SYNTHESIS OF NICKEL SELENITES, THEIR SOLUBILITY AND BONDING IN THEM

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Dedicated to Professor Dr J. Klikorka on the occasion of his 60th birthday.

The solubility diagram of the $NiSeO_3$–SeO_2–H_2O system at 25°C was studied, and on its basis, $Ni(HSeO_3)_2.2\,H_2O$ was prepared. This selenite and $NiSeO_3.2\,H_2O$ were investigated by infrared absorption spectroscopy and by electronic reflectance spectroscopy and their magnetic properties were determined. Based on the infrared spectra, the force constants of the selenium––oxygen bonds were determined and the hydrogen bonding was characterized. The electronic reflectance spectra and the magnetic parameters indicate an octahedral arrangement of the coordination sphere of the nickel cation and characterize the selenite anion as a ligand that in the spectrochemical series assumes a position between the fluoride anion and water and in the nephelauxetic series, between ethylenediamine and the chloride anion.

Preparation of nickel selenites was the concern of Espil[1], Berzelius and Muspratt[2], Boutzoureano[3], Nilson[4], and Makatun and coworkers[5], who synthesized anhydrous nickel selenite and hydrated selenites of the composition $NiSeO_3.n\,H_2O$ $(n = \frac{1}{2}, 1, 2)$. The crystal structure and magnetic properties of $NiSeO_3$ were studied by Kohn and coworkers[6,7], the solubility product was measured by Chukhlantsev and Tomashevskii[8]. The dihydrate $NiSeO_3.2\,H_2O$ was examined by Lieder and Gattow[9], who in a preliminary structure study found the compound isostructural with zinc selenite dihydrate.

Salts with nickel-to-selenium ratios other than 1 : 1 were dealt with by Boutzoureano[3] and Nilson[4], who prepared a compound with the composition $NiSeO_3$.$.SeO_2.3\,H_2O$ by dissolving $NiSeO_3$ in selenious acid and evaporating the solution at 60°C. A similar compound was synthesized later by Lieder and Gattow[10] by precipitation of concentrated selenious acid solution with nickel carbonate; the authors characterized this substance as nickel diselenite trihydrate, $NiSe_2O_5$.$.3\,H_2O$, and determined its crystallographic parameters.

The constitution and symmetry of the selenite, hydrogenselenite, and diselenite anions were determined by Simon and Paetzold[11−13] based on a study of the infrared spectra of the alkali salts. The spectral region of the SeO_3, SeO_2, and $SeOH$

group stretching vibrations was studied in detail by Khanna and coworkers[14] Torrie[15], and Cody and Levitt[16].

The objective of the present work were the preparation of all selenites in the $NiSeO_3$–SeO_2–H_2O system at 25°C, establishment of the optimum conditions for their preparation, and study of their bonding properties.

EXPERIMENTAL

$NiSeO_3 . 2 H_2O$ was prepared by dropwise adding 0·06M sodium selenite solution to boiling 0·05M nickel chloride solution; the chemicals were reagent grade preparations of Lachema, Brno. The deuterated analogue, $NiSeO_3 . 2 D_2O$, was prepared likewise using D_2O, $Ni(DSeO_3)_2 . 2D_2O$ was prepared from $NiSeO_3 . 2 D_2O$, SeO_2 (reagent grade, Lachema, Brno), and D_2O based on the solubility diagram.

The starting material as well as the final product were analyzed gravimetrically: selenium by a modified method after Bode[17], nickel electrogravimetrically after separating of selenium[18]. In the solubility studies, titrimetric methods were employed: selenium(IV) was determined iodometrically[19], nickel, after pH adjustment, was titrated chelatometrically using murexide as indicator[20].

The electronic reflectance spectra were measured in the region of $10\ 000 - 50\ 000\ cm^{-1}$ on a VSU-1 instrument (Zeiss, Jena). The samples were diluted with magnesium oxide in the ratio 1 : 1 or 1 : 2; MgO served also as standard. In the $5\ 000 - 12\ 000\ cm^{-1}$ region the spectra were measured on a Unicam SP 700 instrument in Nujol mulls applied to a filter paper.

The infrared spectra were scanned on a UR 20 spectrophotometer (Zeiss, Jena) over the region of $400 - 4\ 000\ cm^{-1}$. The Nujol mulls were placed in potassium bromide cells. Tripene mulls were in addition applied in the region of the hydroxyl group stretching vibrations.
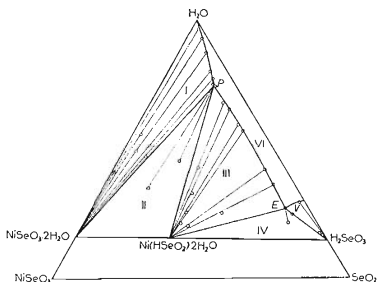

FIG. 1

Solubility diagram of the $NiSeO_3$–SeO_2–H_2O system at 25°C

The magnetic susceptibility was measured on a magnetic balance by the Gouy method[21], using $Co[Hg(SCN)_4]$ as standard.

RESULTS

Study of Solubility in the $NiSeO_3$–SeO_2–H_2O System at 25°C

The wet residue (Schreinemakers) method was used in the solubility study of the $NiSeO_3$–SeO_2–H_2O system. The equilibrium established within 5 to 12 weeks.

The solubility diagram constructed according to Gibbs and Roozeboom is shown in Fig. 1. Obviously, in addition to the starting substances, to which the crystallization fields I and V belong, $Ni(HSeO_3)_2.2 H_2O$ is formed in the system at 25°C (crystallization field III). The equilibrium between the two solids and the solutions of the composition of the peritonic point P or the eutonic point E are characterized by the crystallization fields II and VI, respectively. The compositions corresponding to the two points are 7·1% $NiSeO_3$, 17·9% SeO_2, and 75·0% H_2O, and 8·0% $NiSeO_3$, 64·8% SeO_2, and 27·2% H_2O, respectively. In the field II with the liquid phase

TABLE I

Infrared spectra of $NiSeO_3.2 H_2O$ and $NiSeO_3.2 D_2O$. Relative band intensity and shape: vs very strong, s strong, m medium, w weak, vw very weak; b broad, sh shoulder. Band assignment: v_s and v_{as} symmetric and antisymmetric stretching, respectively, δ bending, ϱ rocking. Band positions $(\tilde{v})$ in cm^{-1}

$\tilde{v}(NiSeO_3.2 H_2O)$	$\tilde{v}(NiSeO_3.2 D_2O)$	$\dfrac{\tilde{v}(NiSeO_3.2 H_2O)}{\tilde{v}(NiSeO_3.2 D_2O)}$	Band assignment
402 w	—	—	$\delta(SeO_3)$
512 s	510 s	1·00	
590 w	450 sh	1·31	$\varrho(H_2O)$
705 sh	705 sh	1·00	$v_{as}(SeO_3)$
730 vs	730 vs	1·00	
810 m	810 m	1·00	$v_s(SeO_3)$
860 m	860 m	1·00	
1 540 w	1 180 vw	1·31	$\delta(OH)(H_2O)$
1 640 w	1 220 w	1·34	
2 200—2 450 w, b	—	—	?
2 965 w	2 230 sh	1·33	
3 170 sh	2 365 sh	1·34	$v(OH)(H_2O)$
3 230 m	2 420 m	1·33	
3 475 m	2 590 m	1·34	

composition given by point P, a phase reaction occurs giving rise to the hydrogen selenite:

$$NiSeO_3 + SeO_2 + 3 H_2O \rightleftharpoons Ni(HSeO_3)_2 . 2 H_2O .$$
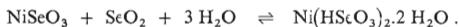
Making use of the diagram, nickel hydrogen selenite dihydrate was prepared. The crystals were collected on an S3 glass filter, washed with chloroform, and dried on air at room temperature to give a green, finely crystalline powder, steady on air at ambient temperature. The results of gravimetric analysis are consistent with the formula: for $Ni(HSeO_3)_2 . 2 H_2O$ (350·7) calculated: 16·74% Ni, 45·03% Se; found: 16·68% Ni, 45·26% Se.

Infrared Absorption and Electronic Reflectance Spectra and Magnetic Susceptibility

The data of the infrared spectra of $NiSeO_3 . 2 H_2O$, $Ni(HSeO_3)_2 . 2 H_2O$, and their deuterated analogues are given in Tables I and II. The band assignment is based on the works of Simon and Paetzold[11-13] and of Cody and Lewitt[16].

The electronic reflectance spectra data are summarized in Table III. The bands were assigned and the crystal field strength Δ and Racah's B parameter were cal-

TABLE II
Infrared spectra of $Ni(HSeO_3)_2 . 2 H_2O$ and $Ni(DSeO_3)_2 . 2 D_2O$. Symbols as in Table I

$\tilde{\nu}(Ni(HSeO_3)_2 . 2 H_2O)$	$\tilde{\nu}(Ni(DSeO_3)_2 . 2 D_2O)$	$\dfrac{\tilde{\nu}(Ni(HSeO_3)_2 . 2 H_2O)}{\tilde{\nu}(Ni(DSeO_3)_2 . 2 D_2O)}$	Band assignment
405 w	—	— }	$\delta(SeO_2)$
515 m	510 m	1·01 }	
570 m	425 w	1·34	$\varrho(H_2O)$
635 m	636 m	1·00	$\nu(SeO)(SeOH)$
735 s	530 s	1·37	$\varrho(H_2O)$
815 s	815 s	1·00	$\nu_{as}(SeO)_2$
850 s	845 s	1·01 }	$\nu_s(SeO_2)$
880 m	870 m	1·01 }	
1 140 m	850 sh	1·34 }	$\delta(OH)(SeOH)$
1 210 sh	900 sh	1·33 }	
1 630 w	1 210 w	1·34	$\delta(OH)(H_2O)$
2 420 w, b	1 800 w, b	1·34 }	
3 040 s	2 360 s	1·29 }	$\nu(OH)(SeOH)$
3 080 sh	2 380 s	7·29 }	
3 440 s	2 560 s	1·34	$\nu(OH)(H_2O)$

culated according to Underhill and Billing[22]. The nephelauxetic parameter β was determined by using the relation $\beta = B/B_0$, where B_0 is Racah's B parameter for the isolated ion (for Ni^{2+}, $B_0 = 1\,030\,cm^{-1}$).

The magnetic parameters obtained are given in Table IV. From the measured specific susceptibilities χ were calculated the molar susceptibilities, which were corrected for the diamagnetism of the cation, anion, and crystal water[23]. The corrected molar susceptibilities χ'_M were used for the calculation of the effective magnetic moments μ_{eff}.

DISCUSSION

In the $NiSeO_3$–SeO_2–H_2O system, an incongruently soluble selenite with the ratio $Ni : Se : H_2O = 1 : 2 : 3$ was found at $25°C$. Based on the solubility diagram, the molar ratio of the starting compounds leading to the maximum yield of this substance was determined to be $NiSeO_3 : H_2SeO_3 : H_2O = 1 : 1.5 : 6.8$. A compound with

TABLE III

Electronic reflectance spectra of $NiSeO_3.2\,H_2O$ and $Ni(HSeO_3)_2.2\,H_2O$

Compound	$\tilde{\nu}$ cm^{-1}	Assignment	Δ cm^{-1}	B cm^{-1}	β
$NiSeO_3.2\,H_2O$	8 500	$^3A_{2g} \rightarrow {}^3T_{2g}$	8 500	827	0.803
	13 500	$^3A_{2g} \rightarrow {}^3T_{1g}\,(F)$			
	24 400	$^3A_{2g} \rightarrow {}^3T_{1g}\,(P)$			
$Ni(HSeO_3)_2.2\,H_2O$	8 400	$^3A_{2g} \rightarrow {}^3T_{2g}$	8 400	880	0.854
	14 000	$^3A_{2g} \rightarrow {}^3T_{1g}\,(F)$			
	24 400	$^3A_{2g} \rightarrow {}^3T_{1g}\,(P)$			

TABLE IV

Magnetic properties of $NiSeO_3.2\,H_2O$ and $Ni(HSeO_3)_2.2\,H_2O$

Compound	χ	χ'_M	μ_{eff} BM
$NiSeO_3.2\,H_2O$	$19.6 \cdot 10^{-6}$	$43.4 \cdot 10^{-4}$	3.26
$Ni(HSeO_3)_2.2\,H_2O$	$13.5 \cdot 10^{-6}$	$47.4 \cdot 10^{-4}$	3.42

this ratio has been described by Boutzoureano[3] and by Nilson[4], but data that would indicate if the compound is hydrated hydrogen selenite or diselenite are lacking. In similar conditions, only hydrogen salts are formed in the case of alkali metals and Mg, Ca, and Sr, whereas only diselenites are found in the case of Ba and Zn (ref.[24]). The infrared spectra give an unambiguous evidence that the new compound arising in the system under study is nickel hydrogen selenite dihydrate.

The force constants of the Se—O bonds were calculated from the positions of the stretching vibrations bands of the SeO_3, SeO_2, and SeOH groups by using Lehman's relation[25], similarly as in the case of magnesium selenites[24]. The data (Table V) show that in the SeO_2 group in the hydrogen selenite anion the force constant is somewhat higher than in the SeO_3 group, while in the SeOH group the force constant is appreciably lower as compared with the SeO_3 group. Similar relations have been

TABLE V
Force constants of the selenium–oxygen bonds in $NiSeO_3.2 H_2O$ and $Ni(HSeO_3)_2.2 H_2O$

Compound	Group	$\tilde{\nu}_s$ cm^{-1}	$\tilde{\nu}_{as}$ cm^{-1}	k_{Se-O} N m^{-1}
$NiSeO_3.2 H_2O$	SeO_3	810	730	450
$Ni(HSeO_3)_2.2 H_2O$	SeO_2	850	815	544
	SeOH	635		316

TABLE VI
Hydrogen bond energies and lengths in $NiSeO_3.2 H_2O$ and $Ni(HSeO_3)_2.2 H_2O$

Compound	E kJ mol^{-1}	$R_{O\cdots O}$ pm
$NiSeO_3.2 H_2O$	18·1	287
	34·2	275
	38·1	273
	51·6	268
$Ni(HSeO_3)_2.2 H_2O$	20·4	285
	44·0	271
	46·6	270
	—	257

established in alkali metal[5] selenites[16,26] as well as in magnesium selenites[24]. The hydrogen bond energies and lengths were calculated from the positions of the hydroxyl group stretching vibration bands; the former were obtained by using the relation suggested by Sokolov[27] (adopted to yield values in kJ),

$$E = 246 \cdot 3 (\tilde{v}_0 - \tilde{v})/\tilde{v}_0 ,$$

where $\tilde{v}$ is the wavenumber of the hydroxyl group stretching vibration in the hydrate and $\tilde{v}_0$ is a reference values, $3\,750\ cm^{-1}$, the wavenumber of the hydroxyl group stretching vibration in a free water molecule. The hydrogen bond lengths were read from the correlation diagrams[28-32] of $\tilde{v}_{OH}$ vs $R_{O \ldots O}$ and averaged. The data are shown in Table VI. In the case of $NiSeO_3.2\,H_2O$, weak to strong hydrogen bonds occur mutually between the water molecules and between the water molecules and the anion, and in the case of $Ni(HSeO_3)_2.2\,H_2O$, mutually between the water molecules and mutually between the anions. Since the hydrogen bonds between the water molecules and the SeO_3^{2-} anion are stronger than between the water molecules themselves, the anion can be classed as positively hydrated[33].

Based on the study of the electronic reflectance spectra, magnetic properties, and the known structure of the isostructural zinc selenite dihydrate[34] it could be proved that the coordination sphere of the nickel cation is constituted by an octahedron made up of donor oxygen atoms, anions, and water molecules, giving rise to a weak crystal field with a high-spin electron arrangement. The crystal field strength is higher in selenite dihydrate than in hydrogen selenite dihydrate, similarly as in the case with the phosphite and hydrogen phosphite anions[35]. The spectrochemical parameters of the hypothetical $[Ni(SeO_3)_6]^{10-}$ anion were determined by the average crystal field method[36] from the electronic reflectance spectra, in analogy with the isostructural compound $ZnSeO_3.2\,H_2O$; the octahedral sphere was deemed composed of two water molecules and four univalent selenite anions. The values $\Delta([Ni(SeO_3)_6]^{10-}) = 8\,300\ cm^{-1}$, $B([Ni(SeO_3)_6]^{10-} = 800\ cm^{-1}$, and $\beta([Ni(SeO_3)_6]^{10-}) = 0 \cdot 78$ were obtained. By using the known values of $g_{Ni^{2+}} = 8\,900\ cm^{-1}$ and $k_{Ni^{2+}} = 0 \cdot 12$ and the relations $\Delta([Ni(SeO_3)_6]^{10-}) = g_{Ni^{2+}} \cdot f_{SeO_3^{2-}}$ and $1 - \beta([Ni(SeO_3)_6]^{10-}) = k_{Ni^{2+}} \cdot h_{SeO_3^{2-}}$, the values of the parameters $f_{SeO_3^{2-}} = 0 \cdot 93$ and $h_{SeO_3^{2-}} = 1 \cdot 86$ were derived. These values characterize the selenite anion as a ligand that in the spectrochemical series assumes a position between the fluoride anion and water, and in the nephelauxetic series, between ethylene diamine and the chloride anion[37].

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