

Halocopper(II) complexes in acetic acid anhydride. I. Spectrophotometric study of the chloro- and bromocopper(II) complexes

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A spectrophotometric study of the systems $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$ (AA, acetic acid anhydride) has established that the two absorption bands in the visible region of the spectrum at 21 000 and 15 350 cm^{-1} , respectively, belong to a single absorbing particle, a complex ion with the ratio of $\text{X}/\text{Cu} = 3$ ($\text{X} = \text{Cl}, \text{Br}$). The complex ions CuX_3^{2-} are formed in AA solutions in appreciable amounts only at a large excess of halides. Their absorption maxima in the visible region occur at 25 000 and 19 300 cm^{-1} . Based on the spectral data, the structure of CuX_3^{2-} ions was assumed to be a distorted tetrahedron, similar to the structure of some compounds of the type A_2CuX_4 in the solid state. Ions $[\text{CuX}_3\text{AA}]^-$ are formed on solvolysis of CuX_3^{2-} and their structures are almost square-planar.

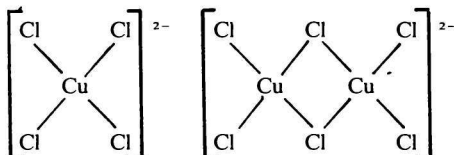
Спектрофотометрическим изучением систем $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$ и $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$ (AA — ангидрид уксусной кислоты) было определено, что абсорбционные полосы в видимой области спектра при 21 000 и 15 350 cm^{-1} принадлежат одной абсорбирующей частице а именно комплексному иону с отношением $\text{X}/\text{Cu} = 3$ ($\text{X} = \text{Cl}, \text{Br}$). Комплексные ионы CuX_3^{2-} возникают в наблюдаемом количестве в ацетангидридовых растворах только при большом избытке галогенида. Максимум поглощения в видимой области спектра находится при 25 000 и 19 300 cm^{-1} . На основе спектральных данных можно сделать заключение, что у ионов CuX_3^{2-} есть структура деформированного тетраэдра, которой характеризуются некоторые соединения типа A_2CuX_4 в твердом состоянии. Ионы $[\text{CuX}_3\text{AA}]^-$ возникают сольволизом ионов CuX_3^{2-} и их структура близка к планарной.

The results of numerous papers dealing with the systems $\text{Cu}(\text{II}) - \text{X}^- - \text{solvent}$ ($\text{X} = \text{Cl}, \text{Br}$) pointed out that such solutions contain complex ions $[\text{CuX}_n]^{2-n}$ ($n = 1-4$) [1-16]. In some cases also the existence of penta- and hexahalocopper(II) complexes has been anticipated [17-19].

There are different opinions as regards the structure and optical properties of tri- and tetrahalocopper(II) complexes. The structure of CuX_3^{2-} has been suggested to be both planar [7-10, 17, 19] and tetrahedral [2, 5, 6, 9]. The complex with the X/Cu ratio of 3 was shown to exist in solutions as planar monomer CuX_3^- [5], planar dimer $\text{Cu}_2\text{X}_6^{2-}$ [8, 12-15] and $[\text{CuX}_3\text{L}]^-$, the solvolysis product of CuX_3^{2-} [2, 6]. In the case of the bromocopper(II) complex, in addition to the above-mentioned possibilities, the existence is considered of the complex ion $[\text{CuBr}_3\text{L}_2]^-$ in which the arrangement of the ligands around the central atom is trigonal bipyramidal with solvent molecules at axial positions [16]. The attribution of the

absorption bands observed in the visible region of the spectrum to the complex compounds formed has not yet been unambiguous.

Studied from our laboratories dealing with chlorocopper(II) complexes in nonaqueous solvents led to an assumption that tri- and tetrachlorocopper(II) complexes absorb in the same spectral region and that the complex ions CuCl_4^{2-} and $\text{Cu}_2\text{Cl}_6^{2-}$ possess in the solution an equal coordination sphere around Cu:



In complex compounds acetic acid anhydride is capable to form dative π bonds similarly as acetone, acetonitrile, acrylonitrile and some other solvents. Interaction of which was extensively investigated with halocopper(II) complexes [20—22]. The systems Cu(II)—Cl^- —AA and Cu(II)—Br^- —AA have not yet been studied. This paper deals with the spectrophotometric study of halocopper(II) complexes in acetic acid anhydride absorbing in the visible region of spectrum, their composition, structure, and conditions of existence. Emphasis is given to the number of complex ions present in the solution under various conditions and to the regions of maximum absorbances of individual complex species.

Experimental

Chemicals and equipments

The following chemicals were used: $\text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, prepared from copper(II) hydroxide carbonate and HClO_4 ; LiCl (anal. grade); LiBr , prepared from Li_2CO_3 and HBr ; acetic acid anhydride, the fraction with b.p. 140—141°C.

Spectrophotometric measurements in the ultraviolet and visible region were carried out with an UV VIS 200 spectrophotometer (Zeiss, Jena) and in the near infrared region with an SF-8 spectrophotometer (LOMO Leningrad).

Analytical procedures

Copper in $\text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was determined complexometrically. Halides in acetic acid anhydride solutions of LiCl and LiBr were determined argentometrically using potentiometric indication.

Bromocopper(II) complexes in acetic acid anhydride are kinetically unstable. To achieve reproducibility of measurements the absorption curves were recorded always 2 min after the preparation of solutions.

Results

Absorption spectrum

The absorption spectra of the system $\text{Cu(ClO}_4)_2 \cdot 6\text{H}_2\text{O—LiCl—AA}$ at various Cl/Cu ratios are shown in Fig. 1. At Cl/Cu ratios from 3 to 10, there is only one absorption band in the visible region of the

spectrum at $21\,000\text{ cm}^{-1}$ with $\epsilon_{\text{max}} = 2400\text{ cm}^2\text{ mM}^{-1}$. In the near infrared region the main absorption band appears at $11\,400\text{ cm}^{-1}$ with $\epsilon_{\text{max}} = 96\text{ cm}^2\text{ mM}^{-1}$. An additional band at about 8800 cm^{-1} has a much lower value of molar absorptivity. According to the values of ϵ_{max} , the absorption band in the visible region represents a charge-transfer band and the bands observed in the near infrared region are the ligand-field bands. In the presence of a large excess of chlorides a new absorption band appears at $25\,000\text{ cm}^{-1}$ and the intensity of the band at $\approx 8800\text{ cm}^{-1}$ increases. The intensity of the original bands

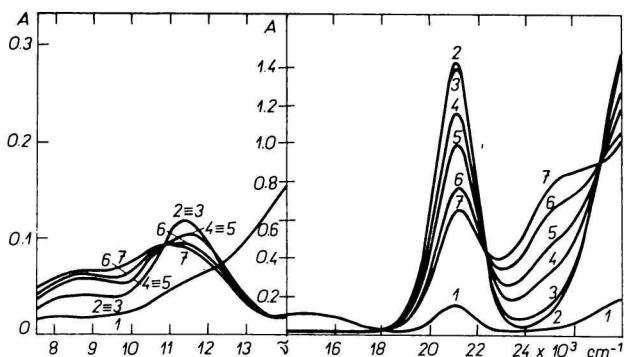


Fig. 1. Effect of chloride ion on the spectrum of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in acetic acid anhydride ($c_{\text{Cu}} = 2 \times 10^{-4}\text{ mol l}^{-1}$).

Cl/Cu ratio: 1. 2; 2. 10; 3. 100; 4. 500; 5. 1000; 6. 2000; 7. 3000.
2 cm cell used above $14\,000\text{ cm}^{-1}$, 5 cm cell below $14\,000\text{ cm}^{-1}$.

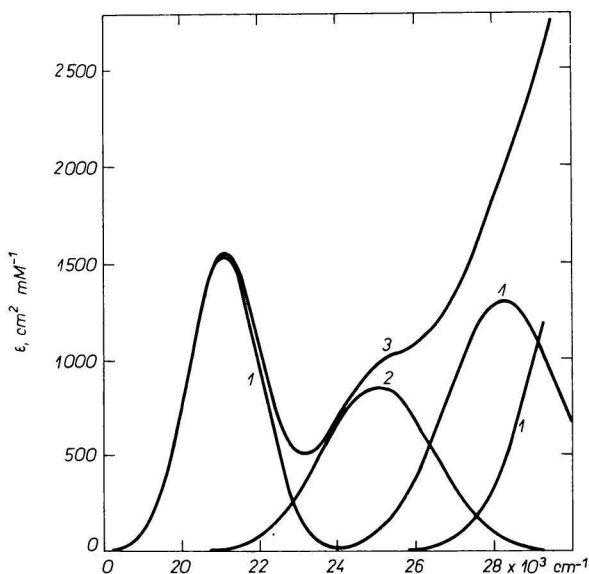


Fig. 2. Analyzed absorption spectrum of the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$.
 $c_{\text{Cu}} = 5 \times 10^{-4}\text{ mol l}^{-1}$, Cl/Cu ratio 1000.

1. Absorption bands of $[\text{CuCl}_3, \text{AA}]^-$; 2. absorption band of CuCl_2^- ; 3. absorption spectrum recorded.

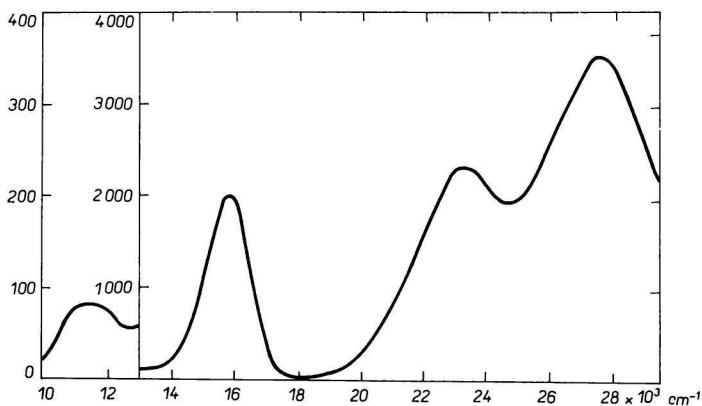


Fig. 3. Absorption spectrum of the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$.
 $c_{\text{Cu}} = 2 \times 10^{-4} \text{ mol l}^{-1}$, $c_{\text{Br}^-} = 6 \times 10^{-4} \text{ mol l}^{-1}$, 2 cm cell.

simultaneously decreases. It is obvious that an equilibrium was established in the solution. Assuming that under given conditions two complex species predominate in the solution (see below), the value of molar absorptivity of the complex with the band at $25\,000 \text{ cm}^{-1}$ as well as the percentual proportion of both complexes can be calculated by means of an analysis of the absorption spectrum of the solution with a Cl/Cu ratio of 1000 (Fig. 2). This treatment showed that in a 10^3 -fold excess of chlorides, the solution contains 63.8% of the component absorbing at $21\,000 \text{ cm}^{-1}$ and 36.2% of the component

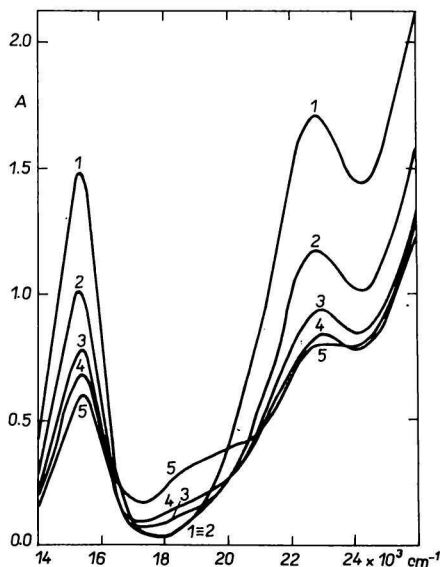


Fig. 4. Effect of bromide ion on the spectrum of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in AA ($c_{\text{Cu}} = 5 \times 10^{-4} \text{ mol l}^{-1}$).
 Br/Cu ratio: 1. 10; 2. 100; 3. 500; 4. 1000; 5. 2000.
 2 cm cell.

absorbing at $25\,000\text{ cm}^{-1}$. The calculated value of ϵ_{max} of the latter component is $2380\text{ cm}^2\text{ mM}^{-1}$. The exact values of $\tilde{\nu}_{\text{max}}$, ϵ_{max} and half-widths δ of the absorption bands, which are assumed to belong to the complex ion $[\text{CuCl}_3\text{AA}]^-$ and are needful for the above-mentioned calculation, were obtained by an analysis of the absorption spectrum of the solution with a Cl/Cu ratio of 10.

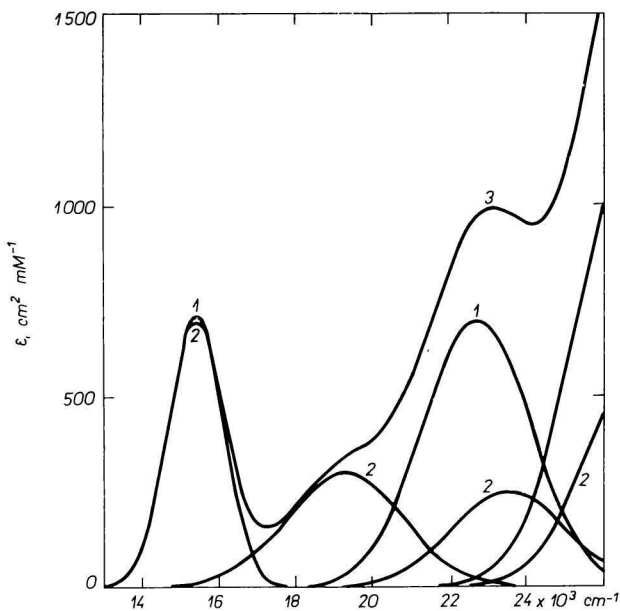


Fig. 5. Analyzed absorption spectrum of the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$.

$$c_{\text{Cu}} = 5 \times 10^{-4}\text{ mol l}^{-1}, c_{\text{Br}} = 1.5\text{ mol l}^{-1}, \text{Br/Cu ratio } 3000.$$

1. Absorption bands of $[\text{CuBr}_3\text{AA}]^-$; 2. absorption bands of CuBr_2^- ; 3. absorption spectrum recorded.

Fig. 3 shows the absorption spectrum of the solution with a Br/Cu ratio of 3. The absorption bands with maxima at $15\,350$, $22\,650$, and $26\,900\text{ cm}^{-1}$ having $\epsilon_{\text{max}} = 2320$, 2520 , and $3670\text{ cm}^2\text{ mM}^{-1}$, respectively, represent the charge-transfer bands. The fourth band at $11\,600\text{ cm}^{-1}$ is a ligand-field band with $\epsilon_{\text{max}} = 133\text{ cm}^2\text{ mM}^{-1}$. The absorbance in the visible region reaches a maximum directly at a Br/Cu ratio of 3 and evidently decreases with an increasing bromide concentration. In a large excess of bromides, the character of the absorption spectrum changes (Fig. 4). A new absorption band appears at $19\,300\text{ cm}^{-1}$. Under the assumption that only two complex species exist in the solution at given conditions, their proportion in the solution and ϵ_{max} value of the complex absorbing at $19\,300\text{ cm}^{-1}$ can be calculated from the data obtained by an analysis of the spectrum of the solution with a Br/Cu ratio of 3000 (Fig. 5). According to our calculations, the above solution contains 60% of the component absorbing at $15\,350\text{ cm}^{-1}$ and 40% of the component absorbing at $19\,300\text{ cm}^{-1}$ with $\epsilon_{\text{max}} = 1500\text{ cm}^2\text{ mM}^{-1}$.

The changes in the absorption spectrum in the visible region are accompanied by changes in the near infrared region. The absorbance of the band around $11\,600\text{ cm}^{-1}$ moderately decreases and a new less intense band is observed at about 9000 cm^{-1} .

*Number and composition of the complexes absorbing
in the visible region*

The assumption, that at X/Cu ratios lesser than 10 only one complex and at higher X/Cu ratios two halocopper(II) complexes absorb in the visible region, can be verified by a simple graphical method proposed by *Coleman et al.* [23]. In the case that only one species absorbs in a given spectral region, according to this method, the value of the determinant $\begin{vmatrix} A_{i1} & A_{i2} \\ A_{21} & A_{22} \end{vmatrix}$ is zero and the plot A_{ij} vs. A_{i0j} gives a straight line which intersects the origin (A_{ij} are the absorbance values of the solutions with varying concentration of the component j at a chosen wavenumber i and at a constant concentration of the second component). If two species absorb in a given spectral region, zero is the value of the determinant of the third order. The plot $(A-A_0)_1$ vs. $(A-A_0)_2$, where 1, 2 are two chosen wavenumbers and A_0 the absorbance of the solution with zero concentration of one of the complex forming components at a given wavenumber, is a straight line passing through the origin. Fig. 6 shows the plot A_{ij} vs. A_{i0j} in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$. At higher Cl/Cu ratios, the plot loses its linear character. As it can be seen in Fig. 7, a straight line was acquired by plotting $(A-A_0)_1$ vs. $(A-A_0)_2$.

These results lead to an assumption that only one complex exists in the system at low chloride concentrations while at higher concentrations two complex species are present. In the complex with a maximum absorbance at $21\,000\text{ cm}^{-1}$, the molar ratio of copper to chloride was found to be 1:3 using the methods of mole ratios and continuous variations (Figs. 8 and 9). These two methods could not be applied for the determination of the composition of the complex having the maximum absorbance at $25\,000\text{ cm}^{-1}$ since it is formed only at a large excess of chlorides.

In the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$, the plot A_{ij} vs. A_{i0j} at a Br/Cu ratios between 2 and 3 gives also a straight line passing through the origin (Fig. 10). Thus under these conditions only one complex absorbs. As bromide is added (up to Br/Cu ratios about 400), the plot A_{ij} vs. A_{i0j} does not change, however, the absorbance decreases. This fact may be due to the formation of a complex which does not absorb in the visible region of spectrum. A deviation from the straight line is observed at Br/Cu

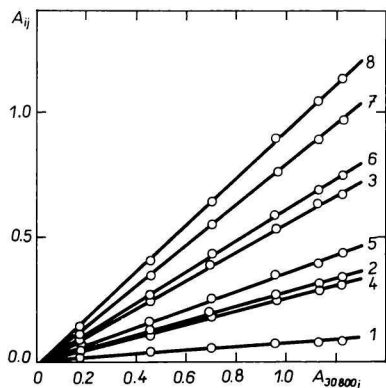


Fig. 6. The plot A_{ij} vs. A_{30800j} in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$.

$$c_{\text{Cu}} = 4 \times 10^{-4} \text{ mol l}^{-1},$$

$$c_{\text{Cl}} = 0.785 - 1.175 \times 10^{-3} \text{ mol l}^{-1},$$

$$\bar{\nu} = 19\,000 - 30\,000 \text{ cm}^{-1}.$$

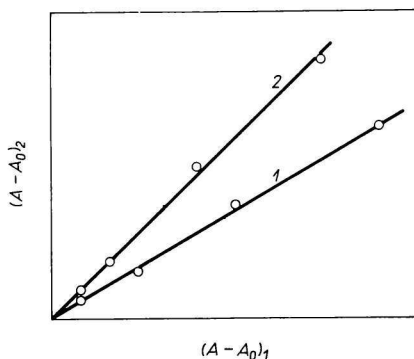


Fig. 7. The plot $(A-A_0)_1$ vs. $(A-A_0)_2$ in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$.

$$c_{\text{Cu}} = 3 \times 10^{-4} \text{ mol l}^{-1},$$

$$c_{\text{Cl}} = 1.5 - 3 \times 10^{-3} \text{ mol l}^{-1}.$$

1. $\bar{\nu}_1 = 24\,000 \text{ cm}^{-1}$, $\bar{\nu}_2 = 21\,000 \text{ cm}^{-1}$;
2. $\bar{\nu}_1 = 20\,500 \text{ cm}^{-1}$, $\bar{\nu}_2 = 25\,000 \text{ cm}^{-1}$.

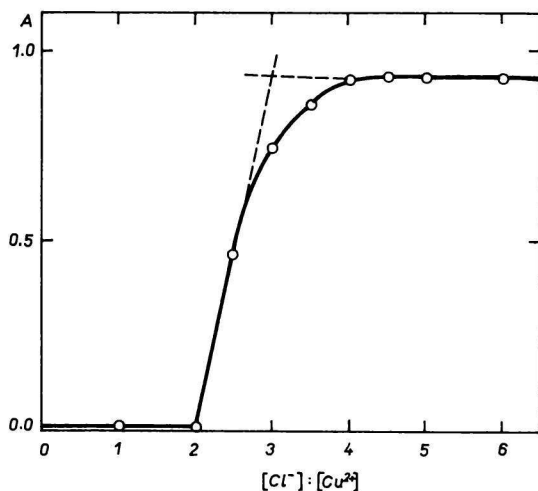


Fig. 8. Absorbance of the system

$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$ as a function of the Cl/Cu ratio.

$c_{\text{Cu}} = 5 \times 10^{-4} \text{ mol l}^{-1}$, $\tilde{\nu} = 21\,000 \text{ cm}^{-1}$, 1 cm cell.

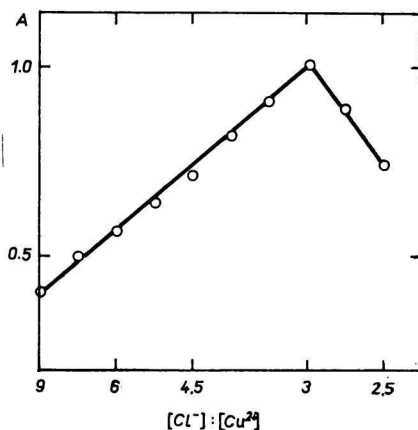


Fig. 9. Absorbance of isomolar solutions of the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$ as a function of the Cl/Cu ratio.

$c_{\text{Cl}} + c_{\text{Cu}} = 5 \times 10^{-3} \text{ mol l}^{-1}$, $\tilde{\nu} = 21\,000 \text{ cm}^{-1}$, 1 cm cell.

ratios higher than 500 when a new absorption band at $19\,300 \text{ cm}^{-1}$ arises. The results cannot be evaluated unambiguously, probably because of a low kinetic stability of the bromocopper(II) complexes in AA. Consequently, the recorded values of absorbances are less reproducible, particularly at higher Br/Cu ratios.

The composition of the complex with a maximum absorbance at $15\,350 \text{ cm}^{-1}$ was examined by the methods of mole ratios and continuous variations (Figs. 11 and 12). According to the results of both methods, the absorption band is attributed to the complex with a ratio of copper to bromide 1:3. The absorption band at $19\,300 \text{ cm}^{-1}$ is observed only at a large excess of bromide. For this reason its composition could not be elucidated by the above-mentioned methods.

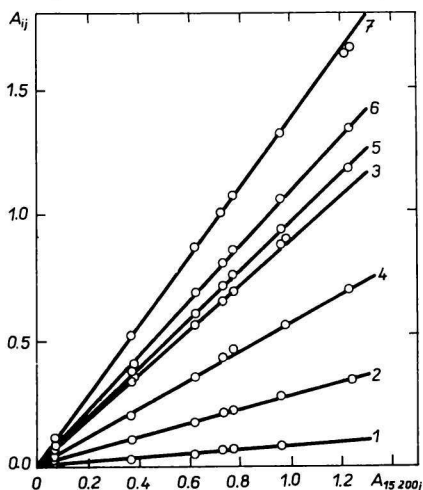


Fig. 10. The plot A_{ij} vs. $A_{15\,200j}$ in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$.

$c_{\text{Cu}} = 5 \times 10^{-4} \text{ mol l}^{-1}$,
 $c_{\text{Br}} = 1 - 1.5 \times 10^{-3} \text{ mol l}^{-1}$,
 $\tilde{\nu} = 13\,000 - 26\,000 \text{ cm}^{-1}$.

Discussion

In the systems $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$ and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$ two complexes are formed showing significant absorbance at $21\,000$ and $15\,350\text{ cm}^{-1}$, respectively. Both absorption bands correspond to a single complex with a Cu/X ratio 1:3. This finding obtained by the method of *Coleman et al.* [23] was further confirmed by the fact that the position of the maxima of the absorption bands did not change with the Cu(II) concentration in the range $5 \times 10^{-5} - 5 \times 10^{-3}\text{ mol l}^{-1}$ at a X/Cu ratio lesser than 10. If two complexes absorb in the same spectral region, the position of the maximum absorbance is usually affected by the changes in the concentrations of a complex-forming reagent [24]. Thus we have proved that in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$ at Cl/Cu ratios 3—10 only one complex is formed. The idea that the absorption band at $21\,000\text{ cm}^{-1}$ is exhibited by two complexes, different in composition but having an identical coordination sphere around Cu, has not been confirmed [13].

The absorption band at $25\,000\text{ cm}^{-1}$ is not observed in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiCl} - \text{AA}$ until the Cl/Cu ratio exceeds 100, contrary to the systems Cu(II)—Cl—acetone [17] and Cu(II)—Cl—acetonitrile [1] in which such band appears in the visible region at a much lower excess of chloride. One can infer from this fact that the stability constants of CuCl_4^{2-} and CuCl_3L^- differ in these solvents.

The electronic crystal spectra of Cs_2CuCl_4 and $[(\text{CH}_3)_4\text{N}]_2\text{CuCl}_4$ [25] with a D_{2d} symmetry of CuCl_4^{2-} [26—28] show absorption bands at $25\,000\text{ cm}^{-1}$ in the visible and around 9000 and 8800 cm^{-1} in the infrared region. Two of these bands ($\tilde{\nu}_{\text{max}} = 25\,000$ and 8800 cm^{-1}) were also observed in acetic acid anhydride solution of chlorocopper(II) complexes at a large excess of chloride ions. Based on these data it is probable that the complex formed in the solution is CuCl_4^{2-} with a structure of distorted tetrahedron.

The situation in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$ is complicated due to a low kinetic stability of the bromocopper(II) complexes in AA. The decrease of absorbance in the visible region at a large excess of bromide may be ascribed to the reduction of Cu(II) to Cu(I) and to the formation of a bromocopper(I) complex absorbing in the ultraviolet region. We assume that the spontaneous redox processes taking place in the solutions of halocop-

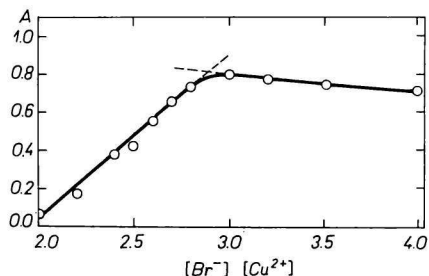


Fig. 11. Absorbance of the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$ as a function of the Br/Cu ratio.

$c_{\text{Cu}} = 5 \times 10^{-4}\text{ mol l}^{-1}$, $\tilde{\nu} = 15\,400\text{ cm}^{-1}$, 1 cm cell.

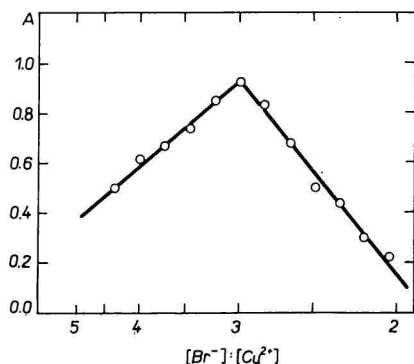


Fig. 12. Absorbance of isomolar solutions of the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$ as a function of the Br/Cu ratio.

$c_{\text{Cu}} + c_{\text{Br}} = 4 \times 10^{-3}\text{ mol l}^{-1}$, $\tilde{\nu} = 15\,400\text{ cm}^{-1}$, 0.5 cm cell.

per(II) complexes in some nonaqueous solvents are caused by an effect of the Cu-solvent bond on the Cu-halogen bond which is most pronounced in the case of the halogen bound in a *trans* position with respect to solvent. When a solvent is capable to form a dative π bond with the central atom, the increase of the positive effective charge on the central atom, as a consequence of electron drawing, creates suitable conditions for a non-polar splitting of the Cu-halogen bond resulting in a reduction of Cu(II) to Cu(I) and a simultaneous oxidation of X^- to X^\cdot [29]. With respect to the structure, acetic acid anhydride is capable to form a dative π bond. This fact may be assumed to support the reduction of Cu(II) to Cu(I) in the studied system.

The complex absorbing at $15\,350\text{ cm}^{-1}$ has the Cu/Br ratio 1 : 3. The absorption band at $19\,300\text{ cm}^{-1}$ is probably exhibited by CuBr_4^{2-} with a D_{2d} symmetry. This we infer from the electronic crystal spectrum of Cs_2CuBr_4 with a D_{2d} symmetry of the complex anion, in which the mentioned absorption band was observed too [30].

The low value of ϵ_{max} calculated for the complex ion CuBr_4^{2-} at $19\,300\text{ cm}^{-1}$ ($1500\text{ cm}^2\text{ mM}^{-1}$) is due to the fact that the basic assumption of the calculation was not fulfilled. Originally, only two complex ions were considered to be present in the solution. However, the concentration of Cu(I) is not negligible and that of CuBr_4^{2-} is in fact lower than the calculated one. Consequently, the real value of ϵ_{max} is higher.

The values of molar absorptivities of CuCl_4^{2-} at $25\,000\text{ cm}^{-1}$ and CuBr_4^{2-} at $19\,300\text{ cm}^{-1}$ confirm that the observed bands are the charge-transfer bands.

The ligand-field band is shifted to the region of lower energy with an increase of the Cl/Cu ratio (Fig. 1). Similar phenomenon, although in a less expressive form, was observed in solutions of bromocopper(II) complexes. This shift can have two reasons:

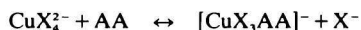
1. Solvent molecules in the coordination sphere are gradually substituted by halogen atoms. The donor atom in acetic acid anhydride is oxygen. Ligand-field energy of oxygen is higher than that of chlorine or bromine. Thus a substitution of the solvent by halogen atoms will result in a shift of the ligand-field band to lower energies.

2. A shift of the ligand-field band in the same direction may also result from a transition of planar arrangement of ligands to a distorted tetrahedral.

In this case, both factors must be considered. An increase of the concentration of free ligands suppresses solvolysis. The symmetry of the complexes CuL_4^{2+} , CuXL_3^+ , CuX_2L_2 , CuX_3L^- , and CuX_4^{2-} is not the same: the deviation from planar arrangement increases with the number of halogen atoms in the inner coordination sphere.

The absorption band at $21\,000\text{ cm}^{-1}$ is ascribed to $[\text{CuCl}_3\text{AA}]^-$, which is a solvolysis product of CuCl_4^{2-} and has a structure of a strongly distorted tetrahedron.

The absorption band at $15\,350\text{ cm}^{-1}$ found in the system $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} - \text{LiBr} - \text{AA}$ is ascribed to the complex $[\text{CuBr}_3\text{AA}]^-$ formed on solvolysis of CuBr_4^{2-} . Based on the spectral data, the shift of the equilibrium



to the solvolysis product appears to be more pronounced in the solutions of bromocopper(II) complexes.

References

1. Manahan, S. E. and Iwamoto, R. T., *Inorg. Chem.* **4**, 1409 (1965).
2. Furlani, C. and Morpurgo, G., *Theor. Chim. Acta* **1**, 102 (1963).
3. Kuzina, M. G., Lipovskii, A. A., and Nikitina, S. A., *Zh. Neorg. Khim.* **16**, 2461 (1971).

4. Kirpichnikova, N. P. and Nalbandian, R. M., *Izv. Akad. Nauk SSSR, Ser. Khim.* **1970**, 1991.
5. Ludwig, W. and Textor, M., *Helv. Chim. Acta* **54**, 1143 (1971).
6. Chugtai, A. R. and Keller, R. N., *J. Inorg. Nucl. Chem.* **31**, 633 (1969).
7. Gill, N. S. and Nyholm, R. S., *J. Chem. Soc.* **1959**, 3997.
8. Gažo, J., *Chem. Zvesti* **10**, 509 (1956).
9. Eswein, R. P., Howald, E. S., Howald, R. A., and Keeton, D. P., *J. Inorg. Nucl. Chem.* **29**, 437 (1967).
10. Howald, R. A. and Keeton, D. P., *Spectrochim. Acta* **22**, 1211 (1966).
11. Scharff, J. P., *Bull. Soc. Chim. Fr.* **1972**, 413.
12. Gažo, J., *Chem. Zvesti* **10**, 612 (1956).
13. Gažo, J., *Chem. Zvesti* **11**, 107 (1957).
14. Gažo, J., *Chem. Zvesti* **11**, 143 (1957).
15. Gažo, J., *Zh. Neorg. Khim.* **3**, 1166 (1958).
16. Barnes, J. C. and Hume, D. N., *Inorg. Chem.* **2**, 444 (1963).
17. Faye, G. H., *Can. J. Chem.* **44**, 1643 (1966).
18. Kosower, E. M., Martin, R. L., and Meloche, V. W., *J. Amer. Chem. Soc.* **79**, 1509 (1957).
19. Spessard, J. E., *Spectrochim. Acta* **26A**, 297 (1970).
20. Gažo, J., *Chem. Zvesti* **15**, 20 (1961).
21. Ondrejovič, G. and Čislova, J. N., *Chem. Zvesti* **20**, 729 (1966).
22. Ondrejovič, G., *Thesis*. Slovak Technical University, Bratislava, 1966.
23. Coleman, J. S., Varga, L. P., and Mastin, S. H., *Inorg. Chem.* **9**, 1015 (1970).
24. Schläfer, H. L., *Kompleksoobrazovanye v rastvorakh*. (Komplexbildung in Lösung; Russian translation.) Khimiya, Moscow, 1964.
25. Willett, R. D., Liles, O. L., Jr., and Michelson, C., *Inorg. Chem.* **6**, 1885 (1967).
26. Helmholtz, L. and Kruh, R. F., *J. Amer. Chem. Soc.* **74**, 1176 (1952).
27. Morosin, B. and Lingafelter, E. C., *Acta Crystallogr.* **13**, 807 (1960).
28. Morosin, B. and Lingafelter, E. C., *J. Phys. Chem.* **65**, 50 (1961).
29. Gažo, J., *Chem. Zvesti* **19**, 826 (1965).
30. Morosin, B. and Lawson, K., *J. Mol. Spectrosc.* **12**, 98 (1964).

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