The Crystal and Molecular Structure of Chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(III)

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The structure of the title compound, $C_{44}H_{28}N_4CoCl$, has been determined by single-crystal X-ray diffraction. The crystals are body-centered tetragonal, with $a=b=13.693(2)$, $c=9.701(2)$ Å, and $Z=2$. The space group was determined to be $I4$ from the measurement of the anomalous dispersion effect. The structure was predicted prior to the X-ray analysis from the calculation of the intermolecular van der Waals energy; the result agreed quite well with the experimentally determined structure. A tetragonal pyramidal five coordination with the chlorine atom at the apex was found for the cobalt atom. The cobalt–chlorine distance is 2.149 (6) Å, about 0.1 Å shorter than those found in ordinary octahedral coordinations.

Previously, cobalt(III) $\alpha,\beta,\gamma,\delta$-tetraphenylporphin complexes with a nitrogenous base, $Cl(L)_nCoTPP$ ($n=1,2$),** were prepared[1] by treating Co(II)TPP with L in an alcoholic solution containing hydrochloric acid, and the octahedral six coordination about the cobalt atom of Cl(pyridine)CoTPP was confirmed by X-ray diffraction.[2] Recently, from a solution without L investigators could isolate single crystals of chloro-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocobalt(III), ClCoTPP,*** whose coordination remained ambiguous from a study of the electronic absorption spectra in various solvents and the solid state.[4] The present paper will deal with the determination of the structure of this compound by the X-ray diffraction technique. The results show a tetragonal pyramidal five coordination about the cobalt atom, with the chlorine atom at the apex.

Experimental

Preparation of Chloro-α,β,γ,δ-tetraphenylporphinatocobalt(III) (ClCoTPP). Co(II)TPP[5] (0.3 g) was suspended in methanol (297 ml) containing concentrated hydrochloric acid (3 ml). When the suspension was stirred at room temperature in an open flask for several hours, the solution gradually changed to reddish purple, and then the whole became a clear solution. The solution was filtered and concentrated under reduced pressure at about 50 °C. The separated crystalline precipitates were collected, washed with water, and then with a small amount of a methanol–water mixture (2:1), dried at room temperature, and recrystallized from methanol and then chloroform–ether (yield, 0.2 g). The crystals thus obtained were again dissolved in a small amount of chloroform, and the solvent was allowed to evaporate slowly to yield ClCoTPP as violet, lustrous, single crystals.

Found: C, 73.45; H, 4.17; N, 7.85; Co, 8.24; Cl, 5.00%. Calcd for $C_{44}H_{28}N_4CoCl$: C, 74.73; H, 3.99; N, 7.92; Co, 8.33; Cl, 5.01%.

Electronic absorption spectrum (methanol), λ/nm ($\varepsilon/10^3$): 575_{sh} (3.8), 541_{max} (14.4), 505_{max} (3.5), 425.5_{max} (250), and 313_{max} (17.0).

Magnetic susceptibility measurements showed diamagnetism.

Measurements of X-Ray Diffraction Intensities and the Space Group Determination. The preliminary Weissenberg photographs showed that the crystals belong to the tetragonal system and that the systematic absences are $h+k+l=2n+1$. Therefore, the possible space groups are $I4$, $I\bar{4}$, or $I4/m$. The diffraction intensities were collected on a Rigaku AFC four-circle diffractometer, with graphite-monochromatized Cu $K\alpha$ radiation, within the range of $2\theta \leq 140°$. The size of the crystal was $0.6\times0.4\times0.2$ mm^3. The ordinary Lorentz and polarization corrections were applied. The effect of the absorption was corrected by North, Phillips, and Mathews's experimental method.[6] The linear absorption coeffecient is 49.8 cm^{-1}. The succssive averaging of equivalent reflections yielded 855 independent reflections with $l \leq 0$. Both cobalt and chlorine atoms have considerably large $\Delta f''$ components for Cu $K\alpha$ radiation. The values of $\Delta f''$ are 3.8 and 0.7 for the cobalt and chlorine atoms respectively.[7] Therefore, in order to determine the space group, all the equivalent reflections were measured for some reflections. A few examples are shown in Table 1. These F_0 values have a four-fold symmetry in the reciprocal space. Therefore, the space group is $I4$.

Crystal data $a=b=13.693(2)$, $c=9.701(2)$ Å, $V=1818.9$ (6) Å^3. Space group $I4$, $Z=2$. $D_c=1.292$ g cm^{-3}.

Prediction of the Structure

The number of general equivalent positions is eight for the $I4$ space group. The number of the molecule in the cell is two. Therefore, the molecule must be located on a special position with a four-fold symmetry. From the shape of the complex, the cobalt atom was taken as the point of origin. The symmetry of the TPP group is 4. The approximate geometry of the porphinato core is well known. The most probable dihedral angle between the porphinato plane and the phenyl plane is about 72°.[2] Therefore, freedom remains in the rotation of the TPP group about the c axis. The van der Waals energy between the TPP groups was calculated in relation to the rotation angle. The energy curve showed two very sharp minima when the Co–N

** This formula represents the composition. TPP: dianion of α,β,γ,δ-tetraphenylporphin. L: nitrogenous base (example, pyridine, *p*-toluidine, *etc.*).

*** The crystal structure of ClCoTPP was previously reported, in Fleischer's review article,[3] to be $I4/m$ with $a=b=13.41$ and $c=9.82$ Å. However, as far as the present authors are aware, no written report about the structure has been published.

TABLE 1. OBSERVED STRUCTURE FACTORS, F_O'S, EXHIBITING 4-FOLD SYMMETRY

Index $\{h\ k\ l\}$	F_O							
	$h\ k\ l$	$-k\ h\ l$	$-h\ -k\ l$	$k\ -h\ l$	$-h\ -k\ -l$	$k\ -h\ -l$	$h\ k\ -l$	$-k\ h\ -l$
4 4 2	32	33	33	32	24	24	24	24
6 4 2	33	34	34	33	33	33	33	33
2 3 3	31	31	31	30	35	36	36	35
6 5 3	20	20	20	20	26	27	27	26
1 5 4	29	28	28	28	29	30	30	29
4 3 5	23	24	23	23	18	19	19	18

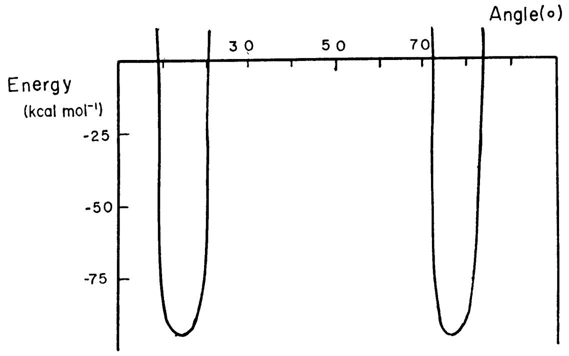


Fig. 1. Van der Waals energy of the tetraphenylporphin molecule. The abscissa is the angle between the Co–N vector and the a axis.

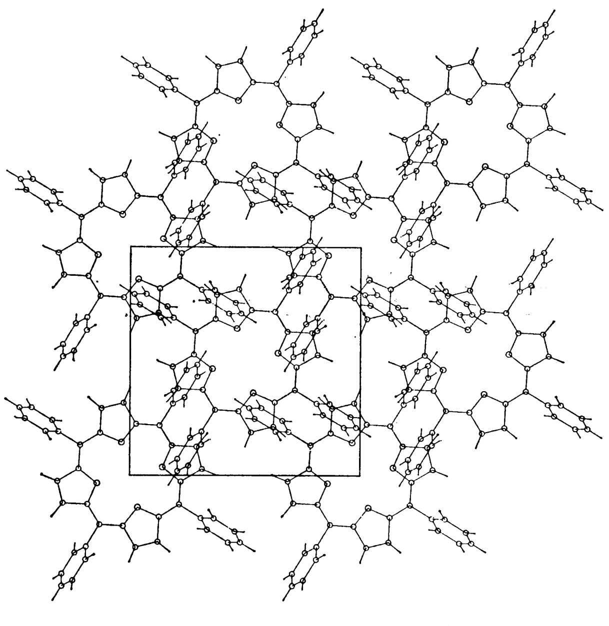


Fig. 2. The predicted structure. c axis projection.

vector makes an angle of 14° or 76° from the a axis (Fig. 1). These two orientations are energetically equivalent for the TPP group. Thus, the packing of the TPP groups in the unit cell was predicted to be as is shown in Fig. 2, or its equivalent, before the diffraction intensities were observed.

Structure Analysis

The structure was easily solved by the ordinary heavy-atom method, independent from the predicted structure, and was refined by the block-diagonal least-squares method. In a difference Fourier map, the peaks corresponding to the hydrogen atoms were very broad; thus, the hydrogen atoms were not included in the structure-factor calculation. The refinement was performed using 855 unique reflections. The final R index, with anisotropic temperature factors, was 8.8%. In order to determine the absolute configuration and verify the space group, the structure factors of the Friedel pair reflections were also calculated. Some of the results are shown in Table 2, while the atomic parameters are given in Table 3. The structure factors

TABLE 2. STRUCTURE FACTORS OF FRIEDEL PAIRS

Index	F_O	F_C
4 4 2	32	33
−4 −4 −2	24	23
6 4 2	33	33
−6 −4 −2	33	32
2 3 3	31	34
−2 −3 −3	35	41
6 5 3	20	19
−6 −5 −3	26	27
1 5 4	29	27
−1 −5 −4	29	30
4 3 5	23	22
−4 −3 −5	18	19

TABLE 3. FRACTIONAL COORDINATES AND ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$)

Standard deviations are given in parentheses. The anisotropic parameters are in the form:

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

Atom	x	y	z
Co	0(0)	0(0)	0(0)
Cl	0(0)	0(0)	2216(7)
N	1396(7)	387(7)	−57(17)
C(1)	1762(8)	1318(9)	−53(19)
C(2)	2833(9)	1317(10)	10(23)
C(3)	3078(9)	356(10)	65(22)
C(4)	2206(8)	−205(9)	−24(20)
C(5)	2180(8)	−1216(9)	−40(20)
C(6)	3140(8)	−1770(9)	−64(23)
C(7)	3672(11)	−1806(13)	1282(23)
C(8)	4568(12)	−2354(14)	1269(29)
C(9)	4882(10)	−2786(10)	−116(34)
C(10)	4350(13)	−2742(12)	−1255(23)
C(11)	3449(12)	−2218(12)	−1251(21)

TABLE 3. (Continued)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	4(0)	4(0)	9(0)	0(0)	0(0)	0(0)
Cl	5(0)	5(0)	7(1)	0(0)	0(0)	0(0)
N	5(1)	5(1)	11(1)	0(0)	0(1)	0(1)
C(1)	5(1)	6(1)	12(2)	0(1)	2(1)	2(1)
C(2)	5(1)	7(1)	19(2)	0(1)	5(1)	−2(2)
C(3)	5(1)	6(1)	17(2)	0(1)	2(1)	2(1)
C(4)	5(1)	5(1)	13(2)	0(1)	3(1)	0(1)
C(5)	5(1)	6(1)	12(2)	0(1)	1(1)	−1(1)
C(6)	5(1)	6(1)	18(2)	0(1)	2(1)	−3(1)
C(7)	5(1)	10(1)	23(4)	1(1)	−2(2)	6(2)
C(8)	7(1)	10(1)	29(4)	2(1)	1(2)	2(2)
C(9)	5(1)	7(1)	31(3)	1(1)	2(2)	−2(2)
C(10)	7(1)	6(1)	31(4)	1(1)	6(2)	0(2)
C(11)	7(1)	6(1)	25(4)	0(1)	6(2)	−2(1)

are given in Table 4.****

Discussion of the Structure

The lattice parameters of the present crystals are significantly different from those referred to by Fleischer.[3] This difference is attributable to the order and disorder structures. For the disorder structure, the chlorine atoms are distributed randomly on both +z and −z sides of the cobalt atom, so that the apparent space group is $I4/m$. We also obtained disordered crystals with a=13.489 and c=9.779 Å from the same crystallization condition. So far, all known five-coordinate structures are disordered. The only known order structure is the six-coordinate $Cl_2Sn(IV)TPP$.[8] Therefore, the present structure is the first example of an order structure with a five coordination. The method of distinguishing between the order and disorder structures was fully discussed by us previously.[9]

The crystal structure is shown in Fig. 3. The cobalt-nitrogen bond makes an angle of 15° from the a axis. The dihedral angle between the phenyl plane and the mean porphinato plane is 75°. These values agree quite well with the predicted structure.

The shortest intermolecular carbon–carbon distance, 3.64 Å, is between the C(2) of the pyrrole group of a molecule and the C(11) of the phenyl group of the neighbouring molecule at the body center position (Fig. 4). The rapid increase in the intermolecular energy against the rotation of the molecule from the equilibrium position is due to the repulsion between phenyl groups of the neighbouring molecules.

The bond distances and angles within the TPP group, averaged over chemically equivalent bonds, are shown in Fig. 5, while the thermal ellipsoids are shown in Fig. 6. In contrast to the previous structure,[2] the porphinato group is quite flat. The maximum deviation of the atom from the mean plane is 0.08 Å for C(3) and less than 0.03 Å for the others. The angle between the mean pyrrole plane and the mean porphinato plane is 2.1°.

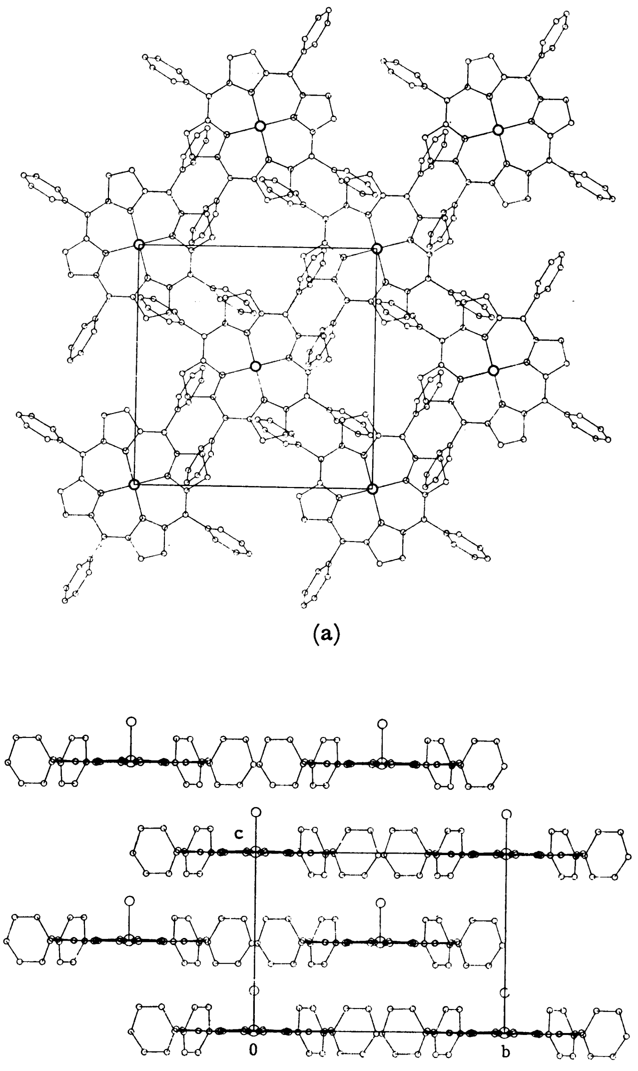


Fig. 3. The crystal structure.
(a) c axis projection. (b) a axis projection.

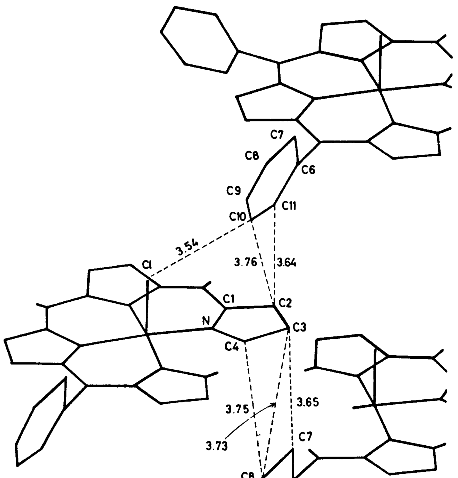


Fig. 4. Intermolecular atomic distances (Å).

**** Table 4 has been submitted to, and is kept, by the office of the Chemical Society of Japan, 1-5 Kanda-Surugadai, Chiyoda-ku, Tokyo 101 (Document No. 7632).

Table 5. Coordination about the metal atom

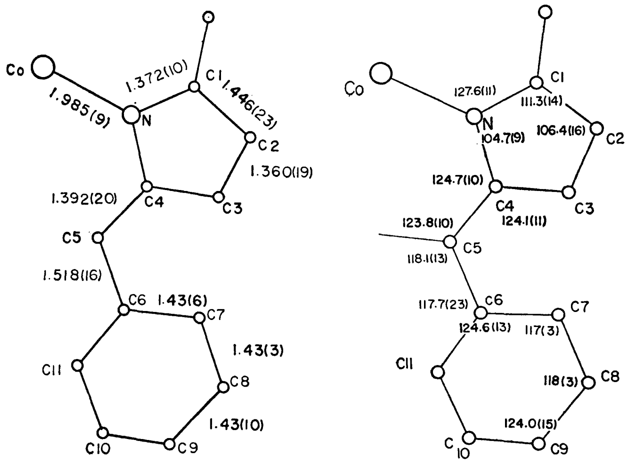
Parameters of cobalt complexes.

Complex	Coordination	Co–Ct$^{a)}$ (Å)	Equatorial Co–N(Å)	Co–Cl (Å)	Ref.
ClCo(III)TPP	Five	0.05	1.985	2.145	This work
Co(III)(N_4)Cl$^{b)}$	Five	0.19		2.509	10
Cl(pyridine)Co(III)TPP	Six	0.	1.98	2.251	2
(1-Methylimidazole)Co(II)TPP	Five	0.13	1.977		11
(NO)Co(II)TPP	Five	0.09	1.978		12
(Piperidine)$_2$Co(II)TPP	Six	0.	1.987		13

Parameters of other five-coordinate metalloporphyrins.

Complex	M–Ct$^{a)}$ (Å)	Equatorial M–N (Å)	Ref.
(NO)Fe(II)TPP	0.211	2.001	14
(MeO)Fe(III)(Meso-P-IX DME)$^{c)}$	0.48	2.073	15
(Pyridine)Zn(II)TPyP$^{d)}$	0.33	2.073	16
(H_2O)Mg(II)TPP	0.273	2.072	17
(Me)Rh(III)OEP$^{e)}$	0.051	2.03	18
ClFe(III)TPP	0.38	2.049	19

a) Ct: Center of the plane of porphin nitrogen atoms. b) See footnote . c) Mesoporphyrin-IX dimethyl ester. d) α, β, γ, δ-Tetrapyridylporphin. e) 1, 2, 3, 4, 5, 6, 7, 8-Octaethylporphin.



(a) (b)

Fig. 5. (a) Bond distances (Å). (b) Bond angles (°).

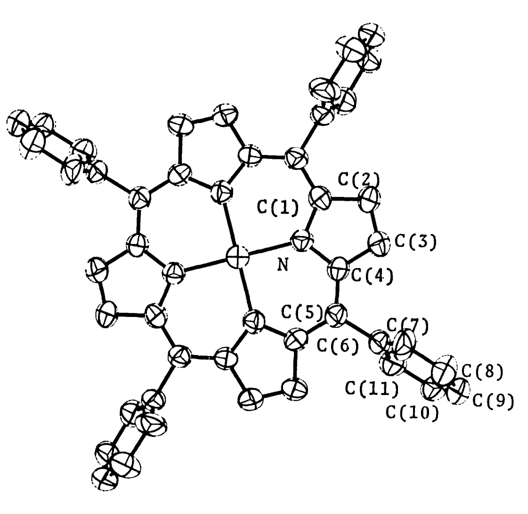


Fig. 6. Thermal ellipsoids of the molecule.

The coordination about the cobalt atom is the tetragonal pyramid, as is shown in Fig. 7. The ordinary cobalt(III) complex has been known to form an octahedral coordination. Recently, Bailey *et al.*$^{10)}$ presented a tetragonal pyramidal structure for the cobalt(III) complex Co(N_4)Cl.† This complex is paramagnetic, in contrast to the present diamagnetism. Several other five-coordinate metalloporphyrins are known. The parameters of these complexes are compared in Table 5. In the present complex, the deviation of the cobalt atom from the mean plane of the nitrogen atoms is very small, and the Co–Cl distance, 2.15 Å, is shorter by about 0.1 Å than those of the ordinary six-coordinate cobalt(III) complexes.$^{2)}$ Since the $d_{x^2-y^2}$ orbital of the central cobalt(III) ion is not occupied in the diamagnetic state and thus the effective radius is reduced, the cobalt ion can be in the central hole of the porphyrin. On the other hand, an occupation of $d_{x^2-y^2}$ orbital in chloro-α,β,γ,δ-tetraphenylporphinatoiron(III) gives rise to a shift of the central metal ion out of the porphinato plane.$^{19)}$ The shortening of Co–Cl bond found in the present work is attributed to an enhanced donation of coordinating Cl^- ion. For an electroneutrality, the axial ligand in the five-coordinate configuration should donate much more than the one in an ordinary six-coordinate configuration. This shortening might be also due to an enhanced donation promoted by a vacancy of d_{z^2} orbital in this diamagnetic complex. In fact, the Co–Cl bond found in a paramagnetic five-coordinate cobalt(III) complex$^{10)}$ is longer by about 0.25 Å than the normal bond. A similar shortening of the axial coordination in a diamagnetic d^6 five-coordinate complex has been reported on the Rh–C-

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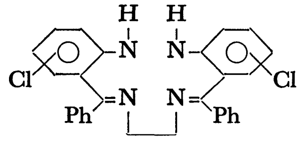
† (N_4) represents



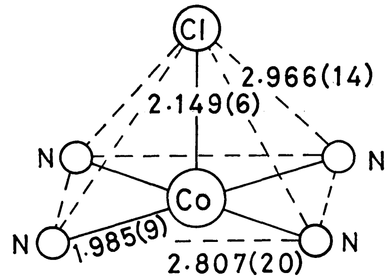


Fig. 7. Coordination about the cobalt atom.

(methyl) bond in octaethylporphinato(methyl)rhodium(III).[18]

The structure of this complex corresponds to a geometry of an intermediate of the S_N1 substitution reaction of six-coordinate cobalt(III) complexes.

The calculations were carried out on the FACOM 230-75 computer of this Institute, using UNICS II program system.[20] The authors are grateful to Professor Hiroshi Kobayashi and Dr. Youkoh Kaizu of the Tokyo Institute of Technology for the discussion on an electronic state of this complex and the measurement of the magnetic properties. The research was supported, in part, by a Scientific Grant (034085) from the Ministry of Education.

References

1) K. Yamamoto and S. Tonomura, *Sci. Papers Inst. Phys. Chem. Res.*, **58**, 122 (1964).

2) T. Sakurai, K. Yamamoto, N. Seino, and M. Katsuta, *Acta Crystallogr.*, **B31**, 2514 (1975).

3) E. B. Fleischer, *Acc. Chem. Res.*, **3**, 105 (1970).

4) K. Yamamoto, 25th Symposium of Coordination Chemistry, Tokyo, October, 1975, p. 331.

5) G. D. Dorough, J. R. Miller, and F. M. Huennekens, *J. Am. Chem. Soc.*, **73**, 4315 (1951).

6) A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr.*, **A24**, 351 (1968).

7) C. H. MacGillavry and G. D. Rieck, ed., "International Tables for X-Ray Crystallography," The Kynoch Press, Vol. III, Birmingham (1962), p. 214.

8) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Am, Chem. Soc.*, **94**, 6689 (1972).

9) T. Sakurai and K. Yamamoto, *Sci. Papers Inst. Phys. Chem. Res.*, **70**, 31 (1976).

10) N. A. Bailey, E. D. McKenzie, and J. M. Worthington, *Inorg. Chim. Acta*, **12**, L31 (1975).

11) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 90 (1974).

12) W. R. Scheidt and J. L. Hoard, *J. Am. Chem. Soc.*, **95**, 8281 (1973).

13) W. R. Scheidt, *J. Am. Chem. Soc.*, **96**, 84 (1974).

14) W. R. Scheidt and M. E. Frisse, *J. Am. Chem. Soc.*, **97**, 17 (1975).

15) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Am. Chem. Soc.*, **87**, 2312 (1965).

16) D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, **92**, 3761 (1970).

17) R. Timkovich and A. Tulinsky, *J. Am. Chem. Soc.*, **91**, 4430 (1969).

18) A. Takenaka, S. K. Syal, Y. Sasada, T. Omura, H. Ogoshi, and Z. Yoshida, *Acta Crystallogr.*, **B32**, 62 (1976).

19) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967).

20) T. Sakurai, H. Iwasaki, Y. Watanabe, K. Kobayashi, Y. Bando, and Y. Nakamichi, *Rep. Inst. Phys. Chem. Res.*, **50**, 75 (1974).