BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2214—2215(1972)

Charge-Transfer Absorption in the Solid Aromatic Diamine Complexes with Picrates

Gunzi Saito and Yoshio Matsunaga
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received December 3, 1971)

Molecular complexes have received considerable attention for many years. Nonetheless, most of those described in the literature are derived from neutral donor and acceptor molecules; relatively little is known about complexes made from neutral molecules and salts. Recently, we reported on the vibrational and electronic spectra of Kofler's ternary complex, α-naphthylamine-pyridine-picric acid (1:1:1), and postulated that the interaction between the amine molecule and the picrate ion is of the charge-transfer type.[1] Our interest in the acceptor strength of the picrate ion has led to a further study of the molecular complexes with picrates. As it seemed highly desirable to have simple counter ions, we chose sodium, potassium, and ammonium picrates. Their electron-acceptor strengths are expected to be comparable with that of *s*-trinitrobenzene; therefore, strong electron-donors must be combined with the picrates if one is to observe the charge-transfer absorption separated from the spectrum of the yellow-colored component. Benzidine, *o*-tolidine, and *o*-dianisidine were thought to be best suited to our purpose. These donors have low enough ionization potentials and were extensively used in the related work to be described in forthcoming papers.

The picrates were prepared by the addition of an aqueous solution of an appropriate carbonate or nitrate to picric acid dissolved in alcohol. The diffuse reflection spectra were recorded on a Beckman DK 2A spectroreflectometer and were plotted using the Kubelka-Munk function, as has been described in a

---

[1] Y. Matsunaga and G. Saito, This Bulletin, **45**, 963 (1972).

previous paper.[2] Our attempts to prepare the solid complexes with sodium picrate from a solution failed except in the case of *o*-dianisidine. With this combination, dark brown-colored crystals were obtained from hot acetone. As is shown in Fig. 1, comparison with the spectrum of sodium picrate clearly indicates the appearance of a weak low-energy absorption upon the complex formation. When an equimolecular mixture of *o*-dianisidine and sodium picrate was thoroughly ground and heated to the melting point of the diamine, the same spectrum could be observed with the product. Therefore, all the other combinations were examined by the latter technique. The spectra of the *o*-dianisidine complexes with potassium and ammonium picrates are also presented in Fig. 1. The strong absorptions around 24 kK common to all three complexes should be assigned to the picrate ion. In the complexes with potassium and ammonium picrates, the maxima of the low-energy absorptions are located at 15.8 and 16.1 kK respectively; see the spectra, the ordinates for which are expanded. The results with all the donors are summarized in Table 1. An examination of the data for each picrate shows a hypsochromic shift going from *o*-dianisidine→*o*-tolidine→benzidine. This shift is nearly parallel to that of the charge-transfer absorption observed in the *s*-trinitrobenzene complexes. These pieces of spectroscopic evidence lead to the conclusion that the weak absorptions are due to a charge-transfer interaction between the diamine and the picrate. The weakness of the charge-transfer absorptions was noted also in Kofler's ternary complex and in a related one;[1] it now appear to be characteristic of the complexes with picrates.

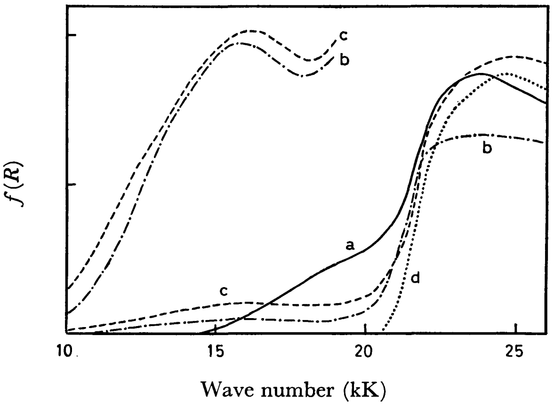

Fig. 1. Diffuse reflection spectra of the *o*-dianisidine complexes with (a) sodium picrate, (b) potassium picrate, (c) ammonium picrate, and (d) sodium picrate alone.

Table 1. The energies of the charge-transfer absorptions appeared in the solid diamine complexes with picrates (in kK)

Donor	Acceptor			
	Na picrate	K picrate	NH_4 picrate	*s*-Trinitrobenzene
None	24.8	23.7	24.2	—
Benzidine	*ca.* 20	16.6	17.0	19.0
o-Tolidine	*ca.* 19	15.8	16.7	17.6
o-Dianisidine	*ca.* 19	15.8	16.1	17.3[a]

a) The composition is known to be 1:2, see Ref. 3.

Although the charge-transfer absorption in the present solid complex is close to that in the corresponding *s*-trinitrobenzene complex, the location is somewhat affected by the kind of cation in the picrate. In Fig. 1, we see that the absorption maximum in the complex with sodium picrate appears at an energy higher by a few kK than that in the complex with potassium or ammonium picrate. This displacement may be, at least qualitatively, interpreted in terms of the polarization theory. The polarizing power of alkali ions is in the order of decreasing ionic radius: $K^+ > Na^+$. Consequently, the sodium ion in the crystal brings about an enhanced partial localization of the electron cloud of the picrate ion. Besides, the constancy of the absorption maximum in the three picrates implies that the lowest vacant orbital, with which the charge-transfer from the diamine is associated, becomes as unstable as the occupied orbital. Thus, the polarization of the picrate ion may account for the shift of the charge-transfer absorption toward the high-energy side. The ammonium ion is known to be a little larger when it rotates freely than the potassium ion. However, the present results suggest that the anion in the ammonium salt is slightly more polarized than that in the potassium salt.

Our finding is unique in the sense that the complex has an anion acting as an electron-acceptor. As early as 1910 Sudborough and Beard reported that potassium *o*-, *m*-, and *p*-aminobenzoates form deeply-colored molecular complexes with *s*-trinitrobenzene.[4] In addition, a black potassium α-anthranolate-*s*-trinitrobenzene complex with a 1 : 2 composition was isolated by Cadre and Sudborough.[5] More recently, several complexes containing the phenazinium ion and related ions were prepared.[6,7] Furthermore, there are some hydrocarbon complexes with tropylium bromide acting as an acceptor.[8] In the cases which have appeared so far in the literature, the complexes are of anionic donors and neutral acceptors or of neutral donors and cationic acceptors.

---

2) K. Abe, Y. Matsunaga, and G. Saito, This Bulletin, **41**, 2852 (1968).

3) J. J. Sudborough, *J. Chem. Soc.*, **109**, 1339 (1916).

4) J. J. Sudborough and S. H. Beard, *ibid.*, **97**, 773 (1910).

5) S. T. Cadre and J. J. Sudborough, *ibid.*, **109**, 1349 (1916).

6) H. Inoue, S. Hayashi, and E. Imoto, This Bulletin, **37**, 336 (1964).

7) A. Ray, A. V. Guzzo, and G. Tollin, *Biochim. Biophys. Acta*, **94**, 258 (1965).

8) S. N. Bhat and C. N. R. Rao, *J. Chem. Phys.*, **47**, 1863 (1967).