Other features of the spectra for this radical agree with this interpretation. The quintet structure that appears when the field is oriented perpendicular to the radical plane suggests that the ^{14}N and the amino group hydrogens couple equally with the electron. When the magnetic field is directed along the *a* axis a group of well-resolved doublets appears in the hyperfine pattern. For this same orientation the doublet structure collapses to the basic seven-line pattern when deuterium replaces hydrogen on the amino group. The maximum doublet splitting attributed to an amino group hydrogen appears in the orientation very near the direction of the maximum value for the methyl group coupling. The maximum coupling of the methyl groups is predicted[7] to occur when the field is in the radical plane and perpendicular to the $C(\alpha)$–$CONH_2$ bond. Theory predicts and observations confirm[10] that the maximum coupling for hydrogen bonded to nitrogen in a nitrogen-centered π radical occurs when the field is in the nodal plane of the nitrogen p orbital and perpendicular to the N–H bond. The minimum coupling for such hydrogen occurs when the field is parallel to the N–H bond. The qualitative features of the spectra associated with the amino group protons for each of the radicals studied agree with these predictions. It is possible that the doublet structure from the amino group proton arises from electron spin density on oxygen with coupling through the hydrogen bond network. This would require an unreasonably large spin density on oxygen to explain the magnitude of the splitting observed (3.1 G in the case of radical **1**).

Acknowledgment. We wish to thank Dr. H. Wallace Baird for his assistance with the X-ray diffraction results.

The Crystal Structure of the Ethyl Grignard Reagent, Ethylmagnesium Bromide Dietherate[1]

L. J. Guggenberger[2a] and R. E. Rundle[2b]

Contribution from the Institute for Atomic Research and the Department of Chemistry, Iowa State University, Ames, Iowa 50010.

Received March 1, 1968

Abstract: An X-ray diffraction study of the ethyl Grignard reagent in diethyl ether was undertaken to establish the structure of this reagent in the solid state. Crystals of $C_2H_5MgBr \cdot 2(C_2H_5)_2O$ are monoclinic with space group $P2_1/c$ and four formula units per cell of dimensions $a = 13.18$ Å, $b = 10.27$ Å, $c = 11.42$ Å, and $\beta = 103.3°$. The structure consists of the packing of discrete monomer units with a bromine atom, an ethyl group, and two ether groups tetrahedrally coordinated to a magnesium atom.

Investigations into the nature of the Grignard reagent have been numerous and diverse in the recent literature. This problem is discussed in two recent reviews[3,4] which testify to the scope of the research done and the problems involved in its interpretation. The purpose of this paper is to present and discuss the details of the crystal structure refinement of the ethyl Grignard reagent. A preliminary account of this work was reported earlier.[5]

Experimental Section

The ethyl Grignard solution was prepared in the conventional way in diethyl ether in about 1 *M* concentration. The details of the solution preparation, purification, and transfer into glass capillaries will not be given here since they are similar to those reported by Stucky in his work[6] on the phenyl Grignard reagent. Single crystals were grown in Lindemann glass capillaries by cooling with a cold nitrogen gas stream. Crystals during growth were consistently prismatic with monoclinic C_{2h} point symmetry. No effort was made to determine the crystal melting point accurately, but it is estimated to be about 15°.

Ethylmagnesium bromide dietherate crystallizes in the monoclinic system with cell parameters of $a = 13.18 \pm 0.03$, $b = 10.27 \pm 0.03$, $c = 11.42 \pm 0.03$ Å, and $\beta = 103.3 \pm 0.3°$. The calculated density on the basis of four formula units per cell is 1.24 g/cm^3. It was not possible to obtain an experimental density. The systematic absences of $\{h0l\}$, $l = 2n + 1$, and $\{0k0\}$, $k = 2n + 1$, establish the space group as $P2_1/c$. All atoms in the cell are in the general positions[7] $\pm(x, y, z;\ x, {}^1/_2 - y, {}^1/_2 + z)$.

The following nine zones of intensity data were measured on the precession camera on two crystals using Zr-filtered Mo Kα radiation: $\{0kl\}$, $\{1kl\}$, and $\{2kl\}$ on the first crystal and $\{h0l\}$, $\{h1l\}$, $\{h2l\}$, $\{hk0\}$, $\{hk1\}$, and $\{hk2\}$ on the second crystal. The data were measured at about −75°. The entire camera was enclosed in a polyethylene tent as this proved to be the only effective way of preventing icing of the capillary. Crystals used were cylindrical in shape with diameter and length of about 0.3 mm.

Timed exposures were taken according to ar^n with $a = 1$ min, $r = 2$, and $n = 0, 1, \ldots, 8$. The intensities were measured by comparison with a series of standard intensities. On those photographs showing mm symmetry, two quadrants were judged and then averaged. A total of 979 observed reflections was judged.

The errors in the structure factors were assigned using a modified Hughes scheme[8] so that

---

[1] Contribution No. 2271; work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] (a) Central Research Department, E. I. du Pont de Nemours and Co., Wilmington, Del. (b) Deceased, Oct 9, 1963.

[3] B. J. Wakefield, *Organometal. Chem. Rev.*, 1, 131 (1966).

[4] E. C. Ashby, *Quart. Rev.* (London), 21, 259 (1967).

[5] L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 5344 (1964).

[6] G. Stucky and R. E. Rundle, *ibid.*, **86**, 4825 (1964); G. Stucky and R. E. Rundle, *ibid.*, **85**, 1002 (1963).

[7] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 99.

[8] "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 328.

Table I. Final Atomic Parameters ($\times 10^4$) with Standard Deviations[a]

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	1413 (2)	−0212 (3)	2113 (2)	67 (1)	106 (3)	94 (2)	−5 (3)	19 (1)	9 (4)
Mg	2762 (4)	0185 (8)	0962 (5)	61 (4)	82 (7)	81 (5)	5 (7)	9 (4)	9 (9)
O(1)	2247 (14)	1824 (14)	0023 (15)	71 (12)	67 (15)	126 (20)	−23 (13)	38 (14)	21 (18)
O(2)	2453 (12)	−1195 (14)	−0374 (14)	58 (11)	84 (15)	102 (16)	8 (13)	6 (12)	−16 (17)
C(1)	4410 (12)	0261 (24)	1726 (15)	34 (9)	98 (21)	80 (15)	−25 (21)	5 (11)	−4 (27)
C(2)	4759 (19)	−0529 (27)	2797 (23)	110 (20)	146 (37)	151 (28)	15 (28)	18 (20)	−75 (32)
C(3)	1147 (13)	2258 (26)	−0480 (18)	28 (12)	175 (34)	62 (16)	32 (22)	32 (15)	21 (32)
C(4)	0930 (21)	3284 (24)	0313 (24)	115 (23)	92 (26)	163 (29)	34 (25)	87 (25)	−33 (29)
C(5)	2989 (28)	2665 (29)	−0336 (31)	85 (26)	143 (35)	110 (38)	3 (31)	−19 (31)	6 (33)
C(6)	3342 (21)	2163 (31)	−1388 (36)	87 (21)	165 (37)	262 (46)	33 (27)	100 (30)	−32 (41)
C(7)	1414 (14)	−1473 (22)	−1071 (21)	36 (13)	113 (28)	127 (25)	9 (18)	57 (17)	−43 (28)
C(8)	1303 (20)	−0886 (28)	−2335 (22)	99 (19)	173 (37)	144 (27)	−4 (29)	53 (19)	−31 (32)
C(9)	3224 (22)	−2111 (27)	−0550 (30)	61 (19)	104 (29)	146 (39)	11 (24)	22 (28)	46 (34)
C(10)	3239 (25)	−3286 (27)	0312 (26)	133 (29)	154 (36)	138 (32)	25 (30)	−49 (29)	16 (34)

[a] The anisotropic temperature factors are of the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

$$\sigma = 4F_{\min}/F_o \qquad F_o < 4F_{\min}$$

$$\sigma = F_o/4F_{\min} \qquad F_o > 4F_{\min}$$

where $F_{\min}$ is the absolute value of the minimum observable structure factor. A small number of questionably weak reflections were called unobserved; the intensities for these were set equal to $I_{\min}/2$, and they were used in the refinement with one-half their weights calculated using the above formulas.

The data were corrected for Lorentz and polarization effects in the usual way. No correction was applied for absorption. The linear absorption coefficient for Mo Kα radiation is 29.1 cm^{-1}. The atom form factors for the neutral atoms were used.[9] The bromine scattering was corrected for the real and imaginary anomalous dispersion contributions using the values listed by Templeton.[10] The function minimized in least squares was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight assigned to each structure factor. The least-squares and Fourier programs were local programs written by Fitzwater.[11]

Solution and Refinement of the Structure

The nine zones of data were scaled together by comparing the structure factors for the same reflections as they appeared on different zones. A three-dimensional Patterson function was computed from which the Br and Mg atom positions were located. The Br positions were obtained by analyzing the Harker sections on the Patterson map while the Mg atom positions were obtained from the Br–Mg vectors. All of the oxygen and carbon atom positions were obtained from an electron density map with the phases determined by the Br and Mg positions.

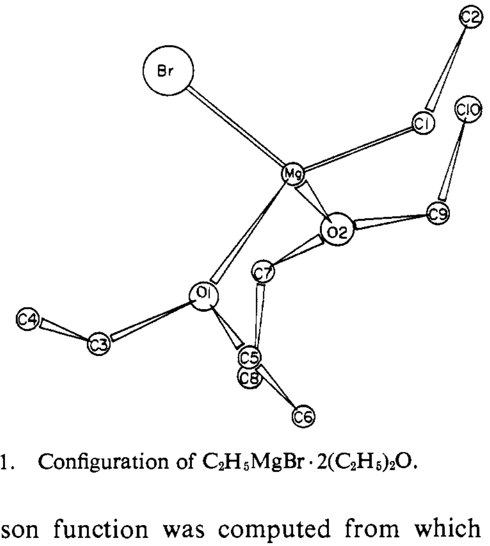


Figure 1. Configuration of $C_2H_5MgBr \cdot 2(C_2H_5)_2O$.

In the initial refinement individual scale factors were refined for each zone of data. After several cycles of least squares with isotropic temperature factors, the conventional R was 0.094. The average values of $w\Delta^2$, where $\Delta = ||F_o| - |F_c||$, were examined for the individual zones of data. As a result, small adjustments were made in the weights of some of the data zones, effectively placing less weight on some of the higher levels of data which were known to be less accurate because of nonuniform spot shapes on photographs of these zones. The equivalent data recorded on more than one zone were averaged, and all of the zones were scaled together using the least-squares refined scale factors. After the averaging process 670 pieces of data remained, including 637 observed reflections. After two cycles of least squares with anisotropic temperature factors, R was 0.087. Sixteen of the 25 hydrogen atoms were located on an electron density difference map close to their calculated positions. These hydrogen atoms were included, but not refined, in the structure factor calculations with isotropic temperature factors of 4.5. A small weighting scheme adjustment was made to the low $(\sin\theta)/\lambda$ data on the basis of the $w\Delta^2$ averages taken in regions of $(\sin\theta)/\lambda$. The refinement was stopped after two more cycles of least squares. A final electron density difference map showed no peaks greater than 0.5 e/Å^3. The final R factors for observed reflections were $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.073$ and $wR = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2} = 0.064$. The corresponding values for all reflections were $R = 0.077$ and $wR = 0.065$. The R and wR for all classes of reflections and all zones of data were in good agreement with the above values.

The final parameters from the refinement of ethylmagnesium bromide dietherate are given in Table I where the numbering system is as shown in Figure 1.[12]

---

(9) H. P. Hansen, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 17, 1040 (1964).

(10) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(11) D. R. Fitzwater, unpublished computer programs, Iowa State University, 1965.

(12) Calculated and observed structure factors for $C_2H_5MgBr \cdot 2(C_2H_5)_2O$ are deposited as Document No. 10010 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

The hydrogen atom positions used in the final refinement are given in Table II.

Table II. Hydrogen Atom Positions ($\times 10^4$)

Atom	x/a	y/b	z/c
H(11)	4615	1278	1984
H(12)	4818	−0040	1051
H(21)	5608	−0416	3103
H(22)	4584	−1543	2550
H(23)	4381	−0225	3483
H(31)	0600	1442	−0512
H(32)	1045	2619	−1423
H(51)	3692	2761	0440
H(52)	2669	3661	−0509
H(71)	0820	−1039	−0666
H(72)	1264	−2542	−1145
H(81)	0551	−1097	−2903
H(82)	1910	−1374	−2741
H(83)	1466	0129	−2262
H(91)	4002	−1654	−0379
H(92)	3047	−2482	−1485

Discussion

The structure of $C_2H_5MgBr\cdot 2(C_2H_5)_2O$ consists of the packing of discrete monomer units such as the one shown in Figure 1. The bond distances and bond angles are given in Table III; the errors have been calculated using the variance–covariance matrix and the program of Busing and coworkers.[13] The anisotropic thermal ellipsoids are depicted in Figure 2.[14] It is apparent from Figure 2 that chemically similar atoms have similar thermal ellipsoids. Also in every case the thermal motion is reasonable for the stereochemistry involved. This is significant in that it suggests that no serious systematic errors were introduced in the scaling of the data or in the method of weighting the data in the refinement.

Table III. Bond Lengths (Å) and Bond Angles (Degrees) with Standard Deviations[a]

Br–Mg	2.48 (1)	Br–Mg–O(1)	103.0 (5)
Mg–O(1)	2.03 (2)	Br–Mg–O(2)	103.7 (5)
Mg–O(2)	2.05 (2)	Br–Mg–C(1)	125.0 (5)
Mg–C(1)	2.15 (2)	O(1)–Mg–C(1)	111.7 (8)
O(1)–C(3)	1.50 (2)	O(1)–Mg–O(2)	101.2 (6)
O(1)–C(5)	1.43 (4)	O(2)–Mg–C(1)	109.6 (7)
O(2)–C(7)	1.44 (2)	Mg–C(1)–C(2)	114.6 (14)
O(2)–C(9)	1.43 (3)	Mg–O(1)–C(3)	128.8 (13)
C(1)–C(2)	1.45 (3)	Mg–O(1)–C(5)	118.9 (15)
C(3)–C(4)	1.46 (3)	C(3)–O(1)–C(5)	112.0 (16)
C(5)–C(6)	1.48 (4)	Mg–O(2)–C(7)	123.1 (11)
C(7)–C(8)	1.54 (3)	Mg–O(2)–C(9)	122.1 (14)
C(9)–C(10)	1.55 (4)	C(7)–O(2)–C(9)	114.0 (16)
		O(1)–C(3)–C(4)	106.7 (17)
		O(1)–C(5)–C(6)	112.7 (24)
		O(2)–C(7)–C(8)	108.2 (17)
		O(2)–C(9)–C(10)	109.0 (25)

[a] The standard deviations of the last significant figures are in parentheses.

It is evident from Figure 1 that the ethyl group, a bromine atom, and two ether groups form a somewhat distorted tetrahedron about a single magnesium atom. The distortion, with the largest angle being 125.0° for angle Br–Mg–C(1), is undoubtedly due to the steric requirements of the groups involved. The bond distances to the Mg atom compare favorably with those calculated on the basis of tetrahedral covalent radii.[15]

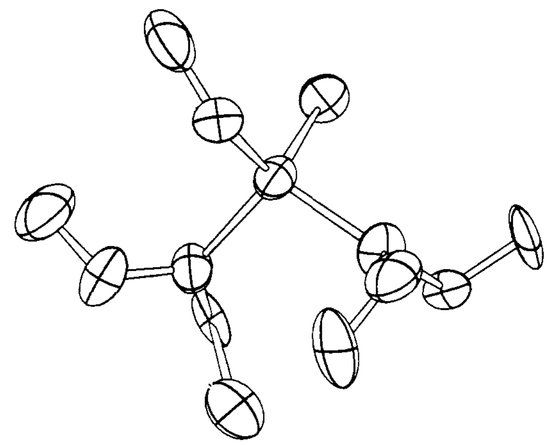
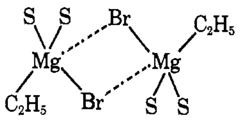


Figure 2. Thermal ellipsoids of $C_2H_5MgBr\cdot 2(C_2H_5)_2O$. The unit depicted here is the mirror image of the one in Figure 1 so that the ether group C(6), C(5), O(1), C(3), C(4) is on the right.

There are no solid-state etherates characterized well enough for a comparison of ether distances and angles. However, the average ether distances and angles of 1.51 (2) Å for C(3)–C(4), 1.45 (2) Å for C(3)–O(1), 109.2 (2.0)° for angle C(4)–C(3)–O(1), and 113.0 (2.0)° for angle C(3)–O(1)–C(5) agree within the errors involved with those determined by electron diffraction.[16] It is significant that the planes defined by the ether methylene carbons and oxygen atoms come within 0.17 Å [C(3), O(1), C(5)] and 0.30 Å [C(7), O(2), C(9)] of passing through the Mg atom. This along with the angles involved demonstrates that the ether oxygens are trigonally bonded to the magnesium. There was evidence in the phenyl Grignard structure[6] for tetrahedral coordination of the ether oxygens to the magnesium, but the ether positions were not well characterized in that case. The configurations assumed by the ether groups themselves are undoubtedly dictated by steric requirements. The dihedral angle between the planes C(3), O(1), C(5) and C(4), C(3), O(1) is 82.2° while the dihedral angle is 83.0° between the planes C(3), O(1), C(5) and C(6), C(5), O(1).

A portion of the packing in the unit cell is shown in Figure 3. It is apparent from Figure 3 that the ether groups occur in layers in the cell. The packing of two monomer units related by the lattice center of symmetry is of interest and corresponds to the following



where S represents the solvent, $(C_2H_5)_2O$. The dashed nonbonding Mg–Br distance is 5.81 Å, thus preventing any association of the Grignard reagent in the solid state. These units are prevented from approaching

---

(13) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE—A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(14) C. K. Johnson, Report No. 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(15) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(16) P. W. Allen and L. E. Sutton, *Acta Cryst.*, 3, 46 (1950).

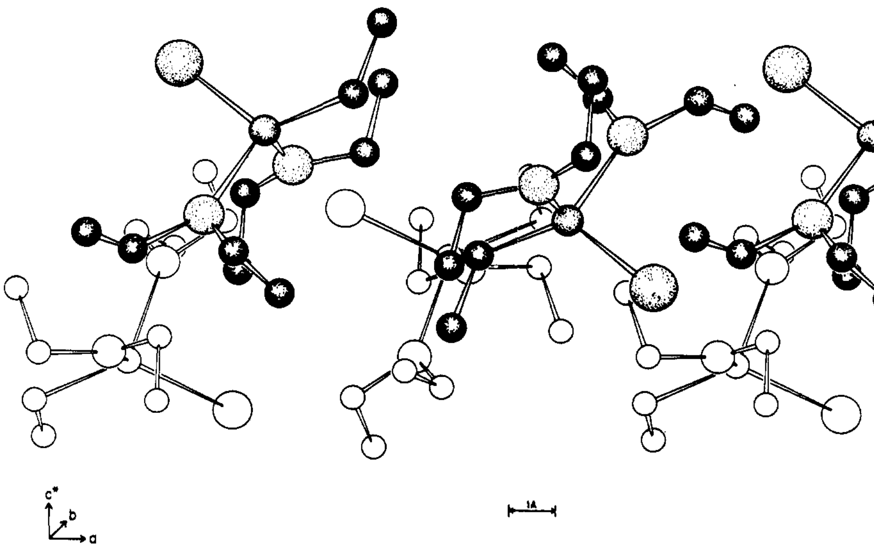


Figure 3. Packing diagram of $C_2H_5MgBr \cdot 2(C_2H_5)_2O$.

any closer by ether contacts between the two units. All nonhydrogen intermolecular contacts less than 4.0 Å were calculated and all nine of the resulting contacts involved ether carbons in some way with the shortest contact being 3.68 Å. Of interest also is the fact that the methylene carbon, magnesium, and bromine atoms for the two center of symmetry related units are coplanar within 0.001 Å. There is nothing crystallographically requiring this. This represents the most efficient mode of packing for these units.

Some previous studies[17] of solid-state Grignard reagents have resulted in a lack of reproducibility and a failure to isolate a species of definite chemical composition. However, the X-ray work done in this area proves that species of definite chemical composition with integral numbers of solvent molecules per magnesium do exist in the solid state. Stucky[6] has shown that the phenyl Grignard reagent $C_6H_5MgBr \cdot 2(C_2H_5)_2O$ exists and is also monomeric in the solid state. Schröder[18] has characterized the phenyl Grignard reagent in tetrahydrofuran, $C_6H_5MgBr \cdot 2C_4H_8O$. The methyl Grignard reagent in tetrahydrofuran reportedly exists as $CH_3MgBr \cdot 3(C_4H_8O)$.[19] This is important in relation to this work since it shows that magnesium will coordinate three of the sterically less demanding C_4H_8O's.

As more structures are becoming available the picture seems to be clearing somewhat with respect to the structure determining aspects of organomagnesium compounds of this type. For the solid state, and possibly for the solution state as well, the coordination about magnesium and the structure assumed depend primarily on the steric requirements of the R group and solvent molecules attached to the magnesium since they put rigid constraints on the number of groups that can approach the magnesium atom. In this context the basicity of the solvent is determined primarily by its steric requirements and secondarily by the electronic nature of the donor atom. This is implied in a comparison of $C_2H_5MgBr \cdot 2(C_2H_5)_2O$ with $CH_3MgBr \cdot 3C_4H_8O$.[19] Also, a related species, magnesium dibromide, coordinates four tetrahydrofurans, $MgBr_2 \cdot 4C_4H_8O$,[20,21] but only two of the sterically more demanding diethyl ethers, $MgBr_2 \cdot 2(C_2H_5)_2O$.[22] The recent crystal structure[23] of $C_2H_5MgBr \cdot (C_2H_5)_3N$ is dimeric with symmetrically bridging bromine atoms and *trans*-ethyl groups. In this case the dimeric configuration is the best way to accommodate the steric requirements of the groups involved.

Much of the controversy over the nature of the Grignard reagent is concerned with the structure in solution. Great care must be taken in extrapolating the solid-state structures to the solution state. This extrapolation is especially tenuous in this case where packing forces are very important since the intramolecular and intermolecular forces will differ in solution. Although there is also evidence for a monomer species in solution,[24] the constitution of the Grignard reagent over a range of concentrations in solution is probably more complicated[3,4] than the situation in the solid state.

---

(17) S. Hayes, *Ann. Chim.* (Paris), 8, 545 (1963); A. Kirrmann, R. Hamelin, and S. Hayes, *Bull. Soc. Chim. France*, 1395 (1963).

(18) F. Schröder, Dissertation, Institut für Anorganische Chemie der Technischen Hochschule, Braunschweig, Germany, 1965.

(19) M. Vallino, Abstracts 3rd Symposium of Organometallic Chemistry, Munich, 1967.

(20) F. Schröder and H. Spandau, *Naturwiss.*, **53**, 360 (1966).

(21) M. Perucaud, J. Ducom, and M. Vallino, *Compt. Rend.*, **264**, 571 (1967).

(22) H. Schibilla and M. LeBihan, *Acta Cryst.*, **23**, 332 (1967).

(23) J. Toney and G. D. Stucky, *Chem. Commun.*, 708 (1967).

(24) A. D. Vreugdenhil and C. Blomberg, *Rec. Trav. Chim.*, **82**, 453 (1963).