

The Relative Stability of Some Nickel (II) Complexes²

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Coordination compounds have received considerable attention because of the belief that an understanding of the forces which hold these combinations together may lead to a better understanding of the general nature of these forces. One indication of the strength of these bonds is to be found in the stability of the complexes. Very little study has been made of the stabilities of the nickel (II) complexes.

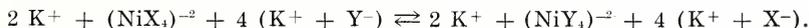
In view of this, a spectrophometric study was made of the relative stabilities of some of the nickel (II) complexes using a Beckman model (DU) spectrophotometer to measure the transmittancy of the various anions in the range 225 $m\mu$ to 400 $m\mu$ at intervals of 10 $m\mu$. Since each complex has certain characteristic features in its transmittancy, it was possible to compare curves of individual anions with those of mixtures of anions and establish relative stabilities of the complexes.

The only values found in the literature for instability constants were for the cyanide, bromide, and citrate complexes. Sartori (1) gives 3.45×10^{-16} for tetracyanonickelate (II); Bobtelsky and Jordan (2) give 4.1×10^{-4} for a citrate complex; and Job (3) gives 6.03×10^{-4} and 1.32×10^{-5} for NiBr_2 and $(\text{NiBr})^-$ respectively in the presence of some HBr , but full details are not given in the article.

H. C. Jones (4) in a series of publications reported studies of absorption spectra of over 2000 different solutions. Very little data are given as to the relative or actual stabilities of the complexes.

Experimental

In order to compare the stability of the complex nickel anions, use was made of reactions of the type:



The original complex was made in solution by adding the proper amount of potassium salt to the simple nickel compound, $(\text{NiX}_2 + 2 \text{KX})$. The solutions were 0.10 M nickel and 0.40 M anion. To the mixture, for comparison purposes, was added an equivalent amount of a second potassium salt (KY) for the possible formation of a complex of nickel with Y. Equilibrium was approached from both directions, i.e. starting with K_2NiX_4 and adding KY; starting with K_2NiY_4 and adding KX. The foregoing statement is true except for measurements using tartrate and thiocyanate, in these cases the potassium salt was added in all cases to the other nickel salts.

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Transmittancy measurements were made with a Beckman model (DU) spectrophotometer. The light source was a hydrogen discharge lamp. Silica cells were used; the one used for the water blank had a cross-section of 1.008 cm, the one for the solutions 1.003 cm. The temperature range was 23°C. to 30.5°C.

All salts were A.C.S. reagent grade except the potassium tetracyanonickelate (II) which was furnished by Dr. W. C. Fernelius. All water used was redistilled.

In figures 1, 2, 3, and 4, it is shown how the relative stability was established. In each figure the ordinate is the percent transmittancy and the abscissa is the wavelength in millimicrons.

The relative stability was established by comparing the transmittancy curve of a mixture of two anions being studied with the transmittancy curve of each anion. The curve of the anion with the mixture more nearly resembled was the curve of the more stable complex.

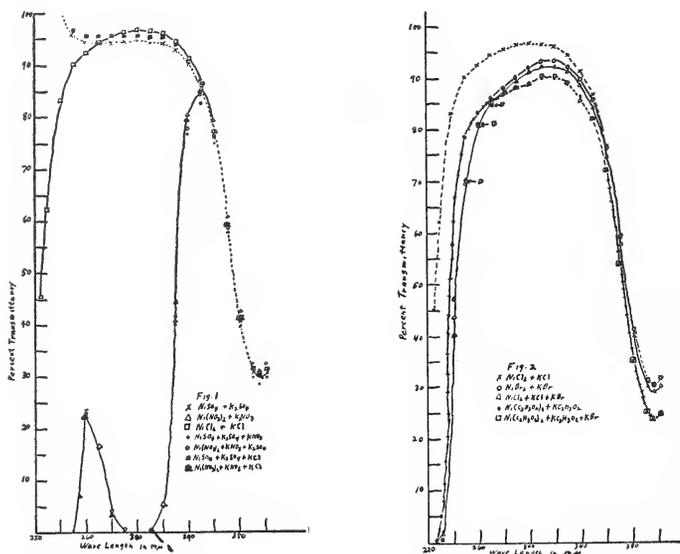


Fig. 1. Transmittancy curves for Nickel (II) complexes of X) Sulfate; Δ) Nitrate; \square) Chloride; \bullet) Sulfate and Nitrate; \circ) Nitrate and Sulfate; \blacksquare) Sulfate and Chloride; \blacktriangle) Nitrate and Chloride.

Fig. 2. Transmittancy curves for Nickel (II) complexes of X) Chloride; \circ) Bromide; Δ) Chloride and Bromide; \bullet) Acetate; \square) Acetate and Bromide.

Figure 1 shows that the sulfate, nitrate, and chloride have about the same degree of stability. The part of the curve from 250 m μ to 340 m μ in the case of all solutions containing nitrate is due to the nitrate ion itself.

Figure 2 shows that the bromide complex is more stable than the chloride complex and that the acetate complex is still more stable.

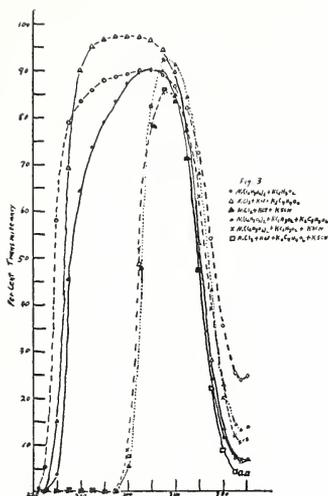


Fig. 3. Transmittancy curves for Nickel (II) complexes of ○ Acetate; △ Tartrate; ▲ Thiocyanate; ● Acetate and Tartrate; X Acetate and Thiocyanate; □ Tartrate and Thiocyanate.

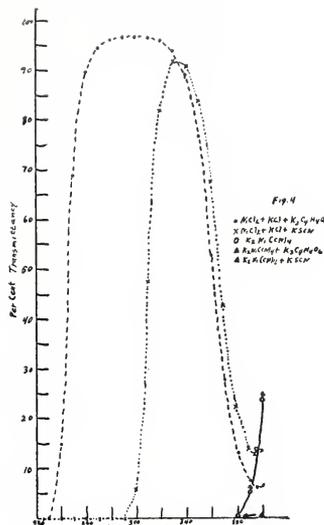


Fig. 4. Transmittancy curves for Nickel (II) complexes of ● Tartrate; X Thiocyanate; ○ Cyanide; ▲ Cyanide and Tartrate; ▲ Cyanide and Thiocyanate.

Figure 3 shows that the tartrate and thiocyanate complexes are both more stable than the acetate complex. The curve for the mixture of tartrate and thiocyanate is about half like one and half like the other so it was concluded that these two complexes had about the same degree of stability.

Figure 4 shows that the cyanide complex is the most stable of the complexes studied.

Results

The relative stability observed for the nickel (II) complexes, the most stable being listed first, is as follows:

Cyanide
Tartrate, Thiocyanate
Acetate

Bromide
Sulfate, Nitrate, Chloride.
Literature Cited

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