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The Charge-transfer Complexes of Metal Chelates of 8-Quinolinol with Various Halogen-substituted *p*-Benzoquinones

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Much attention has been paid to a large number of charge-transfer complexes made from electron donors and acceptors.[1] However, there are few donor molecules that are known to be composed of organic metal chelates. In 1965 the charge-transfer complexes of 8-quinolinol and its copper, palladium, and nickel chelates with *p*-chloranil were first prepared by Bailey *et al.*[2] Recently, we have reported that bis(8-quinolinolato)palladium(II), (Pd(Ox)$_2$), and bis(8-quinolinolato)copper(II), (Cu(Ox)$_2$), form stable crystalline (1:1) charge-transfer complexes with 2,5-diazido-3,6-dichloro-1,4-benzoquinone and 2,5-diazido-3,6-dibromo-1,4-benzoquinone.[3]

In the present work, we found that Pd(Ox)$_2$ and Cu(Ox)$_2$ can also form stable crystalline (1:1) charge-transfer complexes with various halogen-substituted *p*-benzoquinones. Measurements of the diffuse reflection spectra of these solid complexes were attempted in order to study the charge-transfer interaction between the metal chelates of 8-quinolinol and the halogen-substituted *p*-benzoquinones.

The following crystalline complexes were prepared according to a method similar to that described by Bailey *et al.*[2]: Pd(Ox)$_2$-*p*-Bromanil, Pd(Ox)$_2$-*p*-Iodanil, Pd(Ox)$_2$-*p*-QBr$_2$Cl$_2$,[4] Pd(Ox)$_2$-*p*-QBr$_3$Cl,[4] Cu(Ox)$_2$-*p*-Bromanil, Cu(Ox)$_2$-*p*-Iodanil, Cu(Ox)$_2$-*p*-QBr$_2$Cl$_2$, and Cu(Ox)$_2$-*p*-QBr$_3$Cl. The complexes were pulverized and diluted with potassium bromide. The diffuse reflection spectra of these complexes were recorded as the difference in the reflectance between the mixture and pure potassium bromide, as determined 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 Pd(Ox)$_2$ Complexes

The solid-state spectrum of the Pd(Ox)$_2$-*p*-Bromanil complex (Fig. 1, Curve a) shows the band peaks at 14.6 kK and 23.5 kK and a shoulder around 29 kK. The band at 23.5 kK and the shoulder arise from the absorptions due to the component molecules, while the band at 14.6 kK appears in the low-energy region, where neither of the component molecules are absorbed. The value for this low-energy band was found to be close to that for the band of the Pd(Ox)$_2$-*p*-Chloranil complex at 14.8 kK, which Bailey *et al.* assigned to the charge-transfer transition from Pd(Ox)$_2$ to *p*-chloranil. Therefore, the band at 14.6 kK for the Pd(Ox)$_2$-*p*-Bromanil complex is also attributable to the charge-transfer transition from Pd(Ox)$_2$ to *p*-bromanil. These results seem to indicate that the electron affinity for *p*-bromanil is almost the same as that for *p*-chloranil. Since the molecular sizes and the shapes of these acceptors are almost identical, the crystal structure of the Pd(Ox)$_2$-*p*-Bromanil complex may be similar to that of the Pd(Ox)$_2$-*p*-Chloranil complex determined by Kamenar *et al.*[5]

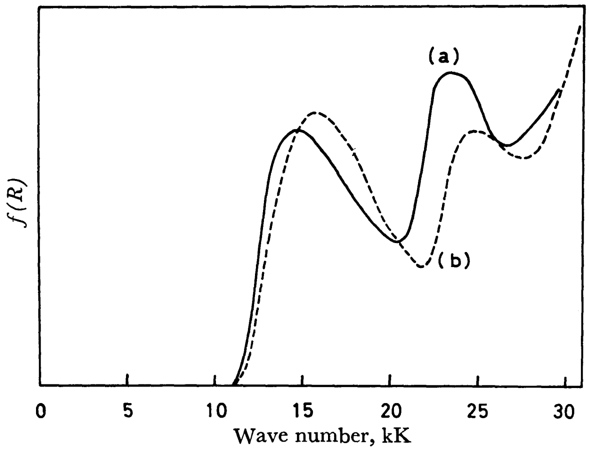

Fig. 1. The solid-state spectra of (a) Pd(Ox)$_2$-*p*-Bromanil and (b) Cu(Ox)$_2$-*p*-Bromanil.

The spectroscopic features for the complexes of Pd(Ox)$_2$ with the other halogen-substituted *p*-benzoquinones are quite analogous to that for the Pd(Ox)$_2$-*p*-

TABLE 1. THE SPECTROSCOPIC DATA ON THE MAXIMUM POSITIONS OF THE CHARGE-TRANSFER BANDS (in unit of 10^3 cm^{-1})

Acceptor	Pd(Ox)$_2$	Cu(Ox)$_2$
p-Chloranil	14.8[a]	15.9[a]
p-Bromanil	14.6	15.9
p-Iodanil	14.3	15.7
p-QBr$_2$Cl$_2$	14.8	16.0
p-QBr$_3$Cl	14.8	16.0

a) Ref. 2.

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

[2] A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc.*, **1965**, 2579.

[3] S. Koizumi and Y. Iida, This Bulletin, **44**, 1436 (1971).

[4] 2,5-Dibromo-3,6-dichloro-1,4-benzoquinone and tribromomonochloro-*p*-benzoquinone are abbreviated as *p*-QBr$_2$Cl$_2$ and *p*-QBr$_3$Cl respectively.

[5] The crystal structure of the Pd(Ox)$_2$-*p*-Chloranil complex has a triclinic symmetry. The planar Pd(Ox)$_2$ and *p*-chloranil molecules, which are alternately stacked, are arranged in planes approximately parallel to the crystallographic (111) plane. See B. Kamenar, C. K. Prout, and J. D. Wright, *J. Chem. Soc.*, **1965**, 4851.

Bromanil complex or for the Pd(Ox)$_2$-*p*-Chloranil complex. The energy values for the charge-transfer bands of the complexes are collected in Table 1. Table 1 shows that the charge-transfer-band positions for the Pd(Ox)$_2$ complexes, practically, do not depend on the acceptors now under investigation. This means that the electron affinities of these halogen-substituted *p*-benzoquinones are very similar to one another.

The Cu(Ox)$_2$ Complexes

The solid-state spectrum of the Cu(Ox)$_2$-*p*-Bromanil complex (Fig. 1, Curve b) shows the band peaks at 15.9 kK and 25.0 kK, and a shoulder around 30 kK. The low-energy band at 15.9 kK can also be assigned to the charge-transfer transition from Cu(Ox)$_2$ to *p*-bromanil; this energy value was found to be in good coincidence with the value for the Cu(Ox)$_2$-*p*-Chloranil complex (15.9 kK).[2] However, we can see that the charge-transfer energy for the Cu(Ox)$_2$-*p*-Bromanil complex is larger than that for the Pd(Ox)$_2$-*p*-Bromanil complex by 1.3 kK. For a common acceptor, the variation in the charge-transfer energy arises mostly from the difference in the ionization potentials of the donor molecules. Therefore, it seems that the ionization potential of Cu(Ox)$_2$ is higher than that of Pd(Ox)$_2$ by about 1.3 kK.

The spectroscopic features of the complexes of Cu(Ox)$_2$ with the other halogen-substituted *p*-benzoquinones are found to be quite similar to those of the Cu(Ox)$_2$-*p*-Bromanil complex. The charge-transfer bands of the complexes are given in Table 1.

Discussion

The solid-state spectra clearly indicate that the ionization potential of a metal chelate of 8-quinolinol is much affected by the species of the central metal ion. The ionization potential of Cu(Ox)$_2$ is appreciably larger than that of Pd(Ox)$_2$. For the above four acceptors, the magnitude of this difference is estimated to be 1.3 ± 0.2 kK (0.16 ± 0.025 eV).

Bailey *et al.* examined the charge-transfer complexes of Cu(Ox)$_2$, Pd(Ox)$_2$ and various aromatic hydrocarbons with common acceptors and compared their charge-transfer energies.[2] By the use of the relationship between the charge-transfer-band energies and the ionization potentials of the donors, they proposed that the values for the ionization potentials of Cu(Ox)$_2$ and Pd(Ox)$_2$ were 7.3 eV and 7.1 eV respectively.[2] The difference in the ionization potentials between Cu(Ox)$_2$ and Pd(Ox)$_2$ is 0.2 eV, which is in good agreement with the value determined by the present investigation.