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STRUCTURAL STUDIES OF ORGANOMETALLIC COMPOUNDS IN SOLUTION

I. MAGNESIUM IODIDE IN DIETHYL ETHER AND TETRAHYDROFURAN *

AGNETA ERICSON and INGMAR PERSSON
Inorganic Chemistry 1, Chemical Centre, P.O. Box 124, 221 00 Lund (Sweden)

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Summary

The structure of 2.8 *M* MgI_2 in diethyl ether solution and that of 1.7 *M* MgI_2 in tetrahydrofuran solution have been determined by large angle X-ray scattering measurements. The measurement on the diethyl ether solution was performed at 44 °C, on a phase crystallizing at approximately 30 °C. In diethyl ether a dimeric structure is found, arranged in a square-planar fashion. The bond lengths are: Mg–I 2.65(2), I–I (diagonal) 3.75(2) and I–I (linear) 5.30 Å. Three diethyl ether molecules are probably coordinated to each magnesium to complete an octahedral arrangement. In tetrahydrofuran the ion MgI^+ from a dissociated complex predominates. In the MgI_2 complex a tetrahedral arrangement is found. In both the MgI^+ and MgI_2 complexes the Mg–I distance is 2.56(2) Å. In the MgI_2 complex the I–I distance is 4.44(4) Å. In both solutions the Mg–O and Mg–C distances were kept fixed at 2.10 and 3.48 Å, respectively. The solubility of MgI_2 in diethyl ether has been shown to be strongly dependent on the water content of the ether; 0.2 *M* was the highest concentration obtained in anhydrous diethyl ether.

Introduction

The crystal structures of several magnesium bromide compounds have been reported, Table 1. A tetrahedral arrangement around the magnesium atom has been established for the solid dietherate of $MgBr_2$ [1], and this arrangement has also been confirmed for the solid dietherates of phenylmagnesium bromide [2] and ethylmagnesium bromide [3]. In tetrahydrofuran, THF, an octahedral arrangement has been

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* *Editorial note*. This paper was accepted for this Journal, even though it is not concerned with organometallic compounds, because it forms the introduction to a planned series concerned with structures of Grignard reagents.

TABLE 1

INTERATOMIC DISTANCES IN SOME MAGNESIUM HALIDE COMPOUNDS

Compound	Mg–Br (Å)	Mg–O (Å)
$MgBr_2$/2DE [a]	3.18, 3.32	2.16, 2.13
$MgBr_2$/4THF [b]	2.625	2.16
PhMgBr/2DE [c]	2.44	2.01, 2.06
EtMgBr/2DE [d]	2.48	2.03, 2.05
$MgBr_2$ [e]	2.34	
MgI_2 [f]	Mg–I 2.52	

[a] Ref. 1. [b] Ref. 4. [c] Ref. 2. [d] Ref. 3. [e] Ref. 22. [f] Ref. 23.

reported [4]. According to Walker and Ashby [5] the degree of association, *i*, of MgI_2 in diethyl ether (DE) is 1 (i.e. monomers are formed) at infinite dilution and then increases with concentration up to a value of 2.6 at 0.5 *M*. In THF solution MgI_2 would be expected to be monomeric, since this solvent has stronger solvating properties than DE. This paper presents the results of a study of the structures of MgI_2 in tetrahydrofuran or diethyl ether by the large angle X-ray scattering technique, LAXS.

Experimental

Solvents. Both DE and THF were distilled over metallic sodium, with benzophenone as an indicator.

Glass apparatus was dried in an oven at approximately 120 °C. All preparations were then carried out under a dry atmosphere in a glove box. Reaction flasks were opened for sampling in the glove box.

Preparative procedure. To prepare the DE solutions of magnesium iodide, mercuric iodide (Fluka) and an excess of magnesium turnings (Merck) were placed in a round-bottomed flask, equipped with a condenser, and diethyl ether was added. The reaction was initiated by heating, and the ether was refluxed until all the red HgI_2 had reacted. The solution had then formed two layers. The colourless solution was filtered to remove residual magnesium and the magnesium amalgam formed. Both layers turned yellowish after a few hours and brown after a day, probably because of generation of iodine. Samples were taken from both layers and added to water. After removal of the iodine by extraction with diethyl ether, it was shown that there was only a five-percent decrease in iodide concentration. The lower phase crystallized at room temperature and the upper layer was removed. The crystalline phase was melted again before being transferred to the glass container used in the X-ray scattering measurements.

Magnesium iodide is soluble in THF, and the THF solutions were prepared by dissolving appropriate amounts of anhydrous MgI_2. Both solvents were dried over freshly cut metallic sodium. The compositions of the studied solutions are given in Table 2.

Solubility measurements. The solutions mentioned above, which were considered anhydrous, and DE solutions of various water contents containing various traces of other organic solvents were used for solubility measurements.

TABLE 2

CONCENTRATIONS (M) OF THE SOLUTIONS INVESTIGATED

Solution	Mg	I	Solvent
THF	1.71	3.42	10.18
DE	2.79	5.58	9.50

The DE taken straight from the distillation apparatus was taken to be slightly aqueous. Dried glass-equipment was still used though, and all preparations were carried out in the glove box. In the case where a glove box was not used and the glass had not been dried in an oven, the solutions were slightly more aqueous, owing to adsorption of water on the glass-surfaces. Water-saturated DE was obtained by shaking the ether with water in a separating funnel.

A few drops of THF or dimethylsulfoxide (DMSO) were added to DE in order to compare the solubility of MgI_2 in these solutions with those in the DE containing small amounts of water. These organic solvents had been dried to the same extent as the ether to which they were added. Magnesium iodide is readily soluble in both THF and DMSO.

Analysis. The solutions of magnesium iodide were analysed for iodide by titration with a standard 0.10 M $AgNO_3$ solution.

X-ray scattering measurements. The X-ray scattering from the free surface of the ether solutions was measured in a θ–θ goniometer of the Seifert GDS type. The solutions were enclosed in a cylindrical thin-walled glass container of a type previously described [6]. Correction for the absorption by the glass container was made. Mo-K_α (λ 0.7107 Å) radiation was used as the X-ray source and the scattered intensities were measured at discrete points, at intervals of 0.335 in $s, s = 4\pi \sin\theta\lambda^{-1}$, between θ-values of 4 and 62 degrees, where the scattering angle is 2θ. An extrapolation of the intensity data at $\theta < 4°$ was necessary because of the liquid meniscus on the glass wall. 40000 counts were collected twice at each point, which gives a statistical error of 0.35%. The measurements of the DE solutions were carried out at $44 \pm 1°$ C and those for the THF solutions at $25 \pm 1°$ C.

Minute droplets on the glass wall are considered to be responsible for the somewhat larger than normal spread between data points.

Data treatment. The measured intensity data were initially corrected for background scattering and polarization, and normalized to a stoichiometric volume, V, containing one Mg atom. The normalization was performed as described before [7]. Scattering factors, f, for the neutral atoms were used, except for H, for which the spherical form factors suggested by Stewart et al., were employed [8].

The contribution from anomalous dispersion, $\Delta f'$ and $\Delta f''$, was considered for all atoms [9]. Incoherent scattering factors [10–12], corrected for the Breit–Dirac effect [13,14], were used. All these corrections were taken into account when calculating the reduced intensities, $i(s)$, from the scaled observed intensities, $I_{obs}(s)$.

$$i(s) = K \cdot I_{obs}(s) - \sum_i n_i \cdot \left[f_i^2(s) + (\Delta f_i'')^2 + \mathrm{del}(s) \cdot I_i^{incoh}(s) \right]$$

where K is the normalization factor, n_i is the number of atoms "i" per stoichiometric volume, and del(s) is the fraction of incoherent radiation reaching the counter [15]. A Fourier transformation was applied, as described previously [16], to obtain the electronic radial distribution function, RDF. Spurious peaks below 1.5 Å were removed from the RDF by a procedure described elsewhere [17].

All calculations were made with the program KURVLR [18], while least-squares refinements were carried out with the PUTSLR [18] and STEPLR [19] programs.

Results

Solubilities of MgI_2 in diethyl ether. When MgI_2 was generated in DE the solution separated into two layers at the end of the reaction. The solubility of MgI_2 in the upper layer, which is saturated, is a function of the water content of the ether, the solubility being much larger in aqueous ether. It was found that DE distilled over metallic sodium which had not been freshly cut contained traces of water. This ether was dried over freshly cut sodium, but comparatively large amounts of metallic sodium were required, since it is only the outermost layer of the surface which is able to react with water, to give sodium hydroxide and hydrogen. The largest solubility found in anhydrous DE was 0.2 M, whereas in the ether which had not been sufficiently dried the solubility was significantly greater. In DE saturated with water the solubility was as large as 0.4 M, Table 3. When small amounts of THF or DMSO were added to anhydrous ether the solubility was lower than in pure ether as can be seen from Table 3, even though MgI_2 is more soluble in THF and DMSO, than in DE. Apparently the addition of small amounts of water or organic solvents changes the physical properties of DE, which determine its ability to dissolve MgI_2, perhaps through hydrogen bonding. The basicity of the impurity may also be an important factor.

X-Ray data. For both solutions investigated, the RDFs show a peak at around 2.6 Å which fits the expected Mg–I distances (Fig. 1). Only the RDF function for the DE solution has a marked shoulder at 3.7 Å that indicates an I–I distance in a dimeric structure. There is also a shoulder around 1.5 Å, and this was assigned to the C–O and C–C distances in DE of 1.408 and 1.516 Å, respectively (see Table 4). The peak around 2.6 Å also incorporates the C–O distance of 2.47 Å. For THF these distances are at 1.538 Å (C–C), 1.428, and 2.37 Å (C–O), Table 4. No intermolecular distances in the solvents were refined.

TABLE 3

THE SOLUBILITY OF MgI_2 IN DIETHYL ETHER UNDER VARIOUS CONDITIONS

Solvent	MgI_2 (M)	MgI_2 (g/l)
DE (fresh Na (s)) + DMSO (dist.)	0.10	28
DE (fresh Na (s)) + DMSO (over CaH_2)	0.14	39
DE (fresh Na (s))	0.20	56
DE (dist.)	0.21	58
DE (dist.) + THF (dist.)	0.21	58
DE (dist.)	0.28	78
DE (dist.)	0.33	92
De (no glovebox, glass not dried)	0.34	95
De (sat. with water)	0.40	111
DE (sat. with water)	0.46	128

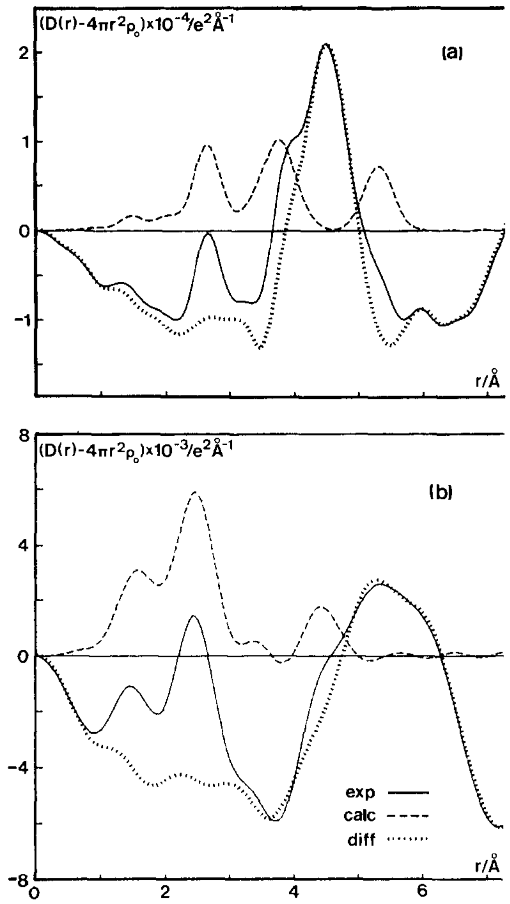

Fig. 1. $D(r)-4\pi r^2\rho_0$ function and calculated peak shape for magnesium iodide in (a) diethyl ether and (b) tetrahydrofuran.

TABLE 4

INTERATOMIC DISTANCES IN DIETHYL ETHER (ref. 26) AND TETRAHYDROFURAN (ref. 27). THE LONG O–C DISTANCES IN BOTH SOLVENTS ARE THE RESULTS OF CALCULATIONS BASED ON THE C–C AND SHORT O–C DISTANCES STATED IN REFERENCES 26 AND 27

Interaction	O–C	O–C	C–C
Diethyl ether			
d (Å) [a]	1.408	2.47	1.516
b (Å²) [b]	0.0005	0.002	0.002
n [c]	2	2	2
THF			
d (Å)	1.428	2.37	1.538
b (Å²)	0.0017	0.0017	0.0017
n [c]	2	2	2

[a] *d* = distance. [b] *b* = temperature coefficient. [c] *n* = number of distances per molecule.

TABLE 5

INTERATOMIC DISTANCES *d* (Å), TEMPERATURE COEFFICIENTS *b* (Å^2) AND NUMBER OF DISTANCES PER MAGNESIUM *n* (Estimated errors are shown in parentheses.)

Interaction	Solvent	*d*	*b*	*n*
Mg–I	DE	2.65(2)	0.003(3)	3.0
	THF	2.56(2)	0.005(2)	1.0
I–I	DE	3.75(2)	0.026(4)	0.5
	DE	5.30	0.018(3)	1.0
	THF	4.44(4)	0.007(5)	0.15
Mg–O	DE/THF	2.10	0.007	3.0/5.0
Mg–C	DE/THF	3.48	0.012	3.0/5.0

In both RDFs there are broad peaks due to interactions between solvent molecules. In the case of DE the peaks are at 4.5–5 Å and 7.5–8.5 Å and in the THF solution at 5–6 Å and 8.5–9.5 Å.

The sum of all the intramolecular reduced intensity contributions $i_{calc}(s)$ is compared with the experimental $i_{obs}(s)$ function, after multiplication by s (see Fig. 3).

For the DE solution, the model selected consists of a dimer arranged in a square-planar fashion. Probably three DE molecules are coordinated to each magnesium to complete an octahedral arrangement around the magnesium atom. The interatomic distances are given in Table 5.

Least-squares refinements of the distance *d* (Å) and the temperature coefficient *b* (Å^2) for the Mg–I and I–I diagonal distances were carried out. In Table 5 only those parameters shown with estimated errors were refined in the least-squares refinements, the others being fixed.

In THF only monomeric magnesium complexes are present. A large proportion of the molecules were assumed to have dissociated into Mg^{2+}, I^- and MgI^+ ions, with the latter predominating. In both the MgI_2 and MgI^+ complexes a tetrahedral arrangement was assumed around the magnesium atom; an octahedral configuration cannot be excluded, but does not give as good a fit as well, and the same is true for the model based on a trigonal bipyramidal configuration. Least-squares refinements were performed on the parameters *b* and *d* for the Mg–I interaction in the range $5 < s < 12$ Å^{-1}. The parameters for the proposed model are given in Table 5, where estimated errors are shown for parameters which were refined.

Discussion

Solutions of magnesium iodide in DE could not be prepared by simply dissolving MgI_2 in DE, so Ashby and Arnott's [20] method, involving refluxing of DE with magnesium turnings and the mercuric halide was used, since this is known to give a very pure product. MgI_2 crystallizes in a closed-packed hexagonal lattice with Mg^{2+} in half the octahedral holes. DE has a fairly low dielectric constant, $\epsilon = 4.3$, and may not be able to bring the ions into solution because the lattice energy is larger than the energy of solvation.

The variation in the solubility of MgI_2 in DE with change in the water content is noteworthy. Water is expected to solvate magnesium more strongly than DE because of its donor properties, which result in a very favourable net enthalpy term. In water itself the entropy term is usually unfavourable since water is a highly structured solvent but for water in an unstructured solvent such as DE, the entropy term for solvation of magnesium by water is more favourable [21].

The interatomic distances for $MgBr_2$ [22] and MgI_2 [23] in gaseous phase have been determined. Both molecules are linear, and the Mg–I and Mg–Br distances are 2.52 and 2.34 Å respectively. There are no structural reports on the etherates of MgI_2 in DE or THF, but the crystal structures of $MgBr_2$ in both solvents have been determined [1,4]. Schibilla and Le Bihan derived Mg–Br distances in the ethyl etherate of 3.18 and 3.32 Å, but these seem unreasonably long, and we prefer to compare our distances in DE with that of 2.44 Å found for phenylmagnesium bromide by Stucky and Rundle [2].

The change in the Mg–I distance on going from DE to THF is due to the fact that in the dimer Mg coordinates three iodine atoms, compared with one or two in the monomer, and that magnesium is six-coordinated in DE and only four-coordinated in THF. In both cases the best fit was obtained with all the Mg–I distances equal.

The formation of a monomer by MgI_2 in THF but a dimer in DE is presumably due to the stronger solvating properties of THF [24]. The dielectric constant for THF, $\epsilon = 7.6$, is larger than that for DE, which accounts for the large degree of dissociation in THF. Solvents with low dielectric constants neutralize charges and charge densities within molecules through ion pair or aggregates formation. At concentrations in the region of 0.5 *M* the charge density is, apparently, minimized by the formation of dimers. Perhaps at higher concentrations this is achieved by the formation of complexes with an even higher degree of association.

It is not unreasonable that MgI_2 should form dimers in DE. LiBr, for example, forms a tetramer in a cubane configuration in DE [25], and preliminary measurements lead us to believe that PhMgBr is tetrameric in DE at concentrations in the region of 2 *M*.

References

1 H. Schibilla and M-T. LeBihan, Acta Cryst., 23 (1967) 332.
2 G. Stucky and R.E. Rundle, J. Am. Chem. Soc., 86 (1964) 4825.
3 L.J. Guggenberger and R.E. Rundle, J. Am. Chem. Soc., 90 (1968) 5375.
4 M.-C. Perucaud and M-T. LeBihan, Acta Cryst., B, 24 (1968) 1502.
5 F.W. Walker and E.C. Ashby, J. Am. Chem. Soc., 91 (1969) 3845.
6 I. Persson, M. Sandström, P. Goggin and A. Mosset, J. Chem. Soc., Dalton Trans., (1985) 1597.
7 Å. Iverfeldt and I. Persson, Inorg. Chim. Acta, 111 (1986) 179.
8 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
9 International Tables of X-ray Crystallography, Kynoch Press, Birmingham, Eng., Vol. 4, 1974.
10 D.T. Cromer and J.B. Mann, J. Chem. Phys., 47 (1967) 1892.
11 D.T. Cromer, J. Chem. Phys., 50 (1969) 4857.
12 A.H. Compton and S.K. Allison, X-ray in Theory and Experiment. Van Nostrand-Reinhold, New York, 1935.
13 G. Breit, Phys. Rev., 27 (1926) 362.
14 P.A.M. Dirac, Proc. Roy. Soc. London, 4 (1926) 195.
15 M. Sandström, I. Persson and S. Ahrland, Acta Chem. Scand., A32 (1978) 607.
16 Å. Iverfeldt and I. Persson, Inorg. Chim. Acta, 111 (1986) 171.
17 H.A. Levy, M.D. Danford and A.H. Narten, Data Collection and Evaluation with X-ray Diffractometer Designed for the Study of Liquid Structure, Report ORNL-3960, Oak Ridge National Laboratory, Oak Ridge, 1966.

18 G. Johansson and M. Sandström, Chem. Scr., 4 (1973) 195.
19 M. Molund, and I. Persson, Chem. Scr., 25 (1985) 197.
20 E.C. Ashby and R.C. Arnott, J. Org. Chem., 14 (1968) 1.
21 S. Ahrland, Pure Appl. Chem., 54 (1982) 1451.
22 P.A. Akishin, V.P. Spiridonov, G.A. Sobolev and V.A. Naumov, Z. Fiz. Khim. SSSR, 31 (1957) 461.
23 P.A. Akishin and V.P. Spiridonov, Z. Fiz. Khim. SSSR, 32 (1958) 1682.
24 I. Persson, Pure Appl. Chem., 58 (1986) 1153.
25 J. Goulon, C. Goulon-Ginet and M. Chabanel, J. Solution Chem., 10 (1981) 649.
26 M. Hayashi and K. Kuwada, Bull. Chem. Soc. Japan, 47 (1974) 3006.
27 A. Almenningen, H.M. Seip and T. Willadsen, Acta Chem. Scand., 23 (1969) 2748.