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Copper(I) Chloride Complex Containing *p*-Benzoquinone as a Ligand

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A new complex $[(NH_4)Cu_3Cl_4(C_6H_4O_2)_{3/2}\cdot H_2O]$ was synthesized from $CuCl_2$, hydroquinone, and NH_4Cl in an aqueous solution, and its structure was characterized on the bases of its UV, IR, and ESR spectra and TGA. On heating, this complex was stable up to 100 °C, but above 120 °C *p*-benzoquinone was released quantitatively. The complex was found to be a polynuclear copper(I) complex containing *p*-benzoquinone molecules and chlorides as ligands, and to be a charge-transfer complex in which π-electrons of the ring carbons of *p*-benzoquinone form coordinate bonds with Cu(I). The formation process of the complex was:

$$3CuCl_2 + 3/2(C_6H_6O_2) + H_2O + NH_4Cl = (NH_4)Cu_3Cl_4(C_6H_4O_2)_{3/2}\cdot H_2O + 3HCl$$

Deep red crystals are inadvertently obtained when $CuCl_2$, hydroquinone, and NH_4Cl are mixed in an aqueous solution. They were found to be a new-type Cu(I) complex, $[(NH_4)Cu_3Cl_4(C_6H_4O_2)_{3/2}\cdot H_2O]$ (to be called BQ-Red hereafter), in which the π-electrons of *p*-benzoquinone form coordinate bonds with Cu(I).

A complex containing a ligand of *p*-benzoquinone has been synthesized by Hashimoto *et al.*[1] In this complex, both of the oxygen atoms of *p*-benzoquinone are coordinated to Cu(I). The IR spectrum of BQ-Red, however, indicates that the oxygens can not be the donor atoms, because the shift of the C=O stretching absorption caused by complexation is only 8 cm^{-1}.

The aim of this paper is to describe a method for synthesizing this interesting complex and its chemical and spectral characteristics. The information obtained from the latter is all in harmony with its structure, which was recently established by an X-ray diffraction study.† The reaction mechanism for the formation of BQ-Red will also be discussed.

Experimental

Materials. The reagents, $CuCl_2$, hydroquinone, and NH_4Cl (Wako special grade), were used without further purification. All the solvents used were purified by repeated distillations.

Apparatus. The IR spectra were taken with Hitachi perkin Elmer Model 125(4000—400 cm^{-1}) and JASCO DS-403G grating(600—200 cm^{-1}) spectrometers. The ESR spectra were measured with a JEOL, Model JES-3BSX, X-band spectrometer. The UV and visible spectra were obtained with a Hitachi EPS-2U spectrometer. The TG and DTA measurements were carried out using a Rigaku denki DPA-001D apparatus, with α-alumina as the standard and in a quartz cell. The elemental analysis of C, H, and N was carried out by means of an auto CHN corder, Model MT-2(Yanagimoto).

Synthesis. NH_4Cl, $CuCl_2$, and hydroquinone were mixed in an aqueous solution. The total concentration of the three components in 100 ml was kept constant(2 M), while the molar ratios of the three were varied as is shown in Fig. 1. Deep red crystals separated out from the solution when 5 M NaOH (10—20 ml) was slowly added to the mixed solution with constant stirring. The crystals were obtained only when the molar ratio of the components lay inside the enclosed area shown by a dotted line (Fig. 1); no red crystals were formed outside of this area. This indicates that the formation of the red crystals depends mainly upon the amount of hydroquinone. When the amount of hydroquinone was smaller than the theoretical one (△), red crystals were easily formed. All the red crystals thus formed has the same composition. The molar ratio at which the largest amount of red crystals(BQ-Red) was formed was, $CuCl_2$: hydroquinone: NH_4Cl=3 : 1 : 1.

BQ-Red is soluble only in aqueous NH_4Cl, and the higher the concentration of NH_4Cl, the better it dissolves. The solution is reddish orange. On the other hand, when the concentration of NH_4Cl is less than 2 M, it is hardly soluble, and it decomposes gradually, forming a yellow solution after 20—30 min. In water, BQ-Red decomposes at once and becomes greenish, with the formation of $CuCl_2$. In methanol, the crystals become white CuCl, and a similar but partial decomposition occurs either in ethanol or in acetone. In 1-pentanol, benzene, ligroin, ether, or petroleum ether, however, the crystals are stable and remain deep red. Since no solvent for the recrystallization was found, the sample of BQ-Red for the analyses was purified by scrubbing it with 1-pentanol and with ether to remove all unreacted substances. Deep-red crystalline plates of BQ-Red were obtained in this way.

Analysis. The copper was determined by titrating it with EDTA after decomposition with a mixture of nitric

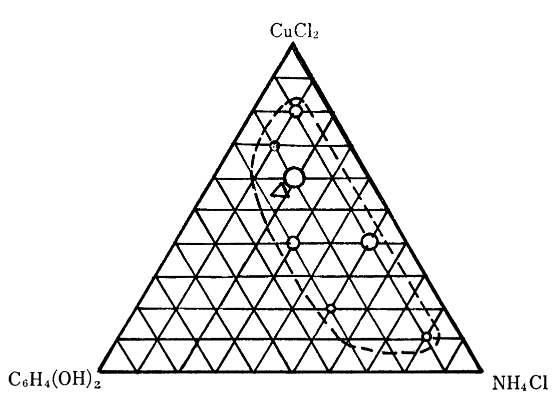

Fig. 1. Molar ratio of the three components for the formation of BQ-Red.
$[Cu]+[C_6H_4(OH)_2]+[NH_4]=2.0$ M.
△: Theoretical value of BQ-Red, Cu:$C_6H_4(OH_2)$: NH_4Cl=6 : 3 : 2.
○: Formation of BQ-Red (size of the circle indicates the amount of BQ-Red formed).

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† A schematic drawing of the established structure of BQ-Red is shown in Fig. A. The details of this X-ray study will be published elsewhere: H. Yamaguchi, T. Uechi, and I. Ueda, manuscript in preparation.

Table 1. Thermogravimetric analysis of BQ-Red

	(I) in air		(II) in Ar		Calcd		State
	Temp (°C)	Weight loss (%)	Temp (°C)	Weight loss (%)	Weight loss (%)		
(A)	25	0	25	0	0		$Cu_3Q_{3/2}NH_4Cl_4H_2O$
(B)	103	29.3	100	28.1	30.6	$-Q_{3/2}$	$Cu_3Cl_3NH_4ClH_2O$
(C)	230	33.6	232	34.0	34.0	$-H_2O$	$(CuCl)_3NH_4Cl$
(D)	390	35.6	270	37.7	37.0	$-NH_3$	$(CuCl)_3HCl$
(E)	450	41.6	—	—	43.9	$-HCl$	$(CuCl)_3$
(F)	540	53.2	—	—	54.9	$-Cl_3+O_3$	3 (CuO)
(G)	—	—	595	83.9	81.7	$-(CuCl)_2$	(CuCl)
					or 82.0	$-Cl_3-Cu_{3/2}$	$(Cu_{3/2})$

Q: $(C_6H_4O_2)$

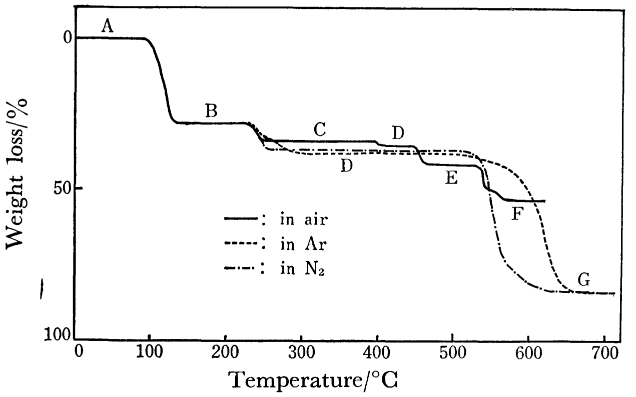


Fig. 2. TG curves of BQ-Red.

acid and perchloric acid(3 : 1).[5] The chlorine was also determined by chelate titration, after the decomposition of the BQ-Red by the Schöniger method[6] and the absorption of the evolved chlorine gas into a basic H_2O_2 solution.[7] Found: C, 20.06; H, 2.31; N, 2.62; Cl, 29.68; Cu, 35.71%. Calcd for $C_9H_{12}NCl_4O_4Cu_3$: C, 20.36; H, 2.26; N, 2.64; Cl, 26.73; Cu, 35.94%.

Results and Discussion

ESR Spectrum (Solid State). The ESR spectra of BQ-Red and $CuCl_2\cdot 2H_2O$ in the solid state were measured. Since the intensities of the obtained spectra depend upon the content of Cu(II), the content of Cu(II) in BQ-Red could be estimated from the data; it was found to be about fiftieth of the total amount of copper in BQ-Red. Thus, the copper in BQ-Red is present as a univalent ion, and BQ-Red appears to be a charge-transfer complex.

Thermogravimetric Analysis. BQ-Red decomposes, with the sublimation of the yellow crystals of *p*-benzoquinone, leaving a green copper salt, within a month at room temperature in the summer. When BQ-Red is heated, the yellow crystals of *p*-benzoquinone sublime from it at about 100 °C. Figure 2 and Table 1 show the TG curves and related data. Experiment (I) was performed in air, and (II), under flowing argon. Both sets of data show that *p*-benzoquinone sublimes endothermically at about 100 °C and that the lattice water is then lost at about 230 °C.

In air (I), the ammonium cation is lost as ammonia at about 390 °C and the chloride anion is lost as HCl at about 450 °C endothermically, and finally stable CuO (F) is obtained.

Table 2. IR spectra of BQ-Red and *p*-benzoquinone

BQ-Red (cm^{-1})	*p*-Benzoquinone (cm^{-1})	Assignment
3500	—	ν(OH) lattice water
3140	—	$\nu(NH_4)$
—	3070	ν(CH)
3015	—	$\nu(NH_4)$
1669	—	$\delta_d(NH_4)$
1647	1655	ν(C=O)
1476	1592	ν(C=C)
1400	—	$\delta_d(NH_4)$
1288	1308	$\delta(CH_2)$ in
1056	1084	$\delta(CH_2)$ in
869	892	$\delta(CH_2)$ out

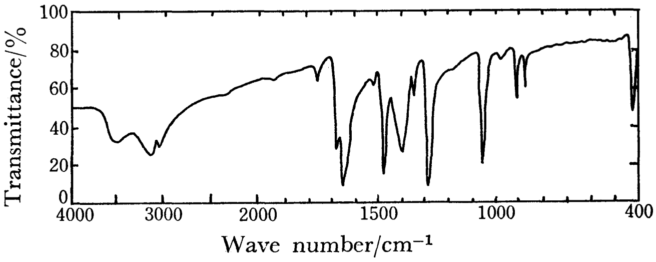


Fig. 3. IR spectrum of BQ-Red.

Under an inert gas, Ar (II), however, these two steps are indistinct, and the weight loss of 37.7% at the (D) point indicates that a compound with the composition of $(Cu_3Cl_3)\cdot HCl$ is formed; this compound remains stable between 270 and 595 °C. Then, at 595 °C, the weight loss suddenly increases until it becomes constant (83.9%, that is, 16.1% of the initial weight of BQ-Red); thereafter, it does not change until 800 °C. In N_2 gas, the TG curve is similar to that obtained in Ar, as is shown in Fig. 2, and the final weight of BQ-Red is 16.1% of the initial weight of BQ-Red, too. Under the inert gases, the final compound probably changes to elementary copper, corresponding to 1/2 of the initial copper content, while the rest sublimes away as chlorides.

Thus, the TG data can be explained in terms of the $[(NH_4)Cu_3Cl_4(C_6H_4O_2)_{3/2}\cdot H_2O]$ formula.

Infrared Spectrum. The IR spectrum of BQ-Red is shown in Fig. 3, while the assignments are sum-

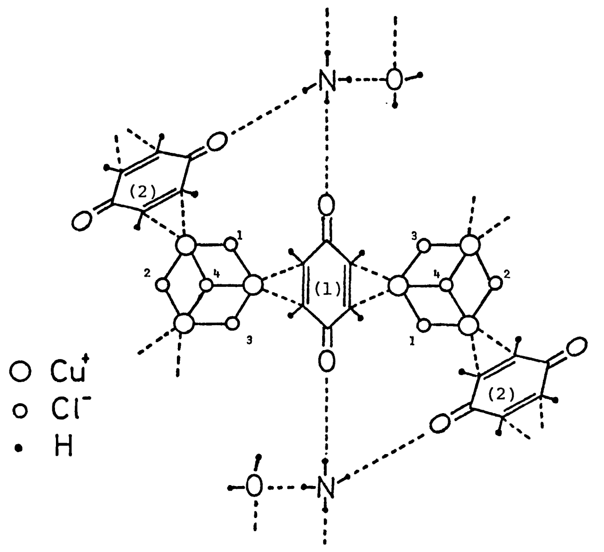


Fig. A. Schematic drawing of the molecular structure of BQ-Red.
$[(NH_4)Cu_3Cl_4(C_6H_4O_2)_{3/2}\cdot H_2O]_{2n}$.

marized in Table 2. Many bands of BQ-Red are similar to those of *p*-benzoquinone; this indicates that the starting material, hydroquinone, changes to *p*-benzoquinone upon the formation of BQ-Red. In the spectrum of BQ-Red, the C=C stretching band of *p*-benzoquinone (1592 cm^{-1}) shifts to 1476 cm^{-1}. It is interesting to note that this kind of shift to lower frequencies is more remarkable in Pt complexes.[8] For example, the C=C stretching frequency of the asymmetrical olefins observed at about 1600 cm^{-1} shifts to 1504 cm^{-1} in $K[PtCl_3(C_3H_6)]H_2O$,[9] although C=C bands of symmetrical olefins are not observed even in such complexes as $K[PtCl_3(C_2H_4)]H_2O$. This suggests that the C=C of the *p*-benzoquinone in BQ-Red is asymmetrically coordinated to Cu. In fact, the results of the X-ray structural analysis shown in Fig. A show clearly that the *p*-benzoquinone(1) has a symmetrical, but *p*-benzoquinone(2) has an asymmetrical, interaction with NH_4^+; this fact may cause some resemblance between them and symmetrical and asymmetrical olefins respectively.

On the other hand, the shift of the C=O stretching absorption caused by complexation is only 8 cm^{-1} in BQ-Red. It can thus easily be deduced that the oxygen atoms of the carbonyl groups of *p*-benzoquinone are not coordinated to Cu(I), but only make hydrogen bonds with NH_4^+. This agrees with the fact that BQ-Red readily decomposes to give *p*-benzoquinone when heated.

In addition, the intensities of the IR bands due to C–H [in-plane(1308, 1084 cm^{-1}) and out-of-plane(892 cm^{-1})] are almost equal to each other in *p*-benzoquinone, but in BQ-Red those of the latter (899 and 869 cm^{-1}) are much weaker than those of the former (1288 and 1056 cm^{-1}). Thus, in the crystals of BQ-Red, the *p*-benzoquinone molecules are arranged in a certain order, so that in-plane deformation vibration is promoted and out-of-plane deformation vibration is disturbed.

The bands of water and the ammonium cation in BQ-Red are clearly observed, as is shown in Fig. 3 and Table 2.

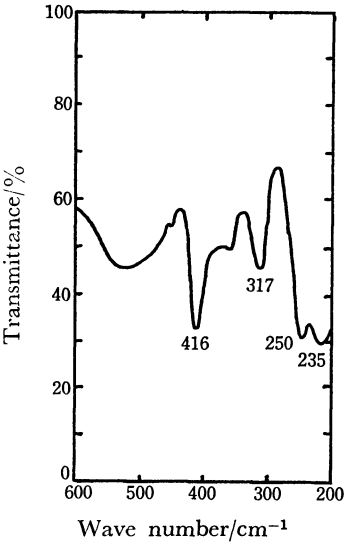


Fig. 4. Far-IR spectrum of BQ-Red.

Far-infrared Spectrum. The characteristic band of a chloride anion bridging two metals is generally observed between 150—350 cm^{-1}, and it is slightly split into two strong bands. It is known[10] that the wave number of the stretching frequency of the bridging chloride, $\nu(M\text{–}Cl)_b$, is lower than that of terminal chloride, $\nu(M\text{–}Cl)_t$. The far-IR spectrum of BQ-Red is shown in Fig. 4. The absorption bands at 235 and 250 cm^{-1} can be assigned to those of $\nu(Cu\text{–}Cl)_b$, and the band at 317 cm^{-1}, to that of $\nu(Cu\text{–}Cl)_t$. Since the former bands are stronger than the latter, most of the chloride ions seem to be combined directly with two Cu atoms. However, the structure shown in Fig. A has no terminal chloride. Since the central Cl(4) is different from the other three (1, 2, and 3) in coordinate number, the band at 317 cm^{-1} may be assigned to the vibration of the central Cl(4).

The band at 416 cm^{-1} is due to the skeletal vibration of *p*-benzoquinone.

UV and Visible Spectra. The spectra of BQ-Red, *p*-benzoquinone, and hydroquinone in 4 M NH_4Cl solutions were also observed. The *p*-benzoquinone is characterized by maxima at 246 nm ($\log \varepsilon=3.95$) and 428 nm ($\log \varepsilon=1.4$), while hydroquinone is characterized by maxima at 222 nm and 290 nm. The spectrum of BQ-Red in the solution has maxima at 246 nm ($\log \varepsilon'=3.8$), 275 nm (shoulder, $\log \varepsilon'=3.3$), 438 nm ($\log \varepsilon'=2.5$), and 800 nm ($\log \varepsilon'=1.6$); this indicates that BQ-Red forms *p*-benzoquinone in solution. However, the red shift of the maximum at 428 nm and the presence of a shoulder at 275 nm suggest the interactions of *p*-benzoquinone with NH_4^+ and H_2O, which are in both the molecule and the solvent.

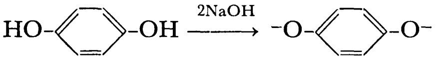
Molecular Structure. Since copper in BQ-Red is univalent, a tetrahedral arrangement of ligands like that in other Cu(I) complexes seems most probable;[11–13] this expectation conforms to the results of the X-ray analysis (Fig. A).

It is known that the coordination number of Cl is usually 1[11,14] or 2.[15] Moreover, Cu(I) complexes with a three-coordinate chloride,[13] and a complex (Cu_4Cl_4)[12] with two two-coordinate and two three-coordinate chlorides, have been reported. However, BQ-Red is different from those reported previously,[11-15] for it contains three two-coordinated and one three-coordinated chlorides.

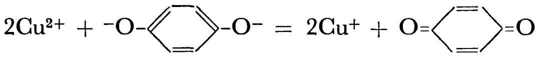
Although the oxygen of the carbonyl group is usually one of the well-known donor atoms, in this complex the π-electrons of the ring carbons of *p*-benzoquinone coordinate to Cu(I) as was reported in the case of a duroquinone complex,[16] in which the π-electrons of $C=C$ of duroquinone coordinate to Ni(II). The coordination of the π-electron of $C=C$ with Cu(I) has often been reported in aromatic complexes;[17-20] for example, the $(C_6H_6)[Cu(OSO_2CF)]_2$ complex[18] is stable up to 100 °C.

Thus, it is established that π-complexing occurs in BQ-Red, though little has been reported with regard to the fact that the copper(I) is π-bonded to a *p*-benzoquinone ring.[21]

Reaction Mechanism. The hydroquinone which is added as a starting material in the synthesis changes to *p*-benzoquinone in the complex formation, but no BQ-Red is formed when *p*-benzoquinone is used instead of hydroquinone, and Cu(II) changes to Cu(I). Thus, the formation process of BQ-Red is:



(1)



(2)

Then, three Cu(I) ions and three chloride ions make a ring:

$$3Cu^+ + 3Cl^- = \text{Ring } (\text{-Cu-Cl-})_3 \quad (3)$$

As $Cu^+(d^{10})$ favors sp^3-hybridization, each Cu(I) accepts an electron pair from a *p*-benzoquinone around it and also combines with another chloride which is located at a center of the crown like ring (Cu_3Cl_3) (*cf.* Fig. A) to give a stable tetrahedral coordination structure:

$$\text{Ring } (Cu_3Cl_3) + NH_4Cl = (Cu_3Cl_3)Cl^- \cdot NH_4^+ \quad (4)$$

Thus, the overall reaction is:

$$3CuCl_2 + 3/2\, C_6H_4(OH)_2 + H_2O + NH_4Cl = \text{BQ-Red} + 3HCl \quad (5)$$

References

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21) The fact that BQ-Red is a polymer, as is shown in Fig. A, agrees with the finding that BQ-Red is insoluble in any common solvent. The volumes of the holes in a polymer which is packed with so many molecules and ions (such as *p*-benzoquinone, Cu_3Cl_3, H_2O, NH_4^+, and Cl^-) may reasonably be said to be similar to those of the NH_4^+ and Cl^- ions; this may be the reason why it is easily soluble only in an aqueous NH_4Cl solution.