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Charge-transfer Complexes between Square Planar Metal Complexes and Some Organic Compounds

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The formation of molecular complexes between square planar metal complexes and organic acceptor [1] or donor [2] molecules was reported by Bailey *et al.* and Schmidt *et al.* These complexes were thought to be held by a so-called Mulliken's charge-transfer molecular interaction [1–3]. This view was supported by the X-ray analysis [4] for the 1:1 complex of bis(1,2-benzoquinonedioximato)nickel(II) and TNCQ*.

Since it appears that the donor–acceptor molecular interaction between metal complexes and organic molecules plays an important role in some biological electron transfer [5], we have initiated a systematic investigation of the charge-transfer complexes of square planar metal complexes with some organic π-donors and/or π-acceptors (*cf.* Table I).

In this paper we report the preliminary results of a spectroscopic study on the charge-transfer complexes of several cobalt(II), nickel(II) and copper(II) complexes of the $[MN_4]$ and the $[MN_2O_2]$ types in solution.

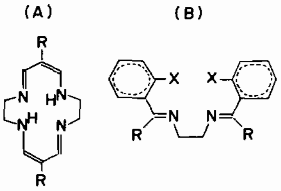

Figure 1. The ligands used in this study and their abbreviations: (A), H_2(A-14) for R = phenyl; H_2(A-14') for R = *p*-tolyl. (B), H_2(salen) for R = H and X = OH; H_2(amben) for R = H and X = NH_2; H_2(aaen) for R = CH_3 and X = NH_2.

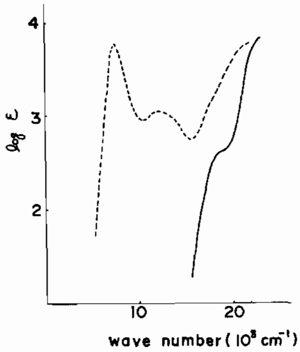

Figure 2. Absorption spectra of [Ni(A-14')], (———), and the 1:1 mixture of [Ni(A-14')] and TCNE, (-------) (in dichloroethane at 20 °C, 5 × 10^{-4} *M*). The spectrum of charge transfer complex was measured immediately after mixing.

As an example, the absorption spectrum of the mixture of [Ni(A-14')]** and TCNE in 1,2-dichloroethane is shown in Fig. 2. New bands were observed at 0.75 μm^{-1} and 1.21 μm^{-1}, the molar extinction coefficients being 5730 and 1140, respectively. By the use of the continuous variation method, the band at 0.75 μm^{-1} was attributed to the formation of the 1:1 molecular complex of [Ni(A-14')] and TCNE. On the other hand, there was practically no change in the absorption spectrum (in the range 0.5–2.0 μm^{-1}), when TCNE was added to a 1,2-dichloroethane solution of nickel(II) complexes of the $[NiN_2O_2]$ type, such as [Ni(salen)]**. This fact indicates that no appreciable molecular complex was formed between TCNE and the $[NiN_2O_2]$ type complex (neither π- nor σ-type). In general, an axial ligation is more difficult in a square planar metal complex with a stronger in-plane ligand field effect than that with a weaker one [6]. Accordingly, the interaction between the $[NiN_4]$ type complex and TCNE should not be of a σ-type but of a π-type, although TCNE coordinates (σ-type) to the metal ion through the nitrogen atom in some organometallic compounds [7].

The interaction between metal complexes and π-donors is entirely different from that of π-acceptors.

TABLE I. Organic π-Acceptors and π-Donors Used in This Study.

	Compound	Abbreviation
π-Acceptor	Tetracyanoethylene	TCNE
	7,7,8,8-Tetracyanoquinodimethane	TCNQ
	1,2,4,5-Tetrachloro-*p*-benzoquinone	Chloranil
π-Donor	N,N,N',N'-Tetramethyl-*p*-phenylenediamine	TMPD
	1,2,4,5-Tetramethylbenzene	Dulene
	Hexamethylbenzene	HMBZ

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*For the abbreviations of the organic reagents, see Table I.

**For the abbreviations of the ligands, see Fig. 1.

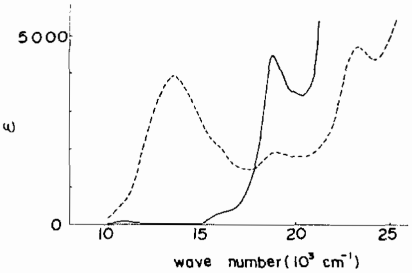

Figure 3. Absorption spectra of [Co(amben)], (———), and the 1:4 mixture of [Co(amben)] and TMPD, (-------) (in DMF at 20 °C, 5 × 10^{-4} *M*).

The addition of π-donors, such as TMPD and Dulene, effected no appreciable change in the absorption spectra of nickel(II) and copper(II) complexes used in this study. However, in the case of the cobalt(II) complexes remarkable changes were observed in the spectra, *e.g.*, a new band appeared at 1.36 μm^{-1} in a solution of [Co(amben)] and TMPD (Fig. 3). The above facts indicate that a new band observed for the mixture of $[CoN_4]$ type complexes and π-donors is due to the electronic transition from π-donors to the unfilled metal d_{yz} orbital [8]. In the case of nickel(II) and copper(II) complexes, such a charge transfer as observed for cobalt(II) complexes is impossible, because all the d_π-orbitals are occupied. More detailed results will be published in a separate paper.

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