BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 629—630 (1973)

The Charge-transfer Complexes of Metal Chelates of 8-Quinolinol with 7,7,8,8-Tetracyanoquinodimethane

Shigeo KOIZUMI and Yôichi IIDA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

(Received June 15, 1972)

Although there have been a large number of charge-transfer complexes made of electron donors and acceptors,[1] there are few donor molecules that are known to be composed of organic metal chelates. In 1962 Melby *et al.* prepared an unusual (1: 1) complex between the copper chelate of 8-quinolinol, Cu(Ox)$_2$, and 7,7,8,8-tetracyanoquinodimethane, TCNQ.[2] Williams and Wallwork investigated the crystal and molecular structure of this complex in order to see whether or not the predominant factor influencing the orientation and packing of the molecules was the charge-transfer interaction between the donor of Cu(Ox)$_2$ and the acceptor of TCNQ.[3]

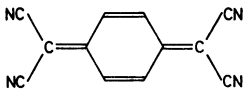

Fig. 1. 7,7,8,8-Tetracyanoquinodimethane (TCNQ).

The present paper will describe the (1: 1) complexes of the copper and palladium metal chelates of 8-quinolinol with TCNQ.[4] The measurements of the diffuse reflection spectra of these solid complexes were attempted in order to ascertain the charge-transfer transitions in the solid-state spectra. We will show that these complexes are essentially charge-transfer complexes, in which the metal chelates of 8-quinolinol act as electron donors, and TCNQ, as an acceptor. On the other hand, we reported earlier on the charge-transfer complexes of Cu(Ox)$_2$ and Pd(Ox)$_2$ with various halogen-substituted *p*-benzoquinones.[5,6] Therefore, the complexes of Cu(Ox)$_2$–TCNQ and Pd(Ox)$_2$–TCNQ are interesting in comparison with these charge-transfer complexes.

Experimental

The crystals of Cu(Ox)$_2$–TCNQ were prepared according to the method of Melby *et al.*[2] They were deposited when boiling solutions of the components in chloroform were mixed and allowed to cool very slowly. The Pd(Ox)$_2$–TCNQ complex was prepared in a way similar to that used for Cu(Ox)$_2$–TCNQ.

These complexes were pulverized and diluted with potassium bromide. The diffuse reflection spectra of the solid complexes were recorded as the difference in the reflectance between the mixture and pure potassium bromide by means of a Beckman DK-2A spectroreflectometer. The solid-state spectra were then obtained by plotting the diffuse reflection spectra using the Kubelka-Munk equation, $f(R)=(1-R)^2/2R$, in which R is the reflectance.

The Cu(Ox)$_2$-TCNQ Complex

According to Williams and Wallwork,[3] this complex crystallizes as black triclinic crystals (space group $P\bar{1}$), with one molecule of the complex in the unit cell. The component molecules are stacked in a plane-to-plane manner, so that the double bond adjacent to one dicyanomethylene group of TCNQ lies over the 5: 8 positions of one donor molecule, while the other double bond is similarly oriented with respect to the benzenoid ring of the centrosymmetrically-related donor molecule. The perpendicular separation of the molecules, in the region of overlap, is approximately 3.2 Å. These crystallographic features, although there appears to be a specific interaction between the dicyanomethylene group of TCNQ and the benzenoid group of the oxinate, are common in structures of the π-π charge-transfer type.

The solid-state spectrum of this complex (Fig. 2, Curve (a)) shows intense band peaks at 12.1 kK and 23.9 kK and a shoulder around 29.6 kK. The high-energy band at 23.9 kK and the shoulder around 29.6 kK arise mostly from the absorptions due to the component molecules, while the broad band at 12.1 kK appears in the low-energy region, where neither of the component molecules absorb. This low-energy band at 12.1 kK seems to be attributable to the charge-transfer transition from the donor of Cu(Ox)$_2$ to the acceptor of TCNQ for the following reasons. In the Cu(Ox)$_2$–*p*-chloranil charge-transfer complex, the corresponding band is located at 15.9 kK.[6,7] The electron

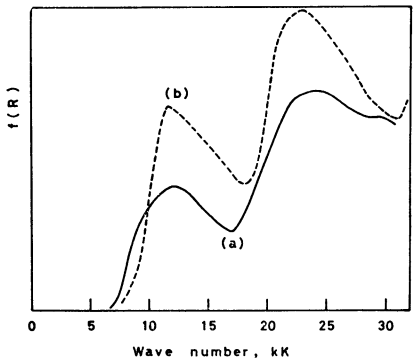

Fig. 2. The solid-state spectra of (a) Cu(Ox)$_2$-TCNQ and (b) Pd(Ox)$_2$–TCNQ.

1) G. Briegleb, "Elektronen-Donator-Acceptor Komplexe," Springer-Verlag, Berlin-Göttingen-Heidelberg (1961).

2) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

3) R. M. Williams and S. C. Wallwork, *Acta Crystallogr.*, **23**, 448 (1967).

4) The palladium chelate of 8-quinolinol is abbreviated as Pd(Ox)$_2$.

5) S. Koizumi and Y. Iida, This Bulletin, **44**, 1436 (1971).

6) Y. Iida, *ibid.*, **44**, 2564 (1971).

7) A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc.*, **1965**, 2579.

affinities of TCNQ and *p*-chloranil have been reported to be $E_A(\text{TCNQ})=1.7$ eV and $E_A(p\text{-chloranil})=1.3_7$ eV respectively.[8] If one assigns the band at 12.1 kK of the $Cu(Ox)_2$–TCNQ complex to the charge-transfer transition, the difference in the charge-transfer energies between these two complexes, $h\nu_{CT}(Cu(Ox)_2\text{–}p\text{-chloranil})-h\nu_{CT}(Cu(Ox)_2\text{–TCNQ})$, should be caused mostly by the difference in the electron affinities between TCNQ and *p*-chloranil. In accordance with this view, the observed value of $h\nu_{CT}(Cu(Ox)_2\text{–}p\text{-chloranil})-h\nu_{CT}(Cu(Ox)_2\text{–TCNQ})=0.47$ eV was found to agree almost exactly with $E_A(\text{TCNQ})-E_A(p\text{-chloranil})=0.3_3$ eV.

The $Pd(Ox)_2$-TCNQ Complex

The assignment of the band at 12.1 kK of the $Cu(Ox)_2$–TCNQ complex to the charge-transfer transition was confirmed by replacing the donor of $Cu(Ox)_2$ by $Pd(Ox)_2$. The ionization potential of $Pd(Ox)_2$ has been reported to be lower than that of $Cu(Ox)_2$ by 0.16 eV.[6,7] For the common acceptor of TCNQ, the difference in the ionization potentials of the donor molecules mainly causes the variation in the charge-transfer energies. Therefore, one can expect that the charge-transfer energy of $Pd(Ox)_2$–TCNQ will be lower than that of $Cu(Ox)_2$–TCNQ by that amount.

Figure 2, Curve (b), shows the observed solid-state spectrum of the $Pd(Ox)_2$–TCNQ complex. It has strong absorption band peaks at 11.6 kK and 22.8 kK and a slight shoulder around 32.0 kK. The high-energy band at 22.8 kK and the shoulder around 32.0 kK are attributable to the absorptions due to the component molecules. The energy value of the low-energy band at 11.6 kK of $Pd(Ox)_2$–TCNQ was found to be lower than that of $Cu(Ox)_2$–TCNQ by 0.06 eV. Therefore, although this energy difference is not sufficient, as is to be expected from the ionization potential difference between $Cu(Ox)_2$ and $Pd(Ox)_2$, one can also assign the low-energy band at 11.6 kK of the $Pd(Ox)_2$–TCNQ complex to the charge-transfer transition from the donor of $Pd(Ox)_2$ to the acceptor of TCNQ. On the other hand, the charge-transfer band of the $Pd(Ox)_2$–*p*-chloranil complex has been reported to be located at 14.8 kK.[6,7] Thus, the difference in the charge-transfer energies, $h\nu_{CT}(Pd(Ox)_2\text{–}p\text{-chloranil})-h\nu_{CT}(Pd(Ox)_2\text{–TCNQ})=0.40$ eV, was again found to agree well with $E_A(\text{TCNQ})-E_A(p\text{-chloranil})=0.3_3$ eV.

Discussion

The crystallographic features and also the marked appearance of the strong charge-transfer absorptions clearly show that the $Cu(Ox)_2$–TCNQ and $Pd(Ox)_2$–TCNQ complexes behave as usual π-π charge-transfer-type complexes. Bailey *et al.* have reported the virtual ionization potentials of the donors of $Cu(Ox)_2$ and $Pd(Ox)_2$ to be 7.3 eV and 7.1 eV respectively.[7] Their electron-donor strengths are of the order of pyrene or perylene in the series of aromatic hydrocarbons.[9] It is interesting to note that the electron-donor strengths of these metal chelates of 8-quinolinol are much influenced by the species of the central metal ions.

8) G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).
9) H. Kuroda, *Nature*, **201**, 1214 (1964).