The Crystal and Molecular Structure of the Copper(I) Chloride Complex Containing *p*-Benzoquinone as a Ligand

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The crystal and molecular structure of the red compound, $[(NH_4)Cu_3Cl_4(C_6H_4O_2)_{1.5}\cdot H_2O]$, has been determined from 2115 X-ray diffraction data collected on an automated four-circle diffractometer. The crystals are monoclinic, with space group $P2_1/c$, and with four formula units in a unit cell of dimensions; $a=7.308(5)$, $b=11.593(7)$, $c=18.359(9)$ Å, and $\beta=90.16(3)°$. The structure was solved by direct methods, and block-diagonal least-squares refinements led to a final discrepancy index, R, of 0.035. The crystal structure is characterized by polymeric, beehive-like layers composed of $Cu_3Cl_4^-$ anions, and centro- and pseudocentrosymmetric *p*-benzoquinone molecules. Each of the *p*-benzoquinone molecules acts as a bridging ligand to the two *trans* $Cu_3Cl_4^-$ anions, with the Cu–C closest distances falling in the range from 2.047(5) to 2.086(5) Å. The NH_4^+ cations and the water molecules are accommodated by a roughly coplanar arrangement within the tunnel-like holes of the beehives, and the NH_4^+ cations are joined to the layers by intra- and interlayer hydrogen bonds of the N–H···O type. The $Cu_3Cl_4^-$ has a distorted cubane-type structure with one corner missing, and each Cu atom has a distorted tetrahedral coordination.

Yamaguchi *et al.* have synthesized a new compound with the composition of $[(NH_4)Cu_3Cl_4(C_6H_4O_2)_{1.5}\cdot H_2O]$ (hereafter abbreviated as BQ-Red), from $CuCl_2$, hydroquinone, and NH_4Cl in an aqueous solution. They have found, on the basis of spectroscopic studies, that this compound in the solid state is a polynuclear π-complex between $Cu_3Cl_4^-$ and *p*-benzoquinone (*p*-BQ).[1] It seems to have been reported few X-ray structural studies of metallic complexes containing *p*-BQ molecules as ligands, and so BQ-Red was expected to be a *p*-BQ complex of Cu(I) chloride of a novel type. The study of the crystal structure of BQ-Red has been carried out by the X-ray diffraction method to reveal the interactions between the $Cu_3Cl_4^-$ anions and the *p*-BQ molecules.

Experimental

Single crystals of this compound were prepared by one of the authors. Preliminary Weissenberg photographs showed the systematic absences of $0k0$, k odd and $h0l$, l odd, indicating the space group $P2_1/c$. The unit-cell parameters were obtained by a least-squares procedure using the 2θ values of 15 reflections measured on a Syntex $P\bar{1}$ four-circle diffractometer with Mo $K\alpha$ radiation. The density was measured by flotation in a methyl-iodide solution. The crystal used for X-ray work was ground to a sphere of 0.38 mm in diameter. The crystal data are given in Table 1.

TABLE 1. CRYSTAL DATA[a]

Formula unit	$Cu_3C_9H_{12}NO_4Cl_4$
Formula weight	530.65
Space group	$P2_1/c$
Density:	
D_m	2.27 g cm^{-3}
D_x	2.266 g cm^{-3}
Cell parameters:	
$a=7.308(5)$ Å	
$b=11.593(7)$ Å	
$c=18.359(9)$ Å	
$\beta=90.16(3)°$	
$V=1555.4(16)$ Å^3	
Number of formula units per unit cell:	$Z=4$
Linear absorption coefficient: (for Mo $K\alpha$ Radiation)	$\mu=49.1$ cm^{-1}

a) The numbers in parentheses, here and elsewhere in this paper, are the e.s.d.'s in the last significant digits.

Intensity data were collected by the θ-2θ scan technique at rates varying from 5.0 to 12.0° min^{-1} and with Mo $K\alpha$ radiation monochromated by a graphite crystal. 2115 independent reflections with 2θ values less than 45° were collected. Of these, 155 reflections with $I<0.7\sigma(I)$ were assigned values of $I=0.7\sigma(I)$ and were given zero weight in the initial refinement. The intensity data were corrected for Lorentz-polarization and absorption effects. The over-all temperature factor and the initial scale factor were obtained by the method of Wilson and were then used to compute the normalized structure factors, $|E|$.

Structure Determination and Refinement

The structure was solved by direct methods using the automatic phasing program MULTAN.[2] An E map calculated using 289 reflections with $|E|>1.5$ revealed the positions of all the Cu and Cl atoms. The other non-hydrogen atoms were obtained from a subsequent Fourier synthesis. Refinement was carried out by block-diagonal least-squares calculations in which the function minimized was $\Sigma\omega(|F_o|-|F_c|)^2$, initially with the unit weight and later with Cruickshank's weighting schemes for all reflections.[3] After refinement with anisotropic temperature factors, the H-atom positions were deduced from the difference Fourier syntheses, and the 35 most intense low-order reflections affected by the second extinction were corrected according to the method described by Stout and Jensen.[4] Refinement including the H atoms was terminated when the shifts of the parameters for the non-hydrogen atoms became less than a quarter of their estimated standard deviations. The final discrepancy index, R, was 0.035 for all reflections. A list of observed and calculated structure factors has been deposited with the office of the Chemical

Table 2. Fractional atmic coordinates and temperature factors

(a) Non-hydrogen atoms.

All values have been multiplied by 10^4. The anisotropic temperature factors are expressed in the form: $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2hkB_{12}+2hlB_{13}+2klB_{23})\}$.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	2173(1)	−301(1)	717(0)	94(1)	45(1)	15(0)	5(1)	5(0)	2(0)
Cu(2)	2157(1)	828(1)	2323(0)	96(1)	39(0)	17(0)	−9(1)	−3(0)	−1(0)
Cu(3)	2187(1)	−1980(1)	2092(0)	98(1)	39(0)	18(0)	6(1)	−7(0)	2(0)
Cl(1)	619(2)	1182(1)	1236(1)	96(2)	49(1)	19(0)	20(1)	−6(1)	−2(1)
Cl(2)	721(2)	−683(1)	2893(1)	110(2)	44(1)	19(0)	−5(1)	11(1)	2(1)
Cl(3)	673(2)	−2033(1)	1008(1)	108(2)	48(1)	19(0)	−13(1)	−11(1)	3(1)
Cl(4)	4457(2)	−486(1)	1728(1)	73(2)	37(1)	14(0)	0(1)	−1(1)	2(0)
O(1)	4339(5)	2270(3)	−113(2)	156(8)	38(3)	27(1)	18(4)	9(3)	3(2)
C(1)	4626(6)	1239(4)	−58(3)	84(10)	49(4)	12(1)	1(5)	10(3)	−1(2)
C(2)	3240(7)	364(4)	−246(3)	92(10)	53(4)	12(1)	23(5)	5(3)	6(2)
C(3)	3579(7)	−792(4)	−208(3)	90(10)	54(4)	10(1)	−10(5)	5(3)	−3(2)
O(2)	4558(6)	3143(4)	1445(2)	214(10)	79(4)	19(1)	−29(5)	−21(3)	14(2)
O(3)	5441(6)	646(4)	3865(3)	228(11)	71(4)	30(2)	−19(5)	−22(3)	18(2)
C(4)	4748(7)	2570(5)	2008(3)	118(10)	40(4)	16(2)	−17(5)	−10(3)	−5(2)
C(5)	3264(6)	2437(4)	2532(3)	99(9)	25(3)	19(2)	6(5)	−13(3)	−3(2)
C(6)	3469(7)	1766(4)	3138(3)	100(10)	43(4)	17(2)	−14(5)	4(3)	−10(2)
C(7)	5234(7)	1209(4)	3314(3)	158(12)	27(4)	18(2)	−11(5)	−22(4)	0(2)
C(8)	6739(7)	1364(4)	2787(3)	94(10)	35(4)	23(2)	15(5)	−18(3)	−8(2)
C(9)	6495(6)	1986(4)	2172(3)	78(9)	45(4)	19(2)	−11(5)	5(3)	−16(2)
O(W)	7595(6)	4005(4)	333(2)	191(10)	85(4)	28(2)	−7(5)	−2(3)	−9(2)
N	1666(7)	3856(4)	442(3)	140(10)	60(4)	32(2)	16(5)	−8(4)	5(2)

(b) Hydrogen atoms.

The hydrogen atoms are labelled in terms of the atom to which they are attached. The coordinate values have been multiplied by 10^3. The average e.s.d. of the isotropic temperature factors is 1.4 Å^2.

Atom	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
H(C2)	233(7)	66(4)	−50(3)	2.0	H(W)1	709(10)	361(7)	−1(4)	7.0
H(C3)	291(6)	−136(4)	−40(3)	2.5	H(W)2	693(11)	433(7)	64(5)	7.8
H(C5)	228(6)	288(4)	248(3)	2.3	H(N)1	207(9)	327(5)	19(4)	5.1
H(C6)	275(7)	175(5)	347(3)	3.2	H(N)2	203(10)	384(6)	88(4)	6.8
H(C8)	771(7)	90(4)	286(3)	2.3	H(N)3	202(8)	452(5)	26(3)	3.9
H(C9)	728(6)	200(4)	182(3)	2.0	H(N)4	53(9)	376(6)	42(4)	6.2

Society of Japan as a Document No. 8036. The atomic scattering factors for Cu^+, Cl^-, O, N, and C_{cov}, and also the anomalous dispersion factors for the first two atoms, were taken from International Tables for X-ray Crystallography,[5] and those for H atom, from Stewart, Davidson, and Simpson.[6] All the calculations were carried out on a FACOM 230-75 computer in the Computer Center of Kyushu University, mainly by the use of the UNICS-II program system.[7] The figures were drawn by the use of the *ORTEP* program.[8] The final atomic parameters are listed in Table 2, along with their estimated standard deviations.

Results and Discussion

Crystal Structure. A projection of the crystal structure down the c axis is shown in Fig. 1, along with the atomic nomenclature scheme, while a stereoscopic illustration viewed along the a axis is shown in Fig. 2. The crystal structure consists of $Cu_3Cl_4^-$ anions, *p*-BQ molecules, NH_4^+ cations, and water molecules. The bond distances(l) and angles(θ) are listed in Table 3.

The $Cu_3Cl_4^-$ anions are arranged with an approximate $\bar{3}$ symmetry around the axis parallel to the a axis and passing through the inversion center at (1/2,1/2,0). Each of the *p*-BQ molecules is sandwiched between these anions in such a mode that the molecular plane is tilted about 99° in relation to the planes defined by the two C atoms and the one Cu atom, as shown in Fig. 3. These *p*-BQ molecules are also in an approximately threefold symmetric arrangement around each anion, with the Cu–C closest distances ranging from 2.047(5) to 2.086(5) Å. Inspection of these Cu–C distances and dihedral angles suggests that π-complexing occurs in BQ-Red. These Cu–C closest distances are shorter than the sum of the relevant Pauling's covalent radii, 2.12 Å.[9] This is indicative of strong interaction between the Cu atoms and the *p*-BQ molecules. It appears that this interaction plays an important role in the stability of the crystal. The distances from the Cu atoms to the centers of their nearest C–C bonds were found to be in the range from 1.953(5) to 1.960(5) Å, with an average value of 1.957 Å. BQ-Red is, to the best of our knowledge, the first reported π-complex

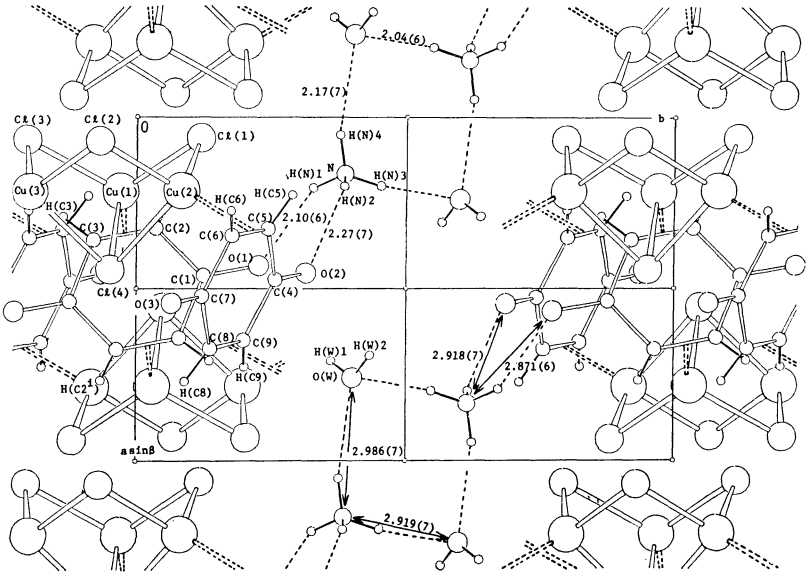

Fig. 1. Crystal structure projected down the c axis. Dashed and double-dashed lines indicate hydrogen bonds and Cu(I)–olefin bonds respectively, and distances in Å. The atoms in (1−x, 1/2+y, 1/2−z) and (x, 1/2−y, 1/2+z) have been omitted for clarity.

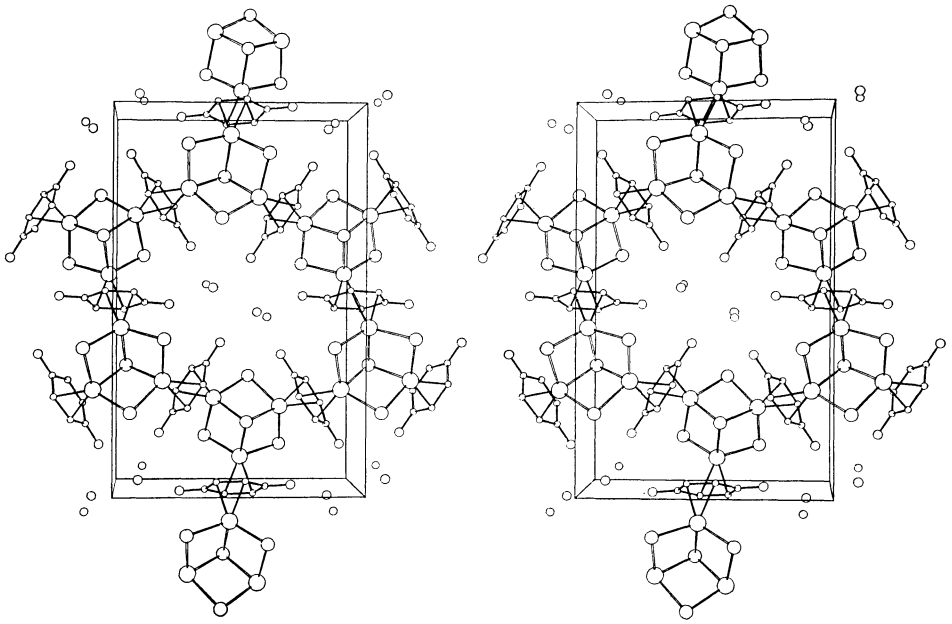

Fig. 2. Stereoscopic view of the crystal structure along the a axis. The center of the cell outline is at the inversion point (1/2, 1/2, 0). The b axis is horizontal, left to right, and the c axis points upward. The H atoms have been omitted for clarity.

where the *p*-BQ molecule bridges two *trans* Cu(I) cations as a di-olefinic ligand, although similar π-complexing has been found in $C_6H_6 \cdot (CuOSO_2CF_3)_2$ where the benzene molecule acts as a bridging ligand to two *trans* Cu(I) cations, with the Cu–C closest distances ranging from 2.09(2) to 2.30(2) Å.[10]

As shown in Fig. 2, each of the $Cu_3Cl_4^-$ anions is surrounded by three *p*-BQ molecules acting as bridging ligands, and these anions and molecules form a polymeric, two-dimensional, beehive-like network extended all over the bc plane. The beehive-like layers are stacked along the a axis, and the holes of the beehive look like tunnels running almost normal to the bc plane.

As shown in Fig. 1, the NH_4^+ cations and the water molecules are accommodated with a roughly coplanar arrangement within the tunnel-like holes of the beehive. The NH_4^+ is linked by hydrogen bonds to two *p*-BQ molecules and one water molecule within a layer, and the NH_4^+ cations and the water molecules in pairs bridge the layers with the hydrogen bonds across the centers of symmetry.

The crystal structure, thus, consists of polymeric,

TABLE 3. BOND DISTANCES AND ANGLES[a)]

(a) Bond distances (l/Å)

Cu(1)–Cl(1)	2.271(2)	Cu(2)–Cl(2)	2.295(2)	Cu(3)–Cl(3)	2.275(2)
Cu(1)–Cl(3)	2.350(2)	Cu(2)–Cl(1)	2.325(2)	Cu(3)–Cl(2)	2.363(2)
Cu(1)–Cl(4)	2.502(2)	Cu(2)–Cl(4)	2.520(1)	Cu(3)–Cl(4)	2.491(1)
Cu(1)–C(3)	2.068(5)	Cu(2)–C(5)	2.069(5)	Cu(3^{ii})–C(9)	2.047(5)
Cu(1)–C(2)	2.082(5)	Cu(2)–C(6)	2.082(5)	Cu(3^{ii})–C(8)	2.086(5)
Cu(1)–C(23)[b)]	1.959(5)	Cu(2)–C(56)[b)]	1.960(5)	Cu(3^{ii})–C(89)[b)]	1.953(5)
O(1)–C(1)	1.218(6)	O(2)–C(4)	1.236(6)	O(3)–C(7)	1.214(7)
C(1)–C(2)	1.474(7)	C(4)–C(5)	1.460(7)	C(6)–C(7)	1.477(7)
C(2)–C(3)	1.364(7)	C(5)–C(6)	1.366(7)	C(8)–C(9)	1.351(7)
C(3)–C(1^{i})	1.491(7)	C(6)–C(7)	1.477(7)	C(9)–C(4)	1.475(7)
C(2)–H(C2)	0.88(5)	C(6)–H(C6)	0.81(5)	C(9)–H(C9)	0.87(5)
C(3)–H(C3)	0.89(5)	C(5)–H(C5)	0.89(5)	C(8)–H(C8)	0.90(5)
O(W)–H(W)1	0.86(8)	N–H(N)1	0.87(6)	N–H(N)3	0.88(6)
O(W)–H(W)2	0.83(8)	N–H(N)2	0.85(7)	N–H(N)4	0.84(7)

(b) Bond angles (θ/°)

Cl(1)–Cu(1)–Cl(3)	108.50(6)	Cl(2)–Cu(2)–Cl(1)	107.77(6)	Cl(3)–Cu(3)–Cl(2)	109.98(6)
Cl(1)–Cu(1)–Cl(4)	95.00(5)	Cl(2)–Cu(2)–Cl(4)	92.44(5)	Cl(3)–Cu(3)–Cl(4)	96.14(5)
Cl(3)–Cu(1)–Cl(4)	93.95(5)	Cl(1)–Cu(2)–Cl(4)	93.19(5)	Cl(2)–Cu(3)–Cl(4)	91.58(5)
C(2)–Cu(1)–C(3)	38.4(2)	C(5)–Cu(2)–C(6)	38.4(2)	C(8)–Cu(3^{ii})–C(9)	38.2(2)
Cu(1)–C(2)–C(3)	70.3(3)	Cu(2)–C(6)–C(5)	70.3(3)	Cu(3^{ii})–C(8)–C(9)	69.3(3)
Cl(1)–Cu(1)–C(23)	124.4(2)	Cl(2)–Cu(2)–C(56)	124.3(2)	Cl(3)–Cu(3^{ii})–C(89)	123.2(2)
Cl(3)–Cu(1)–C(23)	117.5(2)	Cl(1)–Cu(2)–C(56)	119.7(2)	Cl(2)–Cu(3^{ii})–C(89)	117.4(2)
Cl(4)–Cu(1)–C(23)	110.6(2)	Cl(4)–Cu(2)–C(56)	111.3(2)	Cl(4)–Cu(3^{ii})–C(89)	111.5(2)
Cu(1)–Cl(1)–Cu(2)	89.18(5)	Cu(2)–Cl(2)–Cu(3)	89.63(6)	Cu(3)–Cl(3)–Cu(1)	87.10(5)
Cu(1)–Cl(4)–Cu(2)	79.96(5)	Cu(2)–Cl(4)–Cu(3)	81.88(5)	Cu(3)–Cl(4)–Cu(1)	79.35(5)
O(1)–C(1)–C(2)	122.6(4)	O(2)–C(4)–C(9)	120.8(5)	O(3)–C(7)–C(6)	121.6(5)
O(1)–C(1)–C(3^{i})	121.3(4)	O(2)–C(4)–C(5)	121.7(5)	O(3)–C(7)–C(8)	121.4(5)
C(2)–C(1)–C(3^{i})	116.1(4)	C(5)–C(4)–C(9)	117.5(4)	C(6)–C(7)–C(8)	117.1(4)
C(1)–C(2)–C(3)	122.7(4)	C(5)–C(6)–C(7)	121.4(5)	C(4)–C(9)–C(8)	121.8(4)
C(2)–C(3)–C(1^{i})	121.2(4)	C(4)–C(5)–C(6)	121.1(4)	C(7)–C(8)–C(9)	121.0(4)
C(1)–C(2)–H(C2)	112(3)	C(7)–C(6)–H(C6)	113(4)	C(4)–C(9)–H(C9)	114(3)
C(3)–C(2)–H(C2)	123(3)	C(5)–C(6)–H(C6)	125(4)	C(8)–C(9)–H(C9)	123(3)
C(1^{i})–C(3)–H(C3)	111(3)	C(4)–C(5)–H(C5)	118(3)	C(7)–C(8)–H(C8)	114(3)
H(N)1–N–H(N)2	113(7)	H(N)2–N–H(N)3	107(6)	H(N)3–N–H(N)4	113(6)
H(N)1–N–H(N)3	112(6)	H(N)2–N–H(N)4	110(7)	H(N)1–N–H(N)4	102(7)
H(W)1–O(W)–H(W)2	119(7)				

a) The superscripts, here and elsewhere in this paper, refer to the following equivalent positions: none) x, y, z; i) $1-x$, $-y$, $-z$; ii) $1-x$, $1/2+y$, $1/2-z$. b) C(23), C(56), and C(89) are the centers of the C(2)–C(3), C(5)–C(6), and C(8)–C(9) bonds respectively.

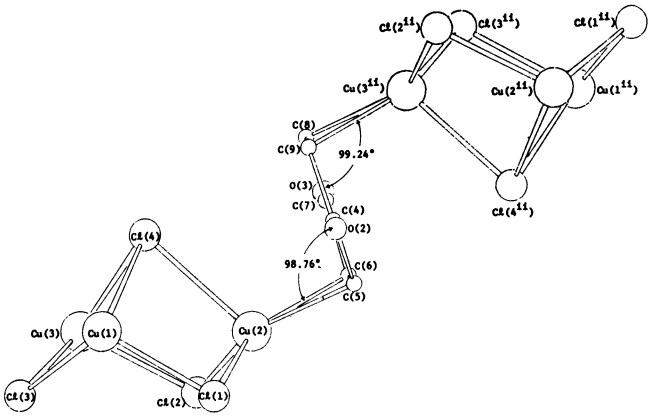

Fig. 3. Edge-on view of the p-BQ molecule lying at the general position. Similarly, the p-BQ molecule lying at the center of symmetry is coordinated to Cu(1) and Cu(1^{i}) so that its molecular plane makes an angle of 98.31° with the plane defined by C(2), C(3), and Cu(1).

beehive-like layers formed by $Cu_3Cl_4^-$ anions and p-BQ molecules, and of intra- and interlayer hydrogen bonds of the N–H···O type within the tunnel-like holes of the beehives.

Molecular Structure. The Cu_3Cl_4 moiety has a cap-like structure with an approximate threefold symmetry axis passing through the apex, Cl(4), and the midpoint of the three Cu atoms. The bond distances in the ring of the six-membered zigzag Cu–Cl chain range from 2.271(2) to 2.363(2) Å, while the three Cu–Cl(4) bonds bridging to the ring have distances ranging from 2.491(1) to 2.520(1) Å. The former and latter values are comparable respectively to the distances of the bidentate- and tridentate-chlorine-to-copper bonds found in other Cu(I) chloride complexes.[11,12] The bond angles within the Cu_3Cl_4 moiety fall into three groups; angles of about 109° between the ring Cl atoms subtended at each Cu atom, angles of about 80° at Cl(4), and the other angles of about 90°. Inspection

of these bond distances and angles suggests that the geometry of the Cu_3Cl_4 moiety may be described also as a distorted cubane-type with one corner missing. It has been found that the Cu_4Cl_4 core of $(P\cdot Ph_3CuCl)_4$ has a cubane-type structure in which each of the four Cu atoms has a distorted tetrahedral coordination, with Cu–Cl bond distances ranging from 2.362(2) to 2.505(2) Å.[13] In BQ-Red, each of the three Cu atoms has a distorted tetrahedral geometry coordinated by three Cl atoms and one *p*-BQ molecule, and the angles at the Cu atoms between the centers of their nearest C–C bonds and Cl atoms vary from 110.6(2) to 124.4(2)°. Such an environment around the Cu atom has also been found in $C_6H_6\cdot CuAlCl_4$, where the Cu atom has a distorted tetrahedral geometry coordinated by three Cl atoms and one benzene molecule acting as a mono-olefinic ligand.[14]

There are two crystallographically independent *p*-BQ molecules, one lying at an inversion center and the other at a general position. The latter has an approximate center of symmetry, though O(3) is the only oxygen atom not involved in hydrogen-bond formation. None of the bond distances or angles in either molecule is significantly different from the values obtained by gaseous electron diffraction.[15] Both molecules are also substantially planar, within the maximum deviations of 0.015 and 0.024 Å from their best-fit planes, despite that each of these molecules bridges two $Cu_3Cl_4^-$ anions with strong interactions.

The thermal-motion analysis has been applied to the three moieties of the $Cu_3Cl_4^-$ and the two independent *p*-BQ molecules in terms of the rigid-body model of translation and libration. The results suggest that both the *p*-BQ molecules behave as non-rigid bodies, in contrast with the Cu_3Cl_4 moiety, which behaves as a rigid body. This may be attributable to the polymeric structure. The thermal-motion corrections of the bond distances and angles were not applied in this work.

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