5	9.1	9.6
13 1 6	5.9	4.8
13 1 7	3.9	4.0
13 2 0	15.3	11.7
13 2 2	8.6	9.6
13 2 4	4.1	5.5
13 3 0	26.0	21.8
13 3 1	5.8	3.8
13 3 2	16.6	17.6
13 3 3	4.2	4.5
13 3 4	8.9	9.4
13 3 6	4.3	3.3
13 4 0	7.7	5.7
13 4 1	35.4	35.2
13 4 2	5.5	5.4
13 4 3	24.5	23.7
13 4 4	2.9	3.9
13 4 5	13.1	10.9
13 5 0	26.4	21.2
13 5 1	14.5	17.2
13 5 2	14.7	16.9
13 5 3	7.3	11.5
13 5 4	6.7	8.7
13 7 0	20.3	15.9
13 7 2	11.9	13.6
13 7 4	6.1	8.9
14 0 0	27.3	21.6
14 0 1	20.9	21.6
14 0 2	20.7	20.8
14 0 3	13.5	14.0
14 0 4	15.2	15.1
14 0 5	4.5	6.1
14 0 6	9.1	7.3
14 1 0	22.4	18.4
14 1 1	5.6	9.0
14 1 2	13.2	14.8
14 1 4	6.2	7.7
14 2 0	15.7	9.8
14 2 1	5.9	6.7
14 2 2	11.3	9.7
14 2 4	7.7	7.5
14 2 6	4.7	3.8
14 3 0	33.8	27.2
14 3 1	14.9	13.1
14 3 2	21.9	22.3
14 3 3	12.1	10.8
14 3 4	11.9	13.1
14 3 5	8.8	6.6
14 3 6	6.0	5.6
14 5 1	28.6	26.1
14 5 3	15.8	19.3
14 6 0	38.9	31.5
14 6 2	19.6	25.5
14 6 4	9.9	13.8
15 1 0	19.8	15.8
15 1 2	12.9	13.4
15 1 4	7.4	8.3
15 1 6	4.0	3.8
15 2 0	11.9	3.1
15 2 1	11.2	8.2
15 2 3	6.5	5.8
15 2 5	3.4	3.0
15 3 0	6.9	4.9
15 3 1	12.3	9.1
15 3 2	3.4	3.9
15 3 3	8.3	7.5
15 3 5	4.3	4.4
15 4 0	25.7	24.4
15 4 1	18.1	17.9
15 4 2	18.1	21.2
15 4 3	11.5	12.6
15 4 4	11.8	13.6
15 4 5	6.9	6.3
15 5 0	11.9	8.4
15 5 1	17.2	17.4
15 5 2	5.7	7.5
15 5 3	7.1	10.9
15 5 4	4.7	4.9
15 6 1	7.9	6.6
15 6 3	5.2	5.0
15 7 0	16.3	11.0
15 7 1	6.0	1.7
15 7 2	7.9	9.5
16 0 0	37.4	37.2
16 0 1	8.9	5.2
16 0 2	25.4	29.2
16 0 3	5.6	4.3
16 0 4	12.5	14.1
16 0 5	3.6	2.8
16 1 0	7.5	7.4
16 1 1	18.8	19.4
16 1 3	10.1	12.2
16 1 5	3.7	4.9
16 2 0	7.8	5.5
16 2 1	22.9	18.7
16 2 2	6.4	5.8
16 2 3	12.9	12.2
16 2 4	3.1	4.2
16 2 5	6.6	5.1
16 3 0	38.6	31.0
16 3 2	26.8	25.8
16 3 4	15.0	15.0
16 4 1	9.4	11.0
16 4 3	5.5	7.5
16 5 0	6.7	3.7
16 5 1	15.8	15.4
16 5 3	9.3	9.4
16 5 4	3.0	3.0
16 6 0	5.3	2.7
16 7 0	11.5	10.4
17 1 1	22.8	22.4
17 1 2	8.7	2.9
17 1 3	13.1	13.8
17 1 5	5.3	5.3
17 2 0	30.6	23.7
17 2 1	7.9	7.5
17 2 2	19.4	18.8
17 2 3	4.2	5.0
17 2 4	9.9	9.5
17 3 0	6.2	6.6
17 3 2	3.6	5.4
17 4 0	14.2	13.2
17 4 2	9.3	10.6
17 4 4	6.6	5.6
17 5 0	6.4	5.6
17 6 0	13.7	13.1
18 0 1	20.3	18.4
18 0 3	12.4	12.9
18 1 0	12.6	9.3
18 1 2	8.5	8.0
18 1 4	3.9	4.9
18 2 0	10.8	9.7
18 2 1	12.7	9.6
18 2 2	6.5	7.0
18 2 3	8.0	6.8
18 2 4	2.7	2.3
18 3 0	15.7	13.4
18 3 1	8.8	8.8
18 3 2	10.2	11.5
18 3 3	4.3	4.9
18 3 4	5.4	7.3
18 4 1	6.7	7.9
18 4 3	3.7	5.3
18 5 0	8.1	4.1
19 1 0	13.4	12.7
19 1 1	5.2	3.3
19 1 2	8.3	10.7
19 1 3	4.4	4.0
19 2 0	4.6	4.4
19 2 1	9.7	9.3
19 2 2	4.0	5.2
19 2 3	5.6	6.0
19 3 0	5.1	4.5
19 3 2	3.0	3.9
19 4 0	10.3	7.2
19 4 2	7.6	7.1
20 0 0	12.1	8.7
20 0 1	14.8	15.9
20 1 0	6.6	8.5
20 1 2	4.3	6.4
20 2 0	6.3	4.8
20 2 1	11.8	12.6
20 2 2	6.7	6.0
20 3 0	13.6	11.3

TABLE IV

BOND LENGTHS (Å.)

Atoms	Distances	Atoms	Distances
NiS_1	2.168 (11)	C_3N_1	1.44 (6)
NiS_2	2.146 (11)	C_2N_2	1.51 (4)
NiN_1	1.86 (2)	C_6N_1	1.33 (4)
NiN_2	1.85 (3)	C_5N_2	1.34 (4)
C_1S_1	1.82 (5)	C_6H_8	1.47 (6)
C_4S_2	1.82 (5)	C_5C_7	1.51 (7)
C_1C_2	1.35 (6)	C_5C_6	1.44 (5)
C_3C_4	1.52 (7)		

TABLE V

BOND ANGLES

Atoms	Angle, deg.	Atoms	Angle, deg.
S_1NiS_2	97.3 (4)	$C_2C_1S_1$	119 (3)
		$C_3C_4S_2$	114 (3)
N_1NiN_2	82.9 (11)		
		$N_1C_3C_4$	112 (3)
N_1NiS_1	172.7 (9)	$N_2C_2C_1$	113 (3)
N_2NiS_2	172.6 (9)		
		$C_3N_1C_6$	120 (3)
N_1NiS_2	89.8 (9)	$C_2N_2C_5$	125 (3)
N_2NiS_1	90.0 (9)		
		$N_1C_6H_5$	111 (3)
NiS_1C_1	96 (2)	$N_2C_5C_6$	113 (3)
NiS_2C_4	100 (2)		
		$N_1C_6C_8$	122 (3)
NiN_1C_3	123 (2)	$N_2C_5C_7$	123 (3)
NiN_2C_2	120 (2)		
		$C_5C_6C_8$	126 (3)
NiN_1C_6	117 (2)	$C_6C_5C_7$	123 (3)
NiN_2C_5	115 (2)		

selected portions of the molecule. The only satisfactory plane through a five-membered ring was through the ring containing the two nitrogen atoms. The equation to this plane is

$$-0.0316X + 0.0092Y + 0.9995Z = 1.6954$$

The departures from this plane are Ni, +0.009; N_1, −0.011; N_2, −0.009; C_5, +0.004; C_6, +0.006; C_7, +0.174; C_8, +0.152 Å.

It will be observed that none of the five atoms in the ring departs significantly from the plane, which is evidence for the delocalization of electrons in this chelate ring. The two methyl groups, however, both lie out of this plane and on the same side. No suitable planes can be constructed through the other two five-membered rings without significant departures of the methylene groups. Accordingly, planes through N_1–Ni–S_2 and N_2–Ni–S_1 were constructed. The equations of these planes and the departures of the carbon atoms are

N_2NiS_2: $-0.0482X + 0.0129Y + 0.9987Z = 1.6855$

C_3, +0.161; C_4, −0.032 Å.

N_3NiS_1: $-0.0604X - 0.0202Y + 0.9980Z = 1.6509$

C_1, +0.348; C_2, −0.124 Å.

All van der Waals contacts less than 4 Å. were calculated. There are 28 such distances, the two shortest being 3.48 Å. between N_2 and C_4 and 3.54 Å. between C_4 and C_5. The closest approaches to a nickel atom from a neighboring molecule are 3.65 Å. for C_3 and 3.71 Å. for N_1. It can therefore be concluded that the nickel atom is four-coordinate in this complex in the solid state.

Acknowledgment.—The authors are grateful to G. A. Jeffrey and R. Shiono for computer programs and to R. Bates for adapting these programs to our requirements. P. J. W. thanks the National Science Foundation for a Fellowship. Financial assistance from the U. S. Atomic Energy Commission is gratefully acknowledged.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Molecular Structure of the Dimer of Bis(*cis*-1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate)cobalt

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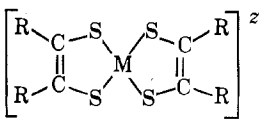
Received August 12, 1965

A three-dimensional X-ray diffraction study has verified the dimeric structure of $(CF_3)_2C_2S_2CoS_2C_2(CF_3)_2$, which has previously been shown to be diamagnetic and dimeric in solution. Dimerization occurs through the unusual Co–S linkages of 2.38 Å. in length which require the Co atom to be 0.37 Å. out of the plane of the S_4 group within each monomer unit. One dimeric molecule is present in the unit cell having parameters $a = 7.98$, $b = 9.89$, $c = 10.12$ Å., $\alpha = 103.0$, $\beta = 98.5$, and $\gamma = 100.8°$. The space group is $P\bar{1}$.

The discovery first by Schrauzer and Mayweg[2] and by Gray, *et al.*,[3] of *cis*-1,2-disubstituted ethylene-1,2-dithiolate complexes



(where z is 0, −1, or −2, R is CF_3, CN, or C_6H_5, and M is a transition metal) has been followed by extensive

(1) National Science Foundation Predoctoral Fellow, 1963–1965.
(2) G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).
(3) H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962).