

Crystallographic Proof for a Dichlorophosphate Compound**The Structure of $\text{Mn}(\text{PO}_2\text{Cl}_2)_2, (\text{CH}_3\text{COOC}_2\text{H}_5)_2$**

JACOB DANIELSEN and SVEND ERIK RASMUSSEN

Department of Inorganic Chemistry, University of Aarhus, Aarhus C, Denmark

The crystal structure of $\text{Mn}(\text{PO}_2\text{Cl}_2)_2, (\text{CH}_3\text{COOC}_2\text{H}_5)_2$ has been determined by three-dimensional Patterson and Fourier methods. Least squares analysis of geometric parameters and isotropic temperature factors has been carried out. Existence of a stable dichlorophosphate compound has been proved. The manganese atom is octahedrally coordinated to six oxygen atoms four of which are bonded to dichlorophosphate ions and two are keto oxygens of the ethylacetate groups. Atomic coordinates, temperature factors and bond lengths are reported with their standard deviations.

A previous publication¹ communicated unit cell dimensions and space group of a compound of analytical composition $\text{MnO}_2\text{P}_2\text{O}_7\text{Cl}_4(\text{CH}_3\text{COOC}_2\text{H}_5)_2$. This compound was first prepared by Bassett and Taylor^{2,3} in 1911. They investigated reactions between metal oxides and phosphorus oxide chloride aiming at the establishment of the molecular structure of apatite and related compounds. It was discovered that oxides of divalent manganese, zinc, magnesium, and calcium react with POCl_3 to yield crystalline products, *e.g.* $\text{CaO}, 2\text{POCl}_3$. The nature of these compounds shows that they are not related to apatite, but might be coordination compounds of metal ions and POCl_3 . A closer investigation of these compounds is planned.

Bassett and Taylor also reported that POCl_3 dissolved in acetone or ethylacetate reacts with several metal oxides. Hydrogen chloride is evolved during the reaction and the oxides are dissolved in the boiling solution. After cooling, crystalline products appear, *e.g.* $\text{MnO}_2\text{P}_2\text{O}_7\text{Cl}_4(\text{CH}_3\text{COOC}_2\text{H}_5)_2$. Our observations and analysis concerning this compound are in full agreement with those of Bassett and Taylor.

All recorded observations indicate that presence of small amounts of water is necessary for the reaction to take place. The chemical reaction can be written: $\text{MnO} + \text{H}_2\text{O} + 2\text{POCl}_3 + 2\text{CH}_3\text{COOC}_2\text{H}_5 = \text{Mn}(\text{PO}_2\text{Cl}_2)_2, (\text{CH}_3\text{COOC}_2\text{H}_5)_2 + 2\text{HCl}$
Compounds of this type are hygroscopic and we selected the manganese compound for X-ray investigation as it was apparently less hygroscopic than other.

EXPERIMENTAL

Chemistry. $\text{Mn}(\text{PO}_2\text{Cl}_2)_2(\text{CH}_3\text{COOC}_2\text{H}_5)_2$ was prepared according to the methods described in Ref.² The chemicals used were of analytical grade. The compound was protected from atmospheric humidity during manipulations.

Chlorine was determined by potentiometric titration with AgNO_3 . Phosphorus was analysed as $\text{Mg}_2\text{P}_2\text{O}_7$. (Found: Cl 28.84; P 12.38. Calc. for $\text{Mn}(\text{PO}_2\text{Cl}_2)_2(\text{C}_4\text{H}_8\text{O}_2)_2$: Cl 28.45; P 12.42). The density of the crystal was measured by flotation technique. The X-ray molecular weight is 500; calc. for $\text{Mn}(\text{PO}_2\text{Cl}_2)_2(\text{C}_4\text{H}_8\text{O}_2)_2$: 498.93.

X-Ray techniques. A crystal of dimensions $1.7 \times 0.8 \times 0.4$ mm was quickly transferred to and sealed in a Lindemann glass tube. As no glove box was available attempts at transferring smaller crystals were unsuccessful as the small crystals rapidly decomposed even at short exposures to air humidity.

Weissenberg and precession data were obtained using filtered Cu- and Mo-radiation. The axis of rotation was c in the Weissenberg exposures and c^* in the precession exposures. Using Mo-radiation the following reflexions were recorded with 30° precession photographs: $0kl - 5kl$, $h0l - h5l$ and $hk0$ reflexions with Weissenberg photographs.

The precession patterns gave rather large spots which could be measured photometrically. Part of the photometric measurements were checked by visual measurements using a calibrated strip. The agreement was generally within 10 %. Consequently all subsequent calculations were based upon the photometrically estimated intensities. Because of the rather large size of the crystal (linear absorption coefficient $\mu = 14.2 \text{ cm}^{-1}$) as well as the size and often irregular shape of the spots, the intensities are of rather low accuracy. They are, however, accurate enough for giving results of chemical significance. 1600 independent reflexions were measured. The intensities were corrected for polarization and Lorentz factors using charts. No absorption correction was applied. Computations were carried out on the digital computers DASK and GIER in "Regnecentralen".

STRUCTURE DETERMINATION

$\text{Mn}(\text{PO}_2\text{Cl}_2)_2(\text{CH}_3\text{COOC}_2\text{H}_5)_2$ is monoclinic with the unit cell dimensions:

$$\begin{aligned} a &= 14.27 \text{ \AA} \\ b &= 13.87 \text{ \AA} \\ c &= 10.04 \text{ \AA} \\ \beta &= 95^\circ 56' \end{aligned}$$

Absent reflexions are: $h0l$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$. Consequently the space group is $P2_1/a$, No. 14. The density is 1.67 g/cm^3 . The unit cell must accommodate four units of $\text{Mn}(\text{PO}_2\text{Cl}_2)_2(\text{CH}_3\text{COOC}_2\text{H}_5)_2$.

Patterson projections yielded coordinates of Mn but no other atoms could be located unambiguously from projections. The full three dimensional Patterson confirmed the position of Mn, and using image seeking methods⁴ all P and Cl positions were found. It was not possible to distinguish between P and Cl atoms from the Patterson, but interatomic distances permitted a reasonable guess at which sites were occupied by P-atoms. The distances from Mn to P and Cl indicated that neither of the latter are bonded to Mn. Using Mn as well as P and Cl as searcher atoms revealed that six lighter atoms, presumably oxygen atoms, formed an octahedron around Mn with Mn—O distances of about 2 Å.

Now the chemically interesting problems were almost solved. The manganese ion was coordinated to PO_2Cl_2 ions and to oxygen atoms of the ethylacetate molecules.

Presumably all light atoms except hydrogens could have been found using image seeking functions, but it proved to be more convenient to calculate a Fourier synthesis using signs determined by the coordinates of the located manganese, phosphorus, chlorine and oxygen atoms. The Fourier synthesis revealed the positions of the remaining oxygen atoms and the carbon atoms.

During this investigation one of us, J.D., applied the Hauptmann-Karle methods and found the same trial structure. Danielsen hopes in a forthcoming publication to describe the procedures used.

Refinement. The R -value of the first structure containing all atoms except hydrogen was 0.312. This value decreased to 0.271 through 3 successive difference Fourier calculations.

Two cycles of least squares analysis computed on an IBM 704 using the Vand-Pepinsky⁵ programme reduced the R -factor to 0.181.

At that stage of the investigation the computer GIER became available to us. An Algol programme was written by J.D. for least squares analysis using individual isotropic temperature factors and the diagonal approximation.

We have terminated our refinement at an R -value of 15 % after some additional cycles. With the low accuracy of our intensity measurements we find it of little significance to make additional refinements, as it seems unlikely that highly accurate bond lengths can be obtained from these data. We believe the structure to be essentially correct from the reasonably good agreement between calculated and observed structure factors.

Atomic scattering factors were calculated using an approximation suggested by Bassi⁶:

$$f_n = Z_n - s^2/(a_n + b_n \cdot s + c_n \cdot s^2 + d_n \cdot s^3 + e_n \cdot s^4), \text{ where } s = \sin\Theta/\lambda.$$

The coefficients were calculated using tabulated f_n values from Intern. Tables Vol. III p. 202–207.

The numerical values are given in Table 1.

Table 1. Coefficients employed in structure factor calculations.

	Mn	Cl	P	O	C
Z	25	17	15	8	6
a	0.002370	0.005301	0.005125	0.011906	0.009567
b	0.013431	0.003105	-0.011894	0.005198	0.006581
c	0.053447	0.020229	0.159443	0.081682	0.098695
d	-0.070090	0.190643	-0.064509	0.095267	0.246354
e	0.062711	-0.159902	-0.015419	-0.042875	-0.166072

CRYSTAL DATA

All pertinent crystal data are presented below.

Crystal system: Monoclinic, unique axis b .

Unit cell:

$$a = 14.27 \text{ \AA} \quad b = 13.87 \text{ \AA} \quad c = 10.04 \text{ \AA} \quad \beta = 95^\circ 56'$$

Table 2. Atomic coordinates, temperature factors, and standard deviations.

	x/a	y/b	z/c	$\frac{\text{\AA}^2}{B}$	$\frac{\text{\AA}}{\sigma(x)}$	$\frac{\text{\AA}}{\sigma(y)}$	$\frac{\text{\AA}}{\sigma(z)}$	$\frac{\text{\AA}^2}{\sigma(B)}$
Mn	0.50908	0.43669	0.24658	0.484	0.0033	0.0037	0.0029	0.044
Cl ₁	0.67176	0.69697	0.15822	4.178	0.0100	0.0101	0.0088	0.18
Cl ₂	0.46612	0.76514	0.06748	3.690	0.0091	0.0097	0.0081	0.16
Cl ₃	0.28184	0.63135	0.39367	6.182	0.013	0.013	0.011	0.26
Cl ₄	0.23465	0.42662	0.49297	5.346	0.011	0.012	0.010	0.22
P ₁	0.54814	0.64584	0.07255	1.113	0.0068	0.0070	0.0056	0.10
P ₂	0.34491	0.50699	0.45203	1.284	0.0070	0.0071	0.0058	0.10
O ₁	0.51277	0.57739	0.16514	2.450	0.019	0.020	0.017	0.35
O ₂	0.56394	0.61861	-0.06532	1.583	0.017	0.018	0.015	0.30
O ₃	0.38135	0.46522	0.33506	1.944	0.018	0.019	0.016	0.32
O ₄	0.40591	0.52296	0.57737	1.854	0.018	0.019	0.016	0.32
O ₇	0.50675	0.28461	0.32085	2.408	0.019	0.021	0.017	0.36
O ₈	0.47793	0.14016	0.40325	2.494	0.020	0.021	0.018	0.37
O ₅	0.63762	0.40497	0.15681	3.01	0.021	0.022	0.019	0.40
O ₆	0.77523	0.38043	0.06951	3.48	0.022	0.023	0.020	0.44
C ₁	0.46787	0.27366	0.54704	5.53	0.045	0.048	0.040	0.93
C ₂	0.48898	0.23877	0.41452	2.29	0.030	0.030	0.027	0.53
C ₃	0.49179	0.09767	0.27777	3.59	0.035	0.037	0.031	0.68
C ₄	0.46893	-0.00597	0.29335	5.54	0.045	0.046	0.040	0.93
C ₅	0.74195	0.28414	0.24111	5.22	0.043	0.046	0.039	0.85
C ₆	0.71121	0.36288	0.15617	2.32	0.030	0.030	0.025	0.49
C ₇	0.74033	0.45674	-0.03469	4.73	0.039	0.041	0.036	0.80
C ₈	0.82529	0.49321	-0.08395	6.00	0.049	0.050	0.044	1.04

Table 3.

Bond lengths in Å		Bond angles in degrees	
Mn—O ₁	2.12	O ₁ —Mn—O ₃	92.6
Mn—O ₃	2.14	O ₁ —Mn—O _{2b}	91.8
Mn—O _{2b}	2.14	O ₁ —Mn—O _{4b}	92.5
Mn—O _{4b}	2.11	O ₁ —Mn—O ₇	176.6
Mn—O ₅	2.17	O ₁ —Mn—O ₅	88.3
Mn—O ₇	2.24	O ₃ —Mn—O _{2b}	93.3
		O ₃ —Mn—O _{4b}	92.5
		O ₃ —Mn—O ₇	89.6
		O ₃ —Mn—O ₅	178.9
		O ₇ —Mn—O _{2b}	85.6
		O ₇ —Mn—O _{4b}	89.9
		O ₇ —Mn—O ₅	89.4
		O ₅ —Mn—O _{2b}	86.1
		O ₅ —Mn—O _{4b}	87.9
		O ₅ —Mn—O _{4b}	172.6
P ₁ —Cl ₁	2.01	Cl ₁ —P ₁ —Cl ₂	101.7
P ₁ —Cl ₂	2.02	Cl ₁ —P ₁ —O ₁	107.7
P ₁ —O ₁	1.46	Cl ₁ —P ₁ —O ₂	106.2
P ₁ —O ₂	1.47	Cl ₂ —P ₁ —O ₁	108.2
		Cl ₂ —P ₁ —O ₂	109.3
		O ₁ —P ₁ —O ₂	122.0
		Mn—O ₁ —P ₁	150.7
P ₂ —Cl ₃	2.01	Cl ₃ —P ₂ —Cl ₄	101.5
P ₂ —Cl ₄	2.01	Cl ₃ —P ₂ —O ₃	107.1
P ₂ —O ₃	1.45	Cl ₃ —P ₂ —O ₄	109.2
P ₂ —O ₄	1.47	Cl ₄ —P ₂ —O ₃	107.3
		Cl ₄ —P ₂ —O ₄	108.4
		O ₃ —P ₂ —O ₄	121.5
		Mn—O ₃ —P ₂	143.0
C ₄ —C ₃	1.49	C ₄ —C ₃ —O ₈	104.8
C ₃ —O ₈	1.42	C ₃ —O ₈ —C ₂	117.3
O ₈ —C ₂	1.38	O ₈ —C ₂ —C ₁	111.5
C ₂ —O ₇	1.18	O ₈ —C ₂ —O ₇	119.9
C ₂ —C ₁	1.48	C ₁ —C ₂ —O ₇	128.3
		C ₂ —O ₇ —Mn	141.5
C ₈ —C ₇	1.45	C ₈ —C ₇ —O ₆	104.5
C ₇ —O ₆	1.54	C ₇ —O ₆ —C ₅	111.8
O ₆ —C ₅	1.35	O ₆ —C ₅ —C ₆	109.7
C ₅ —O ₅	1.20	O ₆ —C ₅ —O ₅	124.5
C ₅ —C ₆	1.43	C ₅ —C ₆ —O ₅	125.7
		C ₅ —O ₅ —Mn	151.3
		Mn—O _{2b} —P _{1b}	141.3
		Mn—O _{4b} —P _{2b}	173.3

Space group $P2_1/a$, No. 14, from extinctions. Density 1.67/cm³. Conventional R -factor 15.1 %, for observed reflections only.

Table 1 gives the coefficients used in calculations of atomic scattering factors, Table 2 atomic coordinates and temperature factors with their standard deviations. To save space calculated and observed structure factors are not printed. The authors will gladly send copies of the table to other crystallographers on request.

Table 3 gives bond lengths and bond angles and Table 4 van der Waals distances.

DISCUSSION

According to the X-ray analysis the compound investigated may be formulated as: $Mn^{2+}(PO_2Cl_2)^-_2 (CH_3COOC_2H_5)_2$.

The hydrolysis of $POCl_3$ has been investigated by Goubeau and Schulz⁷ and by Grunze.⁸ They describe isolation of $HPCl_2O_2$ and precipitation of nitron salts.

Apparently isolation of dichlorophosphoric acid and simple salts of it is connected with considerable experimental difficulties. It is therefore a little surprising that the manganese complex compound is prepared rather easily.

Manganese(II) is octahedrally coordinated to oxygen. Fig. 1 shows a projection of molecules coordinated to a manganese atom. Mn—O octahedra are connected *via* PO_2Cl_2 groups. The two oxygens of PO_2Cl_2 groups are connected

Table 4. Van der Waals distances Å.

$[x, y, z]:a$	$[\bar{x}, \bar{y}, \bar{z}]:b$	$[1/2 - x, 1/2 + y, \bar{z}]:c$	$[1/2 + x, 1/2 - y, z]:d$
		$Cl_{1a} - Cl_{3d} = 3.60$	
		$Cl_{1a} - Cl_{4b} = 4.00$	
		$Cl_{4b} - Cl_{3d} = 4.26$	
	$C_{1b} - Cl_{1a} = 3.76$		$C_{4b} - Cl_{2b} = 3.90$
	$C_{1b} - Cl_{2a} = 3.93$		$C_{4b} - Cl_{3c} = 4.25$
	$C_{1b} - Cl_{3a} = 3.80$		$C_{4b} - O_{8a} = 3.58$
	$C_{1b} - Cl_{4b} = 3.94$		$C_{4b} - O_{6c} = 3.80$
	$C_{1b} - O_{1a} = 3.54$		$C_{4b} - C_{8d} = 3.78$
	$C_{1b} - O_{4a} = 3.64$		$C_{4b} - C_{1a} = 4.11$
	$C_{1b} - O_{3b} = 3.59$		$C_{4b} - C_{4a} = 4.16$
	$C_{1b} - O_{5b} = 3.55$		$C_{4b} - C_{8b} = 4.12$
	$C_{1b} - C_{5c} = 4.29$		$C_{4b} - C_{2d} = 3.61$
	$C_{5a} - Cl_{3b} = 3.90$		$C_{8a} - Cl_{3b} = 3.74$
	$C_{5a} - Cl_{4d} = 3.87$		$C_{8a} - Cl_{1c} = 4.18$
	$C_{5a} - Cl_{2b} = 4.12$		$C_{8a} - Cl_{4b} = 4.26$
	$C_{5a} - O_{7a} = 3.53$		$C_{8a} - Cl_{2d} = 4.12$
	$C_{5a} - O_{8d} = 3.74$		$C_{8a} - O_{3b} = 3.72$
	$C_{5a} - C_{4b} = 3.91$		$C_{8a} - C_{4c} = 3.78$
	$C_{5a} - C_{1d} = 4.29$		$C_{8a} - C_{4d} = 4.12$

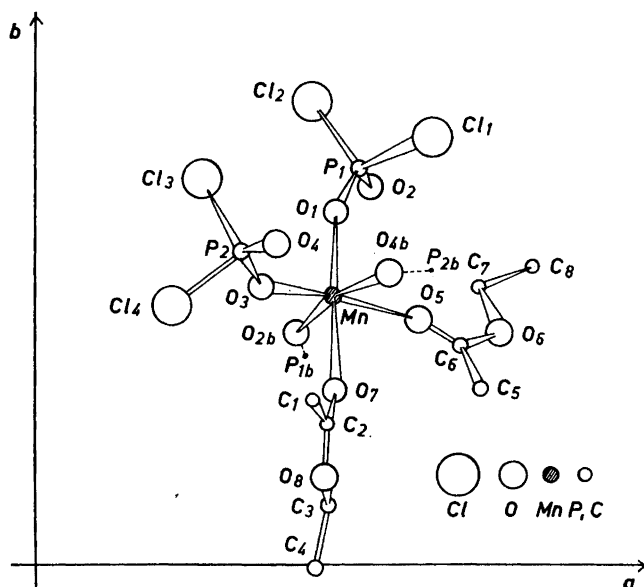


Fig. 1. Projection of molecules coordinated to a manganese atom.

to two adjacent Mn-atoms; this fills four corners of the Mn—O octahedra. The two remaining corners are occupied by keto-oxygen atoms from ethylacetate groups. These oxygen atoms are in *cis* positions. Fig. 2 shows a projection of Mn—O octahedra and PO_2Cl_2 groups. Ethylacetate molecules and chlorine atoms left

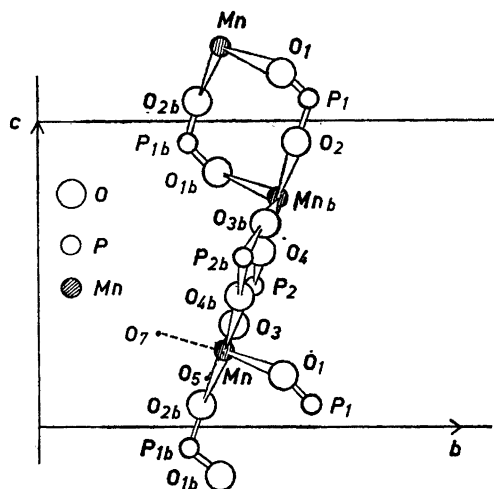


Fig. 2. Projection of Mn—O octahedra and PO_2Cl_2 groups. Ethylacetate molecules and chlorine atoms left out.

out for clarity. Eight membered centrosymmetric rings are formed by manganese, oxygen, and phosphorus. Adjacent rings are almost perpendicular to each other.

The octahedra with connected dichlorophosphate ions and ethylacetate molecules form infinite strings of composition $(\text{Mn}(\text{PO}_2\text{Cl}_2)_2(\text{CH}_3\text{COOC}_2\text{H}_5)_2)$ along the z -axis and along $(1/2, 1/2, z)$. The strings are connected by van der Waals forces. The asymmetric unit of the structure contains two PO_2Cl_2 groups and two ethylacetate groups. Indeterminacy of interatomic distances probably shows up as differences in bond lengths in crystallographically non equivalent molecules of the same kind.

The numerical values of the standard deviations are dependent upon atomic number and the magnitude of the temperature factor. Manganese and phosphorus atoms are located rather accurately and the chlorine positions are apparently well defined too, although the temperature factors are high.

P—Cl and P—O distances are equal in pairs. Differences between corresponding bond lengths are smaller than standard deviations both within a PO_2Cl_2 group and between crystallographically non equivalent PO_2Cl_2 groups. P—Cl and P—O bond distances do not differ significantly from corresponding distances in the POCl_3 molecule.

Distances between oxygen from PO_2Cl_2 groups and manganese differ within the standard deviation only; the mean is 2.13 Å. Distances between keto-oxygens and manganese differ by 0.07 Å. This is about twice the standard deviation of the Mn—O bond and is possibly not significant. The mean of the two keto-oxygen-manganese distances is 2.20 Å. The difference between the two sets of mean Mn—O distances is probably significant. It is reasonable to assume, that the two sets of distances are slightly different.

Bond lengths and bond angles of ethylacetate are poorly defined. Standard deviations of bond lengths vary between 0.06 and 0.11 Å.

The bond lengths however differ in most cases less than one standard deviation from commonly accepted values for bonds of the types in ethylacetate molecules. The differences in corresponding bond lengths in the two crystallographically non-equivalent molecules are in all cases except one less than one standard deviation. The bonds C_3-O_8 and C_7-O_6 are of the same type. Their lengths differ by 0.11 Å. As the standard deviation of the bond length is 0.08 Å, the difference is hardly significant. The carbon-oxygen skeleton of the ethylacetate molecule is approximately planar.

The temperature factors vary in a fashion consistent with details of the structure. Manganese and phosphorus have the smallest B -factors as they are located at the centre of an octahedron and a tetrahedron, respectively. Chlorine atoms have few restrictions of movements and have rather large B -factors. The same is true for carbon atoms C_1 , C_4 , C_5 and C_8 . Atoms which are bonded to several other atoms are more restricted in their movements and have smaller temperature factors. Qualitatively the relative sizes of temperature factors are in agreement with the determined structure but no quantitative significance should be attached to the absolute values.

Interatomic distances between 1.9 and 4.3 Å were calculated to analyse the packing of the molecules. The van der Waals contacts are given in Table 4.

The chlorine atoms, the CH₃ group from the acetyl group and the CH₃ group in the ethyl group play important roles in the packing of the molecules. One rather short Cl—Cl distance of 3.6 Å indicates van der Waals bonding but the other Cl—Cl distances of about 4 Å are too long for strong bonding to occur. Van der Waals bonds are probably formed between CH₃ groups and Cl atoms at distances of between 3.7 and 3.9 Å, and CH₃—O distances of about 3.5 Å also indicate weak bonding. The results obtained for this structure agree, within the experimental error with the commonly accepted values of the van der Waals radii, 1.8 Å for Cl, 2.0 Å for CH₃ and 1.5 Å for O.

Acknowledgements. We thank Professor D. W. J. Cruickshank for suggesting improvements to our least-squares programme and Miss R. Grønæk for carrying out the computations on IBM 704.

We are indebted to *Statens teknisk videnskabelige fond* and *Statens almindelige videnskabsfond* for covering the costs of programming and computations and to *Carlsbergfonden* for supplying a Weissenberg goniometer.

REFERENCES

1. Danielsen, J. and Rasmussen, S. E. *Acta Chem. Scand.* **15** (1961) 1398.
2. Bassett, H. and Taylor, H. S. *J. Chem. Soc.* **99** (1911) 1402.
3. Bassett, H. and Taylor, H. S. *Z. anorg. Chem.* **73** (1912) 75.
4. Buerger, M. J. *Acta Cryst.* **4** (1951) 531.
5. Vand, V. and Pepinsky, R. *Z. Krist.* **111** (1958) 46.
6. Bassi, M. G. *Acta Cryst.* **15** (1962) 617.
7. Goubeau, J. and Schulz, P. *Z. anorg. Chem.* **294** (1958) 224.
8. Grunze, H. *Z. anorg. Chem.* **313** (1961) 316, 323.

Received April 23, 1963.