Short Communications

On the Tendency of the Tetracyano Nickelate(II)Ion to Form Complexes

MIHÁLY T. BECK* and JANNIK BJERRUM

Chemistry Department I. Inorganic Chemistry. The H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

It is well known that in the presence of excess cyanide the colour of tetracyano nickelate(II) solutions becomes more intense. The reason for this change is evidently the formation of higher cyanide complex(es)[1]. There is disagreement about the composition and stability of the complex formed.

According to McCullough, Jones and Penneman[2] the tetracyano nickel(II) complex takes up only one further cyanide forming a pentacyano complex, the absorbancy of which in the visible, especially between $500-375$ mμ, is much greater than that of the tetracyano complex. The stability constant was found to be about 0.2. The infrared study[2] of the same system gave the same results.

Almost simultaneously Blackie and Gold[3] published the results of a magnetic study of the same system. According to their proton magnetic resonance experiments, the tetracyano nickel(II) complex stoichiometrically reacts with two further cyanide ions. From their results it can be estimated that the stability constant of the hexacyano complex (K_5K_6) is at least $10^5 - 10^6$. The authors cited Kisova and Čuprova's spectrophotometric study[4] in support of their result. They did, however,

* Permanent address: Institute of Inorganic and Analytical Chemistry, University of Szeged, Szeged, Hungary.

not know the original paper by Kisova and Čuprova, but only the abstract of it. The results given by the Czechoslovak authors do not support the formation of a *stable* hexacyano complex, but in our opinion rather the formation of an unstable pentacyano complex.

The only difference between the cited spectrophotometric[2] and the magnetic study is that in the case of the latter experiments the authors worked with ammoniacal solutions, the concentration of which was not specified. Therefore we repeated the spectrophotometric study using ammoniacal solutions. However, instead of an increase of stability — which would possibly be expected considering the results of Blackie and Gold's study — a decreasing extent of formation of pentacyano complex with increasing ammonia concentration, or more correctly a fading of colour of solutions on the effect of ammonia, was observed (see Fig. 1a). It was further observed (see Fig. 1b) that a similar fading effect in approximately 1 M cyanide solution was caused by ethylenediamine, pyridine, butylamine, ethanol, methanol, dioxane, etc. Relatively small concentrations of these substances result in great change of absorbancy of solutions, so it is very probable that the reason of this peculiar behaviour is not a change in the spectra properties of species, but rather a change in the concentration of the high absorbing pentacyano nickel(II) complex.

A change of concentration of the pentacyano complex could be independently explained by

(a) a competition between the cyanide ion and the organic substance for a fifth coordination site of the tetracyano complex, assuming that the mixed complex has nearly the same absorbancy as the aquotetracyano nickel(II) complex;

(b) the activity coefficient corresponding to the mass action expression
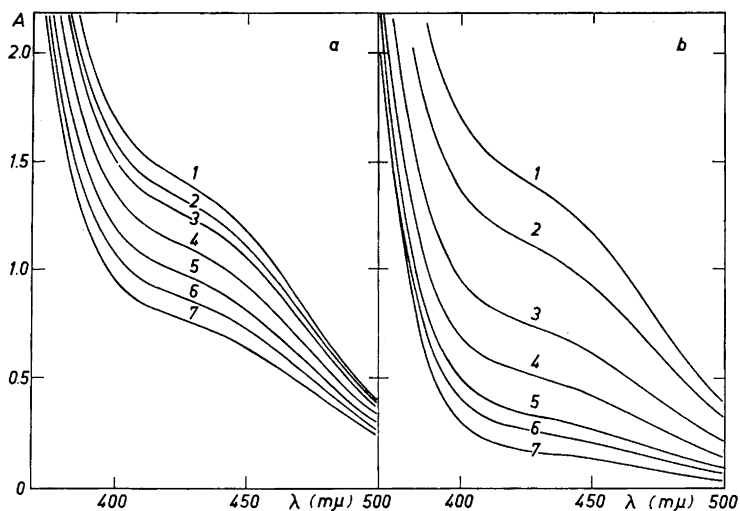
$$F = f_{Ni(CN)_4^{2-}} f_{CN^-} / f_{Ni(CN)_5^{3-}}$$

Fig. 1. The effect of ammonia (*a*), and pyridine (*b*) on the directly measured absorbancy A in 2 cm cells of solutions of the composition: $Ni(CN)_4^{2-}$ 0.04 M, CN^- 0.98 M

ammine conc. (curve nos.)

a: 0 (1), 0.454 M (2), 0.908 M (3), 1.82 M (4), 2.72 M (5), 3.63 M (6), 4.31 M (7).

b: 0 (1), 0.246 M (2), 0.738 M (3), 1.23 M (4), 1.97 M (5), 2.46 M (6), 3.7 M (7).

is supposed to decrease strongly on the effect on the added nonelectrolytes.

It is possible to explain the effect observed on the basis of either assumptions. The fact that molecules the coordination tendency of which is evidently extremely small (*e.g.* alcohols) result in the same effect as the ammines, however, supports the latter explanation. The decrease of the dielectric constant of the medium, which is an important factor in determining the activity coefficients, is practically the same

with the different amines and alcohols [5]. It must be mentioned, however, that the dimethylformamide -- the dielectric constant of which is even greater than that of the water — has the same fading effect.

To elucidate the phenomenon observed, the effect of different salts on the absorbancy of the tetracyano nickel(II) complex and the system $Ni(CN)_4^{2-}-CN^-$ was studied. Added salts cause in all cases an increase of absorbancy and mainly in the visible part of the spectrum. Table 1 shows

Table 1.

$K_2Ni(CN)_4$ 0.01 M

Salt	KCN	KSCN	KI	KBr	KCl	KF	KNO₃
Molarity	0.8	1.94	1.6	1.6	1.8	2	1.8
Δ %/M	747	290	196	26	7.2	7	15.5

$K_2Ni(CN)_4$ 0.01 M, KCN 0.8 M

Salt		KSCN	KI	KBr	KCl	KF	KNO₃
Molarity		1.94	1.6	1.6	1.8	2	1.8
Δ' %/M		26.5	60	45	45	65	20
Δ' %/Δ %		0.09	0.3	1.7	6.3	9.3	1.3

the increase of absorbancy at 400 mμ in per cent per mole/liter of salt.

The great effect of KCN, KSCN, KI and — to a much lesser extent — KBr on the absorbancy of the tetracyano complex can ba interpreted as a consequence of formation of pentacoordinated species. The effect of KCl, KF and KNO_3 seems to be a normal salt effect, however that of the KNO_3 is surprisingly high. The system $Ni(CN)_4^{2-}$ + CN^- is more complicated, and the interpretation in this case is not simple. Evidently the effect observed is the resultant of different factors: the salt effect on the two different absorbing species, and the competition between the cyanide and other anions for the fifth coordination place. The last line of Table 1 is informative and suggests a specific salt effect of KCl and even more of KF on the pentacyano species. In this connection it must be mentioned that Herrington and Kingsbury [6] suggested that the fluoride ion exerts a specific effect on the $Ti(IV)-H_2O_2$ complex. Their conclusion, however, is evidently wrong because the limiting value of absorbancy is reached already at 0.1 M fluoride concentration. The decrease of absorbancy and the shift of the band can be simply explained by the formation of a mixed complex: $Ti(IV)-H_2O_2-F^-$.

For comparison the effect of different salts on the spectrum of a coordinatively saturated cyano complex was also studied. Potassium hexacyanoferrate(II) was measured in the wavelength range 440—380 mμ, and Table 2 summarizes the increase of absorbancy at 380 mμ in per cent per mole/liter of salt.

Table 2.

$K_4Fe(CN)_6$ 0.01 M, $\lambda = 380$ mμ

Salt	KCN	KI	KBr	KCl	KF	KNO_3
Molarity	1.6	1.6	1.6	1.8	2	1.8
Δ %/M	15	10	9	7	11	13

In comparing the data it can be seen that the salt effect as a whole is very small. Therefore, on the basis of these studies the existence of the mixed complexes $Ni(CN)_4SCN^{3-}$, $Ni(CN)_4I^{3-}$ and $Ni(CN)_4Br^{3-}$ as well as that of the pentacyano-Ni(II) complex seems to be well established. The stability order is

$$Ni(CN)_5^{3-} > Ni(CN)_4SCN^{3-} > Ni(CN)_4I^{3-} > Ni(CN)_4Br^{3-}$$
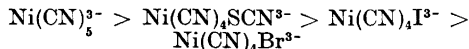
These complexes are very weak ones and therefore it is impossible to give reliable numerical data for their dissociation. Although the paper by McCullough, Jones and Penneman appears correct as a whole, according to our experience the error of K_5 given by the authors seems to be too optimistic.

The results of the present study do not solve the discrepancy between the spectrophotometric and magnetic studies mentioned, but the interpretation of the proton magnetic resonance measurements seems to be incorrect.

Infrared absorption experiments may decide whether the effect of fluoride on the system $Ni(CN)_4^{2-}-CN^-$ is exerted on the activity coefficient expression, or on the pentacyano complex itself. In the latter case there may be a shift of the peak.

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