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The Charge-transfer Complexes of Metal Chelates of 8-Hydroxyquinoline with 2,5-Diazido-3,6-dichloro-1,4-benzoquinone and 2,5-Diazido-3,6-dibromo-1,4-benzoquinone

Shigeo Koizumi and Yôichi Iida
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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Charge-transfer complexes made from electron donors and acceptors have been studied extensively.[1] However, there are few donor molecules that are known to be composed of organic metal chelates. In 1965 Bailey *et al.* prepared the charge-transfer complexes of 8-hydroxyquinoline and its copper, palladium, and nickel chelates with various electron acceptors.[2] Bis(8-hydroxyquinolinato)palladium(II) ($Pd(Ox)_2$) and bis(8-hydroxyquinolinato)copper(II) ($Cu(Ox)_2$) are known to form stable crystalline (1:1) complexes with *p*-chloranil and *p*-bromanil.

On the other hand, the electron-accepting properties of 2,5-diazido-3,6-dichloro-1,4-benzoquinone (p-$Q(N_3)_2Cl_2$), one of the derivatives from *p*-chloranil, have been recently reported by Koizumi and Matsunaga.[3] In the present experiment, we found that $Pd(Ox)_2$ and Cu-

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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. Matsunaga, This Bulletin, **43**, 3010 (1970).

Table 1. The elementary analysis data on the charge-transfer complexes used for this study

Donor	Acceptor	Found (%) C	Found (%) H	Found (%) N	Calcd[a] (%) C	Calcd[a] (%) H	Calcd[a] (%) N
$Pd(Ox)_2$	p-$Q(N_3)_2Cl_2$	43.20	1.85	17.96	44.01	1.85	17.14
$Cu(Ox)_2$	p-$Q(N_3)_2Cl_2$	47.16	2.31	18.10	47.14	1.98	18.32
$Pd(Ox)_2$	p-$Q(N_3)_2Br_2$	37.92	1.70	14.16	38.82	1.62	15.09
$Cu(Ox)_2$	p-$Q(N_3)_2Br_2$	41.12	2.04	15.29	41.19	1.73	16.01

a) The value calculated for the (1:1) complex.

$(Ox)_2$ can also form stable crystalline (1:1) charge-transfer complexes with p-$Q(N_3)_2Cl_2$ and p-$Q(N_3)_2Br_2$.[4] We shall examine the solid-state spectra of these complexes in order to study the charge-transfer interaction between $M(Ox)_2$ and p-$Q(N_3)_2X_2$, where M=Pd or Cu and where X=Cl or Br. The charge-transfer spectra of these complexes are interesting in comparison with those of the complexes of the same metal chelates with p-chloranil or p-bromanil.

Experimental

Four crystalline complexes were prepared according to a method similar to that described by Bailey *et al.*.[2]; $Pd(Ox)_2$-p-$Q(N_3)_2Cl_2$, $Cu(Ox)_2$-p-$Q(N_3)_2Cl_2$, $Pd(Ox)_2$-p-$Q(N_3)_2Br_2$, and $Cu(Ox)_2$-p-$Q(N_3)_2Br_2$. For each of these compounds, the mole ratio of the donor to the acceptor was determined to be (1:1) on the basis of the elementary analysis; the results of this analysis are given in Table 1.

The complexes were pulverized and diluted with sodium chloride. The diffuse reflection spectra of these complexes were recorded as the difference in reflectance between the mixture and pure sodium chloride 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.

Results

The p-*$Q(N_3)_2Cl_2$ Complexes.* The solid-state spectrum of the $Pd(Ox)_2$-p-$Q(N_3)_2Cl_2$ complex (Fig. 1, Curve a) shows band peaks at 29.0 kK, 22.6 kK, and 14.7 kK. The high-energy bands at 29.0 kK and 22.6 kK arise mostly from the absorptions due to the component molecules, while the band at 14.7 kK appears in the low-energy region where neither of the component molecules absorbs. The value for this low-energy band was found almost to coincide with that for the band at 14.8 kK of the $Pd(Ox)_2$-p-Chloranil complex, which Bailey *et al.* assigned to the charge-transfer transition from $Pd(Ox)_2$ to p-chloranil.[2] Therefore, the band at 14.7 kK for the $Pd(Ox)_2$-p-$Q(N_3)_2Cl_2$ complex is attributable to the charge-transfer transition from $Pd(Ox)_2$ to p-$Q(N_3)_2Cl_2$. Judging from these results, the electron affinity for p-$Q(N_3)_2Cl_2$ seems to be essentially the same as that for p-chloranil. Since the molecular sizes and the shapes of these acceptors are almost alike, the crystal structure of the $Pd(Ox)_2$-p-$Q(N_3)_2Cl_2$ complex may be similar to that of the $Pd(Ox)_2$-p-Chloranil complex as determined by Kamenar *et al.*[5]

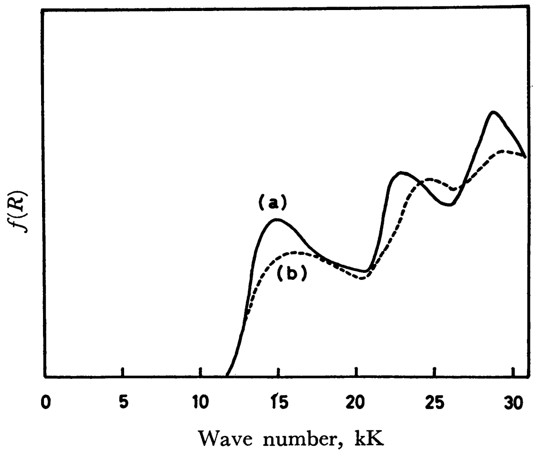

Fig. 1. The solid-state spectra of (a) $Pd(Ox)_2$-p-$Q(N_3)_2Cl_2$ and (b) $Cu(Ox)_2$-p-$Q(N_3)_2Cl_2$.

On the other hand, the solid-state spectrum of the $Cu(Ox)_2$-p-$Q(N_3)_2Cl_2$ complex (Fig. 1, Curve b) shows band peaks at 29.3 kK, 24.6 kK, and 16.0 kK. The low-energy band at 16.0 kK can also be assigned to the charge-transfer transition from $Cu(Ox)_2$ to p-$Q(N_3)_2Cl_2$; this energy value was found to be close to the 15.9 kK value for the $Cu(Ox)_2$-p-Chloranil complex.[2] It is

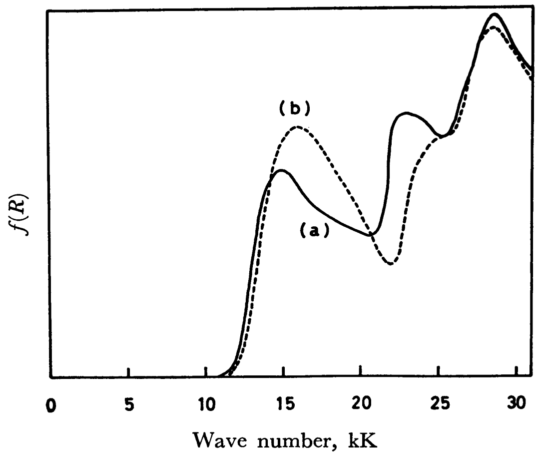

Fig. 2. The solid-state spectra of (a) $Pd(Ox)_2$-p-$Q(N_3)_2Br_2$ and (b) $Cu(Ox)_2$-p-$Q(N_3)_2Br_2$.

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[4] The acceptor of 2,5-diazido-3,6-dibromo-1,4-benzoquinone is abbreviated as p-$Q(N_3)_2Br_2$.

[5] According to an X-ray diffraction study by Kamenar *et al.*, the crystal structure of the $Pd(Ox)_2$-p-Chloranil complex has the 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.*, 4851 (1965).

important to note that the charge-transfer energy for the $Cu(Ox)_2$-*p*-$Q(N_3)_2Cl_2$ complex is larger than that for the $Pd(Ox)_2$-*p*-$Q(N_3)_2Cl_2$ complex by 1.3 kK. For a common acceptor, the great variation in the charge-transfer energy will arise from a difference in the ionization potentials of the donors. Therefore, the ionization potential of $Cu(Ox)_2$ seems to be higher than that of $Pd(Ox)_2$ by about 1.3 kK.

The p-*$Q(N_3)_2Br_2$ Complexes.* The solid-state spectrum of the $Pd(Ox)_2$-*p*-$Q(N_3)_2Br_2$ complex (Fig. 2, Curve a) shows high-energy bands at 28.6 kK and 22.9 kK, and a low-energy charge-transfer band at 14.8 kK. It is interesting to see that the charge-transfer energy for this complex coincides with that of 14.8 kK for the $Pd(Ox)_2$-*p*-Bromanil complex.[6] This leads to a value of the electron affinity for *p*-$Q(N_3)_2Br_2$ close to that for *p*-bromanil.

The $Cu(Ox)_2$-*p*-$Q(N_3)_2Br_2$ complex gives a solid-state spectrum (Fig. 2, Curve b) composed of a high-energy band at 28.3 kK, a shoulder at 25.0 kK, and a low-energy charge-transfer band at 15.9 kK. The energy difference in the charge-transfer transitions between the $Cu(Ox)_2$-*p*-$Q(N_3)_2Br_2$ and $Pd(Ox)_2$-*p*-$Q(N_3)_2Br_2$ complexes was found to be 1.1 kK, which is in good accordance with the 1.3 kK value for the energy difference in the charge-transfer transitions between the $Cu(Ox)_2$-*p*-$Q(N_3)_2Cl_2$ and $Pd(Ox)_2$-*p*-$Q(N_3)_2Cl_2$ complexes.

Discussion

The above-mentioned results on the solid-state spectra clearly indicate that the electron affinities of *p*-$Q(N_3)_2Cl_2$ and *p*-$Q(N_3)_2Br_2$ are essentially the same as those of *p*-chloranil and *p*-bromanil respectively. The azido group thus appears to be as effective as the chlorine or bromine substituent in improving the acceptor strength of *p*-benzoquinone. This conclusion is in good agreement with that given previously by Koizumi and Matsunaga.[3]

On the other hand, the ionization potential of a metal chelate of 8-hydroxyquinoline is very much affected by the species of the central metal ion. This was shown as an appreciable difference in the ionization potentials of $Cu(Ox)_2$ and $Pd(Ox)_2$. Moreover, we examined what kind of metal chelates of 8-hydroxyquinoline can form charge-transfer complexes with *p*-$Q(N_3)_2X_2$, where X=Cl or Br. The preparation of the charge-transfer complexes of $Cd(Ox)_2$, $Hg(Ox)_2$, $Mn(Ox)_2$, and $Ni(Ox)_2$ with *p*-$Q(N_3)_2X_2$ in various solvents was attempted for this purpose. However, no such crystalline compounds could be obtained from these metal chelates.[7] In view of these results, we can see that, for the metal chelates of 8-hydroxyquinoline, not only the magnitude of the ionization potential but also the ability of the formation of the charge-transfer complexes is strongly dependent on the species of the central metal ions.

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[6] Y. Iida, unpublished work.

[7] Although a slight complex formation was detected with $Ni(Ox)_2$, the pure solid charge-transfer complex was not isolated, presumably because of the very poor solubility of $Ni(Ox)_2$ in the suitable solvents.