Crystal Structure and Infrared Absorption Spectra of Magnesium(II) Hydrogen Selenite Tetrahydrate, $Mg(HSeO_3)_2 \cdot 4H_2O$

Zdeněk Mička, Ivan Němec, and Pavel Vojtíšek

Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 Prague 2, Czech Republic

and

Jan Ondráček

Department of Solid State Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

The X-ray structural analysis of $Mg(HSeO_3)_2 \cdot 4H_2O$ has been carried out. The substance crystallizes in a monoclinic system in space group $I\,2/a$. $a = 10.9962(6)$, $b = 7.5517(8)$, $c = 11.6660(9)$ Å, $\beta = 100.92(1)°$, $V = 951.2(1)$ Å³, $Z = 4$, $R = 0.0244$ for 1164 observed reflections. The magnesium atom is surrounded by a coordination octahedron of oxygen atoms from four hydrogen selenite anions and two water molecules. The neighboring octahedra are interconnected through two hydrogen selenite anions and form $\{Mg[Se(OH)O_2]_2(H_2O)_2\}_n$ chains connected by multiple hydrogen bonds. Study of the FTIR vibrational spectra of $Mg(HSeO_3)_2 \cdot 4H_2O$ confirmed that the protons in the hydrogen bonds are localized close to one oxygen atom. Down to a temperature of 77 K, no phase transitions connected with a change in the proton ordering were found for the test compound using vibrational spectroscopy. © 1996
Academic Press, Inc.

INTRODUCTION

The first concrete information on magnesium hydrogen selenites was published by Nilson (1) and Boutzoureano (2), who described the preparation of compounds with compositions corresponding to the formulae $Mg(HSeO_3)_2 \cdot 3H_2O$ and $MgH_4(SeO_3)_3$. The conditions for the preparation of $Mg(HSeO_3)_2 \cdot 4H_2O$ at laboratory temperature were later determined in detail by Ebert and Havlíček (3) on the basis of a study of solubility in the $MgSeO_3$–SeO_2–H_2O system. The symmetry and constitution of the hydrogen selenite anion were determined by Simon and Paetzold (4) using IR spectroscopy. This kind of hydrogen selenite can belong in the group of ferroelectric substances with short hydrogen bonds of the KH_2PO_4 type ("KDP") (5). It is characteristic for this substance that its dielectric prop-

TABLE 1
Basic Crystallographic Data and Data Collection and Refinement Parameters

a	10.9962(6) Å
b	7.5517(8) Å
c	11.6660(9) Å
β	100.92(1)°
V	951.2(1) Å³
Z	4
$D(\text{obs})$	2.305(8) Mg · m⁻³
$D(\text{calc})$	2.460 Mg · m⁻³
Space group	$I\,2/a$
M_r	352.31
$\mu(\text{Mo}K\alpha)$	7.87 mm⁻¹
$F(000)$	680
Crystal dimensions	$0.18 \times 0.28 \times 0.21$ mm
Diffractometer and radiation used	Enraf–Nonius CAD4, Mo$K\alpha$, $\lambda = 0.71073$ Å
Scan technique	$\omega - 2\theta$
No. and θ range of reflections for lattice parameter refinement	20, 22°–24° θ
Range of h, k, and l	$-14 \rightarrow 14$, $-9 \rightarrow 9$, $-15 \rightarrow 15$
No. of standard reflections	3
Standard reflections monitored in interval	120 min.
Intensity fluctuation	0.4%
Total number of reflections measured	4217
θ range	3.23°–28.60°
Value of R_{int}	0.038
No. of unique observed reflections	1164
Criterion for observed reflections	$F_o > 4\sigma(F_o)$
Function minimized	$\Sigma w(|F_o| - |F_c|)^2$
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.0415P)^2 + 0.46P]^{-1}$ $P = (F_o^2 + 2F_c^2)/3$
Parameters refined	82
Value of R	0.0244
Value of wR	0.0616
Value of S	1.052
Ratio of max. least-squares shift to e.s.d. in the last cycle	0.000
Extinction coefficient	0.0034(5)
Max. and min. heights in final $\Delta\rho$ map	0.813, −0.800 e Å⁻³
Source of atomic scattering factors	SHELX93(11), International Tables for X-ray Crystallography (12)
Programs used	SDP (13), SHELX93 (11), PARST (14), PLUTO (15)
Computer used	PDP11/73, PC AT

TABLE 2

Fractional Atomic Coordinates (×10⁴) and Equivalent (for Non-H Atoms ×10³) or Isotropic (for H Atoms ×10³) Displacement Factors with Standard Deviations in Parenthesis

	x	y	z	U_{eq}(Å^2)
Se	4762(1)	1313(1)	3638(1)	15(1)
Mg	2500	325(2)	5000	13(1)
O1	4698(2)	1470(3)	2155(2)	26(1)
O2	5773(2)	−362(2)	3855(2)	18(1)
O3	3401(2)	343(3)	3623(2)	21(1)
O4	1931(2)	−329(3)	1571(2)	28(1)
O5	2500	3001(4)	5000	23(1)
O6	2500	−2362(4)	5000	26(1)
H1O1	4591(37)	2365(58)	1932(35)	30(10)
H1O4	2451(43)	−244(65)	2252(43)	52(13)
H2O4	1408(41)	−566(61)	1720(38)	38(13)
H1O5	2670(33)	3588(45)	4459(31)	22(9)
H1O6	2335(31)	−3031(49)	5492(27)	21(8)

Note. $U_{eq} = \frac{1}{3} E_i E_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

TABLE 3

Bond Lengths (Å) and Selected Angles (°)

Mg–O5	2.021(3)	O5–Mg–O2^i	89.25(6)
Mg–O6	2.029(3)	O5–Mg–O3	89.63(7)
Mg–O3	2.041(2)	O3–Mg–O2^i	89.15(7)
Mg–O2^i	2.105(2)	O3–Mg–O2^{ii}	90.84(7)
		O6–Mg–O3	90.37(7)
		O6–Mg–O2^i	90.75(6)
Se–O1	1.722(2)	O1–Se–O2	95.99(10)
Se–O2	1.671(2)	O1–Se–O3	98.86(10)
Se–O3	1.664(2)	O2–Se–O3	103.84(9)

Hydrogen bonds

Donor–H	Donor ⋯ Acceptor	H ⋯ Acceptor	Donor–H ⋯ Acceptor
O1–H1O1	O1 ⋯ O2^{iii}	H1O1 ⋯ O2^{iii}	O1–H1O1 ⋯ O2^{iii}
0.73(4)	2.674(3)	1.95(5)	173(4)
O4–H1O4	O4 ⋯ O3	H1O4 ⋯ O3	O4–H1O4 ⋯ O3
0.89(5)	2.671(3)	1.79(5)	169(4)
O4–H2O4	O4 ⋯ O1^{ii}	H2O4 ⋯ O1^{ii}	O4–H2O4 ⋯ O1^{ii}
0.66(4)	2.805(3)	2.15(5)	177(5)
O5–H1O5	O5 ⋯ O4^{iv}	H1O5 ⋯ O4^{iv}	O5–H1O5 ⋯ O4^{iv}
0.82(3)	2.698(3)	1.89(4)	168(4)
O6–H1O6	O6 ⋯ O4^v	H1O6 ⋯ O4^v	O6–H1O6 ⋯ O4^v
0.81(3)	2.689(3)	1.88(5)	177(4)

Equivalent positions

^{i} $-x + 1, -y, -z + 1$ ^{iv} $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$

^{ii} $x - \frac{1}{2}, -y, z$ ^{v} $x, -y - \frac{1}{2}, z + \frac{1}{2}$

^{iii} $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ^{vi} $-x + \frac{1}{2}, y, -z + 1$

erties are greatly affected by the dynamics of the hydrogen bonds (6). So the vibrational spectroscopy can be a very useful tool to verify the possibility of phase transitions connected with the proton ordering (7).

This article describes a study of the FTIR spectra of Mg(HSeO$_3$)$_2$·4H$_2$O at laboratory and low temperatures (77 K) and the determination of the crystal structure.
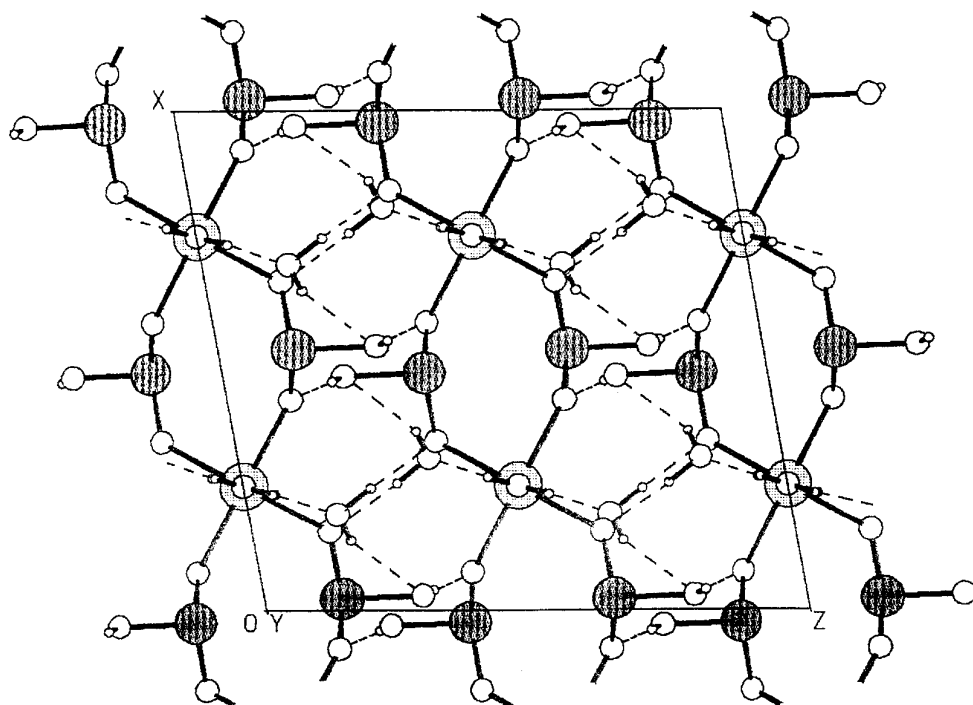
FIG. 1. Packing scheme of Mg(HSeO$_3$)$_2$·4H$_2$O. The hydrogen bonds are designated by dashed lines.
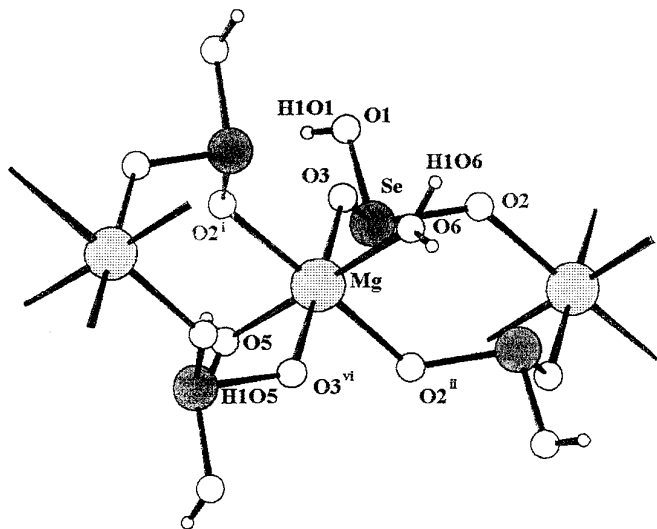
FIG. 2. The surroundings of the magnesium atom in Mg(HSeO₃)₂ · 4H₂O. Equivalent positions are given in Table 3.

EXPERIMENTAL

The tetrahydrate of magnesium hydrogen selenite was prepared by the reaction of $MgSeO_3 \cdot 6H_2O$, SeO_2 and H_2O in the ratios given in the solubility diagram (3). After establishment of equilibrium at 298 K, the slightly pink crystals formed were washed with ethanol and dried at laboratory temperature in the air. The selenium content was determined iodometrically (8) (theoretical 44.82%, found 44.32%) and the magnesium content was found complexometrically using Eriochrome Black T (9) (theoretical 6.90%, found 6.75%).

The X-ray data collection for the $Mg(HSeO_3)_2 \cdot 4H_2O$ single crystal was carried out on an Enraf–Nonius CAD4 four-circle diffractometer (Mo$K\alpha$-radiation, graphite monochromator). The intensities were corrected for the Lorentz and polarization effects. The absorption correction (10) was carried out with minimum and maximum absorption coefficients of 0.930 and 1.136, respectively. The position of the selenium atom was determined from the Patterson map. The positions of the magnesium and oxygen atoms were determined from the calculated Fourier maps. The positions of the hydrogen atoms were found on the differential Fourier maps. The least squares method was employed to refine all the positional parameters and coefficients of the anisotropic displacement factors (for non-H atoms) and the coefficients of the isotropic displacement factors (for H atoms). The basic crystallographic data and the details of the measurement and refinement are summarized in Table 1. A list of the observed and calculated
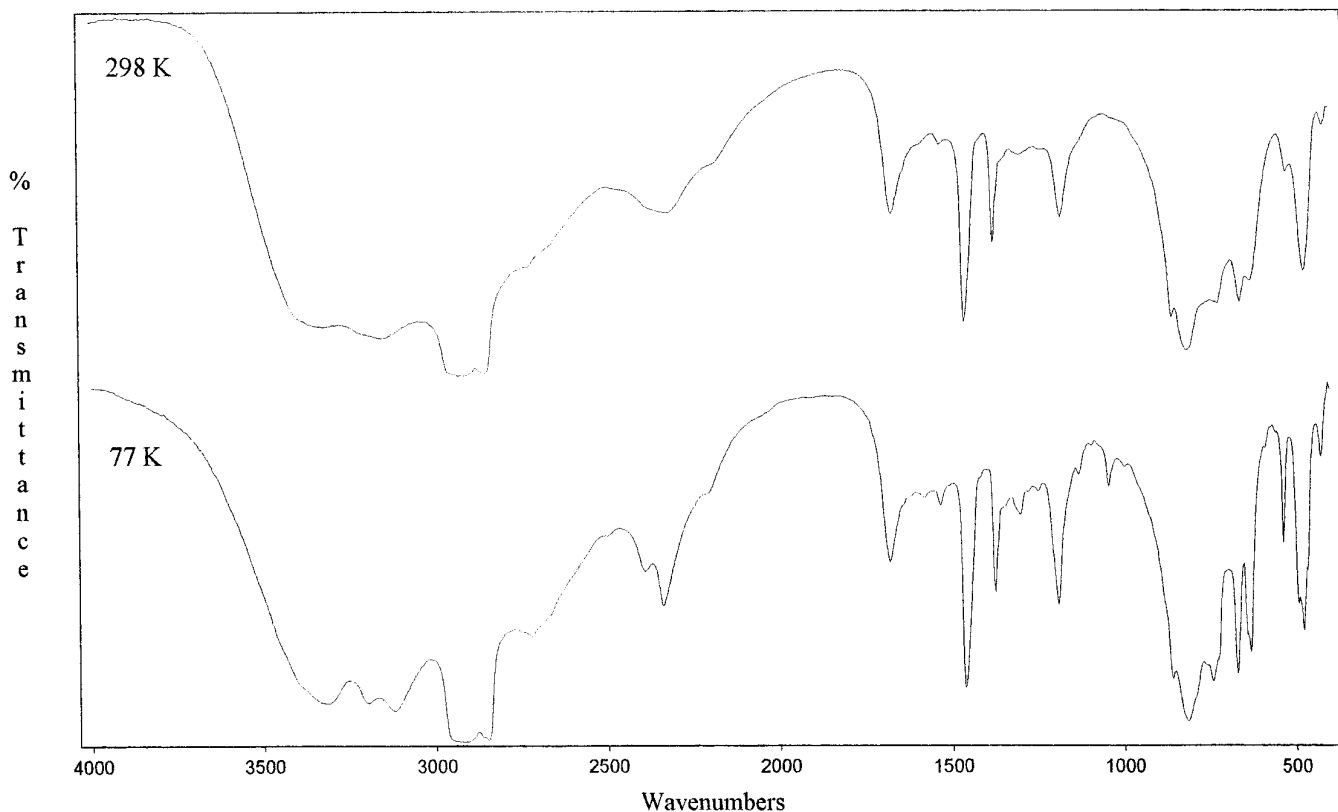

FIG. 3. The infrared absorption spectra of Mg(HSeO₃)₂ · 4H₂O at 298 K and 77 K (Nujol mull).

structural factors and the anisotropic displacement factors can be obtained from the authors on request.

The density of Mg(HSeO$_3$)$_2$·4H$_2$O was determined pycnometrically under xylene.

The FTIR spectra were measured on an ATI Mattson Genesis instrument in the region 4000–400 cm^{-1} by the Nujol and tripene mull techniques (1 cm^{-1} resolution, Beer–Norton medium apodization). The samples were located in a low-temperature cell with potassium bromide windows and the measurement was carried out at laboratory temperature and the temperature of liquid nitrogen (77 K).

RESULTS AND DISCUSSION

Crystal Structure of Mg(HSeO$_3$)$_2$·4H$_2$O

The results of the X-ray structural analysis are given in Table 2 (final values of the atomic parameters) and Table 3 (bonding distances and angles). The packing scheme of atoms is depicted in Fig. 1. The coordination environs of magnesium ion and the atom numbering can be seen in Fig. 2. Each magnesium ion is surrounded by six oxygen atoms forming an octahedron with Mg–O distances in the range 2.021–2.105 Å. The coordination octahedron consists of four oxygen atoms from four hydrogen selenite anions and the two oxygens of the water molecules. The neighboring octahedra are interconnected through two HSeO$_3^-$ anions and from {Mg[Se(OH)O$_2$]$_2$(H$_2$O)$_2$}$_n$ chains connected by multiple hydrogen bonds. Three types of interactions can be distinguished in the extensive system of hydrogen bonds. These are hydrogen bonds of the anion–anion (O1–H1O1 $\cdots$ O2^{iii}), water–anion (O4–H1O4 $\cdots$ O3 and O4–H2O4 $\cdots$ O1^{ii}), and water–water (O5–H1O5 $\cdots$ O4^{iv} and O6–H1O6 $\cdots$ O4^{v}) types (see Table 3). The length of the anion–anion hydrogen bond is in a good agreement with previous results (16).

The pyramidal hydrogen selenite anion has two shorter Se–O bonds and one longer Se–O(H) bond. It follows from the determined bond lengths and angles (Table 3) that the assumed average C_s symmetry of the hydrogen selenite anion is a suitable approximation for the interpretation of the vibrational spectra in the solid phase.

Infrared Spectra

The FTIR spectra obtained for Mg(HSeO$_3$)$_2$·4H$_2$O are given in Fig. 3. The values of the absorption maxima are given in Table 4. Band assignment is based on studies of Ebert and Havlíček (3) and Losoi and Valkonen (17). An analysis of the spectrum obtained at laboratory temperature, directed toward determination of the position and character of the valence vibrations of Se–O(H) and Se–O, and valence and deformation vibrations of the H–O(Se) group, are in agreement with the presence of the hydrogen selenite group. To verify the possibility of a phase transi-

tion, the FTIR spectrum was measured at the temperature of liquid nitrogen. The changes found in the low-temperature spectrum are a result particularly of the temperature effect, accompanied by a narrowing and partial separation of the vibrational bands. A temperature dependence was also observed for the band of the deformation vibration of the SeOH group (1180 cm^{-1}). During cooling, the absorption maximum is shifted to higher wavenumbers (by 12 cm^{-1}) and the band intensity also changes. These changes could be caused by a small shortening of the anion–anion hydrogen bond length on a decrease in the sample temperature. Similar changes were also observed for the hydrogen selenites of the alkali metals of the MHSeO$_3$ type (18).

TABLE 4
Infrared Spectra of Mg(HSeO$_3$)$_2$ · 4H$_2$O (cm^{-1})

298 K	77 K	Assignment
418 w	428 w	
	464 m	δ(SeO$_2$)(ν_3)
472 m	480 m	
	496 m	
524 w	538 m	
	564 w	
	588 w	
632 m	632 s	ν(Se–OH)(ν_1)
660 s	674 s	
733 sh	744 s	ν_{as}(Se–O)(ν_5)
	764 s	
814 s	816 s	
858 s	864 s	ν_s(Se–O)(ν_2)
	998 w	
	1046 w	
	1132 w	δ (SeOH)
1180 m	1192 m	
1238 w	1250 w	
1530 w	1534 w	
1584 sh	1580 w	
1672 m	1684 m	δ (H$_2$O)
2190 sh	2205 sh	ν (H–OSe)
2325 mb	2338 m	
	2392 m	
	2500 sh	
2770 sh	2770 sh	
3150 sb	3120 s	ν (H$_2$O)
	3200 s	
3320 sb	3320 sb	

Note. Intensity scale: w, weak; m, medium; s, strong; b, broad; sh, shoulder.

However, no new ordering of the protons in the hydrogen bonds, that would lead to a phase transition, was observed in the studied temperature range 298–77 K.

The correlation of the position of ν (H–OSe) vibrational bands and the O1 $\cdots$ O2^{iii} distance (see Table 3) corresponding to anion–anion hydrogen bond according to Unterderweide *et al.* (16) cannot be used with respect to the coincidence of the split ν (H–OSe) band with the strong bands of ν (H$_2$O) vibrations.

If the lengths of the hydrogen bonds are compared with the positions of the ν (H$_2$O) vibrational bands in the infrared spectrum, the pair of valence vibrations of the H$_2$O group can be assigned to the water–water and water–anion hydrogen bonds with a length of about 2.7 Å (band at 3150 cm^{-1}) and to the water–anion hydrogen bonds with a length of about 2.8 Å (band at 3320 cm^{-1}). The lengths of the hydrogen bonds determined on the basis of the spectral studies (3), yielding values of 2.81 and 2.69 Å, are very close to the values obtained.

The weak band at 1046 cm^{-1} in the low-temperature spectrum could be assigned to an out-of-plane bending mode γ (SeOH), as in the case of Ca(HSeO$_3$)$_2 \cdot$ H$_2$O (16).

REFERENCES

1. L. F. Nilson, *Bull. Soc. Chim. Fr.* **21,** 253 (1874).
2. B. Boutzoureano, *Ann. Chim. Phys.* **18,** 309 (1889).
3. M. Ebert and D. Havlíček, *Chem. Zvesti* **34,** 441 (1980).
4. A. Simon and R. Paetzold, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.* **64,** 209 (1960).
5. J. C. Burfoot and G. W. Taylor, *in* "Polar Dielectrics and Their Applications." Macmillan & Co., London, 1979.
6. V. H. Schmidt, *in* "The Hydrogen Bond" (P. Schuster, G. Zundel, and C. Sandorfy, Eds.), Part III, p. 1109. North-Holland, Amsterdam, 1976.
7. P. K. Acharya and P. S. Narayanan, *Spectrochim. Acta Part A* **29,** 925 (1973).
8. M. Zh. Ganitskij and V. I. Zelinokrajte, *Zh. Neorg. Chim.* **2,** 1341 (1957).
9. R. Přbil, *in* "Komplexometrie." SNTL, Prague, 1977.
10. N. Walker and D. Stuart, *Acta Crystallogr. Sect. A* **39,** 158 (1983).
11. G. M. Sheldrick, SHELX 93. University of Göttingen, 1993.
12. "International Tables for X-ray Crystallography," Vol. IV. Kynoch, Birmingham, 1974.
13. B. A. Frenz & Associates, Inc., "SDP, Structure Determination Package." College Station, TX, Enraf-Nonius, Delft, 1985.
14. H. Nardelli, "PARST, A System for Computer Routines for Calculating Molecular Parameters from Results of Crystal Structure Analysis." University of Parma, 1982.
15. B. Clegg, PLUTO. University of Göttingen, 1978.
16. K. Unterderweide, B. Engelen, and K. Boldt, *J. Mol. Struct.* **322,** 233 (1994).
17. T. Losoi and J. Valkonen, *Finn. Chem. Lett.* **1,** 1 (1985).
18. Z. Mička, M. Daněk, J. Loub, B. Strauch, J. Podlahová, and J. Hašek, *J. Solid State Chem.* **77,** 306 (1988).