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Abstract

Full Text

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COMPLEX FORMATION IN THE SYSTEM $NiCl_2$–HCl–H_2O

(Presented by Academician I. I. Chernyaev on January 3, 1962)

The uncertainty of information on the chemical nature of the compounds formed in aqueous solutions of Ni(II) halides, obtained from the optical spectra of these solutions ([1–11]), is to a considerable extent due to the difficulties of identifying the frequencies observed in the electronic absorption spectra of such systems. Increasing the concentration of halogen ions in a solution of Ni(II) halides leads only to a smooth shift of the absorption curves into the long-wavelength region, the shift being greater the higher the concentration of the anions, without any substantial change in the contour of the curve.

In the present work we attempt to elucidate the composition and structure of the Ni(II) compounds formed in the system $NiCl_2$–HCl–H_2O by carefully measuring the absorption spectra of this system and comparing them with the spectra of crystalline Ni(II) complexes. For this purpose we selected the following crystalline compounds of divalent nickel: $Ni(ClO_4)_2 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$, $NiCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 2H_2O$, and $NiCl_2$. The structure of the inner coordination sphere of these complexes is shown in Fig. 1 ([12–16]).

Fig. 1. Structure of the nearest environment of the Ni^{2+} ion in crystals: *a* – $Ni(ClO_4)_2 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$; *b* –$NiCl_2 \cdot 6H_2O$; *c* –$NiCl_2 \cdot 2H_2O$; *d* –$NiCl_2$.

The listed preparations, with the exception of $NiCl_2$, were obtained as large single crystals weighing 10–40 g each, both by the static method and by the method of planetary rotation ([17]). Plates measuring $10 \times 25 \times 3$ mm were cut from the crystals; grinding and polishing of the plates were carried out with

Figure 2: absorption curves

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a mixture of emery and crocus with petroleum jelly, and the thickness was measured on an IKV vertical optimeter.

The absorption spectra of the crystalline plates were measured in the region 300–1500 mμ on an SF-11 spectrophotometer, and in the region 400–750 mμ on a two-prism recording SF-10 spectrophotometer. Measurement of the absorption spectrum of small $NiCl_2$ crystals was carried out on a microspectrophotometer and was duplicated by recording the spectrum of the powdered preparation on an SF-10 spectrophotometer.

The absorption curves of the crystals shown in Fig. 2, recorded in natural radiation, show that replacement of water molecules in the hexaaquo ion $[Ni(H_2O)_6]^{2+}$ by Cl^- ions is clearly manifested in the spectrum of the Ni^{2+} ion. Measurement of the spectra of the same preparations in polarized radiation was carried out on an SF-11 spectrophotometer, for which a Frank–Ritter prism was mounted in the latter. It was established that the pleochroism of the crystals studied by us, as in the case of crystalline Co(II) complexes ([18]), reduces to the case of "adsorption" ([19]): changing the orientation of the crystals relative to the plane of vibration of the polarized beam leads to a change in the numerical values of the absorption coefficient, but does not change the frequencies corresponding to the absorption maxima.

Absorption spectra of the system $NiCl_2$—HCl—H_2O were studied on SF-10 and SF-11 spectrophotometers. The concentration of $NiCl_2$ in solution was varied from 10^{-2} g-mol/l to 1 g-mol/l, and the concentration of HCl was varied from 0 to 13 g-mol/l. Absorption curves for several solutions are given in Fig. 3.

At an HCl concentration in solution below 3 g-mol/l, the absorption spectrum of the solution is identical to the spectrum of the octahedral ion $[Ni(H_2O)_6]^{2+}$ in

Fig. 2. Values of the absorption index χ_λ, measured in natural radiation for crystals: 1 —$Ni(ClO_4)_2 \cdot 6H_2O$; 2 —$NiCl_2 \cdot 6H_2O$; 3 —$NiCl_2 \cdot 2H_2O$, 4 —values of the optical density D_λ of $NiCl_2$ crystals

the crystal lattices of $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiSO_4 \cdot 7H_2O$. At a higher HCl concentration the absorption curve of the solution shifts into the long-wavelength region of the spectrum. At $C_{HCl} = 10$ g-mol/l, the absorption curve of a $NiCl_2$ solution has maxima coinciding with those in the spectra of crystals of $Ni(ClO_4)_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$. The absorption curve of a $NiCl_2$ solution in 13 M HCl may be regarded as the sum of the absorption curves of crystals of $Ni(ClO_4)_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, and $NiCl_2 \cdot 2H_2O$.

This gives grounds to suppose that, at high HCl concentrations, an equilibrium exists in solution between the following complexes: $[Ni(H_2O)_6]^{2+}$,

Figure 3: Absorption curves of $NiCl_2$ solutions.

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$[Ni(H_2O)_4(ClH_2O)_2]$, and $[NiCl_4(H_2O)_2]^{2+}$. The monotonic shift of the absorption curve of an aqueous $NaCl_2$ solution, observed with increasing HCl concentration, can be explained in two ways:

1. The concentration of Cl^- anions near $[Ni(H_2O)_6]^{2+}$ ions may produce an additional Stark effect, manifested in a shift of the energy levels of the ion $[Ni(H_2O)_6]^{2+}$. Against such an explanation one may set the following facts: the formation of ion pairs of the type Me^{n+}—H_2O—A^{m-} leads to a small shift of the frequencies in the spectrum of the ion Me^{n+}, of the order of several millimicrons ([20]). In the system $NiCl_2$–HCl–H_2O, however, this shift reaches 30-35 mμ. The coincidence of the absorption curves of dilute aqueous $NiCl_2$ solutions with the absorption curves of crystals of $Ni(H_2O)_6 \cdot 6H_2O$ and $[Ni(H_2O)_6](H_2O)SO_4$ shows that the chemical nature does not cause changes in the spectrum of the Ni^{2+} ion.

The absorption spectrum of a 0.01 *M* $NiCl_2$ solution in 8 *M* $HClO_4$ coincides with

spectrum of a neutral solution of $NiCl_2$, whereas the frequencies in the spectrum of a solution of $NiCl_2$ in 8 *M* HCl are shifted into the long-wavelength region by 15-18 mμ.

2. Cl^- ions, penetrating into the inner coordination sphere of the hexaaquo ion, displace some water molecules from Ni^{2+} and share coordination positions with them. The Ni^{2+}–H_2O distances thereby increase to the point that the water molecules may be displaced into the second coordination sphere. As a result of this process, at high concentrations of Cl^- ions in solution, acid complexes with six inner-sphere substituents may form, for example $[Ni(H_2O)_2Cl_4]$. The gradual change in the Ni–H_2O and Ni–Cl distances leads to a monotonic shift of the energy levels of the Ni^{2+} ion.

Fig. 3. Absorption curves of $NiCl_2$ solutions: **1** –aqueous solution of $NiCl_2$. $[NiCl_2] = 10^{-2}$-1 g-mol/l. **2** –solution of $NiCl_2$ in 10 *N* HCl. $[NiCl_2] = 0.01$ g-mol/l. **3** –solution of $NiCl_2$ in 13 *N* HCl. $[NiCl_2] = 0.01$ g-mol/l. $\bar{x}_\lambda$ – apparent molar absorption coefficient.

The structure of the nearest environment of the Ni^{2+} ion in the crystal $NiCl_2 \cdot 6H_2O$ (14) supports such an assumption.

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