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The d→d Absorption Spectra of Potassium Tris(8-quinolinolato)nickelate(II) in Methanol-Chloroform Mixtures

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The d→d absorption spectra of K[NiQ_3]·EtOH,[1] which was prepared in our laboratory, in MeOH–$CHCl_3$ mixtures have been observed to vary greatly with the change in the ratio of the volume of $CHCl_3$ to that of MeOH. Such a large change in the spectrum cannot be attributed to normal solvent effects, in view of the fact that the absorption spectra of Al(III)Q_3 or Fe(III)Q_3 in various pure and mixed solvents are practically the same.[2]

In the present study, this spectral change was examined with the intention of exploring the basis for this change.

Results and Discussion

The spectra of K[NiQ_3]·EtOH in MeOH and MeOH–$CHCl_3$ mixtures are shown in Fig. 1.[3] The presence of the isosbestic points in Fig. 1 indicates that two species coexist at equilibrium and that normal solvent effects are negligibly small. The plot of the absorbance at 950 nm *vs.* the vol% of $CHCl_3$ shown in Fig. 2 indicates that the complex exists predominantly in one form (Species A) in MeOH, and in another form (B) in 80 vol% or more of $CHCl_3$. The absorption data summarized in Table 1, compared[4] with that[5] of K[Ni(gly)$_3$], suggest that both species, A and B, are six-coordinated (3 O and 3 N atoms of three 8-quinolinolate ligands) complexes.

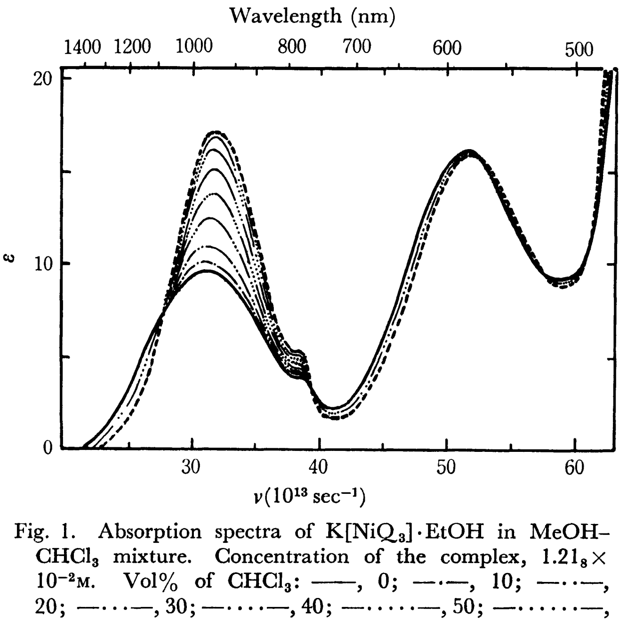

Fig. 1. Absorption spectra of K[NiQ_3]·EtOH in MeOH–$CHCl_3$ mixture. Concentration of the complex, $1.21_8 \times 10^{-2}$ M. Vol% of $CHCl_3$: ——, 0; —·—, 10; —··—, 20; —···—, 30; —····—, 40; —·····—, 50; —······—, 60; —·······—, 70; --------, 80%.

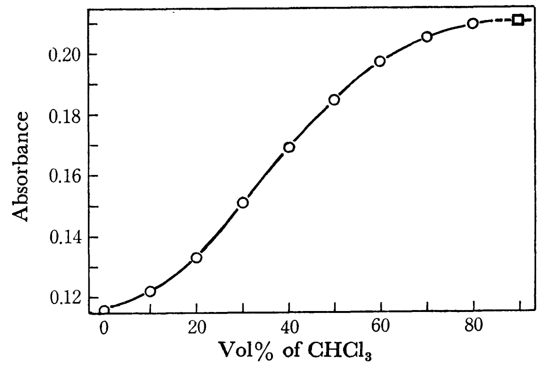

Fig. 2. Variation of absorbance at 950 nm with vol% of $CHCl_3$. Concentrations of the complex: ○: $1.21_8 \times 10^{-2}$ M (a 1 cm cell was used), □: 6.09×10^{-3} M (a 2 cm cell was used).

As is shown in Table 1, with the change from A to B the second band shows little change in either intensity or the position, while the first band shows a small blue shift and a significant increase in intensity. This trend of the spectral change shows a striking resemblance to that of the spectral changes attended by the steric changes from the *mer*-[Co(O,N)$_3$] complexes to the *fac* isomers, which are described in the literature.[6] In DMSO the configuration of MQ_3, where M is Al(III), Co(III), or Rh(III), has been reported by Baker and Sawyer to be a *mer* structure.[7] The same configuration can be expected for the NiQ_3^- ion in MeOH. These facts suggest that the A species has a *mer* structure and that, accordingly, B has a *fac* structure.

The conversion to the *fac* form from the *mer* form may be explained in terms of the ion-pair formation. It is well known that, in the [Co(en)$_2$Cl$_2$]$^+$ system, in various dipolar solvents the ratio of the concentration of the *cis* and *trans* ions varies with the chloride-ion concentration, since the dipolar *cis* ion is stabilized by the ion-pair formation.[8] The *fac*-NiQ_3^-, whose three

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1) In this paper, Q^- represents 8-quinolinol anion.

2) F. G. Zharovskii and V. L. Ryzhenko, *Vis. Kiiv. Univ., Ser. Fiz. Khim.*, **1968**, 56, 62; *Chem. Abstr.*, **71**, 107223t (1969); *ibid.*, **72**, 138055q (1970).

3) Potassium salts or certain solvents instead of $CHCl_3$ showed the same effect. See experimental section.

4) Matsuoka *et al.* drew the conclusion from the study of CoQ_3 and CrQ_3 that the position of 8-quinolinolate ligand in the spectrochemical series is almost same as that of glycinate ligand. (N. Matsuoka, Y. Shimura, and R. Tsuchida, *Nippon Kagaku Zasshi*, **82**, 1637 (1961).)

5) J. Hidaka and Y. Shimura, This Bulletin, **43**, 2999 (1970). (gly) represents glycinate ligand.

6) Data for glycinate, *dl*-alaninate and picolinic acidate ligands as (O, N) are available. J. Fujita and Y. Shimura, This Bulletin **36**, 1281 (1963).

7) B. C. Baker and D. T. Sawyer, *Anal. Chem.*, **40**, 1945 (1968).

8) W. R. Fitzgerald and D. W. Watts, *J. Amer. Chem. Soc.*, **89**, 821 (1967), and references therein.

Table 1. The d→d absorption data[a] of solutions of $K[NiQ_3]\cdot EtOH$ and $K[Ni(gly)_3]$

Complex	Solvent	Band I	Singlet Band	Band II	Band III	Ref.
		ν_{max} ($\log \varepsilon_{max}$)	ν_{max} ($\log \varepsilon_{max}$)	ν_{max} ($\log \varepsilon_{max}$)	ν_{max} ($\log \varepsilon_{max}$)	
$K[Ni(gly)_3]$	H_2O	30.5 (1.01)	39.7 (0.35)	50.2 (0.95)	83.0 (1.18)	5)
$K[NiQ_3]\cdot EtOH$	MeOH	30.9 (0.98)	38.5^{sh} (0.61)	51.5 (1.21)	b)	c)
	$MeOH-CHCl_3$ (20: 80 vol%)	31.9 (1.24)	38.5^{sh} (0.73)	51.9 (1.20)	b)	c)

a) The frequencies are given in 10^{13} sec^{-1}.

b) The third bands could not be observed owing to overlapping of the $\pi-\pi^*$ transition bands.

c) This work.

anionic O atoms are concentrated around the c_3 axis, is expected to have a larger net dipole moment than the *mer* ion, and the formation of the ion pair K^+, NiQ_3^- in $MeOH-CHCl_3$ mixtures with dielectric constants lower than that of MeOH may not be negligible.

Experimental

Reagents and Solvents. All the chemicals used were of a guaranteed reagent quality. The solvents were from freshly-opened bottles of a G. R. quality.[9]

Preparation of Potassium Tris(8-quinolinolato)nickelate(II) Monoethanolate, $K[Ni(C_9H_6ON)_3]\cdot(C_2H_6O)$. A 10.0 g portion of KOH(86%) was suspended (almost dissolved) in 70 ml of EtOH, and the supernatant solution was added to 70 ml of EtOH containing 12.0 g of 8-quinolinol (0.083 mol),[10] after which the mixture was filtered out through a filter paper. To this filtrate, warmed about 70°C, a hot solution of 4.0 g of nickel(II) acetate tetrahydrate (0.016 mol) in 100 ml of EtOH was slowly added without stirring; the resultant clear, deep green, mixed solution was allowed to stand for two days. The fine, deep green crystals obtained were washed with EtOH several times, and dried at room temperature *in vacuo*. The yield, based on the nickel acetate, was 90% (8.3 g).

Found: C, 59.64; H, 4.06; N, 7.39; Q^-, 74.7%. Calcd: C, 60.44; H, 4.20; N, 7.29; Q^-, 75.0%.

The solvent of crystallization (EtOH) was released by heating at 175°C for 6 hr: the complex decomposed slightly. (Found: 8.07%. Calcd: 7.99%).

The complex was recrystallized from MeOH by adding ethanolic KOH, but it was sufficiently pure without recrystallization.

Measurement of Absorption Spectra. A 5.00 ml volume of the $6.09_1\times10^{-2}$M $K[NiQ_3]\cdot EtOH$ methanolic solution and an appropriate volume of $CHCl_3$ were placed in each of a series of 25 ml volumetric flasks, and then each solution was diluted to the mark with MeOH. Each reference solution, containing all the components except the complex, was prepared in a similar manner. After one hour's standing after the initial mixing, each solution was placed in a 1 cm quartz cell and its components determined by means of a Shimadzu MPS-50L spectrophotometer, the transmittance being read at room temperature. No spectral change with time was observed after one day's standing.

Other Systems. In a manner similar to that in the case of $CHCl_3$, the spectra of $K[NiQ_3]\cdot EtOH-MeOH-S$ systems, where S is benzene, dioxane, diethyl ether, acetone, EtOH, KBr, KI, CH_3COOK, KOH, NaOH, *etc.*, were examined. In all cases, the shape of the maximum near 950 nm varied from a rounded hump for the complex–MeOH system to a sharp peak in the presence of S. In the present study, $CHCl_3$ as S was chosen for its greater ability to vary the spectra and for the higher solubility of the complex in this system, though the complex is scarcely soluble in pure $CHCl_3$.

The spectra of the complex–MeOH–KOH system are shown in Fig. 3.

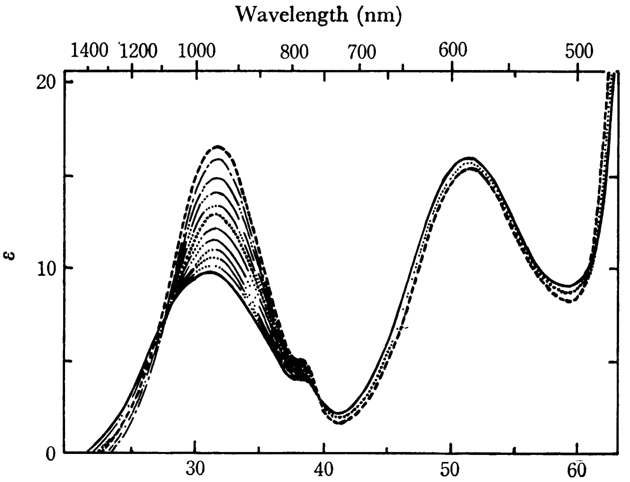

Fig. 3. Absorption spectra of $K[NiQ_3]\cdot EtOH$ in MeOH containing varying amounts of KOH. Concentration of the complex, $1.21_8\times10^{-2}$M. Concentrations of KOH: ——, 0; —··········—, 1.84×10^{-2}; —·········—, 3.68×10^{-2}; —········—, 9.20×10^{-2}; —·······—, 1.47×10^{-1}; —······——, 2.30×10^{-1}; ·········3.68×10^{-1}; —····—, 5.52×10^{-1}; —···—, 9.20×10^{-1}; —··—, 1.47; —·—, 2.30; ------, 3.68M.

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[9] $KNiQ_3$ in the commercially obtained dehydrated MeOH gave an identical spectrum with that of G. R. MeOH solution.

[10] Experimentally, excess KOH and HQ gave fine crystals.