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Features of Structure, Geometrical, and Spectral Characteristics of the $(HL)_2[CuX_4]$ and $(HL)_2[Cu_2X_6]$ ($X = Cl, Br$) Complexes

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1. Introduction

Coordinate compounds of copper(II) are widely spread both as biological objects (metallo-proteins and metallo-enzymes), and in engineering. Among the functions of the copper proteins are: the electron transfer involving the Cu(I)/Cu(II) couple; mono- terminal-oxidases, which form either water or hydrogen peroxide from dioxygen; oxygenases, which incorporate an oxygen atom into a substrate; superoxide degradation to form dioxygen and peroxide; and the oxygen transport. From a structural point of view, there are three main types of biologically active copper centres found in the copper proteins (Cowan, 1993). These are "blue" copper centres, where copper atoms are normally coordinated to two nitrogens and two sulphurs, "non-blue" copper centres, where copper atoms are coordinated to two or three nitrogens as well as oxygens, and copper dimers. The nitrogens come from histidine groups, the sulfur from methionine and cysteine, the oxygens from the carboxylic acid in the protein. So called "non-blue" and dimeric copper-containing proteins are of a great similarity with complex halo (chloro-, bromo-) cuprates (Abolmaali et al., 1998). Thus, studies of structural and spectral characteristics of anionic complex halides of copper(II) can help to explain electronic structures as well as high reactional abilities and selectivities of active sites of copper-containing biopolymers in catalytic processes.

It is also evident that anionic halocuprate(II) complexes are catalytically active species responsible for the increased reactivity in a lot of organic reactions (oxidation and polymerization of phenols, reactions of tertiary amines, dimerization of primary alkyl groups et al.). Various investigations show that catalytic activities of complex copper(II) halides depend upon structures of their coordination polyhedra (Allen et al., 2009).

And finally, cupric halo-complexes relate to classic magneto-active systems containing 3d-metals, magnetic properties of which significantly depend on features of the spatial structure of complex anions (Rakitin & Kalinnikov, 1994).

d^9 -Electronic subshell of Cu(II) is responsible for distortions of symmetry of the coordination polyhedron (Gerloch & Constable, 1994). This deals with the Jahn-Teller effect (as a result of electron-vibrational interactions), and a large spin-orbital interaction constant. These two effects are of comparable values, and this fact complicates the prediction of structures of complexes of such types as well as physico-chemical properties and biological activity of Cu(II) complexes are in many respects determined by features of their structures.

The X-Ray analysis on single crystals can unequivocally determine structures of substances but isolation of single crystals is a complicated process which may not be achieved successively. Thus, a great role should belong to site-methods of structure determination (spectral, magnetic et al). Such correlations like "structure – spectral parameters – magnetic characteristics" help to describe features of the structure of complexes and as a result to predict their possible physical properties and areas of application.

2. Electronic structure and coordination geometry of Cu(II)-compounds

The ground state for the Cu^{2+} cation in its octahedral coordination is ${}^2E_g(t_{2g})^6(e_g)^3$, and the one for the square coordination is ${}^2E_g d_{xz}^2 d_{yz}^2 d_{z^2}^2 d_{xy}^2 d_{x^2-y^2}^1$. The only excited state might relate to ${}^2T_{2g}(t_{2g})^5(e_g)^4$ with the regular and distorted tetrahedral coordination (energy difference 10Dq) (Cotton & Wilkinson, 1966). The maximal coordination number of copper(II) is 6 which relates to octahedral complexes of the $(t_{2g})^6 (e_g)^3 - d_{xz}^2 d_{yz}^2 d_{xy}^2 d_{z^2}^2 d_{x^2-y^2}^1$ or $d_{xz}^2 d_{yz}^2 d_{xy}^2 d_{x^2-y^2}^2 d_{z^2}^1$ configurations. As the $d_{x^2-y^2}$ orbital, when compared to the d_{z^2} one, contains only one electron, it forms stronger Cu-to-ligand bonds. Thus, four planar ligands are stronger joint to the central ion than the two axial ligands which are bounded to Cu(II) along the z-axis. Sometimes the difference is so great that Cu(II) complexes may be considered as square. Most often, the coordination numbers of Cu(II) are 4 (square) or 6 (distorted octahedron). Tetrahedral coordination (T_d symmetry) and distorted tetrahedral coordinations (D_{2d}) also exist. The distorted octahedron is characterized by four short Cu-L bonds at one plane and two longer axial bonds in the trans-position (4+2 coordination) or 2 short and 4 long bonds (2+4 coordination). The square environment of Cu(II) appears as a limiting case of a tetragonal distortion of an octahedron. The copper(II) also forms a lot of complexes with the coordinate number 5. This can be explained by blocking of one of the tops of the octahedron by an e_g -lone electron pair. As a result, a square pyramid is formed (4+1 configuration). The square-pyramidal configuration exists for example in copper(II) pycrate diaquaacetylacetonate and $\text{K}[\text{Cu}(\text{NH}_3)_5](\text{PF}_6)_3$ (Adman, 1991). It usually appears in copper(II) complexes with pyridine and other bases, and is also typical for a Cu- β -alanyl-L-hystidine compound which is used as a model of M-protein interactions (Gerloch & Constable, 1994). In the case that ligands are stereochemically movable, a more symmetric structure of a trigonal bipyramid is formed as in $[\text{CuBr}_5]^{3-}$ or $[\text{CuDipy}_2\text{I}]^+$ (Gillard & Wilkinson, 1963).

The copper(II) forms both cationic and anionic complexes. The anionic ones – cuprates(II) are most often formed in excess of hydrohalic (HCl, HBr), cyanic (HCN) or thiocyanic (HSCN) acids. HI usually reduces Cu(II) into Cu(I). The complex anions of the type of $\text{M}^{+1}[\text{CuX}_3]$ and $\text{M}_2^{+1}[\text{CuX}_4]$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{CN}^-, \text{SCN}^-$) are stabilized by counter-ions the most simple of which are cations of alkaline metals (Willett & Geiser, 1984). For example, the structure of a red CsCuCl_3 (Schluetes et. al., 1966) contains Cu(II) ions octahedrally surrounded by six chloride anions. The CuCl_4^{2-} in a yellow Cs_2CuCl_4 (Helmholz & Kruh, 1952) is in tetragonal distortion. Brownish-red compounds of $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ (Vossos et al., 1963) and KCuBr_3 (Geiser et al., 1986a) consist of planar $\text{Cu}_2\text{X}_6^{2-}$ anions ($\text{X} = \text{Cl}, \text{Br}$) with symmetrical Cu-X-Cu bridges.

Actually, $\text{M}_2[\text{CuX}_4]$, $\text{X} = \text{Cl}, \text{Br}$ compounds with inorganic monovalent cations in the outer sphere can be mostly considered as double salts of a very low stability. For example, for

$[\text{CuCl}_4]^{2-}$ the formation constants were found to be $\log \beta_1 4.0$; $\log \beta_2 4.7$; $\log \beta_3 1.96$; $\log \beta_4 0.23$ (Khan & Schwing-Weill, 1976). The complexes are easily destroyed in polar solvents. Halogen-ions in the inner sphere are easily replaced by other ligands (ammonia, water at al). Majority of complex halides are not stable in air and destroyed by absorption of water vapors.

Much more interesting are anionic halocuprates(II) containing protonated organic molecules as counter-ions. They are stabilized with the help of formation of a system of intra- and intermolecular hydrogen bonds (H-bonds) or extra coordinate bonds via lone electron pairs of donating atoms (N, O, S) or vacant molecular orbitals of organic molecules (so-called dative bonds with the metal-to-ligand charge transfer $\text{M} \rightarrow \text{L}$). The present chapter belongs to development of features of the structures and properties of such type of compounds.

3. Structure characteristics and properties of CuCl_4^{2-} species

Stereochemistry of copper(II) halides is rather rich (Smith, 1976). The latest results are summarized in the review (Murphy & Hathaway, 2003). Two types of coordination exists: the "common" one with ionic radii of about 0.5 \AA and semi-coordinated where the bond lengths are $0.3 - 1.0 \text{ \AA}$ longer (Hathaway, 1982). The shape of coordination polyhedra changes from square planar (Harlow et al., 1975) to distorted tetrahedral (Diaz et al., 1999).

The degree of distortion of CuX_4^{2-} coordination polyhedra is determined by the mean value of the flattening or trans-angle θ (Fig.1). It is evident that the non-distorted tetrahedral configuration (T_d) of CuX_4^{2-} corresponds to mean θ -values up to 109 deg. as the planar distortion increases its value up to 180 deg.

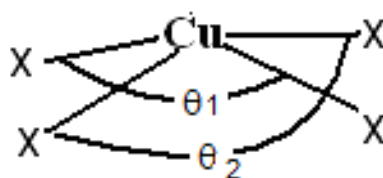


Fig. 1. Determination of the degree of distortion of coordination polyhedra of Cu(II) complexes

3.1 Structure description

Since the last century, a lot of structures of common formulae $(\text{HL})_2\text{CuCl}_4$ and $(\text{HL})_2\text{CuBr}_4$ where L is an organic base were determined by X-Ray crystallography. It was stated that the geometry of CuX_4^{2-} depends upon stability of H-bonds and other electrostatic and steric interactions between counter-ions and halide-ions of tetrahalocuprate(II) fragments (Murphy & Hathaway, 2003). H-bonds flatten the structure towards D_{4h} configuration. The decrease in the abilities of organic cations to form H-bonds with the inorganic anion leads to the decrease in distortion of its tetrahedral geometry. Really, in $\text{Cs}_2[\text{CuX}_4]$ the mean values of trans-angle θ is determined to be 124 deg. for $\text{X} = \text{Cl}$ (Helmholz & Kruh, 1952) and 128.4 deg. for $\text{X} = \text{Br}$ (Morosin & Lingafelter, 1960) which corresponds to slightly distorted tetrahedron, as well as tetrahalocuprates containing diprotonated 3-aminopyridine as counter-ions are characterized by planar structures of inorganic anions ($\theta 170.60 \text{ deg.}$ for tetrachlorocuprate and 170.56 deg. for its bromo-analogue (Willet et al., 1988). More complicated organic compounds provoke intermediate characters of inorganic anions (Table 1).

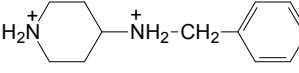
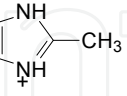
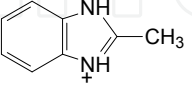
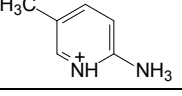
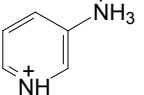
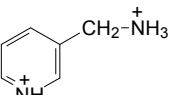
L	$\theta(\text{CuCl}_4^{2-})$, deg	Ref.	$\theta(\text{CuBr}_4^{2-})$, deg	Ref.
Cs+	124	Helmholz & Kruh, 1952	128.4	Morosin & Lingafelter, 1960
	133	Antolini et al., 1981	125.6	Place & Willett, 1988
	134.4	Kovalchukova et al., 2008a	131.64	Koval'chukova et al., 2009b
	134.69	Bhattacharya et al., 2004	134.2	Bhattacharya et al., 2004
	140	Place & Willett, 1987b	137	Place & Willett, 1987b
	170.56	Willet et al, 1988	170.6	Willet et al, 1988
	177.4	Long et al., 1997	178	Long et al., 1997
$\text{H}_3\text{N}^+-\text{CH}_2-\text{CH}_2-\text{NH}_3^+$	180	Tichý et al., 1978	180	Rubenacker et al., 1984

Table 1. Some characteristics of coordination polyhedra of some (HL)₂[CuX₄] structures.

Plotting of degrees of distortion of the CuX₄²⁻ coordination polyhedron *vs.* the type of the halogenide-anion (Fig 2) gives a straight-line dependence with closely related values of $\theta(\text{CuCl}_4^{2-})$ and $\theta(\text{CuBr}_4^{2-})$ for the same organic cations (Koval'chukova et al., 2009b). Thus, the degree of distortion of coordination polyhedron slightly depends upon the nature of X (Cl-, Br-), and is mainly determined by the nature of the organic cation.

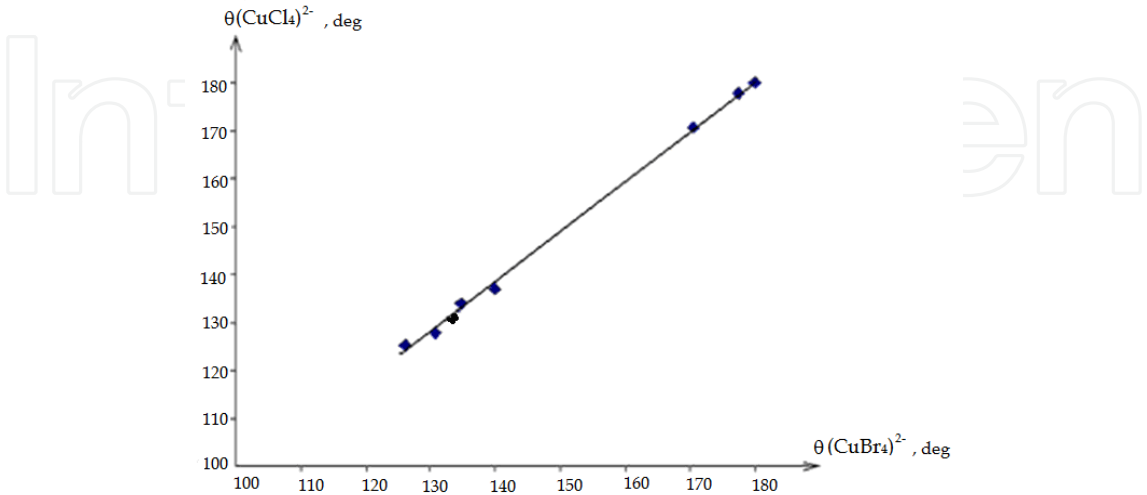


Fig. 2. The dependence of flattening angle of CuX₄²⁻ coordination polyhedron on the nature of inorganic anion (Koval'chukova et al., 2009b).

Among the features of crystal structures of tetrabromocuprates(II) in the D_{4h} configuration stabilized by cations of organic aliphatic amines (such as cyclopentylamine (Luque et al., 2001), phenylethylamine (Arend et al., 1978), methyl(2-phenylethylamine (Willett, 1990)) there are tight interactions of tetrabromocuprate(II) anions. This leads to the appearance of two semi-coordinate bonds with Cu-Br distances 3.0 – 3.1 Å as compared with common 2.41 – 2.45 Å. As a result, the coordination number of copper becomes 6 (4+2 coordination) (Fig. 3).

The same type of (4+2) coordination of Cu^{2+} was found in $(HL)_2[CuCl_4]$, $L = 2\text{-methyl-1,3-di-2-pyridyl-2-propanol}$ (Schlemper et al., 1989). Cu^{2+} ions are in distorted square-bipyramidal coordination. The bridging angles $Cu'ClCu$ are 125.1 and 129.5 deg, and Cu-Cl distances 2.457 and 2.868 Å.

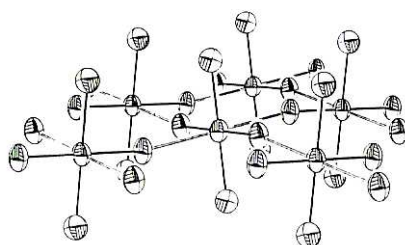


Fig. 3. The formation of a layer of $(CuBr_4)_n$ in $(PhC_2H_4NH_3)_2CuBr_4$ (Arend et al., 1978)

Tetrachlorocuprate(II) ions may also coordinate other d-metals. Paramagnetic metallic ions form bridging anti-spin magnetic chained systems which are of a great interest for physics (Lande et al., 1988). The Cu-Cl distances of bridging fragments may reach 2.325 Å, and those of terminate character shorten till 2.181 Å.

The possibility of bromination of organic cations with using for neutralization of anionic bromocuprates may also take place. That was described for example by (Place & Willett, 1987a). While the formation of anionic tetrabromocuprates(II) containing protonated 2-amino-3-methylpyridine as a counter-ion, partial bromination of an organic specie was observed. Both 2-amino-3-methylpyridinium and 2-amino-5-bromo-3-methylpyridinium cations neutralize the negative charge of tetrabromocuprate anion in the crystal lattice.

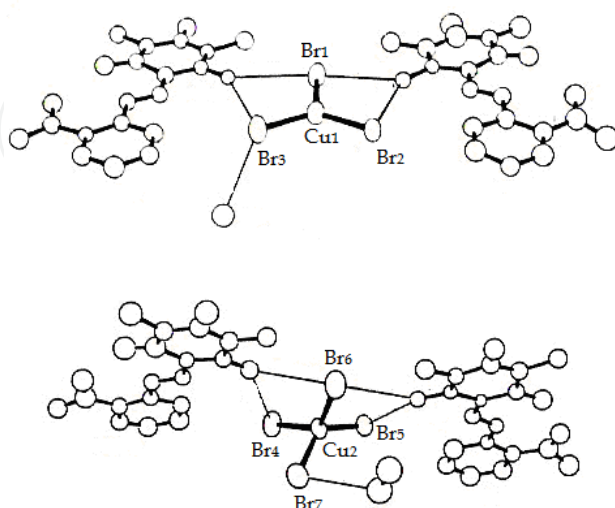


Fig. 4. The crystal structure of $(H_3L)_4(CuBr_3)(CuBr_4) \cdot H_2O \cdot 3CH_3OH$ (Sundberg et al., 1992).

Sundberg and co-workers (Sundberg et al., 1992) showed that while complex formation of CuBr_2 with 6-amino-1,3-dimethyl-5-((2-carboxyphenyl)azo)uracyl (HL) in the presence of HBr, partial reduction of Cu(II) into Cu(I) is observed. As a result, a complex $(\text{H}_3\text{L})_4(\text{CuBr}_3)(\text{CuBr}_4) \cdot \text{H}_2\text{O} \cdot 3\text{CH}_3\text{OH}$ contains copper atoms in oxidation states +2 and +1. The coordination number for Cu(I) is 3 (CuBr_3^{2-} as a planar anion), and 4 for Cu(II) (CuBr_4^{2-} as a distorted tetrahedron). In lattice, both $(\text{H}_3\text{L})_2(\text{CuBr}_3)$ and $(\text{H}_3\text{L})_2(\text{CuBr}_4)$ exist as independent fragments. So the above complex may be considered as co-crystallization of two complexes containing copper in two different oxidation states. Water and methanol molecules have a lattice character (Fig. 4).

As it was intimated (Place & Willett, 1987a), the H-bonding between organic protonated molecules and inorganic tetrahalocuprate(II) anions is not released for structures with $\theta < 132$ deg. Such types of structures are described, for example, for bis(4-azafluorene-9-onium) tetrabromocuprate(II) monohydrate (Kovalchukova et al., 2009a) (θ 130.98 deg.) crystal package of which is present on Fig. 5. It is evident that cations and anions form alternating layers with no H-bonds between them. The only one intermolecular interaction existing in the structure belongs to the hydrated water molecule.

On the other hand, H-bonds are found in the $(\text{H}_2\text{L})[\text{CuBr}_4]$ structure with the flattening angle θ 120 deg (L - 2,4,6-tris(N,N-dimethylamino)methylphenol) (Kovalchukova et al., 2010). The Cu-Br distances in the distorted CuBr_4^{2-} anion range from 2.469(2) to 2.515(1) Å. The minimal Cu-N distance is 3.65 Å, and its value rejects the possibility of formation of a ligand-to-metal coordinate bond. Despite a small value of the flattening angle θ , a hydrogen N-H...Br bond exists between an H-atom of a protonated tertiary amino-group of the organic dication and one of a Br-atom of the inorganic anion (r N-H 1.05; H...Br 2.42; N...Br 3.46 Å; \angle NHBr 169.5 deg.).

Flattening of the CuX_4^{2-} structure increases the number and strength of the H-bonds. As an example, for $(\text{HL})_2[\text{CuX}_4]$ (L = 2-methylimidazolium, X = Cl, θ 134.4 deg (Kovalchukova et al., 2008a); X = Br, θ 132.64 deg (Koval'chukova et al., 2009b)), multiple H-bonds connect counter-ions in crystals (Fig. 6). Similar structures were found for N-benzylpiperazinium tetrachlorocuprate(II) (Antolini et al., 1981) containing an unequally flattened $[\text{CuCl}_4]^{2-}$ tetrahedron (θ 166.4 deg.) (fig. 7) as well as for bis(ethylenediammoniummonobromide) tetrabromocuprate(II), θ 159.2 deg (Anderson & Willett, 1971), and a square-planar limit (θ 180 deg) for creatinium tetrachlorocuprate(II) (Battaglia et al., 1979). Probably H-bondings play the crucial role in these limiting planar structures as compared with crystal packing forces or the cation bulk. Nearly linear strong H-bonds (Fig. 7) produce such a reduction of the ligand-to-ligand electrostatic repulsion to allow a nearly square-planar geometry, favored by the crystal field stabilization (Smith, 1976).

H-bonds change not only bond angles but also Cu-X bond lengths. In (Antolini et al., 1981) the shortest Cu-Cl distances (~ 2.260 Å) were found for chlorine atoms which do not form H-bonds. Abnormally long Cu-Cl bonds (~ 2.334 Å) were determined for Cl-atoms engaged in a strong bifurcate H-bonding (Halvorson et al., 1990). Graphical correlations of parameters of H-bonds, i.e. $r(\text{H-Br})$ on $r(\text{N-Br})$ (Koval'chukova et al., 2009b), $\text{N-H}\cdots\text{Cl}$ angle on $r(\text{Cu-Cl})$ (Kovalchukova et al., 2008a) (Fig. 8, 9) are linear but the dependencies of the NHBr angles on θ (Fig. 10) for tetrachlorocuprates(II) and tetrabromocuprates(II) have opposite derivative signs.

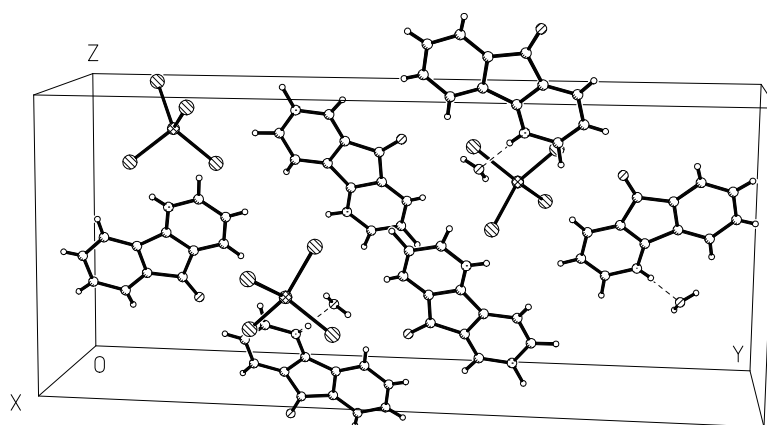


Fig. 5. The crystal package of bis(4-azafluorene-9-onium) tetrabromocuprate(II) monohydrate (Kovalchukova et al., 2009a).

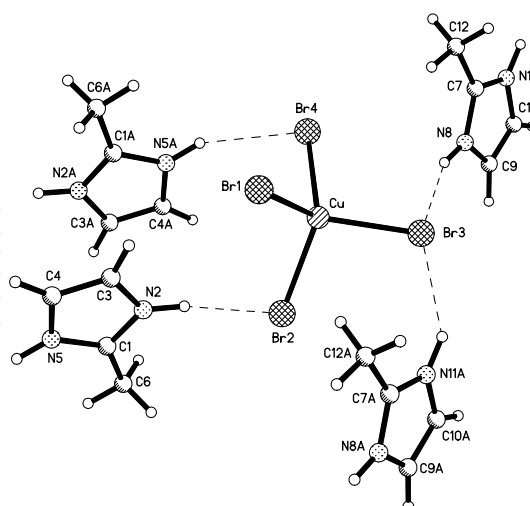


Fig. 6. The formation of H-bonds in the structure of bis(2-methylimidazolium) tetrabromocuprate (Koval'chukova et al., 2009b)

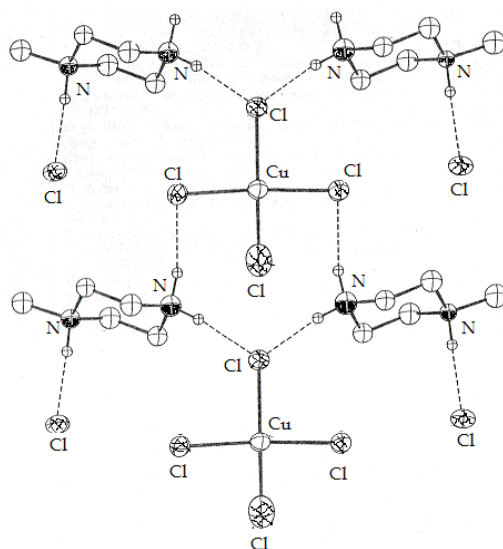


Fig. 7. Hydrogen bonds (dashed lines) in N-benzylpiperazinium tetrachlorocuprate(II). C-bonded H atoms and phenyl rings are omitted for clarity (Halvorson et al., 1990).

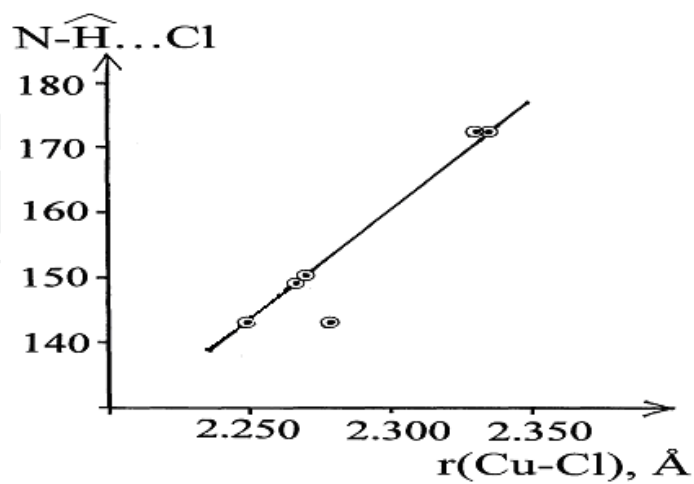


Fig. 8. The dependence of values of bond angles at a bridging H-atom $N - \hat{H}...Cl$ on the Cu-Cl distance for anionic tetrachlorocuprates(II) containing N-protonated organic bases as counter-ions (Kovalchukova et al., 2008a).

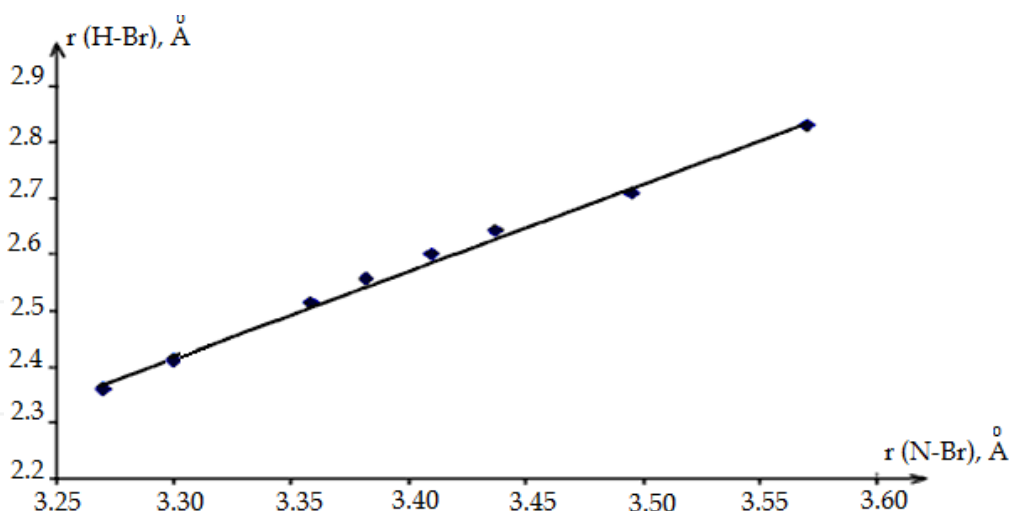


Fig. 9. The dependence of values of H-Br on N-Br distances for anionic tetrabromocuprates(II) containing N-protonated organic bases as counter-ions (Koval'chukova et al., 2009b).

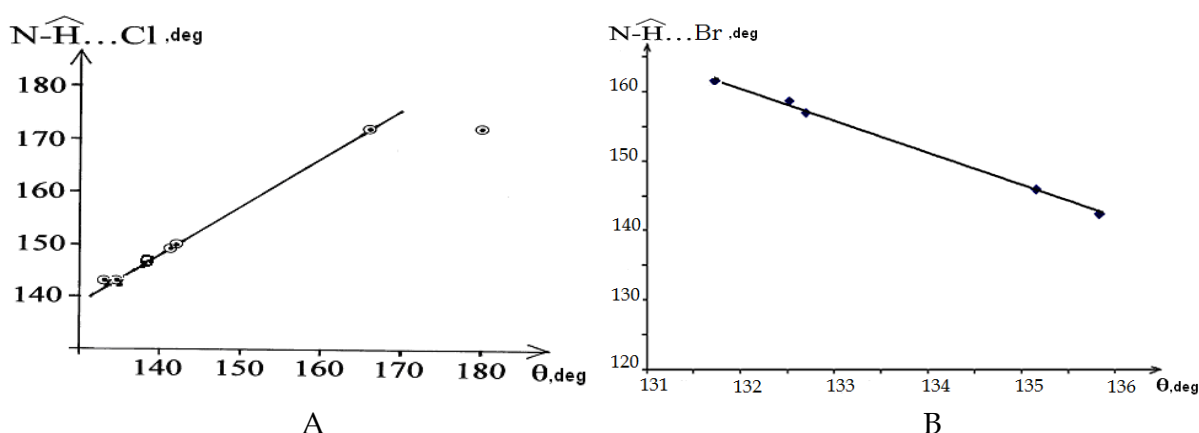


Fig. 10. The dependence of the degree of distortion of coordination polyhedra of anionic tetrachlorocuprates(II) (A) and tetrabromocuprates(II) (B) on the value of bond angles at a bridging H-atom $N-H \cdots X$ ($X = Cl, Br$) (Kovalchukova et al., 2008a; Koval'chukova et al., 2009b).

3.2 Spectral-structural correlations

It is evident that isolation of single crystals for determination of the type of a CuX_4^{2-} coordination polyhedron and degree of its distortion is not always possible. On the other hand, the above parameters mostly affect physico-chemical properties of halocuprates(II). Correlations of spectroscopic characteristics of substances with the features of their crystal structures are useful for these purposes. The major role belongs to electronic spectroscopy. Electronic absorption spectra of $(HL)_2[CuX_4]$, $X = Cl, Br$ are characterized by 3 types of absorption bands. The first ones are d-d transitions of Cu^{2+} cations which lie at 16000 – 5500 cm^{-1} for tetrachlorocuprates(II) and at 9090 – 6000 cm^{-1} for tetrabromocuprates(II). One wide band is present in the spectra at a room temperature as below 77 K it is split into three sharp bands which relate to $^2B_2 \rightarrow ^2A_1$, $^2B_2 \rightarrow ^2B_1$, and $^2B_2 \rightarrow ^2E$ electron transitions (Halvorson et al., 1990). The correlation between the type and degree of distortion of $[CuCl_4]^{2-}$ polyhedra and

maxima of d-d transition bands for D_{2d} and D_{4h} symmetries are described with the help of semi-empiric (McDonald et al., (1988)) and empiric (Wasson et al., 1977) formulae and are presented on Fig. 11, 12.

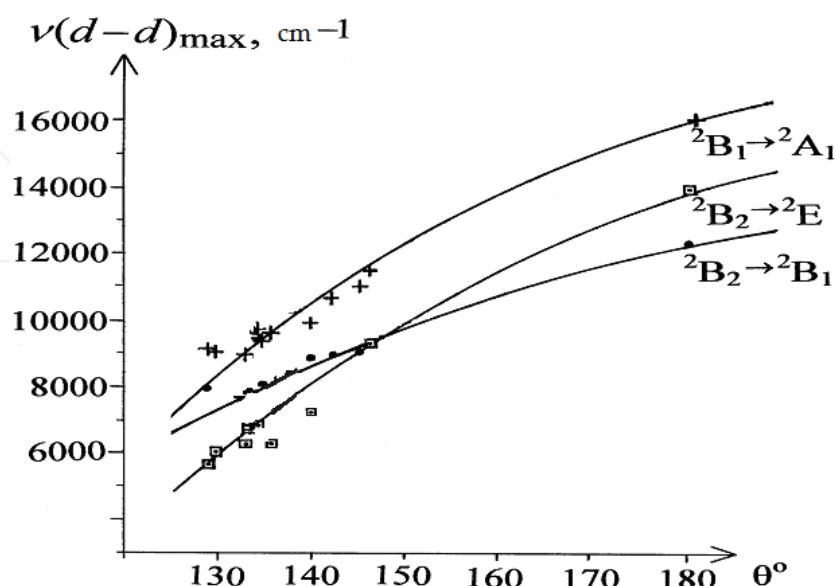


Fig. 11. The dependence of maxima of d-d transition bands in electronic absorption spectra of compounds containing $[\text{CuCl}_4]^{2-}$ anions on the flattening angle of the coordination polyhedron below 77 K (the lines present calculated data (McDonald et al., (1988))).

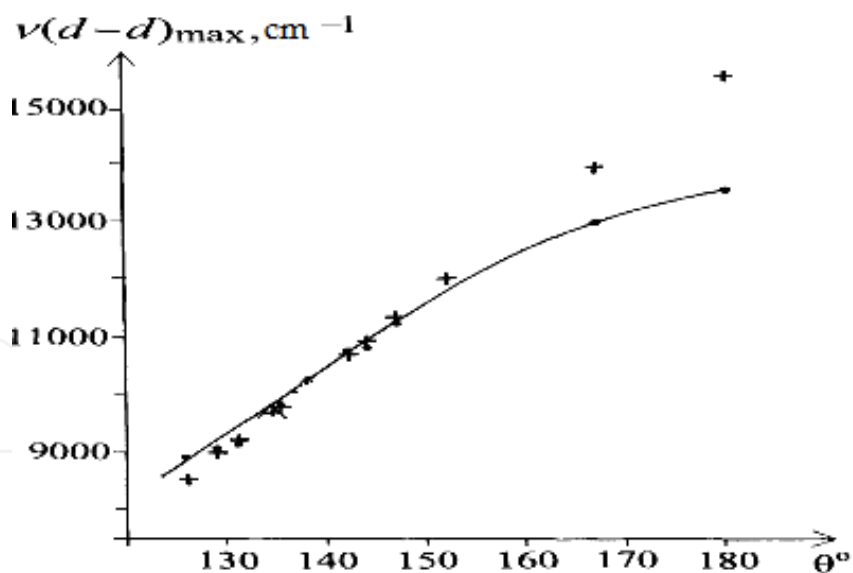


Fig. 12. The dependence of maximum of d-d transition bands in electronic absorption spectra of compounds containing $[\text{CuCl}_4]^{2-}$ anions on the flattening angle of the coordination polyhedron at a room temperature (the lines present calculated data (Wasson et al., 1977)).

The second type of absorption bands in UV and visible parts of electronic spectra of halocuprates(II) relates to $\text{X} \rightarrow \text{Cu}^{2+}$ ($\text{X} = \text{Cl}, \text{Br}$) charge transfer (CT). Their high intensities can be explained by the ability of Cu^{2+} to be reduced into Cu^+ . The transition frequencies are

determined both by the nature of X (Cl, Br) and by the degree of distortion of the CuX_4^{2-} polyhedron (Fig. 13) (Koval'chukova et al., 2009b).

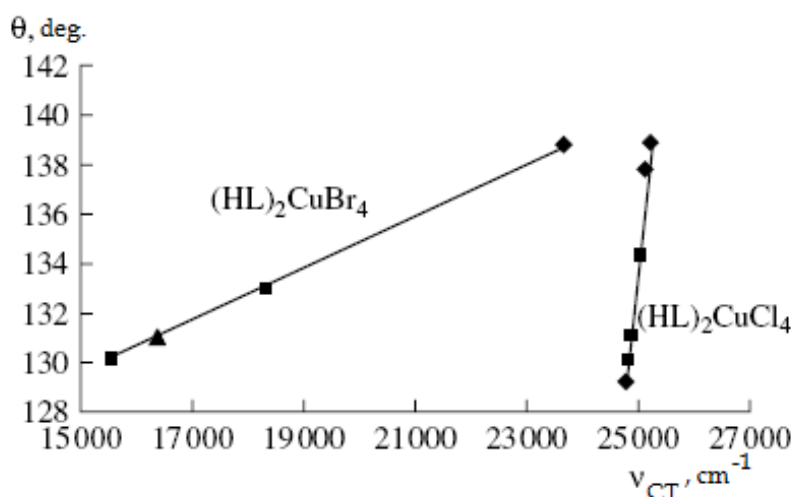


Fig. 13. The dependence of the position of the $\text{X} \rightarrow \text{Cu}^{2+}$ ($\text{X} = \text{Cl}, \text{Br}$) charge transfer bands in the electronic absorption spectra of tetrahalocuprates on the degree of distortion of the anionic polyhedron (Koval'chukova et al., 2009b).

From the data of Fig. 13, empiric formulae for calculation of the degree of distortion of CuX_4^{2-} ($\text{X} = \text{Cl}, \text{Br}$) polyhedra from the position of charge transfer bands in the electronic absorption spectra were obtained:

$$\theta = 0.0272 \cdot \nu_{\text{CT}} - 544.56 \text{ (for } (\text{HL})_2\text{CuCl}_4 \text{ at } R^2=0.9718) \quad (1)$$

$$\theta = 0.001 \cdot \nu_{\text{CT}} + 113.97 \text{ (for } (\text{HL})_2\text{CuBr}_4 \text{ at } R^2=0.9963) \quad (2)$$

$$\nu_{\text{CT}}(\text{CuBr}_4^{2-}) = 272 \cdot \nu_{\text{CT}}(\text{CuCl}_4^{2-}) - 658 \quad (3)$$

The 3rd group of bands in the electronic absorption spectra of halocuprates relates to electron transitions in organic cations. They are of the highest intensities and may overlap with the charge transfer transitions. Unfortunately, the dependence of positions of ligand bonds in the electronic absorption spectra on the nature of H-bonds is not so evident, and no sufficient correlations were found.

The same conclusion was made by Marcotrigiano and co-authors (Grigereit et al., 1987) with using IR spectroscopy data. The attempt to correlate the character of H-bonds in polycrystalline $(\text{H}_2\text{L})\text{CuBr}_4$ ($\text{L} = 1\text{-methylpyperazine}; 2\text{-methylpyperazine}$), as well as $(\text{HL})_2\text{CuBr}_4$ ($\text{L} = 1\text{-methylpyperazine}$) with the shift in ligand absorption bands in IR spectra of complexes with respect to those in corresponding hydrobromides also failed. This might deal with the existence of strong H-bonds of different nature both in complex halocuprates and in initial organic hydrobromides.

4. Structure characteristics and properties of $\text{Cu}_2\text{Cl}_6^{2-}$ structures

As already noted, halide-ions may take place in coordination as bridging ligands. This leads to the formation of dimeric, oligomeric, and even polymeric $\text{Cu}_n\text{X}_{2n+2}^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) anions

(Grigereit et al., 1987). Studies of structures and magnetic properties (O'Bannon & Willett, 1986) of KCuCl_3 and NH_4CuCl_3 showed the existence of characteristic antiferromagnetically-joint dimeric systems, i.e. the formulae of the above substances should be presented as $\text{K}_2\text{Cu}_2\text{Cl}_6$ и $(\text{NH}_4)_2\text{Cu}_2\text{Cl}_6$.

Symmetric dibridged structures of dimeric $\text{A}_2\text{Cu}_2\text{X}_4$ ($\text{X} = \text{Cl}, \text{Br}$) structures are based on $\text{Cu}_2\text{X}_6^{2-}$ dimers in one of the three mostly possible geometric configurations (Fig. 14). The planar dimer A is described by the ϕ -angle and usually has the (4+2) coordination mode (Landee et al., 1988; Bencini & Gatteschi, 1986). The structures present anionic dimers containing two four-coordinated coppers(II) with the D_{2d} geometry. Four coordinate bonds of each metallic atom are formed by Cl-atoms two of which are bridging ligands. Counterions are protonated tetramethylene sulfoxide (Scott & Willett, 1991) or tetrapropylammonium (Landee et al., 1988) cations. The structures are stabilized by axial semi-coordinate Cu-Cl bonds involving the terminate halides in $\text{Cu}_2\text{Cl}_6^{2-}$ anions.

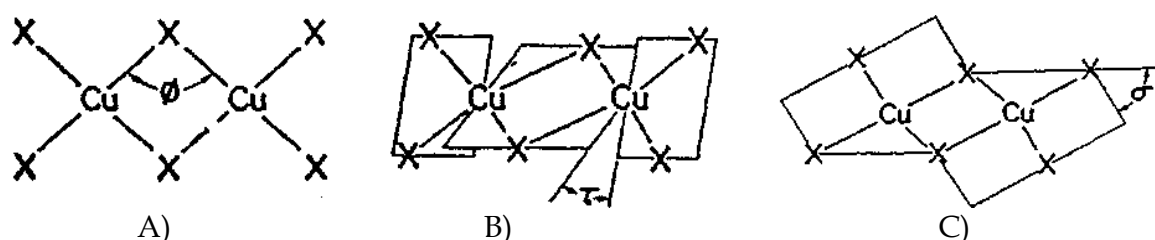


Fig. 14. The types of distortion of $\text{Cu}_2\text{X}_6^{2-}$ anions: A) planar; B) twisted (screwed); C) folded (Willett & Geiser, 1984).

4.1 Planar $\text{Cu}_2\text{X}_6^{2-}$ structures

One of the common types of planar anionic halocuprates(II) is a pseudo-planar dibridged structure (Harlow et al., 1975). Each of Cu(II) atom forms a primary planar square configuration. Variations of the crystal package may exist. For example, this may be presented in the graphical form for KCuCl_3 (Fig. 15a) (Willett et al., 1963), $(\text{H}_2\text{mel})[\text{Cu}_2\text{Cl}_6]$, H_2mel – melaninium cation (Fig. 15b) (Colombo et al., 1985), $(\text{CH}_3)_2\text{CHNH}_3\text{CuCl}_3$ (Fig. 15c) (Roberts et al., 1981) or $(\text{CH}_3)_2\text{NH}_2\text{CuCl}_3$ (Fig. 15d) (Willett, 1966).

Authors (Scott & Willett, 1991) described a crystal structure of bis(tetrapropylammonium) hexabromodicuprate(II) with 6-coordinated copper ((4+2) geometry). The axial coordination involves terminal Br-atoms of neighboring $\text{Cu}_2\text{Br}_6^{2-}$ anions ($r_{\text{Cu-Br}_{\text{axial}}} 2.876 \text{ \AA}$) and N-atoms of organic cations. The coordination polyhedron of Cu^{2+} lies between square-pyramidal and distorted octahedral. The same type of structure was determined for dimorpholinium hexahalodicuprate (II) salts (Scott et al., 1988).

The (4+2) coordination of Cu(II) in planar $\text{Cu}_2\text{Br}_6^{2-}$ anions of dibenzotetrathiafulvalenium hexabromodicuprate(II) (Honda et al., 1985) was achieved with the help of the formation of two $\text{Cu}\cdots\text{S}$ semi-coordination bonds ($r_{\text{Cu-S}}$ from 3.425 to 4.580 \AA).

In bis(4-aminopyridinium) hexabromodicuprate(II) diaquatetrabromodicopper(II) (Place & Willett, 1994) the coordination polyhedron in a planar $\text{Cu}_2\text{Br}_6^{2-}$ is completed to a square pyramidal (coordination number 5) by Br-atoms of a $\text{Cu}_2\text{Br}_2(\text{H}_2\text{O})_2$ fragments as 4-aminopyridinium molecules are not involved in the coordination (Fig. 16). The Cu-Br distances inside the dimer are 2.401 \AA (Cu-Br terminal) and 2.443 \AA (Cu-Br bridging); the $\text{Cu}\cdots\text{Br}$ bond lengths of semi-coordinate bonds lie in the range 2.904 to 3.200 \AA .

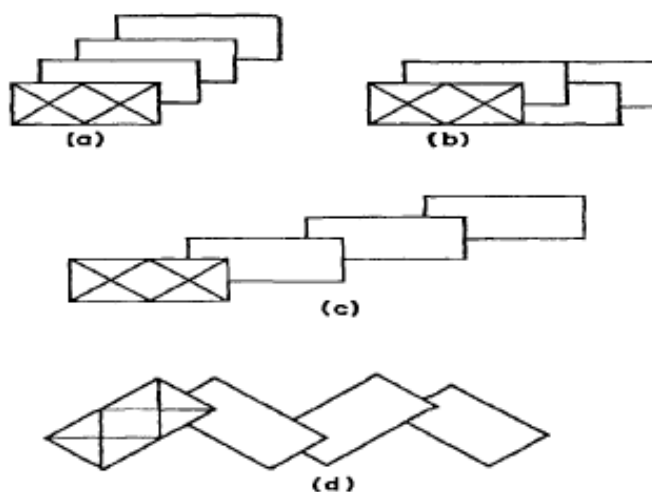


Fig. 15. The crystal package of $Cu_2X_6^{2-}$ dimmers: (a) double chain; (b) “zig-zag” double chain; (c) alternative chain; (d) “zig-zag” alternative chain (Willett & Geiser, 1984).

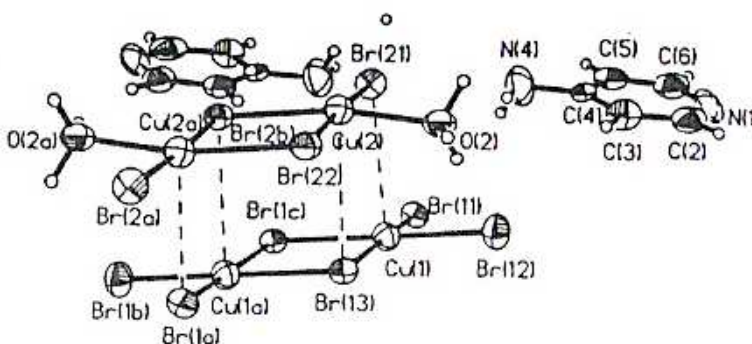


Fig. 16. The crystal structure of bis(4-aminopyridinium) hexabromodicuprate(II) diaquatetrabromodicopper(II) (Place & Willett, 1994) .

4.2 Twisted $Cu_2X_6^{2-}$ structures

The distortion of planar $Cu_2X_6^{2-}$ anions may take place in two directions. The first brings to twisted (or screwed) structures (Fig. 14 B) which are characterized by the twisting angle τ between the bridging Cu_2X_2 plane and two terminate CuX_2 planes. Twisted dimers are most often formed in complexes with large organic cations with a little tendency in formation of the H-bonds. The possibility to form twisted structures relates to the electrostatic repulsion between halide anions which provides the possibility of tetrahedral distortion to the coordination sphere of Cu^{2+} cations.

Such types of twisted $Cu_2X_6^{2-}$ structures were found for example for $(Ph_4As)_2[Cu_2Cl_6]$ (Willett & Chow, 1974), $(Ph_4Sb)_2[Cu_2Cl_6]$ (Bencini et al., 1985), and $(Ph_4P)_2[Cu_2Cl_6]$ (Textor et al., 1974). In the above structures, the coordination geometry of Cu(II) is intermediate between square-planar and tetrahedral. The τ -angle is close to 50 deg. for both the structures.

The authors (Kovalchukova et al., 2008b) report the crystal structure of bis(4-pyridyl-1)-2-phenylpyrido[2,3-a]anthraquinonium-7,12) hexachlorodicuprate(II) which consists of separated organic cations and twisted $Cu_2Cl_6^{2-}$ anions (Fig. 17). The terminal C1(2)-Cu-C1(3)

plane is rotated around the central Cu_2Cl_2 plane through 50.5 deg. The coordinate polyhedron of each Cu(II) atom is a distorted tetrahedron with the bond angles 100.5 (C1(2)-Cu-C1(3)), 96.6 (C1(2)-Cu-C1(1)), 87.5 (Cl(1)-Cu-C1(1^*)), and 92.5 deg. (Cl(3)-Cu-Cl(1^*)). In the crystal, the inorganic anion and planar organic cations form a skeleton structure of H-bonds involving H-atoms at C(24) and C(25) of the pyridine fragment of the cation and Cl(2) and Cl(2*) atoms of the hexachlorodocuprate(II) anion.

Two crystalline phases of $(\text{TMM-TTF})_2[\text{Cu}_2\text{Cl}_6]$ (TMM-TTF = tetra(methylthio)tetrathiafulvalene) were detected by H. Enders (Endres, 1987). They differ in the arrangement of the $(\text{TMM-TTF})^+$ radical cations and the geometry of the $[\text{Cu}_2\text{Cl}_6]^{2-}$ anions. Both of them are of the twisted geometry with the τ -angles of 10.0 (almost planar) and 31.5 deg. This fact reflects the “plasticity” of the coordination sphere of Cu(II).

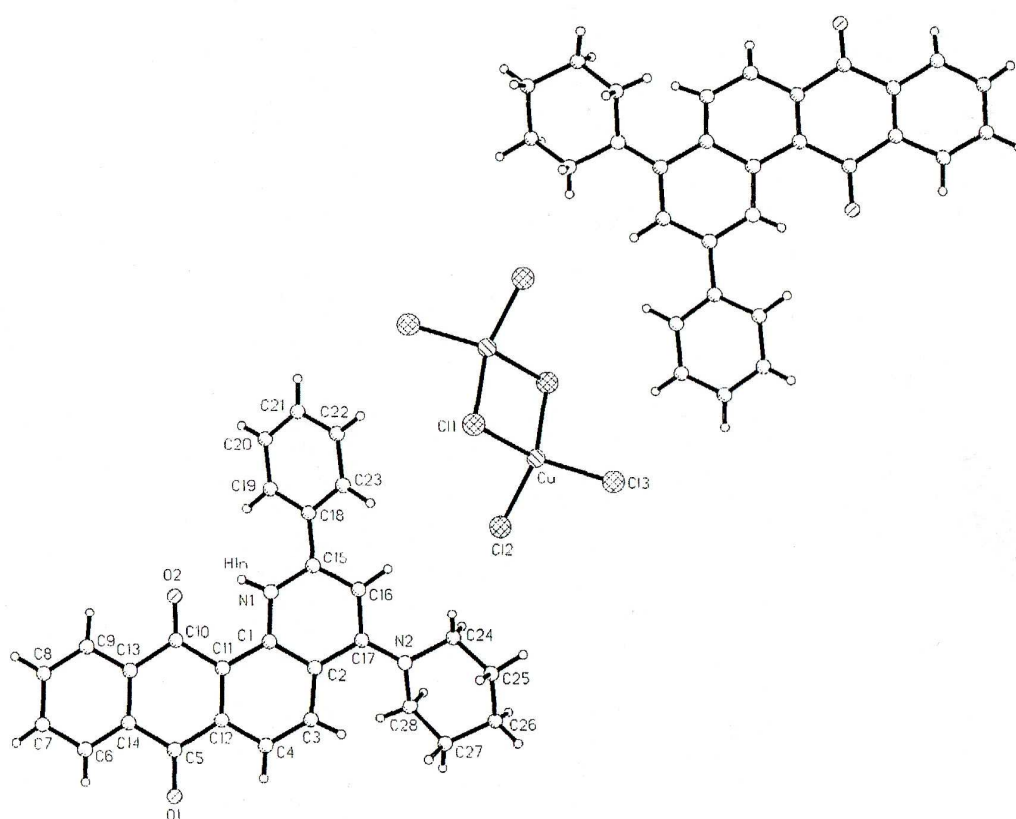


Fig. 17. The crystal structure of bis(4-pyridyl-1)-2-phenylpyrido[2,3-a]anthraquinonium-7,12 hexachlorodocuprate(II) (Kovalchukova et al., 2008b).

4.3 Bifolded $\text{Cu}_2\text{X}_6^{2-}$ structures

The second type of the distortion of a planar $\text{Cu}_2\text{X}_6^{2-}$ anion is known as a folded or “*sedia*” structure (Fig. 14C) where two terminal halide-ions (each one for every side of the dimer) go out of the conjunction plane. This type of distortion is characterized by the σ -angle between the central Cu_2X_2 , and the terminal CuX_3 planes.

The bifolded structures usually have (4+1) type of coordination of Cu(II) ions with the σ -angle inside the interval from 19 to 32.5 deg (Geiser et al., 1986a). The degree of folding of the dimer increases in case if all the five ligands are approaching the copper atom. This leads to the transformation of the coordination polyhedron from square-pyramidal (SP) to the

trigonal-bipyramidal (TBP) one (Fig. 18). Addition of one more coordination bond ((4+2) coordination) increases the Cu-L distances and leads to formation of square-bipyramidal (SBP) structures.

The change in the type of the coordination polyhedron in the folded $\text{Cu}_2\text{X}_6^{2-}$ anions is described by the change in degrees of distortion which are calculated as a mathematical difference of two θ -angles (fig. 18) (Blanchette & Willett, 1988). In case of the square-pyramidal structure (SP), $\theta_1 \approx \theta_2$, as for trigonal-bipyramidal (TBP) configurations the limits $\theta_1 \rightarrow 120^\circ$; $\theta_2 \rightarrow 180^\circ$, $\Delta = \theta_2 - \theta_1 = 60^\circ$. It is evident that the majority of the determined structures are characterized by Cu-Cl distances in the range 2.65 to 2.75 Å, and the Δ range 15 to 30 deg.

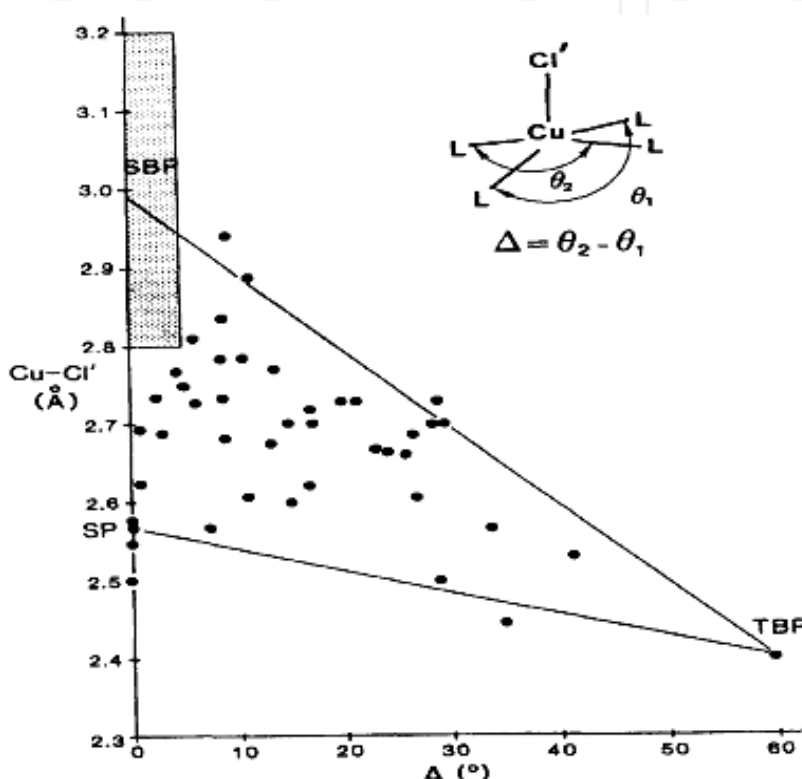


Fig. 18. The dependence of Cu-Cl distances in hexachlorodicuprates(II) on the degree of distortion Δ and the type of coordination polyhedron of Cu(II) (Blanchette & Willett, 1988).

A lot of bifolded five-coordinated halocuprates(II) were reported by various authors and cited in (O'Brien et al., 1988), and three different types of the formation of coordination polyhedra were found. In the first case, all the five coordination sites of Cu(II) are occupied by halide ions. That was described for example for bis(benzimidazolium) hexachlorodicuprate(II) (Bukowska-Strzyzewska & Tosik, 1985). As it was shown (Fig. 19), polymeric slightly bifolded $[\text{Cu}_2\text{Cl}_6^{2-}]_\infty$ chains elongated along the y axis are formed by stacking of $\text{Cu}_2\text{Cl}_6^{2-}$ dimers involving one of the terminal Cl-atom from each side of the monomeric unit. The coordination polyhedra around the Cu atoms of each crystallography independent chain may be described as a distorted square pyramid. The Cu-Cl bond lengths and angles in both crystallography independent anionic chains are not identical. The bridging Cu(1)-Cl(3) and Cu(2)-Cl(6) bonds (2.298 and 2.320 Å, respectively) correlate well to those for other described bonds of such a type (Murray-Rust, 1975). The terminal

Cu–Cl bonds, shorter than the bridging ones, are not equal. The Cu(1)–Cl(1) and Cu(2)–Cl(4) bonds (2.291 and 2.284 Å, respectively) linking the adjacent dimmers, are significantly longer than the terminate Cu(1)–Cl(2) and Cu(2)–Cl(5) bonds (2.245 and 2.256 Å, respectively) which are not involved into the interchain stacking. The Cu...Cu distances inside the $\text{Cu}_2\text{Cl}_6^{2-}$ dimmers are 3.464 and 3.470 Å, as the Cu...Cu distances between the adjacent dimmers are 3.716 and 3.777 Å. The inorganic anions and organic cations are joint by bifurcated H-bonds between NH^+ fragments of benzimidazolium cations and Cl(4) Cl(5) atoms of inorganic anions ($r \text{ N-H}$ 1.00 Å; $r \text{ H...Cl}$ 2.33 – 2.64 Å; $r \text{ N...Cl}$ 3.175 – 3.268 Å; $\angle \text{N-H...Cl}$ 119 – 144 deg.). Another type of H-bonds involves the NH-fragments of the organic cation and Cl(1) atoms ($r \text{ N-H}$ 1.00 Å; $r \text{ H...Cl}$ 2.24 and 2.73 Å for two unequivalent chains; $r \text{ N...Cl}$ 3.216 and 3.396 Å; $\angle \text{N-H...Cl}$ 164 and 124 deg.).

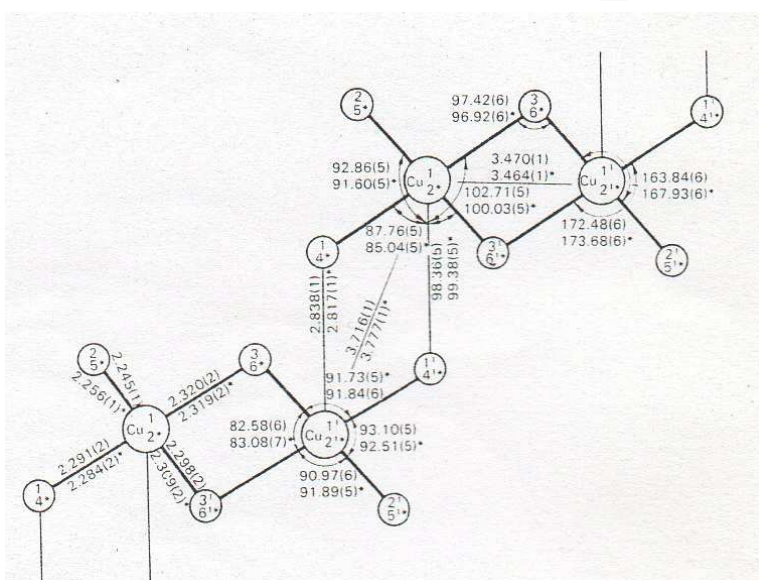


Fig. 19. Bond lengths (Å) and angles (deg.) in the two crystallographically independent $[\text{Cu}_2\text{Cl}_6^{2-}]_\infty$ chains of bis(benzimidazolium) hexachlorodicuprate(II) (Bukowska-Strzyzewska & Tosik, 1985).

Two similar structures of polymeric chlorocuprate(II) containing piperidinium and piperazinium counter-ions (Battaglia et al., 1988) also incorporate unequivalent $[\text{Cu}_2\text{Cl}_6^{2-}]_\infty$ chains joint together by Cu–Cl axial bonds. The $\text{Cu}_2\text{Cl}_6^{2-}$ monomers are bifolded with the σ -angles 29.6 and 23.2 deg. for piperidinium and piperazinium salts respectively. The bifolded distortion gives each Cu(II) ion a (4+1) coordination geometry but the chains differ in their configurations. In the piperazinium hexachlorodicuprate, adjacent dimers are related by unit-cell translation as illustrated on Fig. 15c. From the other hand, in the piperidinium salt the $[\text{Cu}_2\text{Cl}_6^{2-}]_\infty$ fragments are related by a c -glide operation (Fig. 15d). The smallest trans Cl–Cu–Cl angle is 150.43 deg. for the piperidinium salt and 156.8 in the piperazinium one. The equatorial Cu–Cl bond lengths are considerably shorter for the piperidinium complex (average 2.267 Å *vs.* 2.298 Å in the piperazinium one) but the axial semi-coordinate distances are identical (2.612 *vs.* 2.622 Å). The intradimer bridging Cu–Cl–Cu ϕ -angles are 95.5 *vs.* 95.8, and the interdimer bridging Cu–Cl–Cu ϕ' -angles are 87.1 *vs.* 89.1 deg., respectively. The folded structure of $\text{Cu}_2\text{Cl}_6^{2-}$ anions is also observed in bis(4-azfluorene-9-onium) hexachlorodiaquadicuprate(II) dehydrate (Koval'chukova et al., 2009a) but the coordinate

sphere of Cu^{2+} ions differs from previous cases. Both the two central atoms of the dimer are coordinated by four Cl atoms and one water molecule (Fig. 20). The polyhedron $CuCl_4H_2O$ is a distorted square pyramid with one chlorine atom in the axial position. Three Cl atoms and one water molecule form the pyramid basis, and the Cu atom is shifted towards the pyramid top by 0.27 Å. The bridging Cu–Cl distances are 2.274 and 2.307 Å, and the terminal Cu–Cl distances are 2.265 and 2.593 (axial bond) Å. The bifolded $Cu_2Cl_6^{2-}$ dimers (σ 20 deg.) are isolated. The organic cations are adjusted to the inorganic anion via an extra water molecule.

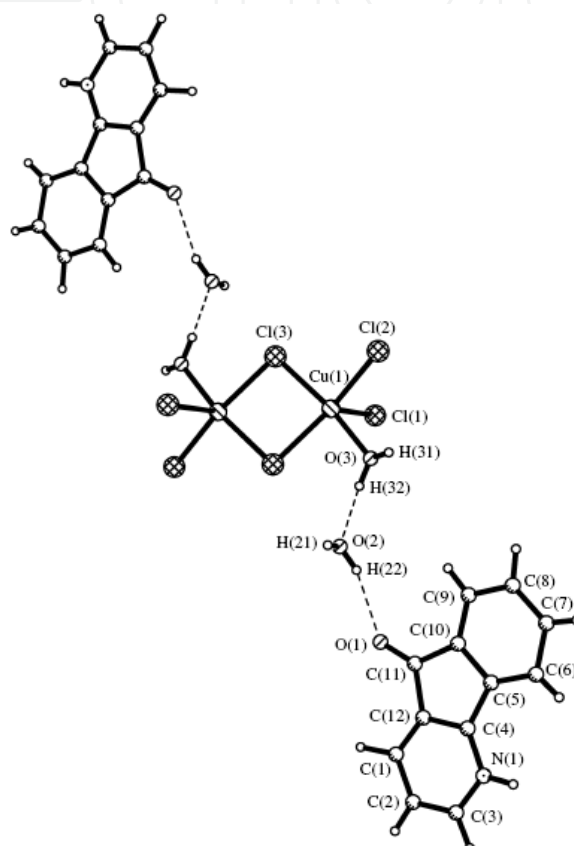


Fig. 20. The crystal structure of $(HL)_2[{\{CuCl_2(H_2O)_2\}_2(\mu-Cl)_2} \cdot 2H_2O$ (L - 4-azfluorene-9-one) (Koval'chukova et al., 2009a)

At the same time, in bis(1-amino-4-azfluorene-9-olium) hexachlorodicuprate(II) (Kuz'mina et al., 2002) the fifth coordinate bond of $Cu(II)$ cations is realized at the expense of the interaction of the lone electron pair of the O-atom of the hydroxo-group of the organic cation which is protonated by its N-heterocyclic atom with a vacant $Cu(II)$ d-orbital (Fig. 21). The $CuCl_4O$ polyhedron represents the form of distorted square pyramid where the O-atom occupies the axial position. All the four Cl atoms lie at one plane (the mean deviation from planarity is 0.055 Å) and the Cu atom is 0.174 Å shifted towards the pyramid top. The hexachlorodicuprate(II) anion has a bifolded configuration ($\sigma = 26.6$ deg.). The bridging Cu–Cl distances (2.299 and 2.324 Å) are a little bit longer than the terminal ones (2.226 and 2.262 Å). In the lattice, the inorganic dimers are adjacent in chains along the x -axis with the help of O–H...Cl hydrogen bonds. The shortest interdimer Cl...Cl contacts in chains are 4.584 Å.

The chains are adjacent in three dimensional skeleton structure via N-H...Cl hydrogen bonds (both N atoms of the pyridine ring and the amino-group are involved in the H-bonding).

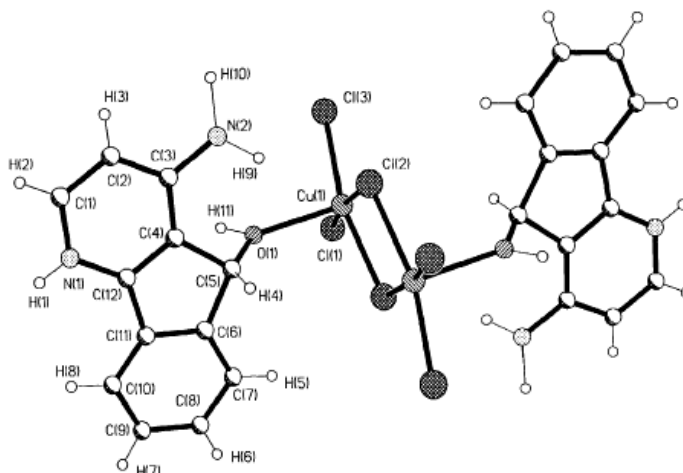


Fig. 21. The crystal structure of bis(1-amino-4-azfluorene-9-olium) hexachlorodicuprate(II) (Kuz'mina et al., 2002).

In the similar structure of bis(3-aminopyridinium) hexabromodicuprate(II) monohydrate (Blanchette & Willett, 1988), one of the terminal coordinate bond is released at the expense of the formation of a Cu-N bond involving the amino-group of the bifolded organic cation (Fig. 22). One of the Br atoms of the inorganic anion forms the axial bond.

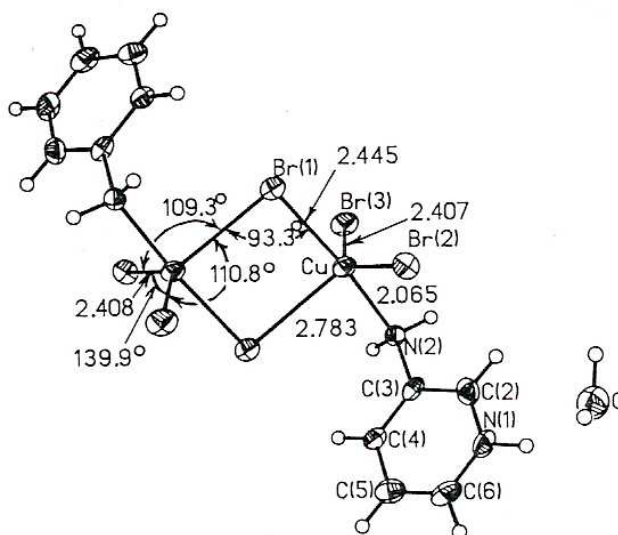


Fig. 22. The crystal structure of bis(3-aminopyridinium) hexabromodicuprate(II) monohydrate (Blanchette & Willett, 1988).

The analogous coordination of Cu(II) atoms via N-atoms of amino-groups of protonated organic bases was described for the co-crystallized bis(3-amino-2-methyl-4H-pyrido[1,2-a]pyrimidine-4-onium) hexachlorodicuprate(II) and 3-amino-2-methyl-4H-pyrido[1,2-a]pyrimidine-4-onium chloride (Kuz'mina et al., 2003) (Fig. 23).

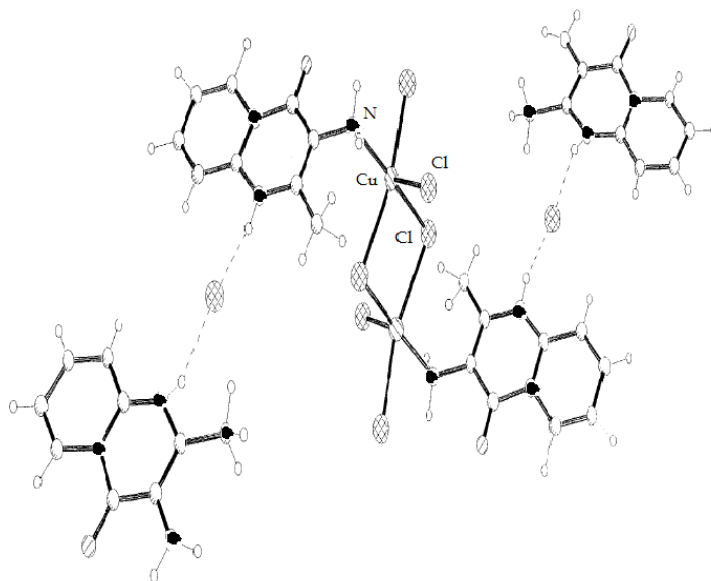


Fig. 23. The crystal structure of co-crystallized bis(3-amino-2-methyl-4H-pyrido[1,2-a]pyrimidine-4-onium) hexachlorodicuprate(II) and 3-amino-2-methyl-4H-pyrido[1,2-a]pyrimidine-4-onium chloride (Kuz'mina et al., 2003).

The fifth coordinate bond is formed via a lone electron pair of an amino-group of the organic cation which is protonated by an N-atom of a heterocycle. The coordination polyhedron $CuCl_4N$ of each Cu atoms in the dimer is a trigonal bipyramid with the N-atom as an axial ligand (r_{Cu-N} 2.080 Å). The Cu-Cl axial distance (2.316 Å) does not differ from the three others. The $Cu_2Cl_6^{2-}$ anion is isolated from other inorganic species and exists as a bifolded centro-symmetric dimer with the folding angle σ 13.3 deg. The structure is stabilized by a set of H-bonds between the H-atoms of the organic molecule and Cl⁻ ions of the inorganic anion.

4.4 Spectral-magneto-structural correlations

Analysis of spectral and structural data of hexachlorodicuprates(II) show linear dependences of positions of the absorption bands relating to the Cl→Cu charge transfer (CT) on the degree of distortion of the anionic polyhedron ($\Delta = \theta_1 - \theta_2$) (Koval'chukova et al., 2009a). From the Fig. 24 it is evident, that the Δ value changes from 0 to 6 deg. in non-distorted or slightly distorted square-pyramidal structures (ν_{CT} 19610 – 19900 cm^{-1}), and from 15 to 50 deg. in trigonal-bipyramidal structures (ν_{CT} 23880 – 24390 cm^{-1}). Thus, the position of the charge transfer bands in the electronic absorption spectra of the compounds of the general formula $(HL)_2[Cu_2Cl_6]$ may characterize the degree of distortion of dimeric coordination polyhedra. The attempt to deduce an analogous dependence for hexabromodicuprate(II) failed because of poor information in the literature.

It is well known that a slight exchange interaction exists in bridging dimeric hexachlorodicuprates and the magnetic behavior depends upon features of the structure of $Cu_2Cl_6^{2-}$ complex anions (Hay et al., 1975; Willett et al., 1983). For the folded structures, the value of the exchange interaction (J/k) is determined by the folding σ -angle and the bridging ϕ -angle. It was determined (O'Brien et al., 1988; Battaglia et al., 1988) that if $\phi = 95 - 96$ deg., the absence of the exchange interaction ($J/k = 0$) is observed at $\sigma = 23$ deg. In the case when $\sigma < 23$ deg., the antiferromagnetic exchange interaction occurs, and the ferromagnetic exchange interaction is observed at $\sigma > 23$ deg. (Fig. 25).

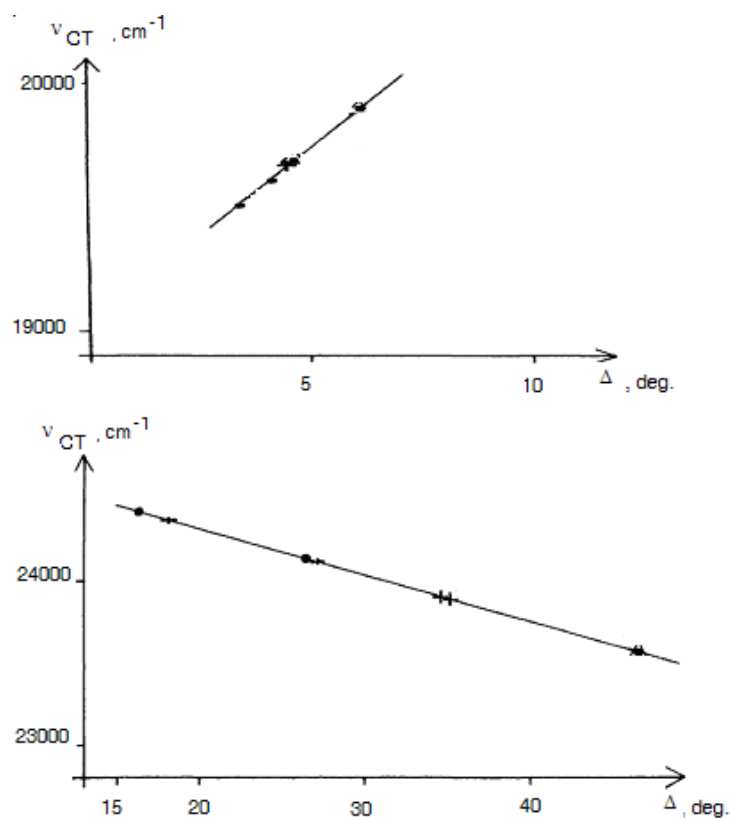


Fig. 24. The dependences of the positions of the absorption bands relating to the Cl→Cu charge transfer (CT) on the degree of distortion of the anionic polyhedron ($\Delta = \theta_1 - \theta_2$) (Koval'chukova et al., 2009a).

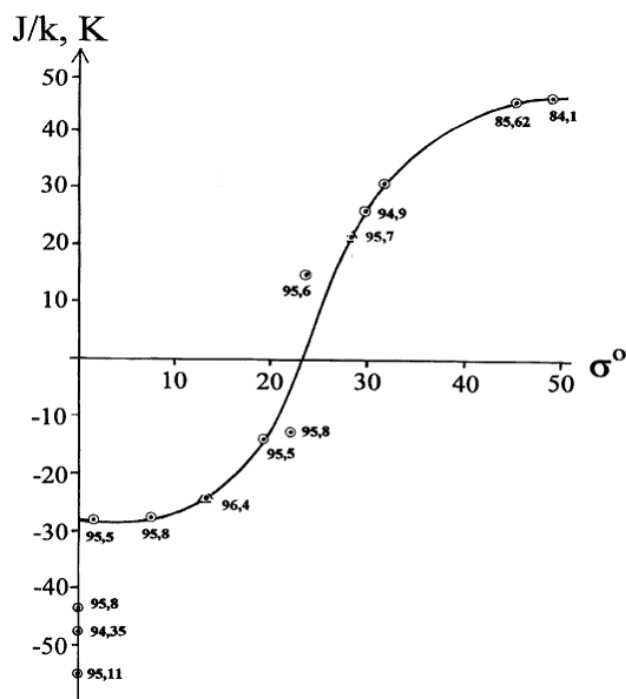


Fig. 25. The dependence of magnetic properties of bifolded hexchlorodicuprates(II) on the folding σ -angle and the bridging φ -angle (O'Brien et al., 1988).

The value of antiferromagnetic depends upon the shape of the coordination polyhedron of Cu(II) atoms: in the bifolded dimeric hexachlorodicuprates(II) the minimal antiferromagnetic exchange is observed for square-pyramidal structures, as well as the maximal one is observed for trigonal-bipyramidal complexes (Hay et al., 1975). The antiferromagnetic exchange increases with shortening of the bridging Cu–Cl bonds and with an increase of the electron density at the bridging atoms. In layered structures $[Cu_2Cl_6]_{\infty}^{2-}$ the existence of short intralayer Cl...Cl contacts (less than 3,94 Å) provoke the intralayer antiferromagnetic interaction which increases with the shortening of Cl...Cl distances (Scott et al., 1988).

5. Conclusion

Anionic halocuprate(II) complexes are of a great interest for scientists because of the areas of their application. They show a large variety in composition and coordinational geometry, and may be presented by mononuclear CuX_2^{2-} species ($X = Cl, Br$) or form $Cu_2X_6^{2-}$ dimers which can exist separately or be arranged in polymeric $[Cu_2Cl_6]_{\infty}^{2-}$ chains. Dimeric structures may exist as planar, twisted, or folded fragments. The coordination number of Cu(II) can change from 4 (tetrahedrons with different degrees of tetrahedral distortion or planar square configuration) to 5 (from the square pyramidal to the trigonal-bipyramidal configurations) and even 6 (more or less distorted octahedra). More complicated structures can also exist despite the event they were out of our interest.

Among the factors controlling on the type and finer details of coordination mode of Cu(II) there is the nature of the cation which neutralizes the negative charge of halocuprate(II) species, i.e. cation size, shape, flexibility, as well as the ability of formation of H-bonds. The nature of the halide atom (Cl or Br) affects the type of the structure much less. Unfortunately the influence of the organic cation on the features of the structure of halocuprates(II) is not unequivocal, and the determination of the crystalline structures not available at every instant. The relationship between the structure and spectral or magnetic properties appeared to be helpful by the prediction of the features of coordination modes, and physical properties as well as possible areas of the application of newly synthesized halocuprates(II).

6. Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grant 10-03-00003-a)

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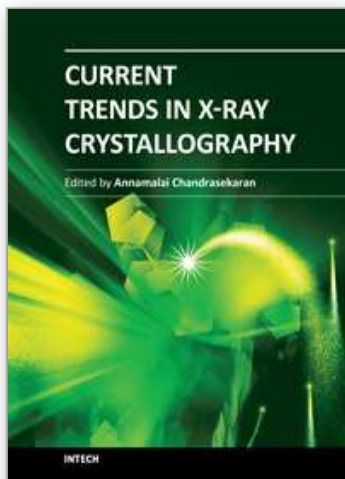
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Edited by Dr. Annamalai Chandrasekaran

ISBN 978-953-307-754-3

Hard cover, 436 pages

Publisher InTech

Published online 16, December, 2011

Published in print edition December, 2011

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