

THE SOLUBILITY OF CUPRIC SELENATE AND THE BONDING CONDITIONS IN THE COMPOUND $\text{Cu}(\text{HSeO}_3)_2$

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Received March 14, 1990

Accepted April 11, 1990

The solubility diagram for $\text{CuSeO}_3\text{-SeO}_2\text{-H}_2\text{O}$ at 298 K was studied for the first time, and was employed to define the conditions for the formation of $\text{Cu}(\text{HSeO}_3)_2$. The bonding conditions including the behaviour of protons in the hydrogen bonds were described for this compound.

Research carried out so far on cupric selenates included preparation methods¹⁻⁷ and study of the thermoanalytical and magnetic properties of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ and CuSe_2O_5 (refs⁸⁻¹⁰). X-ray studies have been carried out on the compounds $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$, CuSe_2O_5 and CuSeO_3 (refs¹¹⁻¹⁵). The complete structure of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ has been determined¹⁶. The molecular spectra have been studied for the compounds, $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$, CuSeO_3 and CuSe_2O_5 (refs¹⁷⁻¹⁸).

This work is devoted to cupric selenate in the framework of a systematic study of selenates, i.e. compounds with potential ferroelectric properties. The solubility diagram for the $\text{CuSeO}_3\text{-SeO}_2\text{-H}_2\text{O}$ system at 298 K was studied and conditions for the formation of $\text{Cu}(\text{HSeO}_3)_2$ were determined; the bonding conditions were characterized on the basis of a study of the physical chemical properties. The behaviour of the protons in the hydrogen bonds was examined, considering possible phase transitions.

EXPERIMENTAL

Selenious acid, employed to study the solubility diagram of $\text{CuSeO}_3\text{-H}_2\text{SeO}_3\text{-H}_2\text{O}$ was prepared from sodium selenate (p.a., Lacema, Brno) on the Dowex 50W-X8 ion exchanger (Fluka AG). Anhydrous cupric selenate was prepared by the reaction of a 0.2M solution of sodium selenate. The molar ratios $\text{CuSeO}_3 : \text{H}_2\text{SeO}_3 : \text{H}_2\text{O}$ were found from the solubility study for optimal yield of the compound $\text{Cu}(\text{HSeO}_3)_2$, equal to 1 : 2, 1 : 1.1. The compound prepared was filtered under suction on a frit, washed with water and acetone and dried in the air. The crystalline blue-green powder obtained is insoluble in water and readily soluble in dilute acids. The values calculated and found (in brackets) for the Cu and Se contents are as follows: 19.88 (19.61) % Cu and 49.44 (49.18) % Se. The deuterated compound $\text{Cu}(\text{DSeO}_3)_2$ was prepared similarly from CuSeO_3 , SeO_2 and D_2O and was employed to study infrared spectra.

Copper was determined gravimetrically as $\text{Cu}(\text{SCN})_2$ (ref.¹⁹) and selenium by the modified Bode method²⁰. In the solubility studies, selenate was determined iodometrically²¹ and copper complexometrically²².

The thermoanalytical properties of the substances were studied thermogravimetrically and by differential thermal analysis using a Derivatograph (MON, Budapest). The heating rate was 5 K min^{-1} in the temperature range 298–873 K. The samples were also studied by a method of gradual temperature increase. They were heated in a regulated electric oven with a temperature increase in steps of 10 K in the temperature range 298–773 K.

The IR spectra were measured in the region $400\text{--}4\,000 \text{ cm}^{-1}$ on the PE-684 instrument (Perkin-Elmer) using a Nujol suspension or the KEL-F technique and a KBr cuvette.

The magnetic properties were measured on magnetic scales according to Vilím²³ using cupric sulphate pentahydrate as a standard.

The diffusion reflectance spectra were measured in the region $10\,000\text{--}40\,000 \text{ cm}^{-1}$ on the VSU-2 UV-VIS spectrometer (Zeiss, Jena). The samples were diluted in a ratio of 1 : 1 or 1 : 2 with magnesium(II) oxide, which was also used as a reference substance.

RESULTS AND DISCUSSION

The solubility diagram for the $\text{CuSeO}_3\text{--SeO}_2\text{--H}_2\text{O}$ system at 298 K obtained by Schreinemaker's method is depicted in Fig. 1. In addition to the initial substances, two additional compounds are formed in the system, $\text{CuSeO}_3 \cdot 2 \text{H}_2\text{O}$ and a substance with the composition $\text{Cu}(\text{HSeO}_3)_2$. This is a slightly incongruent compound that can be prepared only in a slight excess of selenious acid. Study of the polytherms demonstrated that this is the only substance formed in the temperature range 298 to 373 K. Consequently, cupric diselenate CuSe_2O_5 cannot be prepared by heterogeneous reaction in aqueous solution in this region. The character of the solubility diagram for the $\text{CuSeO}_3\text{--SeO}_2\text{--H}_2\text{O}$ system corresponds to that for CoSeO_3 (or NiSeO_3)– $\text{SeO}_2\text{--H}_2\text{O}$, where the given hydrogen selenates are formed as dihydrates^{24,25}.

The results of study of the thermoanalytical properties of $\text{Cu}(\text{HSeO}_3)_2$ are given in Tables I and II. The curves obtained by the gradual temperature increase method differ from the TG curves primarily in a shift of the temperatures for the processes occurring to lower values. It can be seen from the shapes of the thermoanalytical curves $\text{Cu}(\text{HSeO}_3)_2$ that the first step in the decomposition is the dehydration $\text{Cu}(\text{HSeO}_3)_2 \rightarrow \text{CuSe}_2\text{O}_5 + \text{H}_2\text{O}$, occurring at relatively high temperatures (up to 500 K); together with study of the infrared spectra, this fact excludes interpretation of the initial compound as $\text{CuSe}_2\text{O}_5 \cdot \text{H}_2\text{O}$. The mass decrease simultaneously indicates that this compound is also not the monohydrate $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$, which was prepared and studied by X-ray methods earlier¹⁶. Similar dehydration with the formation of diselenate has been observed as the first step in the decomposition of most hydrogen selenates²⁶. Further decomposition of CuSe_2O_5 occurs through gradual formation of the compounds CuSeO_3 and $\text{CuO} \cdot \text{CuSeO}_3$, always with loss of SeO_2 . All the intermediates and final products were identified analytically, by X-ray studies and by infrared spectroscopy.

TABLE I
The thermoanalytical properties of $\text{Cu}(\text{HSeO}_3)_2$ studied by the TG and DTA methods

| TGA | | DTA | | Assignment |
|------------------|------------------|------------------|--------|---|
| temperature K | <i>m</i> , wt. % | temperature K | effect | |
| 298–450 | halt | — | — | $\text{Cu}(\text{HSeO}_3)_2$ |
| 450–510 | 6.1 | 500–515 | endo | decomp. to CuSe_2O_5 and H_2O |
| 510–580 | halt | — | — | CuSe_2O_5 |
| 580–650 | 39.0 | 615–650 | endo | decomp. to CuSeO_3 and SeO_2 |
| 650–680 | halt | — | — | — |
| 680–770 | 57.1 | 735–755 | endo | decomp. to $\text{CuSeO}_3 \cdot \text{CuO}$ and SeO_2 |
| 770–835 | 74.1 | 795–835 | endo | decomp. to CuO and SeO_2 |

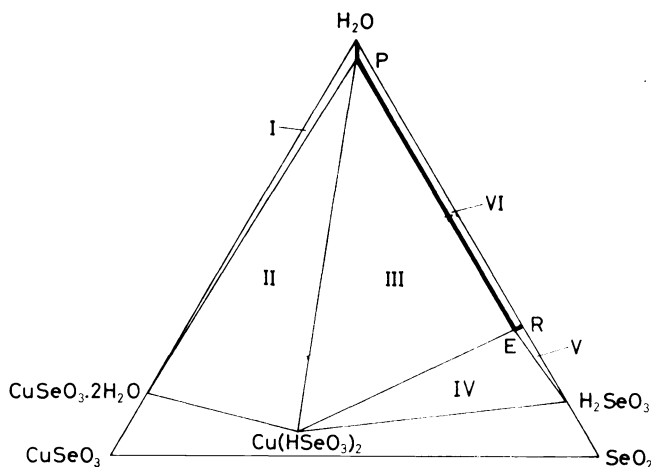


FIG. 1

Solubility diagram of the CuSeO_3 - SeO_2 - H_2O system at 298 K. P peritonic point, E eutonic point, R solubility of SeO_2 in water. I crystallization field of the initial $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ in equilibrium with a saturated solution with composition given by the solubility curve H_2O -P; II crystallization field of the mixture of $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{HSeO}_3)_2$ in equilibrium with a solution with composition given by point P; III crystallization field of $\text{Cu}(\text{HSeO}_3)_2$ in equilibrium with a saturated solution with composition given by the solubility curve P-E; IV crystallization field of the mixture of $\text{Cu}(\text{HSeO}_3)_2$ and H_2SeO_3 in equilibrium with the solution with composition given by point E; V crystallization field of H_2SeO_3 in equilibrium with the saturated solution with composition given by the solubility curve E-R; VI region of unsaturated solutions

The infrared spectra of $\text{Cu}(\text{HSeO}_3)_2$ and $\text{Cu}(\text{DSeO}_3)_2$ are given in Table III. Assignment was carried out according to the literature²⁷⁻²⁹. Analysis of the spectra considered the position and character of the valence vibrations of the $\text{SeO}(\text{H})$ and SeO_2 groups and the deformation vibrations of the $\text{HO}(\text{Se})$ group, as they contribute to the description of the behaviour of the protons in the hydrogen bonds and thus to elucidation of the dielectric properties of acidic selenates. Bands have been found

TABLE II

The thermoanalytical properties of $\text{Cu}(\text{HSeO}_3)_2$ studied by the gradual temperature increase method

| Temperature, | <i>m</i> , wt. % | Assignment |
|--------------|------------------|---|
| 298—400 | halt | $\text{Cu}(\text{HSeO}_3)_2$ |
| 400—490 | 5.6 | decomp. to CuSe_2O_5 and H_2O |
| 490—500 | halt | CuSe_2O_5 |
| 500—630 | 40.5 | decomp. to CuSeO_3 and SeO_2 |
| 630—690 | halt | CuSeO_3 |
| 690—750 | 58.1 | decomp. to $\text{CuSeO}_3 \cdot \text{CuO}$ and SeO_2 |
| 750—770 | halt | $\text{CuSeO}_3 \cdot \text{CuO}$ |

TABLE III

The infrared spectra of $\text{Cu}(\text{HSeO}_3)_2$ and $\text{Cu}(\text{DSeO}_3)_2$

| $\text{Cu}(\text{HSeO}_3)_2$ $\tilde{\nu}(I)$ | $\text{Cu}(\text{DSeO}_3)_2$ $\tilde{\nu}(II)$ | Isotopic ratio | Assignment ^a |
|--|---|-------------------|-----------------------------------|
| 374 w | 368 m | 1.02 | $\delta(\text{SeO})(\text{SeOX})$ |
| 445 s | 445 s | 1.00 | $\delta(\text{SeO}_2)$ |
| 530 s | 510 s | | $\nu(\text{CuO})$ |
| | 555 s | | |
| 635 s | 625 s | 1.02 | $\nu(\text{SeO})(\text{SeOX})$ |
| 765 s | 765 s | 1.00 | $\nu_{\text{as}}(\text{SeO}_2)$ |
| 845 m | 840 m | 1.01 | $\nu_{\text{s}}(\text{SeO}_2)$ |
| 1 210 s | 895 s | 1.34 | $\delta(\text{OX})(\text{SeOX})$ |
| 2 230—2 420 mb (max. 2 375) | 1 700—1 800 mb (max. 1 780) | 1.33 | $\nu(\text{OX})(\text{SeOX})$ |
| 2 540—3 080 mb (max. 2 815) | 1 950—2 370 mb (max. 2 125) | 1.32 | |

^a X is H or D.

for $\text{Cu}(\text{HSeO}_3)_2$ that indicate the presence of HSeO_3^- anions with C_s symmetry and thus also asymmetric proton distribution along the hydrogen bonds in ordered positions with low probability of tunnelling³⁰. These factors would fulfil one of the conditions for potential ferroelectric behaviour of this substance.

Two intense bands ($2\ 375$ and $2\ 810\ \text{cm}^{-1}$) were found in the region of the valence vibrations of the OH group; they can probably be explained on the basis of a non-bonding tunnelling effect³¹ rather than through the presence of hydrogen bonds of various lengths.

The diffusion electron spectra of $\text{Cu}(\text{HSeO}_3)_2$ exhibit only two absorption bands, the first of which ($\tilde{\nu} = 13\ 800\ \text{cm}^{-1}$) corresponds to the energetically close transitions $d_{x^2-y^2} \rightarrow d_{xy}, d_{xz}, d_{yz}, d_{z^2}$ and the second ($34\ 000\ \text{cm}^{-1}$) to charge transfer.

Measurement of the magnetic properties of this compound demonstrated the presence of one unpaired electron and a magnetic effective moment of $\mu_{\text{eff}} = 1.81\ \text{BM}$. These results indicate that the coordination around the cupric cation is octahedral and strongly deformed according to the Jahn–Teller theorem³².

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Translated by M. Štulíková.