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Abstract

Full Text

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CRYSTAL STRUCTURE OF MAGNESIUM METHOXYCHLORIDE

$3Mg(OCH_3)_2 \cdot MgCl_2 \cdot 10CH_3OH$

Metal alkoxyhalides—intermediate products in a number of important organic syntheses—are often also used as catalysts. Compounds of this class are usually not isolated from reaction mixtures, and therefore their physicochemical characteristics are practically absent from the literature.

For an X-ray structural investigation we were offered one of the representatives of the alkoxyhalides—magnesium methoxychloride, synthesized at the Department of Inorganic Chemistry of Moscow University ([1]).

Magnesium methoxychloride is a metastable phase: on contact with alcohol, on grinding, or on heating to 50-60° it immediately decomposes into $MgCl_2 \cdot 6CH_3OH$ and methylate. Transparent colorless crystals become covered in air with a white coating. To obtain the necessary set of X-ray experimental data, the crystals were sealed in glass capillaries, which considerably prolonged the lifetime of the phase but lowered the quality of the X-ray photographs.

Fig. 1. Mg-methoxychloride. Three-dimensional Patterson function $P(uvw)$. The numerator of a fraction is the peak weight, the denominator is the coordinate u in 120ths of the a axis.

At the beginning of the study, both the number of molecules of crystallization alcohol in the chemical formula

Fig. 2. Structure of Mg-methoxychloride, xy projection. Light circles at the centers of octahedra are Mg atoms. Shaded groups are CH_3OH and CH_3O; doubled circles are Cl anions. Beside the circles are indicated the heights of the atoms in fractions of the c axis.

Figure 2: Fig. 2. Structure of Mg-methoxychloride, xy projection. Light circles at the centers of octahedra are Mg atoms. Shaded groups are CH_3OH and CH_3O; doubled circles are Cl anions. Beside the circles are indicated the heights of the atoms in fractions of the c axis.

$$3Mg(OCH_3)_2 \cdot MgCl_2 \cdot n(CH_3OH)$$

remained uncertain.

Kinne ([2]), who first described these crystals, assumed $n = 11$, and then $d_{calc} = 1.32$ g/cm^3 ($d_{exp} = 1.30$ g/cm^3). The results of chemical analysis of the crystals obtained by the authors ([1]) corresponded better to a content of 8 molecules of alcohol, $d_{calc} = 1.15$. Anticipating the results, we indicate that according to the results of the direct X-ray structural investigation the number of molecules of crystallization alcohol was found to be 10, $d_{calc} = 1.28$ g/cm^3.

In a tetragonal cell with parameters $a = 11.37$ Å, $c = 13.75$ Å there are two formula units of composition

$$3Mg(OCH_3)_2 \cdot MgCl_2 \cdot 10CH_3OH;$$

the Fedorov group $D_{2d}^4 = P\bar{4}2_1c$ is determined unambiguously from the systematically absent reflections.

The experimental set of intensities was provided by the layer lines $h0l$–$h5l$ (Weissenberg equi-inclination X-ray goniometer, unfiltered Mo radiation, $\max \sin\vartheta/\lambda = 0.7$).

The intensities were estimated from blackening marks with a step of $\sqrt{2}$. In calculating the structural factors F_{exp}^2, LP factors were taken into account; no absorption correction was introduced.

Fig. 2. Structure of Mg-methoxychloride, xy projection. Light circles at the centers of octahedra are Mg atoms. Shaded groups are CH_3OH and CH_3O; doubled circles are Cl anions. Beside the circles are indicated the heights of the atoms in fractions of the c axis.

The three-dimensional Patterson function, constructed from 440 nonzero reflections, is given in point form in Fig. 1. The heavier Cl and Mg were determined from analysis of the bond peaks ([3]) Cl–Cl and Mg–Mg and of the interaction peaks Cl–Mg ([4]). The discrepancy coefficient for the first model of the structure (Cl and Mg atoms) was 41%. The light O and C were localized at the stage of

Fig. 3. Approximation of a group of four Mg octahedra by the described Laves polyhedron with 12 vertices (truncated tetrahedron).

Figure 3: Fig. 3. Approximation of a group of four Mg octahedra by the described Laves polyhedron with 12 vertices (truncated tetrahedron).

syntheses of the electron density $\rho(xyz)$. A series of successive approximations with all atoms fixed (except hydrogen) led to an R-factor of 23%. Refinement by the least-squares method with allowance for individual thermal corrections reduced R to 13%.

Fig. 3. Approximation of a group of four Mg octahedra by the described Laves polyhedron with 12 vertices (truncated tetrahedron)

The final (at this stage) values of 28 positional parameters and isotropic individual thermal corrections are given in Table 1; interatomic distances calculated from these coordinates are given in Table 2.

The basis of the structure is formed by nearly planar square nets of Cl^{1-} anions, located at the levels 0 and $c/2$. In each net, in checkerboard order, squares occupied by large complexes of 4 Mg atoms alternate with empty squares. Above an Mg complex in the lower net there is an empty square of the upper net, and vice versa. The cationic complex $Mg_4O_6(OH_{10})(CH_3)^{2+}_{16}$ (Fig. 2) is the frequently described large tetrahedron of 4 closely packed Mg octahedra (Fig. 3). At the 12 vertices of the complex and at the 4 centers of its faces are located

Table 1

Mg-methoxychloride. Positional parameters and isotropic individual thermal corrections

Atoms	x/a	y/b	z/c	B_j
Cl	0	0.500	0.045	2.65
Mg	0.110	0.079	0.084	1.00
O_1	0.292	0.064	0.096	2.69
O_2	0.084	0.061	0.228	1.10
O_3	0.140	0.272	0.094	2.49
O_4	0.427	0.401	0.435	1.32
C_1	0.092	0.157	0.315	1.01
C_2	0.361	0.308	0.370	1.80
C_3	0.368	0.063	0.185	2.63
C_4	0.264	0.338	0.094	4.12

Table 2

Mg-methoxychloride. Interatomic distances (Å) in the Mg octahedron

$Mg–O_1$	2.08	$O_1–O_4''$	3.12
$Mg–O_2$	2.02	$O_2–O_4'''$	2.89
$Mg–O_3$	2.20	$O_3–O_4''$	3.17
$Mg–O_4'$	2.09	$O_3–O_4'''$	3.14
$Mg–O_4''$	2.03	$O_4–O_3'$	3.13
$Mg–O_4'''$	2.17	$O_4–O_5'$	3.12
$O_1–O_2$	2.98	$O_4–O_2'$	2.89
$O_1–O_3$	2.93	$O_1–C_3$	1.51
$O_1–O_4'$	3.11	$O_2–C_1$	1.56
$O_2–O_3$	3.09	$O_3–C_4$	1.59
$O_2–O_4'$	2.88	$O_4–C_2$	1.57

10 alcohol groups CH_3OH and 6 groups CH_3O. In the pseudocentered cell, the two Mg complexes related by the plane passing between them, c (or the glide plane n), are mutually rotated about the 4-fold axis by an angle of 7°. Since the multiplicities of the corresponding positions do not agree with the number of organic groups $(12+4)$, these equivalent groups may be regarded as statistically distributed.

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REFERENCES

1. N. Ya. **Turova**, E. P. **Turevskaya**, A. V. **Novoselova**, DAN, **173**, 374 (1967).
2. M. L. **Quinet**, Bull. Soc. chim. Franc. (5), **3**, 1823 (1936).
3. D. **Harker**, J. Chem. Phys., **4**, 381 (1936).
4. S. V. **Borisov**, Kristallografiya, **9**, 603 (1964).

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