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Crystal Structure, Thermal Behavior, and Infrared Absorption Spectrum of Cobalt(II) Hydrogen Selenite Dihydrate $Co(HSeO_3)_2 \cdot 2H_2O$

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The crystal structure, thermoanalytical properties, and infrared absorption spectra of $Co(HSeO_3)_2 \cdot 2H_2O$ are given. The crystals of the substance are monoclinic, with space group $P2_1/n$, a = 7.1357(6) Å, b = 6.8759(6) Å, c = 8.0325(8) Å, β = 113.19(1)°, V = 362.27(6) Å^3, Z = 2, and R = 0.020 for 596 observed reflections. The cobalt atom is located in the center of the coordination octahedron consisting of the oxygen atoms from four hydrogen selenite anions and two water molecules. The structure is linked together by means of a system of hydrogen bonds including those among the $HSeO_3^-$ anions and between the $HSeO_3^-$ anions and water molecules. The thermal decomposition of $Co(HSeO_3)_2 \cdot 2H_2O$ begins at 400 K by gradual liberation of water molecules, leading finally to the formation of cobaltous diselenite (up to 580 K). A further increase in the temperature causes stepwise liberation of selenium dioxide, with formation of cobaltous selenite (up to 760 K) and then cobalt(II) oxide (up to 950 K). No phase transition connected with a change in the proton arrangement was found by vibrational spectroscopy at temperatures down to 77 K. The existence of ferroelectric properties of the $Co(HSeO_3)_2 \cdot 2H_2O$ crystals can be excluded at laboratory temperature, owing to centrosymmetry of the space group. © 1994 Academic Press, Inc.

INTRODUCTION

$Co(HSeO_3)_2 \cdot 2H_2O$ was first prepared and studied by Boutzoureano (1) and Nilson (2). The symmetry and constitution of the hydrogen selenite anion were determined by Simon and Paetzold (3) on the basis of the IR spectra. Hydrogen selenites of this type may be ferroelectrics with short hydrogen bonds of the KDP type. These substances are characterized by the fact that their dielectric properties are strongly affected by the hydrogen bond dynamics (4). In high-temperature paraelectric phases, the hydrogen nuclei move by a rapid, internal bond tunnel effect within the hydrogen bond, while in low-temperature polar phases the protons are completely or partially ordered. A necessary condition for the existence of ferroelectric properties is that the crystal belongs to one of the following crystallographic classes: 1, 2, 3, 4, 6, *m*, *mm*2, 3*m*, 4*mm*, or 6*mm* (5).

This paper deals with the thermoanalytical properties, IR spectra at laboratory and at low (77 K) temperature, and the crystal structure of $Co(HSeO_3)_2 \cdot 2H_2O$.

EXPERIMENTAL

Cobaltous hydrogen selenite dihydrate was prepared by the reaction of $CoSeO_3 \cdot 2H_2O$, SeO_2, and H_2O at ratios determined from the solubility diagram (6). After equilibration at 298 K, the purple crystals formed were washed with ethanol and dried in the air at laboratory temperature. The selenium content was determined iodometrically (7) to be 44.06% (the theoretical content equals 45.00%). The cobalt content was found complexometrically, with the murexide indicator (8) (theory, 16.79%; found, 16.55%).

The thermoanalytical properties of fine crystalline $Co(HSeO_3)_2 \cdot 2H_2O$ were studied by thermogravimetry (TG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC); the method of gradually increased temperature was also used. The TG and DTA curves were obtained in a static air atmosphere on a MOM Derivatograph OD 102 instrument within a temperature

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range of 298 to 870 K and with a temperature gradient of 5 K min^{-1}. Analogous curves were measured on small samples (5 mg), using a Perkin–Elmer TGS-2 apparatus in a dynamic air atmosphere and temperature gradients of 2.5 and 10 K min^{-1}. The DSC measurements were carried out in a Perkin–Elmer DSC-4 calorimeter within a temperature range from 298 to 670 K, at a temperature gradient of 10 K min^{-1}. The samples were further heated in an electric oven at a rate of 10 K per 24 hr, within a range of 298 to 720 K, and the intermediates were analyzed by IR spectroscopy and X-ray powder diffractometry.

The infrared absorption spectra were obtained on a Perkin–Elmer 684 instrument with an on-line 3600 IR data station, from 4000 to 350 cm^{-1}, employing the nujol mull technique. The samples were placed in a low-temperature cell with potassium bromide windows and the measurements were performed at laboratory temperature and liquid nitrogen temperature (77 K). The absorption maxima positions were determined with a precision of ±1 and ±10 cm^{-1} for sharp and broad bands, respectively.

The density of $Co(HSeO_3)_2 \cdot 2H_2O$ was determined pycnometrically in xylene.

The X-ray diffraction data collection of a $Co(HSeO_3)_2 \cdot 2H_2O$ single crystal was carried out on an Enraf-Nonius CAD4 four-circle diffractometer (Mo$K\alpha$ radiation, graphite monochromator). The phase problem was solved by direct methods and the structure refined anisotropically, using the full-matrix least-squares procedure (SHELX76). The H atom positions were found from the difference Fourier map, and their thermal parameters were refined isotropically. The absorption correction (9) was carried out, with minimum and maximum absorption coefficients of 0.835 and 1.270, respectively. The basic crystallographic data and the details of the measurement and refinement are summarized in Table 1. A list of the observed and calculated structure factors and the anisotropic thermal parameters are available from the authors upon request.

RESULTS AND DISCUSSION

Thermal Behavior of $Co(HSeO_3)_2 \cdot 2H_2O$

The thermal decomposition of $Co(HSeO_3)_2 \cdot 2H_2O$ starts at 400 K by gradual liberation of water molecules (see Fig. 1, Table 2). The first step involves liberation of two water molecules up to 450 K, with formation of the dehydrated compound. Another water molecule is immediately released (up to 580 K) and cobaltous diselenite, $CoSe_2O_5$, is formed. This part of the decomposition is connected with destruction of the hydrogen bonds linking the hydrogen selenite groups with water molecules. On a further increase in the temperature, selenium dioxide is released and sublimes, with the formation of cobaltous selenite (up to 760 K) and then cobalt(II) oxide (up to 950 K).

TABLE 1
Basic Crystallographic Data, Data Collection, and Refinement Parameters

a = 7.1357(6) Å	
b = 6.8759(6) Å	
c = 8.0325(8) Å	
β = 113.19(1)°	
V = 362.27(6) $Å^3$	
Z = 2	
D_{obs} = 3.214(2) $g \cdot cm^{-3}$	
D_{calc} = 3.217(1) $g \cdot cm^{-3}$	
Space group $P2_1/n$	
M_r = 350.90	
$\mu(MoK\alpha)$ = 123.16 cm^{-1}	
$F(000)$ = 330	
Crystal dimensions	0.38 × 0.24 × 0.20 mm
Diffractometer and radiation used	Enraf-Nonius CAD4, Mo$K\alpha$, λ = 0.71073 Å
Scan technique	$\omega - 3/4\Theta$
No. and Θ range of reflections for lattice parameter refinement	20, 20–24°Θ
Range of h, k, and l	$-8 \rightarrow 8, -8 \rightarrow 8, -9 \rightarrow 9$
Standard reflections	0 −1 2, −1 0 3
Standard reflections monitored in interval	120 min
Intensity fluctuation	0.4%
Total number of reflections measured	2532
2Θ range	$2\Theta \leq 50°$
Value of R_{int}	0.022
No. of unique observed reflections	596
Criterion for observed reflections	$I \geq 1.96\sigma(I)$
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme	$w = [\sigma^2(F) + 0.0002F^2]^{-1}$
Parameters refined	55
Value of R	0.020
Value of wR	0.022
Value of S	1.13
Ratio of max least-squares shift to e.s.d. in the last cycle	0.000
Max and min heights in final $\Delta\rho$ map	0.76, −0.57 e/$Å^3$
Source of atomic scattering factors	SHELX76 (10), "International Tables for X-Ray Crystallography" (11)
Programs used	SDP (12), SHELX76 (10) SHELXS86 (13), PARST (14)
Computer used	PDP11/73, PC AT

The decomposition can be described by the scheme

$$Co(HSeO_3)_2 \cdot 2H_2O \xrightarrow{-3H_2O} CoSe_2O_5 \xrightarrow{-SeO_2} CoSeO_3 \xrightarrow{-SeO_2} CoO.$$

TABLE 2

Results of TG, DTA, and DSC Measurements on $Co(HSeO_3)_2 \cdot 2H_2O$

TG weight loss (%) T (K)	DTA effect T (K)	DSC effect T (K)	Assignment
16.10 400–580	Endo 390–410 Endo 460–470	Endo 400–405 Endo 460–470	Decomposition to $CoSe_2O_5$ and evaporation of H_2O
37.70 580–670 46.95 710–760	Endo 680–710		Sublimation of SeO_2 and decomposition to $CoSeO_3$
76.25 810–950	Endo 810–900		Sublimation of SeO_2 and decomposition to CoO

An increase in the heating rate does not affect the proposed decomposition mechanism, but the process temperatures increase. The method of gradually increasing temperature was used to confirm the decomposition mechanism, and the intermediates were characterized by X-ray powder diffractometry and IR spectroscopy; the results demonstrated that $CoSe_2O_5$ and $CoSeO_3$ are intermediates in the thermal decomposition of the studied compound. Pure anhydrous $Co(HSeO_3)_2$ could not be isolated because of immediate decomposition.

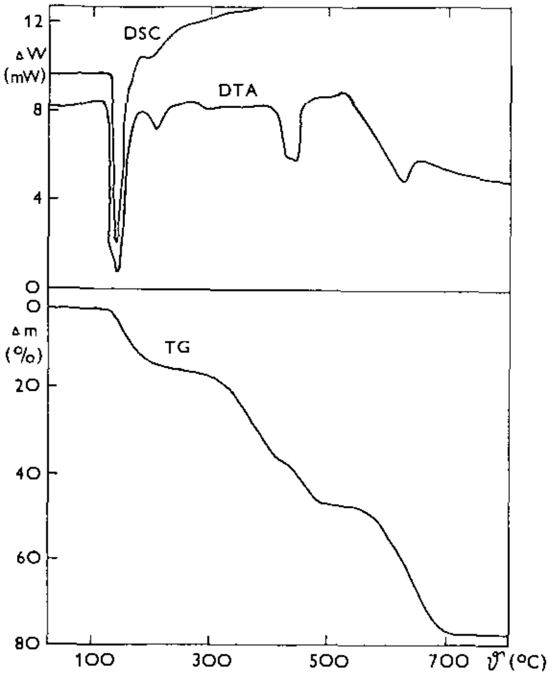

FIG. 1. Thermal behavior of $Co(HSeO_3)_2 \cdot 2H_2O$ in a static air atmosphere. TG: sample weight, 15.29 mg; heating rate, 2.5°C min^{-1}. DTA: sample weight, 5.00 mg; heating rate, 2.5°C min^{-1}. DSC: sample weight, 2.45 mg; heating rate, 10°C min^{-1}.

Crystal Structure of $Co(HSeO_3)_2 \cdot 2H_2O$

The atomic coordinates are given in Table 3, and the bond lengths and angles, including those for the hydrogen bonds, in Table 4. The coordination octahedron around the cobalt atom and the atom numbering can be seen in Fig. 2, and the packing scheme is given in Fig. 3. The coordination octahedron consists of four oxygen atoms from four hydrogen selenite anions and two oxygen atoms from water molecules. Neighboring octahedra are always interconnected through two $HSeO_3^-$ anions and form chains that are interconnected by hydrogen bonds between hydrogen selenite anions. Further hydrogen bonds connect water molecules with the $HSeO_3^-$ anions within the chains.

The determination of the crystal structure confirmed the assumption following from the electronic reflectance spectra and the magnetic properties of $Co(HSeO_3)_2 \cdot 2H_2O$ (6); namely, that the coordination sphere of the cobaltous cations consists of octahedrally arranged oxygen atoms.

TABLE 3

Atomic Coordinates ($\times 10^4$) and Equivalent (For non-H atoms $\times 10^4$) or Isotropic (For H atoms $\times 10^3$) Thermal Parameters

$$U_{eq} = (1/3) \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

	x	y	z	U_{eq}(Å^2)
Co	5000	0	0	101(2)
Se	−532(1)	2309(1)	1236(1)	115(2)
O1	−2570(4)	1658(5)	1636(4)	170(9)
O2	370(4)	4224(4)	2590(4)	167(9)
O3	1104(5)	449(5)	2580(4)	249(10)
O4	3084(5)	2338(4)	15(4)	161(9)
HO3	2431	335	2347	104(29)
H1O4	2813	2927	−1066	46(18)
H2O4	3859	3283	986	59(19)

TABLE 4
Bond Distances (Å) and Angles (°)

Co–O1	2.059(3)	O1 –Co–O4	87.7(1)
Co–O2^{i}	2.122(3)	O1 –Co–O2^{i}	86.2(1)
Co–O4	2.113(3)	O1^{iv}–Co–O4	92.3(1)
		O1^{iv}–Co–O2^{i}	93.8(1)
		O2^{i} –Co–O4	82.7(1)
		O2^{i} –Co–O4^{iv}	97.3(1)
Se–O1	1.669(3)	O1–Se–O2	103.2(1)
Se–O2	1.667(3)	O1–Se–O3	95.9(1)
Se–O3	1.781(3)	O2–Se–O3	100.3(2)

Hydrogen bonds

Donor–H	Donor ··· acceptor	H ··· acceptor	Donor–H ··· acceptor
O3–HO3 1.038(4)	O3 ··· O2^{i} 2.707(5)	HO3 ··· O2^{i} 1.728(3)	O3–HO3 ··· O2^{i} 155.6(2)
O4–H1O4 0.907(3)	O4 ··· O1^{ii} 2.658(5)	H1O4 ··· O1^{ii} 1.779(3)	O4–H1O4 ··· O1^{ii} 162.2(2)
O4–H2O4 0.998(3)	O4 ··· O3^{iii} 2.786(4)	H2O4 ··· O3^{iii} 1.877(3)	O4–H2O4 ··· O3^{iii} 150.0(2)

Equivalent positions

(i) $-x + 1/2,\ y - 1/2,\ -z + 1/2$
(ii) $x + 1/2,\ -y + 1/2,\ z - 1/2$
(iii) $-x + 1/2,\ y + 1/2,\ -z + 1/2$
(iv) $-x,\ -y,\ -z$
(v) $x + 1/2,\ -y - 1/2,\ z + 1/2$

Note. The values of standard deviations for distances and angles involving hydrogen atoms depend on the errors of the oxygen atoms only.

The $HSeO_3^-$ anions is pyramidal, with two shorter Se–O bonds (1.669(3) and 1.667(3) Å) and a longer Se–O(H) bond (1.781(3) Å). It follows from the obtained bond lengths and angles (Table 4) that the assumed C_s symmetry of the hydrogen selenite anions is a suitable approximation for interpretation of the solid-phase vibrational spectra.

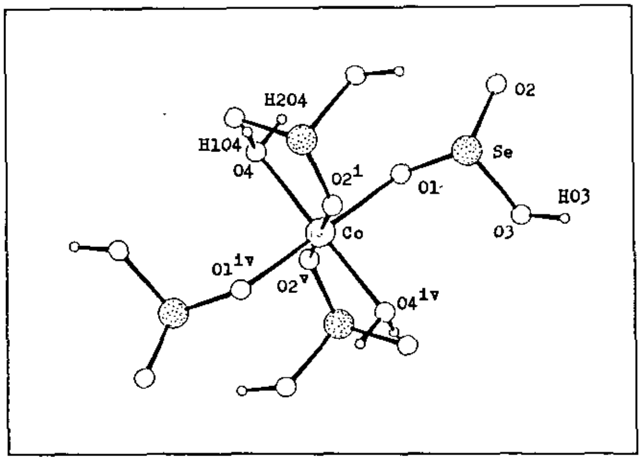

FIG. 2. The coordination octahedron around the cobalt with atom numbering (projection to xy plane). Equivalent positions are given in Table 4.

No water–water hydrogen bond, whose length was estimated on the basis of a spectral study (6), was found in the $Co(HSeO_3)_2 \cdot 2H_2O$ structure. The lengths of the anion–anion and water–anion hydrogen bonds, found in

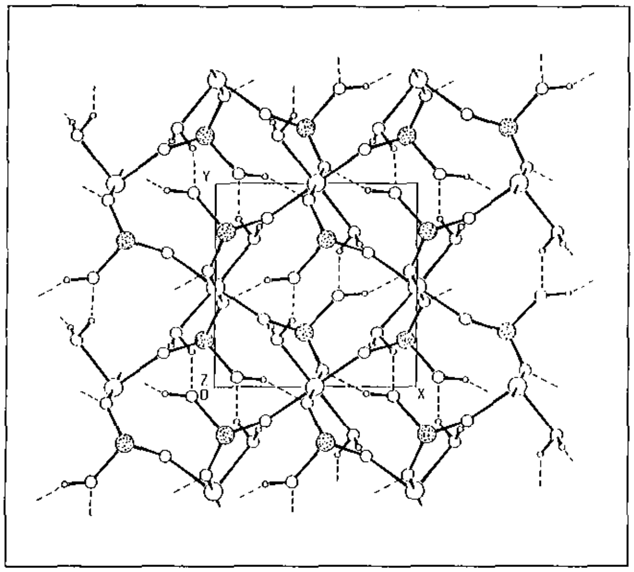

FIG. 3. Packing scheme of $Co(HSeO_3)_2 \cdot 2H_2O$. Dashed lines indicate hydrogen bonds.

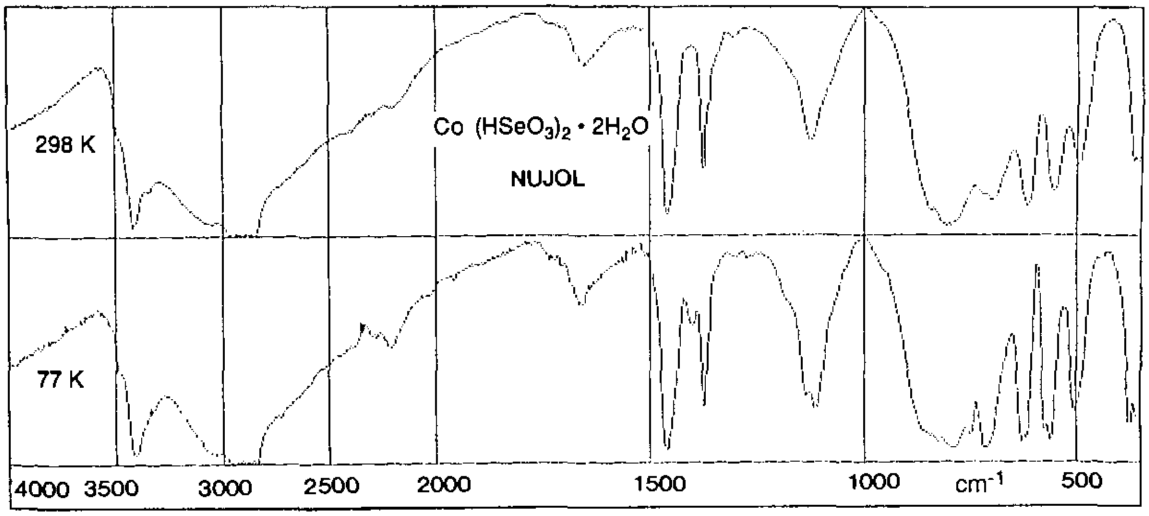

FIG. 4. Infrared absorption spectra of $Co(HSeO_3)_2 \cdot 2H_2O$ at 298 and 77 K.

Ref. (6) from correlation diagrams, are smaller than the values obtained from the structural analysis.

The X-ray structural analysis of $Co(HSeO_3)_2 \cdot 2H_2O$ proved that this compound is isostructural with $Zn(HSeO_3)_2 \cdot 2H_2O$, which was studied (15) by the method of neutron diffraction. The same network of hydrogen bonds seems to be the most important finding of the comparison of these compounds because it confirms the positions of hydrogen atoms found in the structure of $Co(HSeO_3)_2 \cdot 2H_2O$.

Infrared Spectra

The obtained IR spectra of $Co(HSeO_3)_2 \cdot 2H_2O$ are given in Fig. 4. The values of the observed absorption maxima are given in Table 5. An analysis of the spectrum obtained at laboratory temperature, directed toward determination of the position and character of the valence vibrations of SeO(H) and SeO_2, and valence and deformation vibrations of the HO(Se) group are in agreement with the presence of the hydrogen selenite group. From this it follows that protons are arranged nonsymmetrically in the hydrogen bonds coming from the $HSeO_3^-$ anions, with a low probability of tunneling (16). These conclusions primarily follow from the presence of the SeO(H) characteristic vibration at 615 cm^{-1}. The band at 693 cm^{-1} also does not correspond to valence vibrations of the hydrogen selenite group with tunneling protons, but to water molecule vibrations. This fact was verified on the basis of the shift of this band in the study of the deuterates (6). In order to check a possibility of a phase transition, an IR spectrum was obtained at the liquid nitrogen temperature. The changes in the low-temperature spectrum are mainly caused by the temperature effect causing a narrowing and a partial separation of the vibrational bands. Analogous changes have also been observed with hydrogen selenites of the alkali metals of the type $MHSeO_3$ (17). However, within the studied temperature range, 298 to 77 K, the protons in the hydrogen bonds are not rearranged, which would lead to a phase transition. The weak band at 1301 cm^{-1} could be assigned to a deformation vibration of the SeOH group in short hydrogen bonds, on the basis of its position. The bands at 1266, 1298, and 1401 cm^{-1} in the low-temperature spectrum could be interpreted analogously.

TABLE 5
Infrared Spectra of $Co(HSeO_3)_2 \cdot 2H_2O$ (cm^{-1})

298 K	77 K	Assignment
357 m		$\delta_{as}(HSeO_3)$ (ν_6)
368 m	374 m	
497 m	504 m	$\delta(SeO_2)$ (ν_3)
553 m	562 m	$\rho(H_2O)$
	572 sh	
615 s	624 s	$\nu(SeO)(SeOH)$ (ν_1)
693 s	711 s	$\rho(H_2O)$
	751 m	
797 s	787 s	$\nu_{as}(SeO)(SeO_2)$ (ν_5)
842 sh	828 sh	$\nu_s(SeO)(SeO_2)$ (ν_2)
	855 sh	
1122 m	1111 m	$\delta(SeOH)$
	1130 sh	
	1266 w	
1301 w	1298 w	
	1401 m	
1650 mb	1660 m	$\delta(H_2O)$
2190 mb	2210 mb	$\nu(OH)(SeOH)$
3340 sh	3330 sh	
3410 s	3410 s	$\nu(OH)(H_2O)$
3490 sh	3490 sh	

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

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