

TABLE III  
BOND ANGLES AND INTERATOMIC DISTANCES  
 $Mg_4Br_6O \cdot 4C_4H_{10}O^a$

Atoms	Distance, Å.	Atoms	Angle, deg.
Br <sub>1</sub> -Br <sub>2</sub>	4.555 ± 0.005	O <sub>2</sub> -Mg-Br <sub>2</sub>	87.36 ± 0.3
Br <sub>1</sub> -Br <sub>2</sub> (II)	4.438 ± 0.005	O <sub>2</sub> -Mg-Br <sub>2</sub> (III)	88.48 ± 0.3
Br <sub>2</sub> -Br <sub>2</sub> (II)	4.516 ± 0.003	O <sub>2</sub> -Mg-Br <sub>1</sub>	86.61 ± 0.3
Br <sub>1</sub> -Mg	2.613 ± 0.009	O <sub>2</sub> -Mg-O <sub>1</sub>	179.80 ± 0.7
Br <sub>2</sub> -Mg	2.617 ± 0.008	Br <sub>1</sub> -Mg-Br <sub>2</sub>	121.14 ± 0.3
Br <sub>1</sub> -Mg (II)	2.578 ± 0.008	Br <sub>1</sub> -Mg-Br <sub>2</sub> (III)	117.53 ± 0.3
Br <sub>1</sub> -O <sub>2</sub>	3.192 ± 0.002	Mg-Br <sub>1</sub> -Mg (I)	75.93 ± 0.4
Br <sub>1</sub> -O <sub>2</sub>	3.168 ± 0.003	Mg-Br <sub>2</sub> -Mg (III)	75.33 ± 0.3
Br <sub>1</sub> -O <sub>1</sub>	3.45 ± 0.02	Mg-O <sub>1</sub> -C <sub>1</sub>	127.85 ± 6.04
Br <sub>2</sub> -O <sub>1</sub>	3.43 ± 0.02	Mg-O <sub>1</sub> -C <sub>3</sub>	118.85 ± 2.9
Br <sub>2</sub> -O <sub>1</sub> (II)	3.38 ± 0.02	Mg-O <sub>1</sub> -C <sub>2</sub>	136.44 ± 3.6
Mg-O <sub>1</sub>	2.11 ± 0.02	Mg-O <sub>1</sub> -C <sub>4</sub>	114.82 ± 2.4
Mg-O <sub>2</sub>	1.952 ± 0.008		
O <sub>1</sub> -C <sub>1</sub>	1.33 ± 0.09		
O <sub>1</sub> -C <sub>3</sub>	1.44 ± 0.05		

<sup>a</sup> Subscripts correspond to Table I. Roman numeral suffix denotes the subscripted atom has been operated on by the following: (I)  $\bar{x}\bar{y}\bar{z}$ ; (II)  $\bar{y}\bar{x}\bar{z}$ ; (III)  $y\bar{x}\bar{z}$ .

from the ethyl Grignard solution produces a reagent in which there is but one magnesium atom per molecule,<sup>15</sup> in contrast to most previous work which has suggested dimers or polymers. Oxidation products such as the one reported here, or perhaps their precursor, are likely

(15) A. C. Vrengdenhal and C. Blomberg, *Rec. trav. chim.*, **82**, 453 (1963).

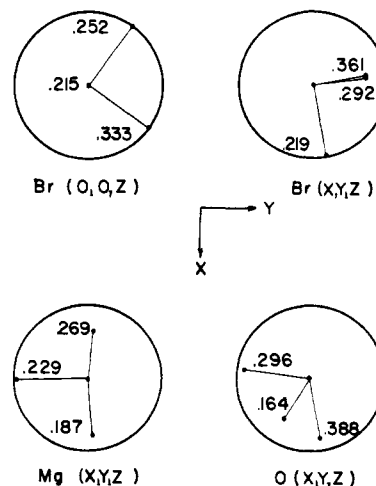


Fig. 3.—Stereograms of anisotropic thermal ellipsoids of Br, Mg, and O atoms on [001]: the magnitudes of the displacements along the axes of the ellipsoids are given in Ångstrom units.

suspects for occluding work on the nature of Grignard reagents, especially in determining their degree of polymerization. Further structural investigations of organomagnesium and organomagnesium halide systems are being made.

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

## The Constitution of the Grignard Reagent, Phenylmagnesium Bromide Dietherate<sup>1</sup>

By G. STUCKY AND R. E. RUNDLE<sup>2</sup>

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In the crystalline state  $C_6H_5MgBr \cdot 2C_4H_{10}O$  consists of a magnesium atom tetrahedrally coordinated to two diethyl ether molecules, a phenyl group, and a bromide atom. There is no evidence of intermolecular interactions between molecules. Some structural properties of crystalline diphenylmagnesium dietherate are briefly discussed.

### Introduction

In an earlier note<sup>3</sup> the partial structure of the Grignard reagent,  $C_6H_5MgBr \cdot 2C_4H_{10}O$ , and evidence suggesting the existence of the same species or possibly a higher etherate in solution were presented. The purpose of this paper is to present in greater detail the structural properties of the Grignard system,  $C_6H_5MgBr$  in diethyl ether.

### Experimental

A 1.5 *N* solution of  $C_6H_5MgBr$  was prepared by the conventional method of slowly adding a mixture of bromobenzene and diethyl ether to an excess of magnesium. All operations were carried out in previously vacuum- and infrared-dried apparatus under a dry, oxygen-free atmosphere of nitrogen or argon. The procedure used to purify the phenylmagnesium bromide was that described by Strohmeier for diphenylmagnesium dietherate.<sup>4</sup>

The Grignard reagent was transferred under an argon atmosphere to one side of an L-shaped container. Crystallization of the reagent was obtained by cooling the solution to Dry Ice temperature and then allowing the temperature to increase slowly. The excess mother liquid was then decanted to the other side of the L-tube, and pure ether was thermally distilled from

the mother liquor back to the crystals. The crystals were allowed to melt (m.p. 15–20°), and the recrystallization process was repeated several times. By using a partial vacuum and liquid nitrogen to freeze the excess ether and impurities in one side of the L-tube, the liquid reagent was poured into capillaries, n.m.r. tubes, or other suitable containers attached directly to the L-tube. Three samples gave an average Br/Mg ratio of  $1.02 \pm 0.02$ . A positive chemical test was obtained for a metal-carbon bond.<sup>5</sup> Because of the volatility of the diethyl ether and entrainment of the ether in the microcrystals, some excess diethyl ether remained in the melt; however, proton magnetic resonance measurements showed that the diethyl ether to phenyl ratio was no greater than 2.17. An ether content lower than 2 moles/mole of phenylmagnesium bromide gave a sirupy substance in which crystallization could not be induced.

Single crystals for X-ray investigation were grown inside a soft glass, thin-walled capillary by cooling with a cold nitrogen gas stream. The transparent crystals were dendritic and thermally distilled inside the capillary. To minimize the distillation, the crystals were grown with the long crystal axis at a right angle to the nitrogen stream; the dimensions of the crystals still changed with time, however, so that the quality of the X-ray was affected.

An ether/methyl ratio of 2.08 to 1 has been found for a similar low temperature crystalline complex of methylmagnesium bromide in diethyl ether. The crystal structure of the related unsolvated derivative,  $[(CH_3)_2Mg]_n$ , has been independently obtained by one of the authors (G. S.) and by E. Weiss of Cyanamid Research in Geneva. This compound has an orthorhombic cell with  $a = 5.96$ ,  $b = 11.44$ ,  $c = 5.44$  Å. (parameters of G. S.),

(1) Contribution No. 1409; work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) (a) Chemistry Department, University of Illinois, Urbana, Ill.; (b) deceased, Oct. 9, 1963.

(3) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963).

(4) W. Strohmeier, *Ber.*, **88**, 1218 (1955).

(5) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

space group  $Ib\bar{a}m$ , and is isostructural with  $[(CH_3)_2Be]_n$ . The Mg-Mg distance is 2.72 Å. (a detailed report of the structure will be given by E. Weiss in the *Journal of Organometallic Chemistry*).

### Collection of Data

Space group and unit cell determinations were obtained from precession data from  $\{0kl\}$ ,  $\{1kl\}$ ,  $\{2kl\}$ ,  $\{hk0\}$ ,  $\{hkl\}$ , and  $\{hk2\}$  reciprocal lattice nets. The crystal class is orthorhombic with  $a = 12.25 \pm 0.04$ ,  $b = 12.81 \pm 0.04$ ,  $c = 11.02 \pm 0.04$  Å. The observed extinctions were:  $\{h00\}$ ,  $h = 2n + 1$ ;  $\{0k0\}$ ,  $k = 2n + 1$ ;  $\{00l\}$ ,  $l = 2n + 1$ ; space group  $P2_12_12_1$ . The observed density was 1.17 g./cm.<sup>3</sup> vs. the calculated density for four molecules of  $C_6H_5MgBr \cdot 2C_4H_{10}O$ , 1.27 g./cm.<sup>3</sup>. Kitaigorodskii's<sup>6</sup> packing coefficient is about 0.64 which is in the range of expected values for organic crystals. Two-dimensional  $\{hk0\}$  precession intensity data and three-dimensional General Electric XRD-5 diffractometer data were collected at a temperature of  $-50^\circ$  with 895 independent reflections being recorded. Standard reflection intensities were taken every 4 hr. during data collection, so as to correct for the change in position of the crystals with time. The two-dimensional  $\{hk0\}$  data were judged visually by two observers and an average intensity for a given reflection was obtained from the equivalent sets  $\{hk0\}$ ,  $\{\bar{h}k0\}$ ,  $\{h\bar{k}0\}$ ,  $\{\bar{h}\bar{k}0\}$ . Because the precise crystal size was not determinable, no attempts were made to apply absorption corrections to the data. The absorption coefficient for Mo  $K\alpha$  is  $M = 25.48$  cm.<sup>-1</sup>, and the maximum  $MR$  value was estimated to be 0.7 ( $R$  = maximum crystal radius). In addition to the usual Lorentz and polarization effects, corrections were made for the variation of the standard reflections with time and for the anomalous scattering of the bromine atoms.

### Determination of the Structure

The weighted reciprocal lattice gave some indication as to the nature of the packing in the crystal. For reflections  $\{hk0\}$ ,  $k$  odd reflections were weak or missing; for  $[h00]$ , even orders were relatively strong; and for  $\{h0l\}$ ,  $h + l$  odd reflections were weak. Both of the pseudo-extinctions could be explained if the atoms in the crystal had approximate mirror symmetry about the plane  $x = 0$ . Since the even orders of (200) were all relatively strong, the major atom densities must occur in layers with a spacing of  $\sim a/2n$ . This agreed with the observation that the needle axis of the crystal was in the [100] direction, implying that the molecules packed in this direction.

The pinacoidal projections of  $P2_12_12_1$  were used to confirm the results obtained from a three-dimensional Patterson calculation. The plane group to space group transformations are listed in Table I. Space

TABLE I

TRANSFORMATION BETWEEN SPACE GROUP COORDINATES OF  $P2_12_12_1$  AND THE COORDINATES OF THE PROJECTIONS OF  $P2_12_12_1$ , ON (100), (010), AND (001) USING PROJECTIONS OF THE TWOFOLD SCREW AXES AS ORIGINS

Description	Transformation
$xyz$ from $x'y'$ (001)	$x = x' + 1/4, y = y'$
$xyz$ from $y''z''$ (100)	$y = y'' + 1/4, z = z''$
$yyz$ from $x'''z'''$ (010)	$z = z''' + 1/4, x = x'''$

(6) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961.

group coordinates were chosen in accordance with Vol. 1 of the "International Tables for X-ray Crystallography." The Patterson section  $U = 0$  is shown in Fig. 1. From this section and the section  $U = 1/2$ , bromine, magnesium, and rough phenyl carbon positions were determined. The bromine-oxygen vectors gave oxygen coordinates of the type  $x, y, z$  and  $\bar{x}, y, z$ , completing the tetrahedral coordination of the magnesium atom. These results were confirmed by two-dimensional electron density projections calculated using the structure factor signs for a bromine atom at  $x = 0, y = 0.095, z = -0.114$ , and a magnesium atom at  $x = 0, y = 0.274, z = 0$ . In the (010) projection the phenyl groups were found to lie at right angles to the plane of projection, and as they are very nearly centered about  $z = 1/4$ , the two sets of phenyl carbons at  $0, y, z$  and  $0, 1/2 + y, 1/2 - z$  overlap. Two-dimensional least squares gave  $R = \sum |F_{\text{obsd}} - F_{\text{calcd}}| / \sum F_{\text{obsd}} = 0.216$  for  $\{hk0\}$ , 0.158 for  $\{h0l\}$ , and 0.171 for  $\{0kl\}$ . The best agreement for the three-dimensional data was 0.178 at this stage of refinement (Table II).

### Refinement of the Structure

The nature of the distortion of the structure from the pseudo-mirror symmetry and the positions of the ether carbon atoms were not defined by the two-dimensional analysis. Least-squares and three-dimensional Fourier and difference Fourier analysis of the data showed that the entire molecule is tipped slightly from the  $x = 0$  plane. Because of the quality of the data, least-squares refinement of the carbon parameters within the restraints of known phenyl and diethyl ether molecular parameters was unsuccessful (Fig. 2 and Table III). The two- and three-dimensional Fouriers, however, do give sufficient resolution so that rough carbon positions can be obtained. From a three-dimensional Fourier calculated with bromine, magnesium, oxygen, and phenyl carbon contributions (carbon parameters constrained to a benzene ring configuration), the ether molecules were found to be tetrahedrally bonded to the magnesium atom (Fig. 3). In addition, the methyl groups are rotated about the methylene-oxygen bond so that the intramolecular distances between the methyl and bromine and the methyl and phenyl atoms are maximized. Intramolecular packing considerations support this model, as there are more stringent requirements on the rotation of the methyl groups away from the phenyl, bromine, and magnesium atoms for a trigonally coordinated ether molecule. The crystal structure can be considered as a nearly planar layer of bromine, magnesium, and phenyl groups alternating with a layer of ether molecules (Fig. 4 and 5). The molecules are packed about the  $2_1$  axis parallel to [100] so that the oxygen atoms of each molecule are approximately packed against the bisector of the bromine-magnesium-phenyl carbon angle of the molecules directly above and below them. The oxygen, bromine, and magnesium  $x$ -parameters indicate that the bromine-magnesium-phenyl carbon plane is tilted about  $7^\circ$  from  $x = 0$ . Bromine and magnesium positions alone eliminate the possibility of a bridged structure. The closest magnesium-magnesium approach is about 6.1 Å., the closest bromine-bromine distance within a phenyl layer is more than 6.4 Å., and the bromine-bromine distance between layers is greater than 6.1 Å.



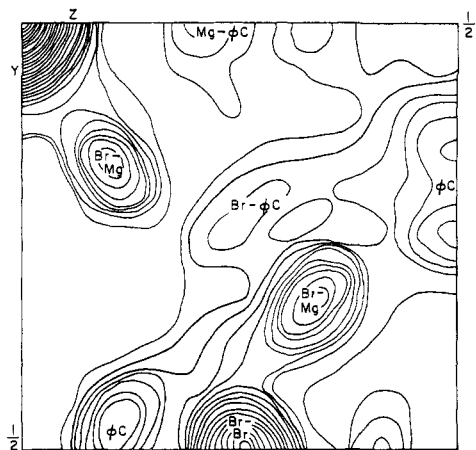


Fig. 1.—Three-dimensional Patterson section,  $U = 0$ , of  $C_6H_5MgBr \cdot 2C_4H_{10}O$ .

compares with the expected covalent bond length of 2.17 Å. Whereas the high symmetry of the  $Mg_4Br_6O$  polyhedron led to disorder of the ether molecules in  $Mg_4$

TABLE III

ATOMIC PARAMETERS FOR  $C_6H_5MgBr \cdot 2C_4H_{10}O$  ISOTROPIC TEMPERATURE REFINEMENT

Atom	$x$	$y$	$z$	$B$
Br	-0.0158	0.0924	-0.1169	2.88
$\sigma$	0.0005	0.0004	0.0005	
Mg	-0.001	0.267	-0.031	3.95
$\sigma$	0.002	0.002	0.002	
O <sub>1</sub>	-0.112	0.349	-0.125	5.22
$\sigma$	0.004	0.004	0.005	
O <sub>2</sub>	0.136	0.340	-0.098	4.91
$\sigma$	0.004	0.004	0.005	
C <sub>6</sub> H <sub>5</sub> C <sub>1</sub>	-0.00	0.29	0.18	6.85
C <sub>6</sub> H <sub>5</sub> C <sub>2</sub>	-0.02	0.22	0.22	5.67
C <sub>6</sub> H <sub>5</sub> C <sub>3</sub>	0.02	0.19	0.37	10.16
C <sub>6</sub> H <sub>5</sub> C <sub>4</sub>	-0.00	0.29	0.41	10.06
C <sub>6</sub> H <sub>5</sub> C <sub>5</sub>	0.02	0.37	0.37	11.08
C <sub>6</sub> H <sub>5</sub> C <sub>6</sub>	-0.02	0.37	0.24	8.85
C <sub>11</sub>	-0.12	0.35	-0.28	2.64
C <sub>12</sub>	-0.22	0.43	-0.03	
C <sub>13</sub>	-0.19	0.31	-0.27	6.18
C <sub>14</sub>	-0.18	0.50	-0.08	5.61
C <sub>21</sub>	0.17	0.28	-0.32	10.70
C <sub>22</sub>	0.10	0.45	-0.10	9.83
C <sub>23</sub>	0.22	0.25	-0.32	3.06
C <sub>24</sub>	0.21	0.49	-0.03	6.14

TABLE IV

BOND DISTANCES AND ANGLES FOR  $C_6H_5MgBr \cdot 2C_4H_{10}O$  Br, Mg, AND O ATOMS

Description	Distance or angle
Br-Mg	2.44 ± 0.02
Mg-O <sub>1</sub>	2.01 ± 0.04
Mg-O <sub>2</sub>	2.06 ± 0.04
Br-Mg-O <sub>1</sub>	103.26 ± 1.57
Br-Mg-O <sub>2</sub>	109.84 ± 1.38

$Br_6O \cdot 4C_4H_{10}O$ ,<sup>8</sup> there appears to be no disorder in this Grignard dietherate.

It is of interest that the ether appears to be approximately tetrahedrally coordinated to magnesium in the Grignard but trigonally coordinated to magnesium in  $Mg_4Br_6O \cdot 4C_4H_{10}O$ . This difference may arise partly for steric reasons, but it is noteworthy that as the coordination number of magnesium increases so should the ionic character of the magnesium-oxygen bond.

(8) G. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **86** 4821 (1964).

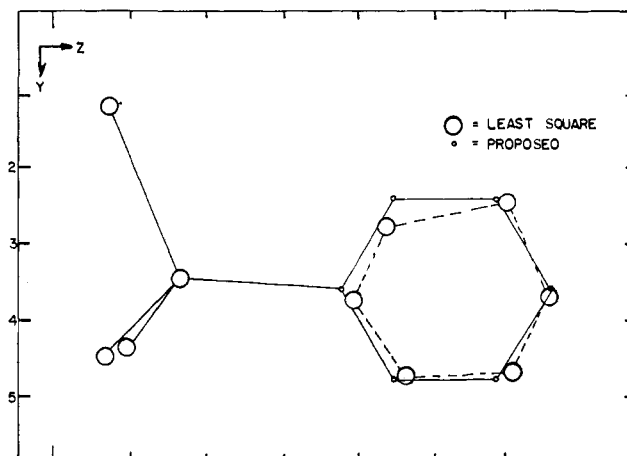


Fig. 2.—Difference between phenyl carbon model  $y$ - and  $z$ -coordinates and those given by least squares (distances are in Ångstrom units).

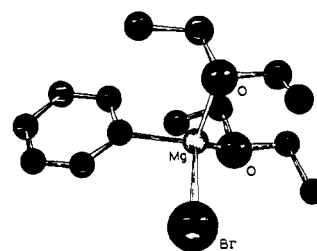


Fig. 3.—Molecular configuration of  $C_6H_5MgBr \cdot 2C_4H_{10}O$ .

The trigonal configuration is more characteristic of expectations for ionic bonding, while a tetragonal configuration is the one expected if covalent bonding is structure determining, and the change in ionic character of the Mg-O bond may well be significant to the change in configuration.<sup>8a</sup>

The existence of tetrahedrally coordinated monomers is also probable for  $(C_6H_5)_3CMgBr \cdot 2C_4H_{10}O$ ,<sup>9</sup>  $C_2H_5MgI \cdot 2C_4H_{10}O$ ,<sup>10</sup> and  $(C_6H_5)_2Be \cdot 2C_4H_{10}O$ .<sup>11</sup> Bridged species are implied by the existence of crystalline monoetherates of  $CH_3MgI \cdot (C_6H_{11})_2O$ <sup>12</sup> and  $C_{10}H_7MgBr \cdot C_4H_{10}O$ <sup>10</sup> and the polymeric characteristics of unsolvated  $(C_6H_5)_2Mg$  and  $C_6H_5MgBr$ . It does not seem unreasonable to expect that steric effects will prove to be the structure-determining factors for the above two monoetherates.

Single crystals of the phenylmagnesium bromide di-tetrahydrofuran complex have been isolated by F. Schröder at the Institut für Anorganische Chemie der Technischen Hochschule, Braunschweig. The  $C_6H_5MgBr \cdot 2C_4H_8O$  molecules are packed in a monoclinic cell, space group  $P2_1/c$ . A complete three-dimensional X-ray investigation of this compound is being carried out and will be published in Schröder's Dissertation, Braunschweig, 1964.

### Diphenylmagnesium Dietherate

$(C_6H_5)_2Mg$  was prepared by heating diphenylmercury with an excess of magnesium in an evacuated bomb

(8a) NOTE ADDED IN PROOF.—L. Guggenberger and R. E. Rundle have completed the three-dimensional structure of the ethyl Grignard reagent,  $C_2H_5MgBr \cdot 2C_4H_{10}O$ . This compound is also monomeric and the only significant difference between the two Grignard structures is that the magnesium atom is only 0.2 Å. out of the ether C-O-C plane. More details concerning the structure will be published in the near future.

(9) M. Gomberg and W. Bachmann, *J. Am. Chem. Soc.*, **52**, 2455 (1930).

(10) W. Schlenk, Dissertation, University of Charlottenburg, 1929.

(11) G. Wittig and P. Hornberger, *Ann.*, **577**, 20 (1952).

(12) T. Zerewitinoff, *Ber.*, **41**, 2244 (1908).

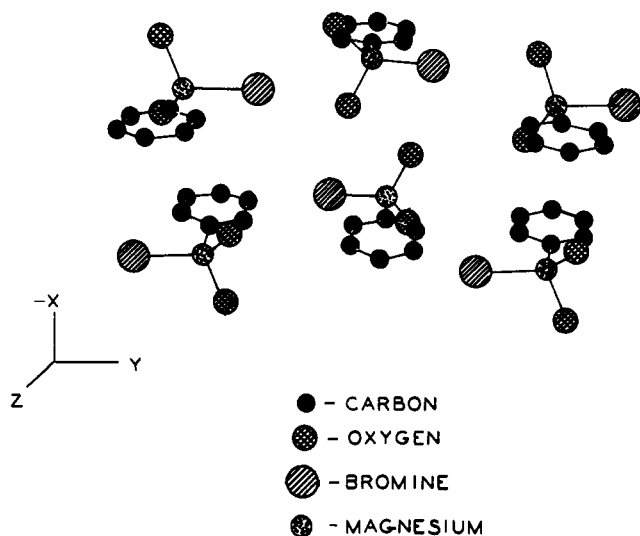


Fig. 4.—Packing of  $C_6H_5MgBr \cdot 2C_4H_{10}O$  molecules in the crystal (ether carbons omitted for clarity): molecules in the center are at  $(\bar{x}, 1/2 + y, 1/2 - z)$  and  $(1/2 - x, \bar{y}, 1/2 + z)$ ; *i.e.*, the magnesium atoms in a layer are approximately  $(0, 1/2, 1/2)$  apart. The molecules at the sides represent one translation of the unit cell in the  $y$  direction (see text for additional details).

tube for 5 to 6 hr. at  $205^\circ$ . Unchanged diphenylmercury was removed by leaching with benzene. The diphenylmagnesium was then dissolved in anhydrous diethyl ether and separated from the magnesium and mercury present by filtration. Further purification was achieved by the crystallization process described above for the phenylmagnesium bromide.  $(C_6H_5)_2Mg \cdot 2C_4H_{10}O$  has characteristics almost identical with those of  $C_6H_5MgBr \cdot 2C_4H_{10}O$ ; *e.g.*, it becomes sirupy and polymeric if more than two ethers of solvation are removed, and the melting points of both are similar and only slightly below room temperature. The crystals are also similar in appearance; the needle-axis direction in the case of  $(C_6H_5)_2Mg \cdot 2C_4H_{10}O$  is [101]. X-Ray crystallographic measurements give  $a = 14.21$ ,  $b = 7.87$ ,  $c = 17.69 \text{ \AA}$ ,  $\beta = 91.4^\circ$ , with  $\{hkl\}$ ,  $h + k = 2n + 1$  extinctions. Statistical tests and packing theory imply the space groups  $C2/m$  or  $C2$ , depending on whether the molecule does or does not have  $2/m$  symmetry.<sup>6</sup> The observed density of the solid,  $1.09 \pm 0.07 \text{ g./cm.}^3$ , and Kitaigorodskii's packing coefficient, 0.65, agree with four molecules of  $(C_6H_5)_2Mg \cdot 2C_4H_{10}O$  per unit cell, calculated density,  $1.095 \text{ g./cm.}^3$ . Proton magnetic resonance results confirmed the ether/phenyl ratio of 1. The concentrated reagent is inflammable in air and gives a positive test for a metal-carbon bond.<sup>5</sup> All crystallographic and n.m.r. results to date are consistent with a tetrahedrally coordinated magnesium atom and a monomeric molecule. A qualitative comparison of the n.m.r. spectra of  $(C_6H_5)_2Mg \cdot 2C_4H_{10}O$  and  $C_6H_5MgBr \cdot 2C_4H_{10}O$  has been given previously.<sup>3</sup> Further X-ray and resonance structural investigations of the above and other organometallic systems are currently being made.

### Discussion

It has been shown recently that the chemical shifts in the proton spectra of *concentrated* solutions of  $C_2H_5MgC_2H_5 \cdot \text{ether}$  are not the same as those of the Grignard reagents  $C_2H_5MgX \cdot \text{ether}$ ,<sup>13</sup> in agreement with the results found for  $C_6H_5MgBr \cdot \text{ether}$  and  $(C_6H_5)_2Mg \cdot \text{ether}$ .<sup>3</sup>

(13) H. Roos, and W. Zeil, *Z. Elektrochem.*, **67**, 28 (1963).

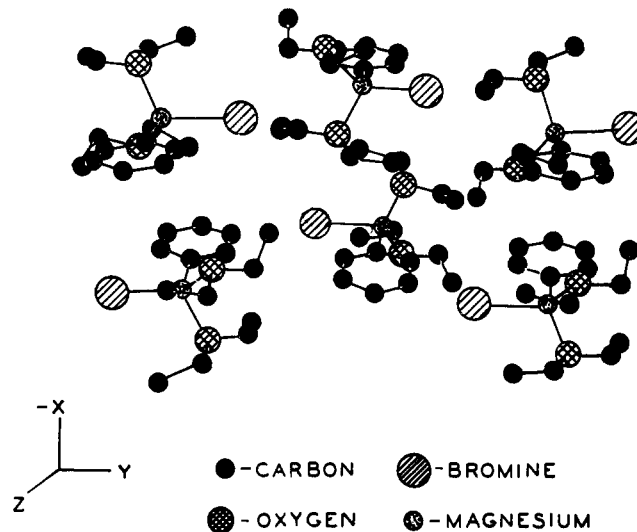
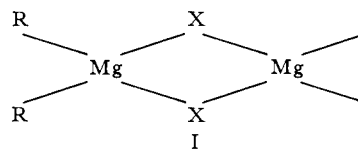
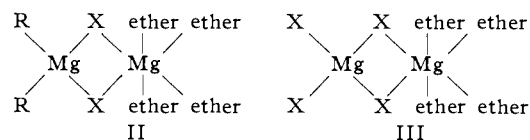


Fig. 5.—Packing of  $C_6H_5MgBr \cdot 2C_4H_{10}O$  molecules in the crystal (ether carbon atoms included): see caption for Fig. 4.

It should be pointed out that it would be surprising if there were not a difference, since the presence of the bromine atom would be expected to affect the alkyl or aryl and ether proton spectra of the often proposed structure I (ethers omitted) as well as the proton spectra



of the molecular species described in this paper. N.m.r. concentration dependent studies of the ethyl Grignard reagent in diethyl ether<sup>13</sup> also imply the existence of a compound with the same Mg/ether ratio of 1:2 which is found in the crystalline state for most Grignard reagents and which is predicted by thermodynamic measurements of the heats of solvation of Grignard compounds.<sup>14,15</sup> The observation that the differences between the resonance frequencies of the  $CH_3$  and  $CH_2$  protons of the diethyl ether in magnesium iodide solution are the same as the difference between the frequencies of the other  $CH_3$  and  $CH_2$  groups in an ethylmagnesium iodide solution has been interpreted as implying that the ether molecules are coordinated to essentially the same species in the two solutions. The molecular species postulated for the Grignard reagent in solution is II and the magnesium halide is formulated as III in



diethyl ether. The results of vapor pressure measurements made on magnesium bromide are relatively consistent, however, and indicate that at room temperature the species in diethyl ether solutions is largely monomeric<sup>16,17</sup> (Table V). It would seem that a more consistent conclusion would be that the species present in

(14) W. C. Tzschelinzeff, *Ber.*, **39**, 773 (1906).

(15) J. Lifschitz and O. E. Kalberer, *Z. physik. Chem. (Leipzig)*, **102**, 393 (1922).

(16) W. Slough and A. H. Ubbelohde, *J. Chem. Soc.*, 108 (1955).

(17) A. D. Vreugdenhil and C. Blomberg, *Rec. trav. chim.*, **82**, 453, 461 (1963).

TABLE V

DEGREE OF ASSOCIATION OF MAGNESIUM BROMIDE IN  
DIETHYL ETHER AND TETRAHYDROFURAN

Degree of association	Solvent	Ref.
1.05	Diethyl ether	14
1.09 1.17	Diethyl ether	15
1.00	Tetrahydrofuran	15

most Grignard solutions is largely monomeric  $\text{RMgX} \cdot 2(\text{ether})$ , in accordance with the recent vapor pressure measurements of the ethyl Grignard solution<sup>17</sup> and the species found in the solid state of phenylmagnesium bromide dietherate.<sup>3</sup>

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## The Magnetic Properties of Nickel(II) Complexes Containing a Macrocyclic Ligand and the Existence of a High Spin–Low Spin Equilibrium

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The effect of an axial perturbation produced by a series of anions on the magnetic properties of a nickel(II) ion in the planar field produced by a closed macrocyclic ligand containing four donor nitrogen atoms, tetra-benzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine, has been examined. With  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ , and  $\text{B}(\text{C}_6\text{H}_5)_4^-$ , the resultant complexes are diamagnetic and therefore have singlet ground states. With  $\text{I}^-$ ,  $\text{NO}_3^-$ , and  $\text{NCS}^-$ , the resultant complexes exhibit moments consistent with triplet ground states. However, for the anions  $\text{Cl}^-$  and  $\text{Br}^-$ , moments intermediate between these two extremes were observed. Measurements of the variation of magnetic susceptibility as a function of temperature between 110 and 300°K. were made. An equilibrium between singlet and triplet states has been assumed to explain the non-Curie–Weiss temperature dependence of the chloride and bromide salts. The calculated enthalpy values for the chloride and bromide are comparable with thermal energies. The entropy changes are small, as expected, but not that predicted by change in spin multiplicity alone.

### Introduction

The effect of a series of ligands of increasing strength on the spin state of certain transition metal ions is expected to produce high-spin compounds for weak field ligands and low-spin compounds for strong field ligands. Consequently, the magnetic moments of such metal complexes are expected to lie in the region of the two extremes, this indeed being the case with the majority of examples. However, a number of complexes of iron, cobalt, and nickel exhibit magnetic moments which lie between these two extremities. The temperature dependence of the magnetic susceptibilities of such compounds would not be expected to follow the usual Curie–Weiss behavior because the apparent magnetic moments of the anomalous compounds are expected to be strongly temperature dependent.

The assumption of an equilibrium between high- and low-spin isomers to explain anomalous magnetic behavior is not new and was proposed by Bozza<sup>1</sup> as long ago as 1933. Cambi and Szego,<sup>2</sup> also around this time, used this concept to explain the anomalous room temperature magnetic moments and non-Curie–Weiss temperature dependence of the magnetic susceptibilities of a series of iron(III) complexes with dialkyl dithiocarbamates. Recent work<sup>3</sup> has confirmed the anomalous room temperature magnetic moments for these compounds. Cambi also proposed an equilibrium between isomers with one and three unpaired electrons to explain the temperature dependence of susceptibility of some cobalt(II) complexes.<sup>4</sup> Theorell and Ehrenberg<sup>5</sup> and George, Beetlestone, and Griffith<sup>6</sup> obtained

spectral and magnetic data for ferrimyoglobin fluoride, cyanide, and hydroxide. Measurements of the magnetic susceptibility between 1 and 30° showed that the susceptibilities of both the high-spin fluoride and the low-spin cyanide follow the Curie law, but that of the hydroxide shows a non-Curie temperature dependence. This was interpreted as arising from an equilibrium between high- and low-spin forms, spectral data being presented to substantiate this conclusion.

The room temperature magnetic moments of some octahedral cobalt(II) complexes with  $\alpha$ -diimines obtained by Figgins and Busch<sup>7</sup> are "intermediate" in value, and an equilibrium mixture of isomeric high-spin and low-spin forms was again suggested. Variation of the magnetic moment of bis(2,6-pyridinedial dihydrazone)cobalt(II) iodide between 80 and 373°K. was explained on the basis of a thermal equilibrium between doublet and quartet states.<sup>8</sup> Other examples of this type of equilibrium for cobalt(II) complexes containing similar ligands have recently been observed by Curry, Burke, and Busch,<sup>9</sup> and Stoufer.<sup>10</sup>

Spin-state isomerism in the case of nickel(II) has been a subject of interest and contention for a number of years. Maki<sup>11</sup> first reported the phenomenon for salicylaldehyde complexes. Her interpretation, as extended by Ballhausen and Liehr,<sup>12</sup> required that the relative energies of the singlet and triplet states be very sensitive to the nature of two ligands located axially, above and below the metal atom which is otherwise bound to a planar array of donor atoms. Most simply, so long as the axial ligands compare closely

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