Acta Cryst. (1985). C**41**, 8–10

Magnesium Dichloride Hexahydrate, $MgCl_2.6H_2O$, by Neutron Diffraction*

BY P. A. AGRON AND W. R. BUSING

Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, *USA*

(*Received* 6 *April* 1984; *accepted* 25 *September* 1984)

Abstract. $M_r = 203{\cdot}31$, monoclinic, $C2/m$, $a = 9{\cdot}8607\,(2)$, $b = 7{\cdot}1071\,(2)$, $c = 6{\cdot}0737\,(2)$ Å, $\beta = 93{\cdot}758\,(2)°$ based on $\lambda(\mathrm{Cu}\,K\alpha_1) = 1{\cdot}54051$ Å; $V = 424{\cdot}74\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}5895\,(3)$, $D_m = 1{\cdot}593\,(3)$ g cm^{-3}, room temperature; for neutrons $\lambda = 1{\cdot}077$ Å, $\mu = 2{\cdot}434$ cm^{-1}, $F(000) = 28{\cdot}836$ fm. Final $R = 0{\cdot}0548$ based on all 813 independent neutron diffraction intensity measurements. The structure can be considered to be composed of $Cl^-(H_2O)_3Mg^{2+}$-$(H_2O)_3Cl^-$ groups with crystallographic point-group symmetry $2/m$. These also have additional pseudo-symmetry $\bar{3}m$ with the $\bar{3}$ axis along the $Cl^-\cdots Mg^{2+}\cdots Cl^-$ line. The O(1)–H(2) and O(2)–H(4) bonds are roughly parallel to this axis and are directed toward the Cl^- ions within each group. The O(1)–H(1) and O(2)–H(3) vectors point away from the $\bar{3}$ axis and form approximately straight hydrogen bonds to Cl^- ions of neighboring groups.

Introduction. This single-crystal neutron diffraction study of $MgCl_2.6H_2O$ was undertaken as part of a program to locate the H atoms precisely and to investigate the role of water in simple salt hydrates.

Experimental. Lattice parameters determined by least-squares refinement based on X-ray diffractometer measurements of Bragg angles for 12 high-angle reflections ($2\theta = 120$ to 130°) using Cu $K\alpha_1$ ($\lambda = 1{\cdot}54051$ Å) radiation. These results agree with earlier reported values (Andress & Gunderman, 1934; Sorrell & Ramey, 1974). D_m taken from Sorrell & Ramey (1974).

Crystals for neutron diffraction studies were obtained by controlled slow growth in a desiccator by seeding a saturated solution of $MgCl_2$. Two selected crystals (volume 3·93 and 11·58 mm^3) were mounted on quartz fibers and completely enclosed in thin quartz envelopes with the bases sealed in wax. It is our experience that crystal hydrates protected in this manner show no signs of deterioration, even after years of storage.

Table 1. *Fractional coordinates* (×10^4) *and equivalent isotropic thermal parameters*, B_{eq}(Å^2)

Standard errors are given in parentheses.

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Mg	0	0	0	2·0
Cl	3176 (1)	0	6122 (2)	2·8
O(1)	2019 (1)	0	1095 (3)	3·5
O(2)	−429 (1)	2067 (2)	2233 (2)	3·9
H(1)	2372 (3)	0	2583 (6)	5·0
H(2)	2693 (4)	0	83 (8)	7·0
H(3)	209 (2)	2997 (3)	2784 (4)	4·5
H(4)	−1161 (2)	1984 (4)	3151 (4)	5·9

813 neutron diffraction intensities measured at the Oak Ridge Research Reactor (Busing, Smith, Peterson & Levy, 1964) to $(\sin\theta)_{\max}/\lambda = 0{\cdot}71$ Å^{-1} with $\lambda = 1{\cdot}077$ Å, corrected for absorption (Busing & Levy, 1957), index range: $-14 \geq h \geq 14$, $0 \geq k \geq 10$, $0 \geq l \geq 9$, average transmission factors 0·58 and 0·68 for the large and small samples respectively. Least-squares refinement based on F^2 starting from X-ray structure (Andress & Gunderman, 1934) with H atoms located on expected hydrogen bonds to Cl^- ions. $w = 1/[\sigma_c^2 + (0{\cdot}03\,F^2)^2]$, where σ_c is the standard error of F^2 based on counting statistics. Variables included scale factors, coordinates, anisotropic temperature-factor coefficients and an isotropic extinction parameter (Zachariasen, 1967) for the larger sample. The smaller crystal showed no appreciable extinction. Data from

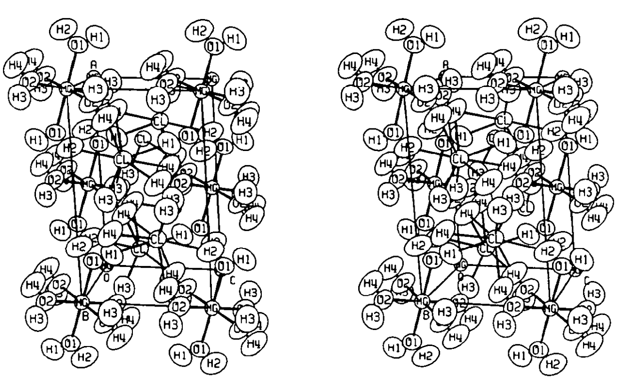


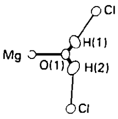
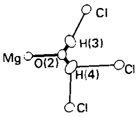
Fig. 1. Stereoscopic drawing of the unit cell of $MgCl_2.6H_2O$. The direction of view is roughly perpendicular to the mirror plane.

---

* Research sponsored by the Divisions of Materials Sciences and Chemical Sciences, US Department of Energy, under contract DE-AC05-84OR21400 with the Martin Marietta Energy Systems, Inc.

0108-2701/85/010008-03$01.50

Table 2. *Distances and angles involving water molecules and hydrogen bonds in* $MgCl_2.6H_2O$

	Distances (Å)				Angles (°)	
	Mg—O	O—H	H···Cl	O···Cl	O—H···Cl	H—O—H
			2·242 (3)	3·189 (2)	179·1 (3)	
		0·947 (4)				
	2·057 (1)					113·2 (4)
		0·935 (4)				
			2·483 (5)	3·298 (2)	145·8 (4)	
			2·206 (2)	3·160 (1)	174·6 (2)	
		0·958 (2)				
	2·062 (1)					110·3 (2)
		0·942 (2)	2·500 (2)	3·294 (1)	142·0 (2)	
			2·904 (3)	3·499 (1)	122·3 (2)	

the two samples combined for final refinement: $R = 0{\cdot}0548$, $wR = 0{\cdot}0794$, $S = 1{\cdot}265$ including all 813 independent reflections. $(\Delta/\sigma)_{\max}$ on final cycle 0·004. Neutron scattering factors used: Mg, 5·32; Cl, 9·580; O, 5·803; and H, −3·740 fm (Shull, 1972).

Computer programs used: lattice-parameter refinement (Busing, Ellison, Levy, King & Roseberry, 1968; Busing, 1970); absorption correction, *ORABS* (Wehe, Busing & Levy, 1962); structure-factor least squares, *XFLS* (Busing, Martin & Levy, 1962); function and error calculation, *ORFFE* (Busing, Martin & Levy, 1964); and crystal-structure illustration, *ORTEP* (Johnson, 1976).

Discussion. Table 1 lists the fractional coordinates and equivalent isotropic thermal parameters for $MgCl_2.6H_2O$.*

Fig. 1 is a stereoscopic drawing of a unit cell with the mirror plane approximately parallel to the page. The O atoms form an almost perfect octahedron about the Mg^{2+} ion, with Mg—O(1) and Mg—O(2) distances of 2·057 (1) and 2·062 (1) Å respectively, and with octahedral angles ranging from 88·67 (5) to 91·33 (5)°. Each water molecule is coordinated to one Mg^{2+} ion, unlike the arrangements observed for $CaCl_2.6H_2O$ and $SrCl_2.6H_2O$ (Jensen, 1940; Agron & Busing, 1969) and for $BaCl_2.2H_2O$ (Padmanabhan, Busing & Levy, 1978). In the latter hydrates, some or all of the water molecules are shared by two cations. The differences in coordination and packing may be attributed to the larger size of these cations. X-ray and neutron diffraction determinations of the $AlCl_3.6H_2O$ structure (Buchanan & Harris, 1968) show an octahedral coordination of six water molecules about the small Al^{3+} ion. In contrast, the hexahydrates of the transition-metal chlorides (Cr^{3+}, Andress & Carpenter, 1934; Co^{2+}, Shchukarev, Stroganov, Andreev & Purvinskii, 1963; Mizuno, 1960; Ni^{2+}, Mizuno, 1961; Kleinberg, 1969) have two Cl^- ions and four water molecules coordinated octahedrally to the cation, even though these metals are about the same size as Mg^{2+} (Pauling, 1969).

Table 2 lists the distances and angles involving water molecules and hydrogen bonds in $MgCl_2.6H_2O$. The O—H distances are in the normal range for water molecules. The eight H atoms (from eight water molecules) coordinated to each Cl^- ion may be described as in a trigonal-prism arrangement with two H atoms projecting from two of the prism faces (Fig. 1). The H···Cl distances range from 2·21 to 2·90 Å, the shortest distances corresponding to O—H···Cl groups that are nearly linear. A comparison of the H—O—H angles of the two water molecules shows that the water with the larger angle has the shorter Mg—O distance. This is consistent with bonding effects observed in other hydrates (Chidambaram, 1962; Chidambaram, Sequeira & Sikka, 1964; Hamilton & Ibers, 1968; Datt & Ozerov, 1972).

References

Agron, P. A. & Busing, W. R. (1969). Chem. Div. Ann. Rep. ORNL-4437, p. 118. Oak Ridge National Laboratory, Tennessee.

Andress, K. R. & Carpenter, C. (1934). *Z. Kristallogr.* **87**, 446–463.

Andress, K. R. & Gunderman, J. (1934). *Z. Kristallogr.* **87**, 345–369.

Buchanan, D. R. & Harris, P. M. (1968). *Acta Cryst.* B**24**, 954–960.

Busing, W. R. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 319–330. Copenhagen: Munksgaard.

Busing, W. R., Ellison, R. D., Levy, H. A. King, S. P. & Roseberry, R. T. (1968). *The Oak Ridge Computer-Controlled X-ray Diffractometer*, Report ORNL-4143. Oak Ridge National Laboratory, Tennessee.

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180–182.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.

---

* Lists of anisotropic temperature-factor coefficients and observed and calculated squares of neutron diffraction structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39741 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, CH1 2HU, England.

BUSING, W. R., SMITH, H. G., PETERSON, S. W. & LEVY, H. A. (1964). *J. Phys. (Paris) Colloq.* **25**, 495–496.
CHIDAMBARAM, R. (1962). *J. Chem. Phys.* **36**, 2361–2365.
CHIDAMBARAM, R., SEQUEIRA, A. & SIKKA, S. K. (1964). *J. Chem. Phys.* **41**, 3616–3622.
DATT, I. D. & OZEROV, R. P. (1972). *Sov. Phys.-Crystallogr.* **17**, 383–401.
HAMILTON, W. C. & IBERS, J. A. (1968). In *Hydrogen Bonding in Solids*. New York: Benjamin.
JENSEN, A. T. (1940). *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **17**(9), 1–17.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KLEINBERG, R. (1969). *J. Chem. Phys.* **50**, 4690–4696.
MIZUNO, J. (1960). *J. Phys. Soc. Jpn*, **15**, 1412–1420.
MIZUNO, J. (1961). *J. Phys. Soc. Jpn*, **16**, 1574–1580.
PADMANABHAN, V. M., BUSING, W. R. & LEVY, H. A. (1978). *Acta Cryst.* B**34**, 2290–2292.
PAULING, L. (1969). *The Nature of the Chemical Bond*, 3rd ed., pp. 514–518. Ithaca: Cornell Univ. Press.
SHCHUKAREV, S. A., STROGANOV, E. V., ANDREEV, S. N. & PURVINSKII, O. F. (1963). *Zh. Strukt. Khim.* **4**, 56–58.
SHULL, C. G. (1972). Personal communication. The values were measured by L. KOESTER.
SORRELL, C. A. & RAMEY, R. R. (1974). *J. Chem. Eng. Data*, **19**(1), 31–32.
WEHE, D. J., BUSING, W. R. & LEVY, H. A. (1962). *ORABS*. Report ORNL-TM-229. Oak Ridge National Laboratory, Tennessee.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1985). C**41**, 10–13

Electron-Density Distribution in Crystals of Lithium Nitrite Hydrate, $LiNO_2.H_2O$, at 120 K

BY S. OHBA, T. KIKKAWA AND Y. SAITO

Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, *Kohoku-ku, Yokohama* 223, *Japan*

(*Received* 11 *May* 1984; *accepted* 25 *September* 1984)

Abstract. $M_r = 70{\cdot}96$, monoclinic, $P2_1/c$, $a = 3{\cdot}306\,(1)$, $b = 14{\cdot}242\,(1)$, $c = 6{\cdot}396\,(1)$ Å, $\beta = 106{\cdot}14\,(1)°$, $V = 289{\cdot}3\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}63$ Mg m^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70926$ Å, $\mu = 0{\cdot}157$ mm^{-1}, $F(000) = 144$, $T = 120\,(1)$ K, final $R = 0{\cdot}028$ for 1512 observed unique reflections. The lone-pair electron of the nitrite O atom was observed as separate peaks of 0·28 (4) e Å^{-3} on the difference synthesis at 110–115° to the N—O bond axis and 0·50–0·55 Å from the O nucleus, suggesting sp^2 hybridization. N—O bonding and N lone-pair electrons were also observed as peaks of 0·25 (4) and 0·47 (4) e Å^{-3}, respectively.

Introduction. Charge distribution in $[Co(NO_2)_6]^{3-}$ has been studied experimentally (Ohba, Toriumi, Sato & Saito, 1978) as well as theoretically by an *ab initio* MO method (Ohba, Kitaura, Morokuma & Saito, 1979). The theoretical deformation density showed sp^2 hybridization of the O atoms, whereas the experimental density suggested *sp* hybridization. To resolve the disagreement, the electron-density distribution of an NO_2^- ion not coordinated to a metal atom has been studied. An attempt with $AgNO_2$ was unsuccessful because of the large anisotropic thermal vibrations of NO_2^- (Ohba & Saito, 1981). Crystal structures of alkaline and alkaline-earth nitrites have not been reported except for $NaNO_2$ (Kay & Frazer, 1961), KNO_2 (Solbakk & Strømme, 1969) and $Ba(NO_2)_2.H_2O$ (Abrahams, Bernstein & Liminga, 1980). Charge distribution in ferroelectric crystals of $NaNO_2$ has been investigated by Iwata, Koyano & Shibuya (1979) and Ito (1984). However, $NaNO_2$ has a non-centrosymmetric structure and hence includes phase approximations (Ito & Shibuya, 1977). For its advantage in valence/core electron ratio (Stevens & Coppens, 1976), Li was selected as a counter ion. We determined the structure of $LiNO_2.H_2O$, which is centrosymmetric, and obtained the deformation density at 300 (1) K. Quite independently, almost the same results on $LiNO_2.H_2O$ at 295 K were reported by Hermansson & Thomas (1983). However, the resolution of the deformation density was not sufficient to discuss the hybridization of the nitrite O atoms; therefore a redetermination was carried out at 120 K.

Experimental. Crystals of $LiNO_2.H_2O$ grown from filtrate of mixture of LiCl and $AgNO_2$ aqueous solution by slow evaporation under sulfuric acid in a desiccator. Hygroscopic, nearly spherical crystal of 0·5 mm diameter sealed in glass capillary with dry N_2 gas. Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. There is a possibility that the crystal is twinned, where the twinned cells are related by a mirror plane perpendicular to **a** (Hermansson & Thomas, 1983) and they cannot be

0108-2701/85/010010-04$01.50