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THE STEREOCHEMISTRY OF POLYNUCLEAR COMPOUNDS OF THE MAIN GROUP ELEMENTS* $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$, A TETRAMERIC GRIGNARD REAGENT**

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SUMMARY

The reaction of ethyl chloride with magnesium in tetrahydrofuran (THF) yields a compound which has been determined by a single crystal X-ray diffraction study to be a tetrameric Grignard reagent, $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$. This organometallic complex crystallizes into the space group C_2h^5-$P2_1/c$ with two molecules per unit cell. The cell dimensions are: $a = 12.128(3)$ Å, $b = 16.750(4)$ Å, $c = 10.972(3)$ Å, $\beta = 104.02(2)^\circ$. A full matrix least squares refinement based upon 919 observed reflections measured by diffractometer techniques yielded a final unweighted R-factor of 0.102. The molecule lies on a crystallographic inversion center and contains a total of five four-membered bridging units consisting of magnesium and chlorine atoms. The two independent magnesium atoms in $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$ exhibit five and six coordination. Two three-coordinated bridging chlorine atoms are also present in the molecule.

INTRODUCTION

Until the early 1960's, the primary question concerning the physical nature of the Grignard reagent was whether the unsymmetrical RMgX species had anything other than possibly a transitory existence in solution. A detailed structural investigation[2,3] of the crystalline product formed by cooling a phenylmagnesium bromide diethylether solution first demonstrated in detail the stability of the monomeric disolvated $C_6H_5MgBr(C_4H_{10}O)_2$. It was obvious, however, that the structure of the Grignard reagent must depend upon the nature of the groups coordinated to the magnesium atom since crystalline products with empirical formulae $CH_3MgI(C_5H_{11})_2O$[4] and $C_{10}H_7MgBr(C_2H_5)_2O$[5] had been isolated and reported by Zerewitinoff[4] and Schlenk[5]. These materials have the common feature of sterically bulky organic groups coordinated to the magnesium atoms. Magnesium, like beryllium[6], undoubtedly is capable of forming isolable compounds which contain three-coordinate

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* For the previous paper see ref. 1.

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magnesium if the steric requirements of the ligands are sufficiently stringent. However, the three-coordinate species, while thermodynamically stable with respect to increased solvation, may not be thermodynamically stable with respect to attack by a base with smaller steric requirements. Thus, it may be more favorable for a given RMgX (solvent) moiety to form an oligomer by self-association through halogen bridges than to be solvated with additional bulky organic molecules. The possibility of oligomerization was also suggested by the association measurements of Slough and Ubbelohde[7], who were the first to recognize that exposure of the Grignard reagent to oxygen results in anomalously high molecular weights in solution*. The Grignard reagent, $C_2H_5MgBr[N(C_2H_5)_3]$[8,9], is solvated by the relatively large $(C_2H_5)_3N$ group and is comparable in this respect to the compounds isolated by Zerewitinoff and Schlenk. Single crystal analysis showed that, in the solid state, $C_2H_5MgBr[N(C_2H_5)_3]$ is a dimer with four-coordinate magnesium and bridging bromine atoms[10]. The triethylamine groups were *trans*, thus resulting in a minimization of non-bonded interactions among the groups coordinated to the magnesium atom. The dimeric molecular structure, which was favored by Ashby and Becker[11] for tetrahydrofuran (THF) solvated $C_2H_5Mg_2Cl_3$ (Fig. 1), at first glance seems reasonable in light of the above structural data, *i.e.*, one would predict the material to be a disolvated dimer. Recently, however, Vallino[12,13] has observed that with THF the tri- and tetrasolvated organomagnesium reagents, $CH_3MgBr(C_4H_8O)_3$ and $(C_6H_5C{\equiv}C)_2Mg(C_4H_8O)_4$, are monomeric compounds with five and six coordinate magnesium respectively. This strongly suggests that coordination numbers higher than four might be expected for the magnesium atoms in $C_2H_5Mg_2Cl_3(C_4H_8O)_n$. As discussed above, for mono-solvated magnesium atoms, higher coordination numbers can be achieved by association through chlorine bridges or by increased solvation. The purpose of this study was to determine which of these possibilities were realized for $C_2H_5Mg_2Cl_3$ and to elucidate in detail the molecular geometry of the resulting Grignard reagent.

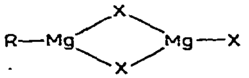

Fig. 1. Proposed structure for $(C_2H_5)Mg_2Cl_3$ (ref. 11).

EXPERIMENTAL

A 0.5 molar solution of C_2H_5MgCl was prepared by the addition of ethyl chloride to excess magnesium in a rapidly stirred solution of tetrahydrofuran. After the exothermic reaction ceased, a small amount of the solution was filtered into a Schlenk tube[14] which was later taken into a dry argon atmosphere inside a glove box. Approximately 50 ml of the solution was then transferred into a flask and the excess THF was slowly removed under vacuum yielding a crystalline solid. Several attempts were made to measure the density, but the crystals apparently easily lose THF and an accurate value could not be obtained.

A crystal with maximum dimensions of 0.26 × 0.39 × 0.52 mm was taken directly from solution and sealed in a thin-walled glass capillary for X-ray examination. On

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* This is probably due to the formation of species such as $Mg_4Br_6O(C_4H_{10}O)_4$. See ref. 15.

the basis of systematic absences observed on precession photographs (*h0l*, *h1l*, *0kl*, *1kl* zones; absences *h0l*, $l=2n+1$: *0k0*, $k=2n+1$), the space group is $P2_1/c$. Eleven reflections were carefully centered on a Picker four-circle diffractometer from which lattice constants: $a=12.138(3)$ Å*, $b=16.750(4)$ Å, $c=10.972(3)$ Å, $\beta=104.02(2)°$, were determined by the least squares refinement of $(\sin\theta)/\lambda$ values. The lattice parameters and their corresponding standard deviations were obtained by using a program, B101[16], which also determines the diffractometer orientation and angle settings. The above crystallographic data are consistent with two molecular units of $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$ per unit cell.

Three dimensional intensity data were collected manually on a Picker four-circle diffractometer using Cu-$K\alpha$ radiation. The crystal was mounted with the c^* axis parallel to the length of the capillary. A take-off angle of 1.7° was found to provide 75% of the maximum intensity for a strong reflection. Collimators of 1 mm and 2 mm diameters for the incident and diffracted beams, respectively, were used for the data collection. A 0.0005 inch nickel foil filter was placed at the opening of a scintillation counter detector mounted 21 cm from the crystal.

The θ–2θ scan technique, with a scan speed of 1.0°/minute, was used to collect all data. *hkl* and $\bar{h}\bar{k}l$ reflections with $2\theta < 50°$ were scanned for 72 sec (1.2°), while a scan time of 84 sec (1.4°) was used for peaks with $2\theta \geqslant 50°$. Individual background counts of 20 sec were measured before and after each scan. All peaks were recorded on a chart recorder thus allowing each peak to be accurately centered and their shapes to be observed. Periodic measurements on a standard reflection were made in order to check the crystal and the diffractometer stability. Small intensity drifts were noted near the end of the data collection and these reflections were treated separately. Mosaicity of the crystal was checked by a narrow-source, open counter ω scan. The average half width of the peak profiles was approximately 0.1°.

A total of 1832 independent reflections were measured to $2\theta_{max}=100.0°$. Corrections for background and Lorentz-polarization effects were made in the usual way, using Prewitt's program ACAC[17]. Of the 1832 reflections measured, 894 were found to be unobserved ($I_{obs} < 3\sigma$) where $\sigma=(\text{total number of counts}+\text{background counts})^{\frac{1}{2}}$. These were assigned an intensity equal to the standard deviation of the background intensities in their respective locations. Ten peaks were found for which $I_{obs} < (I_{bkg} - 3\sigma)$ and were rejected. The linear absorption coefficient for Cu-$K\alpha$ is 44.5 cm^{-1} and absorption corrections were made using program ACAC[17]. No corrections were made for secondary extinction. Atomic scattering factors[18] for neutral carbon, oxygen, magnesium, and chlorine atoms were taken from standard tables. The atomic scattering factor tables for hydrogen atoms were those of Stewart, Davidson and Simpson[19]. Corrections for the real and imaginary components of anomalous dispersion[20] were applied to the magnesium and chlorine scattering factors.

SOLUTION AND REFINEMENT

The composition of the molecule was determined from the solution of the

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* Numbers in parentheses here and in succeeding discussions are estimated standard deviations in the least significant digits.

structure. A three-dimensional Patterson map[21] yielded a possible chlorine position 1.67 Å from a crystallographic inversion center. A three-dimensional electron density calculation with phases based upon this lone chlorine atom yielded no peaks from which the other parts of the molecule could be resolved.

At this point, the symbolic addition procedure of Karle and Karle[22] was used to obtain the phases directly from the magnitudes of the normalized structure factors. Program FAME[23] was used to perform the various statistical tests and to generate a listing of the Σ_2-type interactions. Seven reflections, chosen on the basis of high E magnitudes and large numbers of interactions among 250 reflections having $|E| > 1.44$, were given letter symbols by FAME. These 250 reflections were then used in a series of programs, MAGIC-LINK-SYMPL[23], for the calculation of the Σ_2-relationships and the related probabilities. Three of the seven symbolic reflections were arbitrarily assigned + signs to fix the origin. The other four symbols were assigned + and − signs in different combinations. After five iterations MAGIC had determined 245 knowns.

Two combinations, I and II, with 18 and 25 contradictions respectively were used as input data for E-map calculations. Map I (combination I) showed large peaks about the inversion center (0,0,0), while Map II (combination II) showed large peaks about the inversion center $(0,\frac{1}{2},0)$. Coordinates of the five most intense peaks found in each E-map were assigned the weight of a magnesium atom and used in independent Fourier calculations. The "R"-factor obtained for combination I was 0.35 while that for combination II was 0.52. Attention was then focused on interpreting the "chemical sense" of Map I. Three peaks in Map I were reassigned to chlorine atoms based upon their sizes relative to the other two peaks. The R-factor then decreased to 0.30. The coordinates of three oxygen atoms and one carbon atom were then obtained from the next cycle of Fourier calculation. Subsequently, a difference Fourier map indicated the positions of the carbon atoms in the THF rings and the terminal carbon atom of the ethyl group. Inclusion of all twenty-two non-hydrogen atoms of the $C_2H_5Mg_2Cl_3(C_4H_8O)_3$ unit into a structure factor calculation followed by several cycles of least-squares refinement of the positional parameters reduced the "R"-factor to 0.21. Refinement was carried out using a full-matrix least-squares program, ORFLSD, a modified version of the Busing and Levy program, ORFLS[24]. Weights were determined according to the scheme:

$$\sigma(\mathrm{F}) = \frac{F \cdot K}{2I}\left[IPC + \left(\frac{TP}{TB}\right)^2 (BG_\mathrm{A} + BG_\mathrm{B}) + (\lambda \cdot I)^2\right]^{\frac{1}{2}}$$

in which K = scale factor, F = structure factor, I = observed intensity, IPC = integrated peak count, TP = time of peak scan, TB = total background count time $(BG_\mathrm{A} + BG_\mathrm{B})$, BG_A, BG_B = background counts at the end of each scan and $\lambda = 0.02$.

The weighted and unweighted "R"-factors are defined respectively as:

$$R_w = (\Sigma w||F_o| - |F_c||^2 / \Sigma w|F_o|^2)^{\frac{1}{2}}$$

$$R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$$

Two cycles of refinement of the isotropic temperature factors, positional parameters and the overall scale factor reduced the "R"-factor to 0.17. Consistently large isotropic thermal parameters were obtained for the THF and ethyl groups. The values were approximately 8–9 cm^2 for THF oxygen atoms, 11 cm^2 for the carbon atom of the ethyl group coordinated to the magnesium atom, and 11–18 cm^2 for the remainder of the carbon atoms. A difference Fourier calculated at this point showed anisotropic contributions with maxima as large as 1.8 e/Å^3 about the carbon atom positions.

A difference Fourier calculated with C(12), C(13) and the carbon atoms of the ethyl group omitted showed indications of disorder with two peaks approximately 2.0 e/Å^3 above background within bonding distance (1.5 Å) of the methylene carbon atom of the ethyl group. In addition, the peaks corresponding to C(12) and C(13) of a THF ring were extremely elongated in the direction normal to the C(14)–O(1)–C(11) plane. The five membered THF ring is capable of existing in a number of puckered configurations as indicated in Fig. 2.

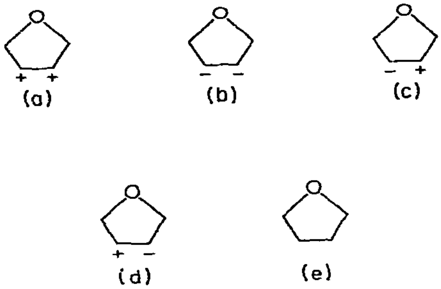

Fig. 2. Possible configurations for C_4H_8O. + = carbon atom position above the plane of the paper. − = carbon atom position below the plane of the paper.

A careful examination of structures containing this group[11,12,25–28] showed that all of the above configurations have been found in the solid state. The thirty-two THF hydrogen atoms were included in their calculated positions assuming H–C–H angles of 109°28′, C–H distances of 0.98 Å and isotropic thermal parameters of 10 Å^2. Anisotropic temperature factors were introduced for all twenty-two non-hydrogen atoms. The ethyl carbon atom was assigned a two-fold disorder associated with a rotation of the terminal carbon atom about the Mg(2)–C(1) bond. The carbon atoms, C(12) and C(13), were treated in two different ways. Refinement was first attempted with ordered C(12) and C(13) atoms and anisotropic temperature factors for all atoms. Non-positive definite matrices for the thermal coefficients of these atoms were obtained. The disorder was then treated by placing four carbon atoms into the region of electron density of C(12) and C(13), although there were no resolved distinct electron density peaks present. These atoms were refined isotropically. The interatomic distances obtained for this THF ring indicate that the refinement of this group was only partially successful. We believe, however, that the electron density associated with C(12) and C(13) has been fitted in as physically a meaningful fashion as possible. Although no conclusions are justified by the experimental results, it appears that the disorder of this five-membered ring is a combination of (c) and (d) above (Fig. 2). All of the THF carbon atoms in this structure are apparently undergoing large thermal displacements. This is consistent with the above observation that THF is readily lost by the crystalline solid. The refined values of R and R_w were 0.102 and 0.125 respectively. A difference Fourier revealed no peaks above background (1.5 e/Å^3).

The final positional and anisotropic thermal parameters are given in Tables 1 and 2 respectively. The final observed and calculated structure factors (observed reflections only) are shown in Table 3. The bond distances and angles, computed with program ORFFE[29] are in Tables 4 and 5. An important criterion for the correctness of the structure is that there be no unusually close approaches between non-bonded atoms. All of the intermolecular contacts (Table 4) are observed to be well outside the limits for van der Waals contacts.

TABLE 1

POSITIONAL PARAMETERS FOR $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$[a]

Atom	*X*	*Y*	*Z*
Mg(1)	−0.0698(5)	0.0240(4)	0.1295(6)
Mg(2)	0.2367(5)	−0.0242(5)	0.2062(7)
Cl(1)	0.0877(4)	0.0772(3)	0.0428(5)
Cl(2)	0.2196(4)	−0.1030(4)	0.0192(6)
Cl(3)	0.0725(5)	−0.0540(3)	0.2828(5)
O(1)	−0.1986(14)	−0.0301(14)	0.1999(17)
C(11)	−0.2074(30)	−0.1061(28)	0.2284(47)
C(12A)	−0.2890(73)	−0.1098(51)	0.3088(71)
C(12B)	−0.3385(75)	−0.1332(52)	0.2060(96)
C(13A)	−0.3669(62)	−0.0588(50)	0.2777(79)
C(13B)	−0.3688(91)	−0.0768(103)	0.1472(126)
C(14)	−0.3070(70)	−0.0050(30)	0.1847(68)
O(2)	−0.582(12)	0.1132(12)	0.2588(13)
C(21)	−0.0347(55)	0.1146(20)	0.3760(38)
C(22)	−0.0386(56)	0.1837(33)	0.4493(38)
C(23)	0.0138(34)	0.2189(21)	0.3795(51)
C(24)	−0.0387(33)	0.2005(21)	0.2450(35)
O(3)	0.3273(17)	−0.1187(18)	0.3182(18)
C(31)	0.3694(35)	−0.1935(29)	0.2963(47)
C(32)	0.4236(26)	−0.2217(25)	0.4166(45)
C(33)	0.3715(53)	−0.1780(52)	0.5010(45)
C(34)	0.3855(36)	−0.1055(26)	0.4343(71)
C(1)	0.3659(21)	0.0674(19)	0.2753(38)
C(2A)	0.3763(51)	0.1413(46)	0.2047(61)
C(2B)	0.3225(72)	0.1293(67)	0.3033(86)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

DISCUSSION OF THE STRUCTURE

The molecular structure of $(C_2H_5Mg_2Cl_3 \cdot 3C_4H_8O)_2$ is shown in Fig. 3 and Fig. 4. In Fig. 4, the carbon atoms of the THF rings and terminal ethyl carbon atom have been omitted to illustrate some of the details of the skeletal structure more clearly. The molecule lies on a crystallographic inversion center with a unique [Mg(1)–Cl(1)]$_2$ bridging unit located around this inversion site. The molecular symmetry, however, approximates *2/m–C$_{2h}$*. The chlorine atom Cl(1) in the [Mg(1)–Cl(1)]$_2$ bridging unit becomes three-coordinate by bonding to a third magnesium atom, Mg(2). The other two independent chlorine atoms, Cl(2) and Cl(3), are two-coordinate, being bonded to Mg(2) as well as to Mg(1). The presence of the center of inversion requires that the ring system Mg(1)–Cl(1)–Mg(1)′–Cl(1)′ be planar. The deviation from planarity of the atoms in Mg(1)–Cl(2)–Mg(2)′–Cl(1)′ and in Mg(1)–Cl(1)–Mg(2)–Cl(3) are given in Table 6. Program BEPLAI[30] was used for this calculation.

The Mg–Cl bond lengths are of four different types; (1) six-coordinate magnesium atom to two-coordinate chlorine atom, (2) five-coordinate magnesium atom to two-coordinate chlorine atom, (3) six-coordinate magnesium atom to three-coordinate chlorine atom and (4) five-coordinate magnesium atom to three coordinate chlorine atom. The observed distances are: type (1), Mg(1)–Cl(2) (2.51 Å) and Mg(1)–Cl(3) (2.47 Å); type (2), Mg(2)–Cl(2) (2.41 Å) and Mg(2)–Cl(3) (2.40 Å); type (3), Mg(1)–Cl(1) (2.50 Å); type (4), Mg(2)–Cl(1) (2.79 Å). The observation that the five-coordinate Mg–Cl distances [type (2)] are shorter than the six-coordinate Mg–Cl distances of type (1) is as expected[31]. As the coordination number decreases, nonbonded repulsion forces between ligands at a given distance from the nucleus are decreased so that shorter metal–ligand distances are possible. A Mg–Cl distance of 2.39 Å is predicted from the tetrahedral radii of Pauling[31], while the distance predicted for six-coordinate ionic Mg–Cl is approximately 2.50 Å[31,32]. The fact that the ob-

TABLE 2

THERMAL PARAMETERS[a,b] ($\times 10^{-4}$) FOR $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Mg(1)	135(7)	53(4)	147(9)	2(4)	29(6)	−9(5)
Mg(2)	119(7)	67(5)	227(12)	2(4)	−13(7)	−20(6)
Cl(1)	137(5)	40(3)	166(7)	−4(3)	18(5)	−5(4)
Cl(2)	140(6)	69(4)	201(9)	30(3)	2(5)	−14(4)
Cl(3)	167(6)	62(3)	186(8)	7(3)	17(5)	13(4)
O(1)	149(19)	69(11)	347(31)	16(11)	131(19)	23(15)
C(11)	210(45)	123(27)	777(121)	31(27)	199(57)	171(46)
C(12A)[b]	14.6(23)					
C(12B)[b]	14.2(26)					
C(13A)[b]	15.0(22)					
C(13B)[b]	15.6(38)					
C(14)	590(98)	136(34)	887(145)	98(58)	552(105)	182(63)
O(2)	202(17)	91(11)	132(20)	−9(11)	39(14)	−37(13)
C(21)	639(152)	58(21)	532(66)	30(45)	32(38)	−151(31)
C(22)	1045(145)	181(44)	412(74)	75(59)	567(93)	18(42)
C(23)	385(61)	184(35)	397(87)	−140(36)	129(66)	−203(51)
C(24)	424(64)	65(20)	300(55)	−5(27)	90(49)	5(29)
O(3)	187(24)	151(20)	178(28)	63(16)	−64(18)	4(17)
C(31)	243(47)	105(28)	546(107)	28(29)	74(56)	44(47)
C(32)	192(38)	153(31)	480(86)	35(24)	−40(47)	207(45)
C(33)	546(94)	387(85)	366(89)	−206(74)	367(83)	−174(70)
C(34)	246(53)	91(27)	731(141)	41(27)	−98(67)	76(49)
C(1)	141(29)	89(20)	522(79)	−5(19)	−41(35)	−97(36)
C(2A)[b]	12.7(19)					
C(2B)[b]	15.8(32)					

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. Anisotropic temperature factors are of the form $\exp[-(b_{11}\cdot h^2+b_{22}\cdot k^2+b_{33}\cdot l^2+b_{12}\cdot h\cdot k+b_{13}\cdot h\cdot l+b_{23}\cdot k\cdot l)]$.
[b] Isotropic temperature factors are of the form $\exp(-B\cdot\sin^2\theta\cdot\lambda^{-2})$.

(*continued* p. 14)

TABLE 3 OBSERVED AND CALCULATED STRUCTURE FACTORS IN ELECTRONS FOR $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$

H	L	OBS	CAL
******K= 0******			
0	2	1121	1167
1	2	353	385
-1	2	646	613
-1	4	803	870
1	6	405	438
-1	8	237	215
2	0	79	87
2	2	290	337
-2	2	764	764
2	4	851	761
2	6	672	595
-2	6	95	107
2	8	86	84
-2	8	247	279
-2	10	102	127
3	0	1094	1201
3	2	73	63
3	4	563	544
-3	4	521	410
-3	6	164	76
3	8	152	126
-3	10	110	105
4	0	217	212
4	2	347	320
-4	2	379	326
4	4	327	300
-4	4	560	518
4	6	96	79
-4	8	97	85
5	0	166	70
-5	2	116	97
5	4	134	126
-5	4	228	208
5	6	144	163
-5	6	424	429
-5	10	83	37
6	0	795	816
-6	2	273	287
6	4	244	211
7	0	1006	962
7	2	293	269
-7	2	103	90
7	4	257	272
-7	4	238	231
7	6	122	83
-7	6	177	217
8	0	263	223
-8	2	106	82
8	4	230	199
-8	4	196	229
8	6	123	106
-8	6	110	66
-8	8	119	106
-9	2	203	215
9	4	232	228
-9	8	106	130
-10	4	84	41
******K= 1******			
0	2	58	57
0	3	361	348
0	6	123	128
1	0	681	632
1	1	398	523
-1	1	933	810
1	2	795	793
1	3	245	274
-1	3	394	355
-1	4	193	197
1	5	441	458
-1	7	482	478
2	0	82	88
-2	0	85	88
2	1	156	196
-2	1	707	749
2	2	542	573
-2	2	677	632
-2	3	225	244
-2	4	144	126
2	5	813	828
-2	5	183	164
2	6	218	199
-2	6	78	64
-2	7	440	393
-2	8	144	96
-2	9	128	117
3	0	291	329
3	1	588	624
-3	1	308	345
3	2	548	576
-3	2	596	553
3	3	92	154
-3	3	139	153
-3	4	237	197
3	5	632	575
-3	5	67	76
3	6	229	228
-3	8	82	59
-3	9	106	96
4	1	110	31
-4	1	363	339
4	2	323	315
-4	2	920	1009
4	3	59	51
-4	3	479	443
-4	4	79	45
4	5	126	131
-4	5	686	637
4	6	75	65
-4	6	259	245
-4	7	139	142
5	0	287	293
5	1	191	166
-5	1	67	67
5	2	57	49
-5	2	393	413
5	3	63	36
-5	3	429	382
5	4	72	127
-5	4	120	109
5	5	90	46
5	6	97	70
-5	6	264	259
5	7	174	139
6	0	240	212
6	1	428	446
-6	1	416	443
6	2	162	169
-6	3	116	132
6	4	195	204
-6	4	106	126
6	5	122	146
-6	5	106	91
6	7	82	95
7	0	123	28
7	1	132	116
-7	1	593	680
7	2	75	8
7	3	106	134
7	5	148	110
-7	5	158	127
-7	7	187	181
8	1	105	83
-8	1	196	199
8	5	275	250
-8	5	77	85
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0	5	114	119
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1	2	71	79
1	3	124	139
1	4	77	68
-1	4	195	216
1	5	147	166
1	6	177	208
-1	6	149	167
2	0	737	712
2	1	610	635
2	2	425	397
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2	3	199	190
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2	4	315	434
-2	4	138	124
2	5	210	192
-2	5	222	238
2	6	158	158
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-2	8	177	170
-2	10	92	73
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3	2	353	329
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3	3	335	347
-3	3	460	477
3	4	472	535
-3	4	124	187
3	5	522	465
-3	5	247	235
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-3	7	93	92
-3	8	144	112
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4	2	135	150
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4	3	60	50
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4	4	74	107
-4	4	371	357
4	5	108	182
-4	5	476	502
-4	6	202	185
4	7	210	163
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5	1	232	221
-5	1	59	78
5	2	110	112
-5	2	165	181
5	3	232	289
-5	3	251	240
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5	7	170	155
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6	2	199	210
6	3	350	339
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7	2	224	237
7	3	177	184
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7	6	76	68
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-8	3	135	170
8	4	119	94
-8	6	96	96
-8	7	78	44
9	1	125	137
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-9	4	80	94
-9	8	103	82
-10	3	100	127
-10	5	107	100
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0	4	84	123
0	6	117	117
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1	2	155	156
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1	3	155	142
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1	4	96	64
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1	5	367	347
-1	6	188	246
2	0	707	626
2	1	226	229
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2	2	1180	1096
-2	2	300	338
2	3	793	761
-2	4	97	94
2	5	545	525
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-2	6	206	200
-2	7	273	237
2	8	99	88
3	0	459	396
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3	4	99	161
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3	5	221	253
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-3	10	90	55
4	0	185	196
4	1	101	116
-4	1	66	46
4	2	501	513
-4	2	1150	1131
-4	3	544	550
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6	6	110	96
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-6	9	74	19
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-7	1	229	212
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-7	3	179	201
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-7	5	86	93
-7	7	110	106
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11	6	76	34
******K= 4******			
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0	3	644	703
0	4	569	502
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1	5	175	122
1	6	96	106
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-1	7	204	203
1	8	84	90
2	0	408	327
2	1	592	523
-2	1	371	322
2	3	292	253
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2	4	107	138
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2	5	294	302
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2	6	228	241
2	7	124	97
-2	7	321	317
2	8	101	116
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3	2	859	798
-3	2	137	97
-3	3	316	311
3	4	231	209
-3	4	176	194
3	5	306	360
-3	5	463	425
-3	6	71	60
3	7	185	165
-3	8	117	125
4	0	162	174
4	1	92	69
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4	2	153	147
-4	2	467	487
4	3	95	143
-4	6	89	74
4	7	173	204
5	1	142	155
-5	1	72	70
-5	2	383	415
5	3	251	272
-5	3	230	236
5	4	81	57
-5	4	112	98
-5	5	232	239
-5	8	112	147
-5	10	84	68
6	0	220	164
-6	1	239	231
6	2	308	314
-6	2	151	131
6	3	371	362
-6	3	187	208
6	4	106	151
-6	4	84	104
-7	0	78	89
7	1	79	68
-7	1	162	159
7	2	170	218
-7	2	198	205
-7	3	178	162
7	4	78	98
-7	4	340	319
-8	1	99	93
8	2	97	67
8	3	131	125
-8	3	89	135
-8	4	239	221
-8	7	95	67
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-10	5	143	131
******K= 5******			
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0	4	300	278
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0	6	77	67
0	7	91	72
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-1	2	79	63
-1	3	733	866
1	4	87	60
-1	5	198	205
1	6	254	219
-1	6	110	128
1	7	183	151
2	0	215	215
2	1	185	177
-2	2	71	68
2	3	327	530
-2	3	74	46
2	4	111	167
-2	4	266	307
2	5	68	90
-2	5	165	157
2	6	184	152
-2	6	190	206
2	7	204	220
2	8	139	103
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-3	4	307	291
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-3	5	70	52
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4	6	317	93
-4	6	94	118
4	7	95	66
-4	7	140	140
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5	3	225	227
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5	6	96	95
-5	6	144	122
-5	7	157	161
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-6	1	200	188
6	2	199	181
6	3	374	329
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6	5	112	77
-6	5	121	79
-6	6	79	62
6	7	74	24
-6	7	77	59
7	1	202	208
7	2	254	232
7	3	95	140
-7	3	434	410
-7	5	178	192
8	1	102	48
8	2	228	260
-8	3	230	221
-8	4	99	54
-8	7	123	35
9	1	204	210
9	2	127	123
9	3	106	128
-9	4	112	131
-10	4	92	89
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0	3	708	717
0	4	360	386
0	5	117	144
0	7	85	81
1	0	395	356
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-1	2	291	272
1	3	408	832
-1	3	103	68
-1	4	479	573
-1	5	168	193
1	8	117	161
2	0	269	246
2	1	180	169
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2	3	73	50
-2	3	86	64
2	4	245	233
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2	5	125	122
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2	6	167	148
2	7	148	161
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2	8	96	175
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-3	1	276	273
3	3	86	91
3	4	73	110
3	5	113	70
-3	5	301	284
3	7	190	200
-3	7	208	231
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4	1	372	359
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4	5	100	109
4	6	84	68
4	7	114	128
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-5	1	121	105
5	2	95	72
-5	2	91	98
-5	3	177	188
5	4	203	233
5	5	144	163
-5	8	149	159
6	0	213	194
6	1	261	230
-6	1	135	149
6	2	226	247
-6	2	165	223
6	3	148	121
-6	3	414	415
6	4	173	204
-6	4	202	206
6	5	106	134
7	0	188	198
7	1	98	97
-7	1	140	152
7	2	95	127
-7	2	115	140
7	3	253	255
-7	3	235	222
-7	4	411	395
-7	5	75	19
8	1	78	77
8	2	130	108
8	3	121	141
-8	4	239	234
-8	5	114	125
-9	1	89	65
9	2	178	177
-9	5	170	188
-10	5	96	99
******K= 7******			
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0	6	134	87
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1	3	234	251
-1	3	361	388
1	4	87	92
-1	4	244	259
1	5	145	124
-1	5	134	161
-1	6	99	170
2	0	313	282
2	1	291	273
-2	1	225	245
-2	2	179	177
-2	3	109	140
2	4	252	244
-2	4	571	595
-2	5	176	189
2	7	107	92
3	0	447	360
3	1	554	509
-3	1	391	415
-3	2	407	415
-3	3	65	82
3	4	119	149
3	5	176	164
3	6	128	143
-3	6	101	88
4	0	480	466
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-4	2	146	152
4	4	155	159
-4	4	189	213
4	5	112	99
-4	5	151	139
5	0	260	231
5	1	273	281
-5	1	92	96
-5	2	325	359
5	3	212	206
5	4	226	195
5	5	86	77
-5	9	113	112
6	0	108	90
6	1	215	193
-6	1	82	61
-6	2	214	259
6	3	158	179
-6	3	292	304
6	4	118	161
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-6	9	79	69
7	0	130	128
7	2	199	199
7	3	96	107
-7	3	338	322
7	5	96	108
-7	6	84	27
-7	7	88	62
8	1	108	72
8	2	172	192
-8	3	79	90
-8	4	90	90
-8	5	84	63
9	1	115	118
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-9	5	87	31
-9	6	69	36
******K= 8******			
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0	3	278	298
0	4	301	238
0	5	197	200
0	6	128	132
1	0	255	234
1	1	255	259
-1	1	281	302
-1	2	100	135
1	3	291	218
-1	3	143	119
-1	4	233	255
1	5	140	146
1	8	95	114
2	0	505	496
-2	1	226	206
2	3	92	87
-2	4	434	471
-2	5	304	334
2	7	93	93
2	8	89	146
3	1	462	446
-3	1	606	605
-3	2	122	131
3	3	283	272
-3	3	187	160
3	4	107	117
-3	5	116	135
3	7	105	97
-3	7	130	144
4	0	322	307
4	1	530	456
-4	1	154	169
-4	2	133	114
-4	3	190	191
4	4	317	259
4	5	103	99
-4	5	111	121
-4	7	142	159
-4	8	115	150
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5	1	129	94
-5	2	191	204
5	3	262	216
-5	3	70	65
5	4	232	194
-5	5	137	111
-5	6	79	67
5	7	90	110
-5	7	95	78
6	0	179	182
6	1	177	156
-6	2	110	118
-6	3	193	243
-6	4	109	110
6	5	149	116
-6	5	76	50
6	6	96	79
-6	6	106	64
7	3	108	109
-7	3	73	60
7	4	91	60
-7	4	181	147
7	5	94	98
8	3	75	74
-8	5	133	116
-9	1	96	105
-9	5	109	119
-10	3	79	46
-10	4	76	60
******K= 9******			
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0	3	275	268
0	4	301	286
1	0	177	182
1	1	181	166
-1	1	114	121
1	3	263	248
-1	3	70	104
-1	4	94	124
1	5	154	132
1	6	144	108
-1	6	152	212
1	7	119	116
2	0	433	402
2	1	96	76
-2	1	524	591
-2	2	380	379
2	3	234	242
2	4	200	185
-2	4	212	259
-2	5	77	100
3	0	418	337
3	1	209	214
-3	1	443	450
-3	2	452	444
3	3	116	140
-3	4	100	89
3	5	109	104
-3	5	143	180
4	0	425	408
4	1	455	400
-4	1	175	143
-4	2	93	95
-4	3	203	188
4	4	199	208
-4	4	139	168
4	5	189	179
-4	5	85	88
5	0	227	219
5	1	301	275
-5	2	181	191
-5	3	298	300
5	4	239	246
-5	4	127	137
-5	6	77	79
6	1	79	36
-6	1	81	86
-6	2	82	61
-6	3	218	219
6	5	105	99
-6	6	109	119
7	0	135	96
7	1	77	109
-7	1	103	107
-7	5	100	88
-7	6	169	149
8	0	111	110
8	1	74	37
-8	2	79	75
9	0	105	85
-9	0	90	85
-9	2	149	160
******K=10******			
0	0	311	282
0	1	127	99
0	5	280	262
0	7	161	204
-1	1	414	381
-1	2	177	216
1	3	119	131
1	5	231	227
2	0	174	150
-2	1	746	715
2	3	181	181
-2	3	133	109
-2	4	166	179
2	6	206	206
3	1	178	137
-3	1	408	425
-3	2	84	66
-3	3	82	61
-3	4	148	162
4	0	170	149
4	1	243	254
-4	1	123	126
4	3	134	139
-4	3	83	89
4	4	93	128
4	5	114	114
5	0	157	159
5	1	219	225
-5	2	101	109
5	3	159	187
5	4	100	136
-5	5	89	108
-5	6	104	85
-6	2	83	105
6	5	113	74
7	1	83	73
-7	1	81	51
-7	2	138	158
8	0	77	38
-8	1	171	180
-9	1	163	181
******K=11******			
-1	1	107	72
-2	1	88	101
-2	2	329	349
-3	1	108	103
-3	2	190	190
-3	4	149	145
-4	2	127	84
-4	3	128	141
-5	1	107	115
-5	3	135	146
-5	4	77	71
-6	0	95	118
-6	1	113	119
-7	0	78	107
-7	3	122	104
-8	0	136	148
-8	2	124	115
-9	2	140	166
******K=12******			
-1	1	424	411
-1	2	301	347
-2	1	497	496
-2	2	186	190
-2	3	82	82
-2	4	83	61
-3	1	99	121
-3	2	126	140
-3	3	91	100
-4	3	93	78
-6	2	131	137
-8	1	153	191
******K=13******			
-1	1	125	128
-1	2	108	111
-1	3	116	120
-2	1	202	205
-2	2	184	205
-2	3	102	136
-3	0	104	116
-3	1	123	137
-3	3	95	98
-5	1	97	126
******K=14******			
-1	2	127	113
-2	0	117	135
-2	1	86	108
-2	2	139	124
-4	0	108	129
-4	1	84	83
-5	0	139	149
-5	1	84	45
******K=15******			
-1	0	82	64
-2	0	94	122
-2	1	148	136
-3	0	140	158
-3	1	115	106

TABLE 4 INTERATOMIC DISTANCES FOR $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_4$[a]

Atoms	Distance (Å)	Atoms	Distance (Å)
Bond distances			
Mg(1)–Cl(1)	2.495(9)	C(11)–C(12A)	1.48(6)
Mg(1)–Cl(1)'	2.508(10)	C(11)–C(12B)	1.61(7)
Mg(1)–Cl(2)	2.506(9)	C(13A)–C(14)	1.66(7)
Mg(1)–Cl(3)	2.472(9)	C(13B)–C(14)	1.42(8)
Mg(2)–Cl(1)	2.792(9)	C(21)–C(22)	1.42(5)
Mg(2)–Cl(2)'	2.406(10)	C(23)–C(24)	1.49(5)
Mg(2)–Cl(3)	2.395(11)	C(31)–C(32)	1.41(4)
		C(33)–C(34)	1.45(4)
Mg(1)–O(1)	2.11(2)	Avg.	1.49
Mg(1)–O(2)	2.04(2)		
Mg(2)–O(3)	2.14(2)	C(12A)–C(13A)	1.26(8)
		C(12A)–C(13B)	1.89(9)
Mg(2)–C(1)	2.19(3)	C(12B)–C(13A)	1.56(9)
C(1)–C(2A)	1.48(5)	C(12B)–C(13B)	1.15(9)
C(1)–C(2B)	1.24(6)	C(22)–C(23)	1.25(6)
O(1)–C(11)	1.32(4)	C(32)–C(33)	1.44(4)
O(1)–C(14)	1.35(3)	Avg.	1.43
O(2)–C(21)	1.25(4)		
O(2)–C(24)	1.49(4)		
O(3)–C(31)	1.40(4)		
O(3)–C(34)	1.32(4)		
Avg.	1.36		
Non-bonded distances less than 3.5 Å			
Cl(1)–Cl(2)'	3.455(8)	O(2)–O(1)	2.92(2)
Cl(1)–Cl(3)'	3.469(8)	Cl(2)–C(14)	3.25(3)
Cl(1)–Cl(1)'	3.336(10)	Cl(2)–C(31)	3.49(3)
		Cl(3)–C(21)	3.37(4)
O(1)'–Cl(1)	3.36(1)	Cl(3)–C(11)	3.41(3)
O(1)–Cl(2)	3.24(1)		
O(1)–Cl(3)	3.22(1)	O(1)–C(21)	3.42(4)
O(2)–Cl(1)	3.34(1)	O(3)–C(1)	3.20(4)
O(2)–Cl(2)	3.21(1)	C(34)–C(1)	3.36(5)
O(2)–Cl(3)	3.20(1)		
O(3)–Cl(2)'	3.24(1)		
O(3)–Cl(3)	3.21(1)		
Intra-ring non-bonded distances			
C(11)–C(14)	2.07(6)	O(1)–C(12A)	2.25(5)
C(21)–C(24)	2.02(6)	O(1)–C(12B)	2.43(5)
C(31)–C(34)	2.09(5)	O(1)–C(13A)	2.44(5)
		O(1)–C(13B)	2.15(6)
C(11)–C(13A)	2.27(7)	O(2)–C(22)	2.36(3)
C(11)–C(13B)	2.01(8)	O(2)–C(23)	2.26(3)
C(14)–C(12A)	2.20(7)	O(3)–C(32)	2.21(3)
C(14)–C(12B)	2.20(7)	O(3)–C(33)	2.19(3)
C(21)–C(23)	1.84(5)		
C(24)–C(22)	2.26(5)		
C(31)–C(33)	2.25(4)		
C(34)–C(32)	2.02(4)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The prime notation refers to atoms related to those in Table 1 by a center of inversion operation $(xyz \rightarrow \bar{x}\bar{y}\bar{z})$.

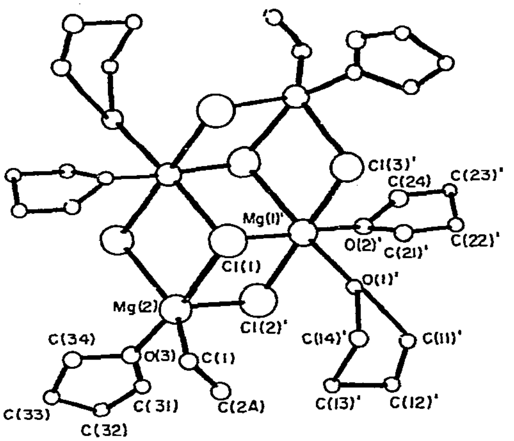
TABLE 5

INTERATOMIC ANGLES FOR $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$ [a]

Atoms	Angle (°)	Atoms	Angle (°)
Cl(1)–Mg(1)–Cl(2)	93.7(3)	Cl(1)–Mg(2)–C(1)	95.4(10)
Cl(1)–Mg(1)–Cl(1)'	83.6(3)	Cl(2)'–Mg(2)–C(1)	125.9(12)
Cl(1)'–Mg(1)–Cl(2)	87.1(3)	Cl(3)–Mg(2)–Cl(1)	127.6(11)
Cl(1)–Mg(1)–Cl(3)	88.6(3)	O(3)–Mg(2)–C(1)	95.4(16)
Cl(1)'–Mg(1)–Cl(3)	94.3(3)		
Cl(2)–Mg(1)–Cl(3)	177.5(5)	Mg(1)–Cl(1)–Mg(1)'	96.4(3)
Cl(1)–Mg(1)–O(1)	175.5(7)	Mg(1)–Cl(1)–Mg(2)	88.5(3)
Cl(1)'–Mg(1)–O(1)	92.9(6)	Mg(1)'–Cl(1)–Mg(2)	89.8(3)
Cl(2)–Mg(1)–O(1)	88.9(6)		
Cl(3)–Mg(1)–O(1)	88.9(6)	Mg(1)–Cl(2)–Mg(2)	99.5(3)
Cl(1)–Mg(1)–O(2)	94.2(6)		
Cl(1)'–Mg(1)–O(2)	175.4(7)	Mg(1)–Cl(3)–Mg(2)	98.8(4)
Cl(2)–Mg(1)–O(2)	89.0(6)		
Cl(3)–Mg(1)–O(2)	89.7(6)		
O(1)–Mg(1)–O(2)	89.6(8)		
Cl(1)–Mg(2)–Cl(2)'	83.0(3)		
Cl(1)–Mg(2)–Cl(3)	83.6(3)		
Cl(2)'–Mg(2)–Cl(3)	106.1(4)		
Cl(1)–Mg(2)–O(3)	169.2(7)		
Cl(2)'–Mg(2)–O(3)	90.6(7)		
Cl(3)–Mg(2)–O(3)	89.9(7)		
Mg(1)–O(1)–C(11)	128(2)	C(11)–C(12A)–C(13A)	112(5)
Mg(1)–O(1)–C(14)	128(2)	C(11)–C(12A)–C(13B)	72(6)
Mg(1)–O(2)–C(21)	134(2)	C(11)–C(12B)–C(13A)	92(5)
Mg(1)–O(2)–C(24)	129(2)	C(11)–C(12B)–C(13B)	91(6)
Mg(2)–O(3)–C(31)	136(2)	C(14)–C(13A)–C(12A)	97(5)
Mg(2)–O(3)–C(34)	121(2)	C(14)–C(13A)–C(12B)	87(5)
		C(14)–C(13B)–C(12A)	82(6)
C(11)–O(1)–C(14)	101(3)	C(14)–C(13B)–C(12B)	117(6)
C(21)–O(2)–C(24)	95(3)	C(21)–C(22)–C(23)	87(5)
C(31)–O(3)–C(34)	101(3)	C(24)–C(23)–C(22)	110(5)
		C(31)–C(32)–C(33)	105(5)
O(1)–C(11)–C(12A)	107(3)	C(34)–C(33)–C(32)	89(5)
O(1)–C(11)–C(12B)	112(3)		
O(1)–C(14)–C(13A)	108(3)		
O(1)–C(14)–C(13B)	102(4)		
O(2)–C(21)–C(22)	125(4)		
O(2)–C(24)–C(23)	98(3)		
O(3)–C(31)–C(32)	104(3)		
O(3)–C(34)–C(33)	104(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. The prime notation refers to atoms related to those in Table 1 by a center of inversion operation ($xyz \to \bar{x}\bar{y}\bar{z}$).

served Mg–Cl distance if decreased from 2.47 Å [Mg(1)–Cl(3)] to 2.40 Å [Mg(2)–Cl(3)] while the Mg–O distance is slightly lengthened [Mg(1)–O average distance 2.07 Å, Mg(2)–O(3) 2.14 Å] implies that the chlorine atom is competing more effectively for a coordination site, *i.e.* is a better base than the THF molecule. The Mg(2)–Cl(1) [type (3)] distance (2.79 Å) is longer than the Mg(1)–Cl(1) [type (4)] distance (2.50 Å)



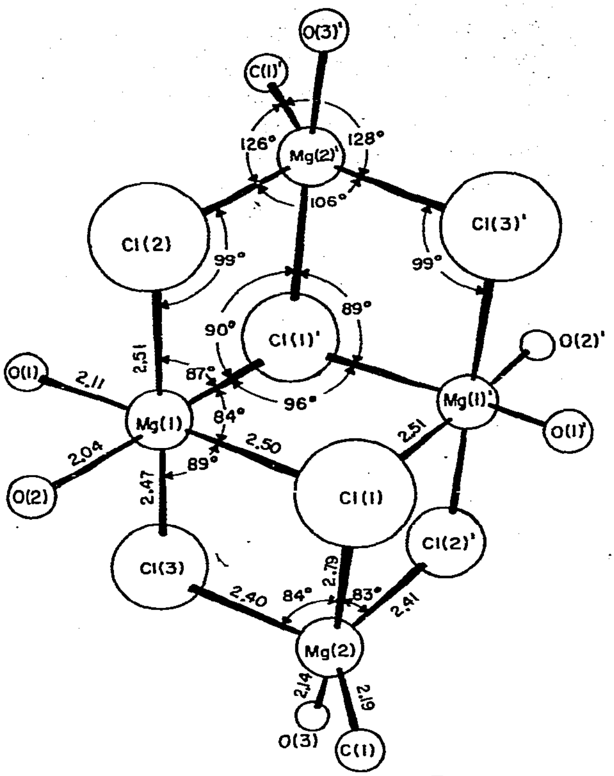


Fig. 3. Molecular structure of $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$. The crystallographic symmetry is $\bar{1} = C_i$.

Fig. 4. Molecular structure of $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$ illustrating selected bond distances and angles.

TABLE 6

MEAN PLANE RESULTS FOR FOUR-MEMBERED $(MgCl)_2$ RINGS IN $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$

Atom	Distance	Atom	Distance		
				Ring	Mg(2)–Cl(3)–Mg(1)–Cl(1)
				Eqn.	$0.0280X + 0.7537Y + 0.6566Z = 1.2477$
Mg(2)	0.059(9)	Cl(1)	−0.056(6)		
Cl(3)	−0.066(6)	Mg(1)	0.063(8)		
				Ring	Mg(1)–Cl(2)–Mg(2)'–Cl(1)'
				Eqn.	$0.8671X + 0.4460Y - 0.2218Z = 1.1611$
Mg(1)	−0.062(7)	Mg(2)	−0.058(8)		
Cl(2)	0.066(6)	Cl(1)	0.054(5)		

which is opposite to what is expected with the decrease in the magnesium coordination number. We believe that this dichotomy is due to the fact that bonding or van der Waals intramolecular contacts to Cl(1) include three chlorine atoms less than 3.5 Å away, two oxygen atoms, three magnesium atoms and one ethyl group. The interaction of Cl(1) with Mg(2) is only one contribution to the total potential energy surface of Cl(1) so that the Mg–C(1) bond length is not necessarily indicative of the nature of that particular interaction. In contrast, Cl(2) and Cl(3) have six bonding or van der Waals contacts with only one Cl–Cl distance less than 3.5 Å.

The five coordination observed about Mg(2) approximates that of a trigonal bipyramid with O(3) and Cl(1) at the apices and Cl(2)', Cl(3) and Cl(1) in the equatorial positions. The sum of the equatorial angles is 360° so that Mg(2), Cl(3), Cl(2)' and C(1) are coplanar. The largest deviation from 90° for an axial–Mg–equatorial angle is Cl(1)–Mg(2)–Cl(2)' (83.0°).

The geometry about Cl(2) is of some interest, with the three coordinated magnesium atoms at nearly right angles to each other. This implies that the three sets of lone pair electrons in the *p* orbitals of the Cl^- ion are being used as donor electrons. As pointed out above, however, this geometry may be determined by intramolecular contacts rather than the electronic requirements of this chlorine atom. The fact that the chlorine atom can simultaneously coordinate to three magnesium atoms greatly expands the structural possibilities for organomagnesium chlorides.

This is the first tetrameric Grignard reagent which has been structurally characterized. The results are entirely consistent with our previous observation[10] that the geometries of organomagnesium reagents are largely determined by the steric requirements of the groups coordinated to the magnesium atom· The effective volumes of various bases appear to be in the order $(C_2H_5)_3N > (C_2H_5)_2O \approx HC(C_2H_4)_3N$[33] $> C_4H_8O$. It is apparent from the structural data which are now available that small changes in the type of organic group or solvent can result in a completely different type of organomagnesium species. This is most obvious in the THF series: $MgBr_2(THF)_4$[26], $C_6H_5C{\equiv}CMgBr(THF)_4$[12], $CH_3MgBr(THF)_3$[11] and $C_6H_5MgBr(THF)_2$[25]. The relatively close approach (3.1 Å) of the *ortho* protons to the magnesium atom is apparently sufficient to result in the formation of the tetracoordinate $C_6H_5MgBr(THF)_2$ rather than a tri-solvated molecule. It is interesting to note that exchanging a CH_3-moiety for a bromine atom decreases the coordination number from six to five. In the structure of $[C_2H_5Mg_2Cl_3(THF)_3]_2$, the units are $C_2H_5MgCl_3(THF)$ and $MgCl_4(THF)_2$. Models show that the terminal carbon atom of the ethyl group effectively blocks out one coordination site on the magnesium atom. It would appear, then, that only with secondary, or tertiary, organic groups will Grignard reagents which are solvated with THF be less than five-coordinate.

There are a number of systems with solvated diethyl ether in which the magnesium atom is four-coordinate. Examples are $C_6H_5MgBr(C_4H_{10}O)_2$[3], $C_2H_5MgBr(C_4H_{10}O)_2$[34], $MgBr_2(C_4H_{10}O)_2$[35], and $[(CH_3)_2COMgBr(C_4H_{10}O)]_2$[36]. The only known example of a higher coordination number with diethyl ether is $Mg_4Br_6O(C_4H_{10}O)_4$[8] which contains five-coordinate magnesium. The effect of solvent is emphasized by a comparison of the crystalline products $MgBr_2(C_4H_{10}O)_2$[35] with $MgBr_2(THF)_4$[26], and $C_2H_5MgBr(C_4H_{10}O)_2$[34] with $[C_2H_5MgBr(C_2H_5)_3N]_2$[10]. In short, the formation of $[C_2H_5Mg_2Cl_3(THF)_3]_2$, rather than the dimeric species originally proposed by Ashby and Becker[11] (Fig. 1), is consistent with the requirement of obtaining the maximum coordination number compatable with the steric requirements of the ligands.

The above discussion does not lead to any conclusion as to why $C_2H_5Mg_2Cl_3$ is formed rather than, for example, C_2H_5MgCl. From the available structural and physical data, the equilibria shown in Fig. 5 for the Grignard reagent seem plausible. General formulae for which specific magnesium compounds have been isolated are

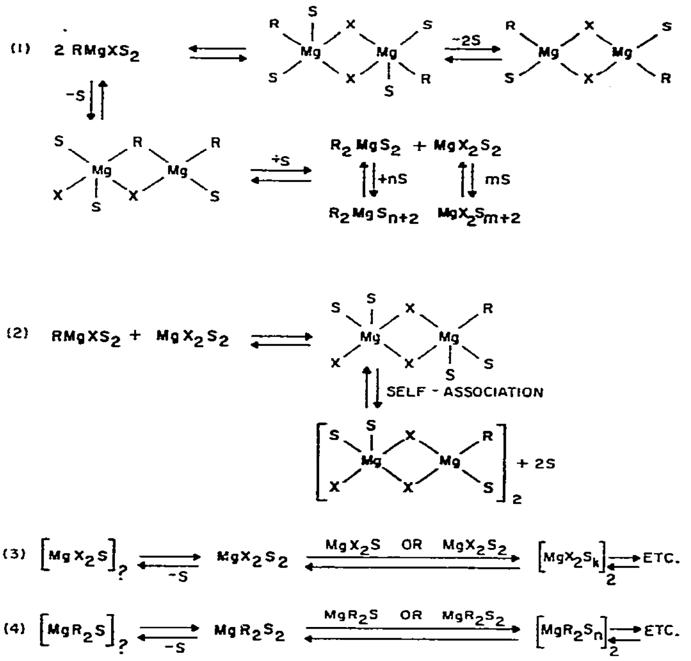


Fig. 5. Possible equilibria for the Grignard reagent in solution. General formulae for which specific magnesium compounds have been isolated are indicated in bold type. S = ether or amine, R = hydrocarbon, X = Cl, Br, I.

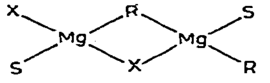
indicated in bold type. The role of the solvent is of obvious importance and cannot be neglected in any consideration of the Grignard reagent[37]. In solution, the degree of solvation may be higher than in the solid state. Thus, five-coordinate species in diethyl ether solutions and six-coordinate organomagnesium species in THF solutions can be expected to be present to a significant extent. The disproportionation or association of the Grignard reagent is regarded as originating from the competition of a halogen or organic group with a solvent molecule for a coordination site at the magnesium atom in the same way that Scala and Becker[37] have proposed to explain the solvent dependency of the reaction of benzonitrile with the Grignard reagent, C_2H_5MgBr in solvents of varying basicity. The term "basicity" as used here refers not to the enthalpy of solvation, but to the total free energy of reactions of the type

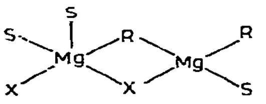
$$\mathrm{RMgXS}_n + \mathrm{S} \rightleftharpoons \mathrm{RMgXS}_{n+1} \tag{5}$$

$$\mathrm{RMgXS}_n + \mathrm{RMgXS}_m \rightleftharpoons (\mathrm{RMgXS}_k)_2 + p\mathrm{S} \qquad (p = n+m-2k) \tag{6}$$

Steric effects are therefore implicitly included. The reactions (5) and (6) emphasize the point that the structure of the Grignard reagent will depend upon the concentration of the basic solvent, S. At high concentrations of RMgX in a relatively weak base, equilibrium (5) will be shifted to the left, which, in turn, will result in the increased probability of reaction (6) proceeding to the right.

Upon concentration of the Grignard reagent, two possibilities exist. The first is that monomeric RMgXS_n or dimeric $[\mathrm{RMgXS}]_2$ will precipitate depending upon the relative base strengths of the halogen atom and the solvent used. The second possibility is that the Grignard solution will yield R_2MgS_n and MgX_2S_m. This is most likely to occur if R if a good bridging group relative to X so that the probability of forming mixed bridge intermediates* such as:





instead of dihalogen bridged species is enhanced; and, if the magnesium halide formed is of limited solubility in the solvent used. This conclusion is supported by the observation of Salinger and Mosher[42] that only R_2Mg is left in solutions of Grignard reagents prepared in THF from alkyl iodides. Methyl and ethyl Grignard reagents can also be expected to form mixed bridge complexes more readily than secondary, tertiary or longer chain primary alkyl groups and enhance the probability of precipitating either $MgCl_2$ as apparently observed by Salinger and Mosher[43] or $CH_3Mg_2Cl_3$ and $C_2H_5Mg_2Cl_3$ as reported by Ashby and Becker[11]. The situation is complicated by the number of magnesium halide species possible. Evans and Rowley[43] have isolated crystalline $MgBr(C_2H_5)_2O$, $MgBr_2[(C_2H_5)_2O]_2$ and $MgBr_2[(C_2H_5)_2O]_3$. The monoetherate is stable to 13° and the dietherate to 28°. On the other hand, the monoetherate of $MgCl_2(C_2H_5)_2O$, which is probably associated, has been reported to be the stable form at room temperature[44].

The exceptional ability of the chlorine atom to bridge two or more metal atoms is undoubtedly why chloro-Grignard reagents form dimeric and higher oligomers[39,45]. Equilibrium (2) particularly required that the halogen atom be a good bridging atom so that the tendency to form $[RMg_2X_3S_3]_2$ can be expected to decrease in the series $Cl > Br > I$. If the organic groups or solvent molecules coordinated to the magnesium atom are sufficiently large, for example, $(C_2H_5)_2O$ or $(C_2H_5)_3N$, the higher coordination numbers required for the formation of $[RMg_2X_3S_3]_2$ are not as easy to achieve and equilibrium (2) is, for all practical purposes, eliminated. The possibility of a similar association involving the dihalogen-bridged species of equilibrium (1) should also be noted. In the THF–ethyl Grignard system, the structural results suggest that a halogen atom and a THF molecule would be replaced by one ethyl group so that a compound $[C_2H_5MgClTHF]_4$ might be expected with all magnesium atoms five coordinate. This, however, would require bridging C_2H_5 groups. A polymeric structure with 3-coordinate Cl atoms might be more reasonable, but still less probable than the formation of $[C_2H_5Mg_2Cl_3(THF)_3]_2$. The details of the structural features expected for $[RMgXS_k]_n$, $n > 2$ molecules are obscure. In any case, trimeric or higher polymeric forms of magnesium reagents must be the most insoluble species present in solution.

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* The first mixed-bridge organometallic species to be isolated and structurally characterized, $(CH_3)_5Al_2N(C_6H_5)_2$, was recently reported by Magnuson and Stucky[38]. Mixed-bridge intermediates in the Grignard system have been proposed by Ashby and Smith[39], Whitesides and Roberts[40], and Fraenkel and Dix[41].

The THF groups in $[C_2H_5Mg_2Cl_3(C_4H_8O)_3]_2$ are apparently thermally disordered and no conclusions concerning the details of their coordination to the magnesium atoms are justified. The Fourier and least-squares analyses are only sufficient to confirm their general disposition with respect to the rest of the molecule. The Mg(2)–C(1) distance of 2.19 Å compares favorably with other reported magnesium–carbon distances[33,34].

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