The Crystal and Molecular Structure of Tetrakisthiocyanatobis-(triphenylphosphine)cobalt(II)mercury(II) in Dimer Form, $[CoHg(SCN)_4\{(C_6H_5)_3P\}_2]_2$

Hisashi KINOSHITA,* Mamoru SHIMOI,† and Akira OUCHI†

Department of Chemistry, Faculty of Liberal Arts, Shizuoka University, Ohya, Shizuoka-shi 422

†*Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153*

(Received November 15, 1984)

The crystal and molecular structure of the title metal complex was determined by the X-ray diffraction method. The crystal is triclinic, with the space group $P\bar{1}$, $Z=1$, $a=11.934(2)$, $b=14.642(9)$, $c=11.801(6)$Å, $\alpha=90.41(5)$, $\beta=94.04(2)$, and $\gamma=83.82(2)°$. The final R value for 6928 reflections is 0.065. The cobalt(II) atom is in a tetrahedral geometry, ligated by four nitrogen atoms of the thiocyanato (SCN) ligands, while the mercury(II) atom is in a trigonal-bipyramidal geometry, where two phosphorus atoms of both the triphenylphosphine ligands bond axially and three sulfur atoms of SCN's equatorially; however, these Hg-S bonds are very long. Thus, the pairs of cobalt(II) and mercury(II) atoms are linked by one SCN bridge, forming a sixteen-membered ring of $Co_2Hg_2(SCN)_4$, and this ring is linked with the next ones on both sides in the a-axis direction with two longer bondings.

Tetrakisthiocyanatocobalt(II)mercury(II), $CoHg(SCN)_4$ (**1**), is known as a "diamond-like" three-dimensional polymeric type of complex where each metal atom is linked with four metal atoms of another kind by thiocyanate (SCN) bridges. Its structure was clarified by Jeffery,[1] and its characteristic structure was discussed by Wells.[2a] Some of its Lewis-base adducts were also synthesized,[3,4] and the structures of the pyridine (py) adduct, $CoHg(SCN)_4(py)_2$,[5] and of *N,N*-dimethylformamide (dmf), $CoHg(SCN)_4(dmf)_2$,[6] were also elucidated. In both of the adducts, the cobalt(II) atom is in the octahedral geometry, and the mercury(II) atom, in the tetrahedral configuration, although the three-dimensional network by the SCN bridges was retained. Because of the octahedral geometry of cobalt(II) in the adducts, they are reddish in color. On the other hand, Makhija has also obtained the title complex, which is deep blue in color; this fact shows that it contains tetrahedral cobalt(II) atoms.[4] Mainly on the base of infrared absorption spectral considerations, Makhija proposed a monomer structure for it, where a cobalt atom and a mercury atom are bridged by two SCN ligands. According to his formula, the cobalt(II) atom is bonded with two phosphorus atoms of triphenylphosphine (Ph_3P) ligands as well as two nitrogen atoms of SCN ions while the mercury(II) atom is ligated by four sulfur atoms of SCN ions. This formula was not yet been proved by the single crystal X-ray diffraction method, and the former concept receives some support even now.[3,7,8] Although cobalt(II) complexes including phosphine derivatives have been reported elsewhere,[9-11] as the ligands are soft ones, they may prefer to bond with the mercury(II) atom, which is softer than cobalt(II).[12] The observed affinity of Ph_3P in the title complex seems to be higher than those of dmf or *N,N*-dimethylacetamide (dma). When the dmf or dma adduct $CoHg(SCN)_4L_2$ (where L=dmf or dma) in its solid phase was left standing in an acetonitrile solution of Ph_3P, they turned into the title Ph_3P adduct rapidly and the base was removed, on the other hand, when the title complex was stirred in an acetonitrile solution of dmf or dma, no substitution reaction occurred. Therefore, we were not able to believe the traditional formula; we have now determined its structure by the single-crystal X-ray diffraction method.

Experimental

Synthesis of Tetrakisthiocyanatobis(triphenylphosphine)-cobalt(II)mercury(II) (2). Although the title complex was synthesized by Makhija from the tetrahydrofuran (thf) adduct of **1**, $CoHg(SCN)_4(thf)_2$, which had itself been obtained from cobalt(II) and mercury(II) thiocyanates and thf, we could obtain the title complex **2**, easier by the following method.

The complex, **1**, obtained by Figgis' method,[13] was finely powdered (2.0 g, 4.1 mmol) and then poured into 20 cm^3 of an acetonitrile solution containing Ph_3P (2.4 g, 9.2 mmol), after which the mixture was stirred for 6 h at the ambient temperature. The addition reaction occurred rapidly, and the solid product thus obtained was filtered off, washed by acetonitrile, and dried on silica-gel in a vacuum desiccator. Yield, 3.5 g, (85%). By the gradual evaporation of the filtrate, some additional crop was obtained in larger-crystal grains, some of which were used for the X-ray diffraction measurement. Anal. of the main and the additional crops: ($Co_2Hg_2C_{80}H_{60}N_8P_4S_8$) Co, C, H, N. The infrared and visible absorption spectra of the product were similar to those reported by Makhija.[4]

Intensity-data Collection. A crystal with the dimensions of 0.3×0.3×0.4 mm^3 was used for the measurement without shaping. The crystallographic data are: $Co_2Hg_2C_{80}H_{60}N_8P_4S_8$, F.W.=2032.87, triclinic, space group $P\bar{1}$, $Z=1$, $a=11.934(2)$, $b=14.642(9)$, $c=11.801(6)$ Å, $\alpha=90.41(5)$, $\beta=94.04(2)$, $\gamma=83.82(2)°$, $V=2045(1)$ Å^3, $D_m=1.64(3)$, $D_x=1.65$ g cm^{-3}, $\mu(Mo\,K\alpha)=4.56$ mm^{-1}. The reflections within the range of $3°<2\theta<50°$ were collected on a Rigaku AFC-6A automated four-circle X-ray diffractometer with graphite monochromated Mo $K\alpha$ radiation, the θ—2θ scan technique being employed (scan speed, 4° min^{-1} in 2θ; scan width, $1.20+0.5\tan\theta$). The crystal was stable during the exposure to X-rays. Of the 7243 independent reflections thus obtained, 6928 with $|F_o|>3\sigma(|F_o|)$ were selected and used for the structure determination. The intensities were corrected for the Lorentz and polarization factors, but no correction was

made for absorption and extinction.

Structure Determination. The structure was solved by the heavy-atom method. The positions of the cobalt(II), mercury(II), and some sulfur and phosphorus atoms were deduced from a three-dimensional Patterson map, while the other non-hydrogen atoms were located by means of successive Fourier syntheses. Their positional, isotropic, and then anisotropic thermal parameters were refined by the block-diagonal least-squares method. The positions of all the non-hydrogen atoms were found. All the hydrogen atoms were fixed at calculated positions with B_{iso}=10.0 (the C–H length was assumed to be 1.08 Å). In the last cycle of the refinement, all the parameter-shifts of the non-hydrogen atoms were less than $\sigma/3$.

All the calculations were carried out on a HITAC M-200H computer at the Computer Center of The University of Tokyo, using the local version of the UNICS program system.[14] The atomic scattering factors were taken from the tables.[15]

Results and Discussion

The final atomic parameters of non-hydrogen atoms are listed in Table 1,[16] while the bond lengths and bond-angles are tabulated in Table 2.[16] The perspective drawings around the cobalt(II) and mercury(II) atoms, together with the numbering scheme, are shown in Figs. 1 and 2. The crystal packing diagram is shown in Fig. 3, while the schematic drawing to show the bondings in a unit cell is in Fig. 4.

The cobalt(II) atom is tetra-coordinated and is in a tetrahedral geometry, where four nitrogen atoms of four SCN ions are ligated. Although S(3) of the SCN does not bond with any metal atom, the other three SCN ligands bridge to three mercury(II) atoms, as is shown in Fig. 4. The average Co–N bond length is 1.954 Å, which is not much different from the sum of the respective atomic radii (Co=1.25, N=0.70 Å).[17] The average Co–N–C angle is 173.48°, and these atoms are almost collinear, although the deviation from 180° is a little larger than that of **1** (178.66°).[1]

The mercury(II) atom is bonded with two phosphorus atoms of the respective Ph_3P ligands in an approximately collinear geometry (P–Hg–P=166.63(10)°), and the average Hg–P bond length is 2.430 Å, which is about the same as the sum of the two atomic radii (Hg=1.50, P=1.10 Å).[17] Three sulfur atoms of the SCN ligands take their positions about perpendicular to the P–Hg–P axis, and the sulfur atoms as well as the central metal atom are almost on one plane: the average positional deviation of the atoms from the plane is 0.043 Å (maximum 0.085 Å for Hg). The S–Hg–P angles are between 81.4 to 100.2° (90.6° on the average). The S(1)–Hg–S(2^i) angle (101.0°) is a little smaller than the other two (133.6 and 125.0°). From these angular observations, the geometry around the mercury(II) atom is thought to be trigonal-bipyramidal; however, the bond lengths of Hg–S are long (Hg–S(1)=2.990(3), Hg–S(2^i)=2.745(4), and Hg–S(4^{ii})=3.323(4) Å), while the atomic radii of the two atoms are Hg=1.50 and S=1.04 Å.[17] In many mercury(II) compounds where the sulfur atom is ligated to the metal atom, the Hg–S bond length is found to be about 2.5 Å. Even in the related complexes, the normal values are shown to be writen

Table 1. Final atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (B_{eq}/Å^2), with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å$^{2a)}$
Co	7995(1)	3149(1)	6016(1)	4.5
Hg	3340.2(4)	2493.7(3)	4400.1(4)	3.6
S(1)	5286(3)	1097(2)	5071(3)	4.7
S(2)	5638(3)	5914(2)	5423(4)	6.0
S(3)	9320(4)	2648(4)	9816(4)	8.3
S(4)	10704(3)	2349(3)	3365(3)	5.4
C(1)	6183(9)	1832(7)	5379(9)	4.0
C(2)	6605(10)	5043(8)	5656(10)	4.4
C(3)	8851(10)	2812(8)	8532(11)	5.0
C(4)	9813(9)	2641(7)	4306(10)	3.9
N(1)	6829(8)	2332(6)	5620(9)	5.1
N(2)	7241(8)	4410(7)	5807(9)	5.1
N(3)	8528(8)	2926(8)	7586(9)	5.8
N(4)	9186(8)	2863(7)	4980(8)	4.9
P(1)	2687(2)	2414(2)	6297(2)	3.3
P(2)	3692(2)	2306(2)	2403(2)	3.6
C(11)	3274(9)	3344(7)	1591(9)	3.9
C(12)	2410(10)	3972(8)	1948(9)	4.4
C(13)	2131(11)	4799(9)	1383(11)	5.5
C(14)	2710(12)	5004(8)	490(11)	5.5
C(15)	3548(12)	4384(10)	105(11)	5.9
C(16)	3839(11)	3559(9)	678(10)	5.4
C(21)	5196(9)	2035(9)	2224(10)	4.8
C(22)	5884(11)	2720(11)	2477(13)	6.8
C(23)	7041(12)	2545(13)	2322(14)	8.3
C(24)	7464(11)	1729(11)	1941(14)	7.4
C(25)	6792(13)	1048(11)	1685(14)	7.9
C(26)	5625(10)	1206(9)	1840(11)	5.5
C(31)	2962(9)	1381(7)	1805(9)	3.9
C(32)	3038(10)	564(8)	2385(11)	5.0
C(33)	2474(11)	−167(9)	1987(11)	5.6
C(34)	1827(12)	−56(9)	962(12)	6.2
C(35)	1726(12)	734(10)	395(12)	6.5
C(36)	2289(11)	1478(9)	796(10)	5.2
C(41)	1896(9)	1440(7)	6407(8)	3.6
C(42)	2236(11)	644(8)	5841(11)	5.2
C(43)	1622(12)	−119(9)	5876(12)	6.2
C(44)	656(11)	−33(9)	6438(13)	6.4
C(45)	316(11)	767(10)	6966(14)	7.1
C(46)	909(10)	1504(9)	6980(12)	5.8
C(51)	1857(8)	3437(7)	6717(9)	3.8
C(52)	1656(10)	3586(9)	7832(10)	5.2
C(53)	1045(11)	4402(10)	8174(11)	6.3
C(54)	677(11)	5063(9)	7389(13)	6.1
C(55)	886(11)	4926(9)	6278(13)	6.0
C(56)	1472(10)	4119(8)	5935(10)	4.4
C(61)	3891(9)	2288(8)	7345(8)	3.9
C(62)	4575(10)	2996(9)	7420(9)	5.2
C(63)	5516(11)	2923(11)	8182(11)	6.6
C(64)	5766(11)	2164(11)	8867(11)	6.4
C(65)	5078(13)	1477(10)	8799(11)	6.9
C(66)	4109(11)	1529(8)	8036(10)	5.1

a) The isotropic temperature factors were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

TABLE 2. SELECTED BOND LENGTHS AND BOND ANGLES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond length	l/Å	Bond length	l/Å
Co-N(1)	1.962(10)	Co-N(2)	1.975(9)
Co-N(3)	1.934(14)	Co-N(4)	1.948(11)
Hg-S(1)	2.991(3)	Hg-S(2^{i})	2.745(4)
Hg-S(4^{ii})	3.322(4)	Hg-P(1)	2.429(4)
Hg-P(2)	2.432(4)	Co···Hg	5.920(2)
Co···Co^{i}	8.699(4)	Hg···Hg^{i}	8.768(4)
Co···Hg^{i}	6.421(4)	Hg···Co^{ii}	6.754(2)
S(1)-C(1)	1.619(11)	S(2)-C(2)	1.637(11)
S(3)-C(3)	1.589(16)	S(4)-C(4)	1.615(13)
C(1)-N(1)	1.140(15)	C(2)-N(2)	1.139(14)
C(3)-N(3)	1.16(2)	C(4)-N(4)	1.152(17)
P(1)-C(41)	1.804(11)	P(1)-C(51)	1.791(11)
P(1)-C(61)	1.823(12)	P(2)-C(11)	1.808(12)
P(2)-C(21)	1.822(11)	P(2)-C(31)	1.800(12)

Bond angle	ϕ/°	Bond angle	ϕ/°
N(1)-Co-N(2)	105.8(4)	N(1)-Co-N(3)	108.1(5)
N(1)-Co-N(4)	106.9(5)	N(2)-Co-N(3)	111.0(5)
N(2)-Co-N(4)	112.3(4)	N(3)-Co-N(4)	112.3(5)
S(1)-Hg-P(1)	89.58(10)	S(1)-Hg-P(2)	91.26(10)
P(1)-Hg-P(2)	166.65(12)	S(1)-Hg-S(2^{i})	101.01(9)
S(2^{i})-Hg-P(1)	100.22(11)	S(2^{i})-Hg-P(2)	92.71(11)
S(4^{ii})-Hg-P(1)	88.36(10)	S(4^{ii})-Hg-P(2)	81.41(10)
S(4^{ii})-Hg-S(1)	133.53(8)	S(4^{ii})-Hg-S(2^{i})	125.02(9)
Hg-S(1)-C(1)	95.8(4)	Hg-S(2^{i})-C(2^{i})	108.6(4)
Hg-S(4^{ii})-C(4^{ii})	111.2(5)	Hg-P(1)-C(41)	110.1(4)
Hg-P(1)-C(51)	113.8(4)	Hg-P(1)-C(61)	110.0(4)
Hg-P(2)-C(11)	112.5(4)	Hg-P(2)-C(21)	111.0(4)
Hg-P(2)-C(31)	109.8(4)	Co-N(1)-C(1)	177.4(10)
Co-N(2)-C(2)	165.4(9)	Co-N(3)-C(3)	178.5(13)
Co-N(4)-C(4)	173.0(10)	S(1)-C(1)-N(1)	178.0(11)
S(2)-C(2)-N(2)	176.9(10)	S(3)-C(3)-N(3)	178.7(15)
S(4)-C(4)-N(4)	178.9(12)		

Key to the symmetric operations: i, 1.0−x, 1.0−y, 1.0−z; ii, −1.0+x, y, z.

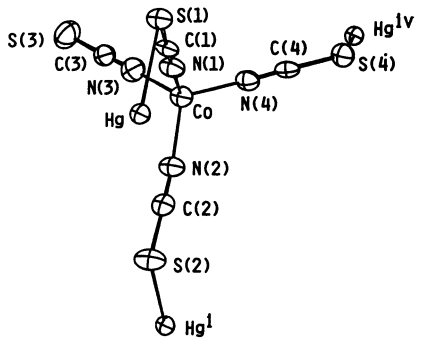

Fig. 1. Perspective drawing of the complex around the cobalt(II) atom with the numbering scheme (Key to the symmetric operations; i, 1.0−x, 1.0−y, 1.0−z; iv, 1.0+x, y, z).

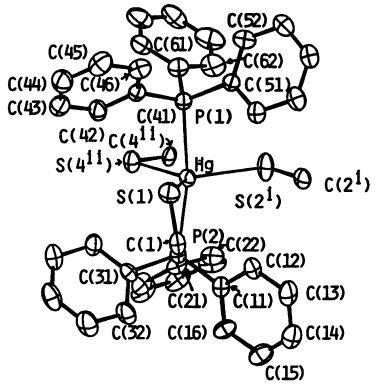

Fig. 2. Perspective drawing of the complex around the mercury atom with the numbering scheme (Key to the symmetric operations; i, 1.0−x, 1.0−y, 1.0−z; ii, −1.0+x, y, z).

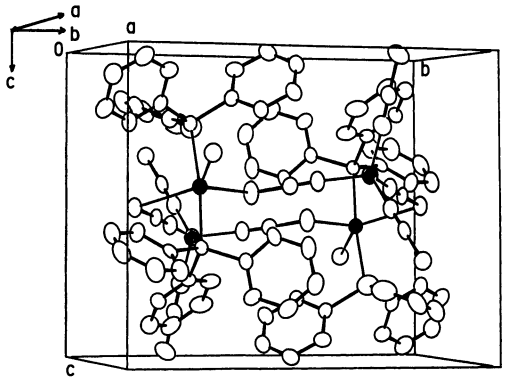

Fig. 3. Crystal packing diagram of the complex.

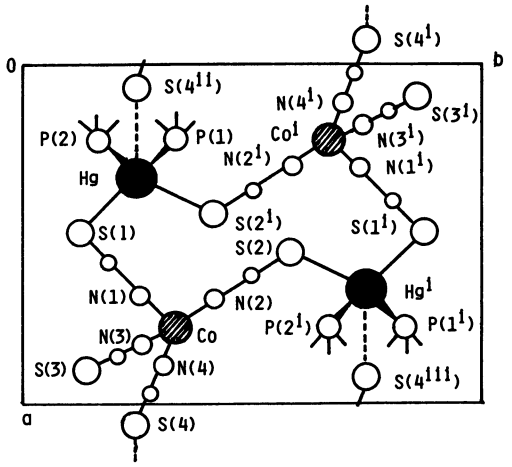

Fig. 4. Schematic presentation to show the bondings in a unit cell (Key to the symmetric operations; i, 1.0−x, 1.0−y, 1.0−z; ii, −1.0+x, y, z; iii, 2.0−x, 1.0−y, 1.0−z).

as follows: $CoHg(SCN)_4$, 2.558(4) Å;[1] $CoHg(SCN)_4(dmf)_2$, 2.539 Å on the average,[5] $CoHg(SCN)_4(py)_2$, 2.525 Å on the average;[6] and $Hg(SCN)_2(Ph_3P)$, 2.503 Å[18] and 2.528 Å[19] on the average.

Although there has been no report about such an elongated Hg-S bond as is found in this complex, it is a well-known fact that, in some multi-coordinated mercury(II) complexes, several groups of bond lengths are found;[2b] for example, in $HgSO_4 \cdot H_2O$, which is in about an octahedral geometry around the central metal atom, two Hg-O bond lengths of one axis are normal, while the other four equatorial Hg-O lengths are much longer.[20] As Ph_3P is a base which is softer than SCN,[12] it is not impossible that the Hg-P bonds take priority over the Hg-S bonds in the title complex; however, as the Hg-S bond has commonly been thought to be a typically strong bond, this kind of the long Hg-S bond has rarely been reported.

The trigonal-bipyramidal configuration of the ligating atoms around the central mercury(II) atom in its complexes has been reported in only a few cases, such as $(CH_3)_3SHgI_3$[23] and $Hg(SCN)_2(Ph_3P)$.[18,19] In these complexes, however, the axially ligating atoms take abnormally far positions: Hg–I=3.52 and 3.69 Å in the former, and Hg–N=2.74 and 2.89 Å in the latter complex. On the other hand, in the title complex, the equatorially bonded atoms are still farther apart; such a type of mercury(II) complex has not previously been reported.

The Hg–S–C angles in the title complex are 95.79 (S(1)), 108.65 ($S(2^i)$), and 111.14° ($S(4^{ii})$). In comparison with the other thiocyanato complexes of mercury(II), where the angles are about 95—98°, and where even the large one in $Hg(SCN)_2(Ph_3P)$ is only 104.5°,[18] these angles in the title complex, especially the latter two, are exceptionally large.

As Hg–$S(4^{ii})$ is longer than the other two Hg–S bonds, a sixteen-membered ring including two mercury(II) and two cobalt(II) atoms which are linked by four SCN^- ions, as is shown in Fig. 4, is considered to be the unit structure, which is linked to the next ones on both sides by means of two relatively long bondings (Hg–$S(4^{ii})$); they lie parallel to the a-axis as a ladder lying perpendicular to the bc-plane. No bridgings are found in either the b- or the c-axis direction between the rings. This type of structure is unique and has never been reported for the thiocyanate-bridged metal complexes.

As Porai-Koshits has already shown, the mixed complex $CoHg(SCN)_4(tu)_4$ (where tu=thiourea) consists of discrete $[Hg(tu)_4]^{2+}$ and $[Co(SCN)_4]^{2-}$ ions, and both of them are bonded only electrostatically; all thiocyanato sulfur atoms are far from the mercury(II) atoms.[24] Therefore, the title complex is thought to belong to an intermediate group between the three-dimensional polymeric-type complexes such as **1** and those consisting of discrete anionic and cationic complexes such as the thiourea adduct of **1**.

References

1) J. W. Jeffery and K. M. Rose, *Acta Crystallogr., Sect B*, **24**, 653 (1968).

2) A. F. Wells, "Structural Inorganic Chemistry," 5th ed, Clarendon Press, Oxford, U. K.,(1984), a) pp. 63—140, b) p. 1158.

3) P. P. Singh, *Coord. Chem. Rev.*, **32**, 33 (1980), and the references cited in it.

4) R. Makhija, L. Pazdernik, and R. Rivest, *Can. J. Chem.*, **51**, 438 (1973).

5) A. L. Beauchamp, L. Pazdernik, and R. Rivest, *Acta Crystallogr., Sect B*, **32**, 650 (1976).

6) M. R. Udupa and B. Krebs, *Inorg. Chim. Acta*, **42**, 37 (1980).

7) R. Makhija, L. Pazdernik, and R. Rivest, *Can. J. Chem.*, **51**, 2987 (1973).

8) P. P. Singh and A. K. Gupta, *Inorg. Chem.*, **17**, 1 (1978).

9) W. E. Hatfield, M. Rowley, and R. Swindells, *J. Chem. Soc., A*, **1966**, 950.

10) J. Bradburg, K. P. Forest, R. G. Nuttall, and D. W. A. Sharp, *Spectrochim. Acta, Part A*, **23**, 2701 (1967).

11) M. Shimoi, A. Ouchi, T. Uehiro, Y. Yoshino, S. Sato, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **55**, 2371 (1982).

12) R. G. Pearson, *Science*, **151**, 172 (1966).

13) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1958**, 4190.

14) "Universal Crystallographic Computation Program System (UNICS)," ed by T. Sakurai, Crystallographic Society of Japan, Tokyo (1967).

15) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV, pp. 72, 150.

16) The positions of the hydrogen atoms, the final thermal parameters, the final F_o—F_c table, and some supplemental bond length and bond angle data are deposited as Document No. 8519 at the office of the Editor of the *Bull. Chem. Soc. Jpn.*

17) L. Pauling," The Nature of the Chemical Bond," 3rd ed, Cornell University Press, N. Y. (1960), pp. 246, 256.

18) C. Gagnon and A. L. Beauchamp, *Acta Crystallogr., Sect B*, **35**, 166 (1979).

19) R. C.M akhija, R. Rivest, and A. L. Beauchamp, *Can. J. Chem.*, **57**, 2555 (1979).

20) C. Stahlhandske, *Acta Crystallogr., Sect B*, **36**, 23 (1980).

21) G. A. Barclay and A.Cooper, *J. Chem. Soc.*, **1965**, 3741.

22) D. Hall, A. J. McKinnon, and T. N. Waters, *J. Chem. Soc., A*, **1966**, 615.

23) R. H. Fenn, *Acta Crystallogr.*, **20**, 20 (1966).

24) A. Korczynski and M. A. Porai-Koshits, *Rocz. Chem.*, **39**, 1567 (1965).