# Halocopper(II) complexes in acetic acid anhydride. II.
# Composition and properties of chlorobromocopper(II) complexes

Z. BIELA, T. OBERT, and J. GAŽO

*Department of Inorganic Chemistry, Slovak Technical University,*
*880 37 Bratislava*

A spectrophotometric study of the system $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl—LiBr—AA (AA, acetic acid anhydride) showed that at a X/Cu ratio of 3 (X = Cl + Br) there is an equilibrium among the complex ions $[CuCl_3AA]^-$, $[CuCl_2BrAA]^-$, $[CuClBr_2AA]^-$, and $[CuBr_3AA]^-$ present in the solution. Each complex ion exhibits its own absorption band in the visible region of the spectrum. Exact $\bar{v}_{max}$ values were obtained by an analysis of the Gaussian curves of the absorption spectra of solutions with various Cu : Cl : Br ratios: $\bar{v}_1 = 15\ 350\ cm^{-1}$, $\bar{v}_2 = 17\ 000\ cm^{-1}$, $\bar{v}_3 = 18\ 850\ cm^{-1}$, $\bar{v}_4 = 20\ 980\ cm^{-1}$. The approximately calculated values of $\varepsilon_{max}$ correspond to those characteristic for charge-transfer bands. According to the spectral data, the symmetry of the complex anion is not substantially affected by changes in the coordination sphere.

Спектрофотометрическим изучением системы $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl—LiBr——AA (AA = ангидрид уксусной кислоты) было найдено, что при отношении X/Cu = 3 (X = Cl + Br) существует (в растворе) равновесие между $[CuCl_3AA]^-$, $[CuCl_2BrAA]^-$, $[CuClBr_2AA]^-$ и $[CuBr_3AA]^-$ Каждому комплексному иону принадлежит изолированная абсорбционная полоса в видимой области спектра. Точные значения $\bar{v}_{max}$ были определены из спектров абсобции растворов с разным отношением Cu : Cl : Br через гауссовские кривые: $\bar{v} = 15\ 350\ см^{-1}$, $\bar{v}_2 = 17\ 000\ см^{-1}$, $\bar{v}_3 = 18\ 850\ см^{-1}$, $\bar{v}_4 = 20\ 980\ см^{-1}$. Вычисленные приблизительные значения $\varepsilon_{max}$ соответствуют значениям характерным для полос с переносом заряда. Из спектральных данных вытекает, что симметрия комплексного аниона существенно не изменяется при изменении координационной сферы.

So far, only few papers dealing with the formation of chlorobromocopper(II) complexes in solutions have been published [1—4]. Little [1—3] or no [4] attention has been paid to the number of complex species formed in the solution and to their composition. A spectrophotometric study of the system Cu(II)—$Cl^-$—$Br^-$—acetone has proved the existence of complex ions $[CuCl_3Br]^{2-}$ and $[CuCl_2Br]^-$, and electrochemical methods revealed the existence of a series of compounds of intermediate composition $[CuCl_xBr_{3-x}]^-$ and $[CuCl_xBr_{4-x}]^{2-}$, where $x = 0$—3 and 0—4, respectively.

The aim of the present work was to determine the number of chlorobromocopper(II) complexes formed under the given conditions in the system $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl——LiBr—AA and to elucidate their composition and structure. The spectrophotometric study of the systems $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl—AA and $Cu(ClO_4)_2 \cdot 6H_2O$—LiBr—AA [5] represents a theoretical basis of this investigation.

## Experimental

### Chemicals and equipments

The following chemicals were used: $Cu(ClO_4)_2 \cdot 6H_2O$, 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.

Absorption spectra in the ultraviolet and visible region were recorded with an UV VIS 200 spectrophotometer (Zeiss, Jena) and in the infrared region with an SF-8 spectrophotometer (LOMO Leningrad).

Absorption spectra were analyzed under the following assumptions:

a) The absorption bands of individual components are symmetric Gaussian curves.

b) The sum of the absorption bands of all components gives the recorded absorption curve.

The whole calculation procedure was programmed for a high-speed computer GIER in the ALGOL IV language.

### Analytical procedures

Copper in $Cu(ClO_4)_2 \cdot 6H_2O$ was determined complexometrically. Halides in AA solutions of LiCl and LiBr were determined argentometrically in solutions diluted with water.

## Results

### Absorption spectrum

Addition of LiBr to AA solution of chlorocopper(II) complex results in gradual changes of the orange colour of the solution to the red, bluegreen, and, at Cl/Br ratios exceeding 2.5, to a green colour, typical for the complex $CuBr_3L^-$ (L, solvent molecule). In addition to the absorption bands of $[CuCl_3AA]^-$ and $[CuBr_3AA]^-$ ($\bar{\nu}_{max} = 21\,000$ and $15\,350$ cm$^{-1}$), two new absorption bands were observed in the visible region of the absorption spectrum around 18 900 and 17 000 cm$^{-1}$.

The absorption spectra in the near infrared region have the same character as those of $[CuCl_3AA]^-$ and $[CuBr_3AA]^-$, i.e. the absorption band around 11 500 cm$^{-1}$ with a relatively low value of molar absorptivity (Table 1).

The regions of absorption spectra (in the visible region) of the solutions with Cu : Cl : Br ratios

*Table 1*

Absorption maxima and molar absorptivities of ligand-field bands of $[CuCl_xBr_{3-x}AA]^-$

| Cu : Cl : Br ratio in solution | $\bar{\nu}_{max}$ cm$^{-1}$ | $\varepsilon_{max}$ cm$^2$ mM$^{-1}$ |
|---|---|---|
| 1 : 3 : 0 | 11 360 | 93 |
| 1 : 2 : 1 | 11 520 | 100 |
| 1  1 : 2 | 11 550 | 126 |
| 1 : 0 : 3 | 11 580 | 133 |

*Table 2*

Molar absorptivities of charge-transfer bands and equilibrium concentrations of [CuClBr$_2$AA] and [CuCl$_2$BrAA]$^-$

| Cu : Cl : Br ratio in solution | 18 850 cm$^-$ | | 17 000 cm$^-$ | |
| --- | --- | --- | --- | --- |
| | $c$ mol l$^-$ | $\varepsilon$ cm$^2$ mM$^-$ | $c$ mol l$^-$ | cm$^2$ mM |
| 1 2 : 1 | $2.35 \times 10^{-4}$ | | $9.66 \times 10$ | |
| | | 1360 | | 2320 |
| 1 1 : 2 | $1.25 \times 10^{-4}$ | | $1.37 \times 10^{-4}$ | |

1 1 : 2 and 1 : 2 : 1 which show the two new absorption bands in a sufficient intensity, were analyzed as Gaussian curves (Figs. 1 and 2). The data indispensable for calculations were obtained by an analysis of the absorption spectra of chloro- and bromocopper(II) complexes in AA [5]. The absorption band exhibited in the visible region by [CuCl$_3$AA] showed $\bar{v}_{max} = 20\,980$ cm$^{-1}$, $\varepsilon_{max} = 2400$ cm$^2$ mM$^{-1}$ and
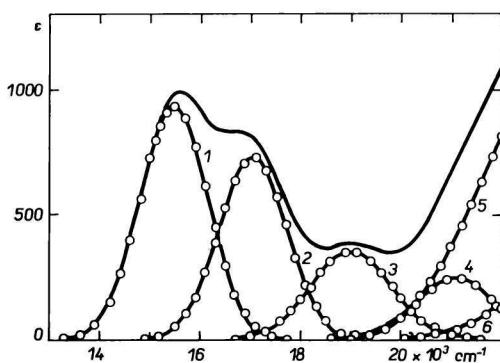


*Fig. 1.* Absorption spectrum of the system Cu(ClO$_4$)$_2 \cdot$6H$_2$O—LiCl—LiBr—AA analyzed as Gaussian curves.

$c_{Cu} = 5 \times 10^{-4}$ mol l$^{-1}$, $c_{Cl} = 5 \times 10^{-4}$ mol l$^{-1}$, $c_{Br} = 10^{-3}$ mol l$^{-1}$.

*1.* and *5.* absorption bands of [CuBr$_3$AA]$^-$ ; *2.* and *6.* absorption bands of [CuClBr$_2$AA]$^-$ : *3.* absorption band of [CuCl$_2$BrAA]$^-$ ; *4.* absorption band of [CuCl$_3$AA]$^-$

halfwidth $\delta = 950$ cm$^{-1}$. The absorption bands of [CuBr$_3$AA]$^-$ have $\bar{v}_{max} = 15\,350$ cm$^{-1}$, $\varepsilon_{max} = 2320$ cm$^2$ mM$^{-1}$, $\delta = 860$ cm$^{-1}$ ; $\bar{v}'_{max} = 22\,650$ cm$^{-1}$, $\varepsilon'_{max} = 2520$ cm$^2$ mM$^{-1}$, $\delta'_{max} = 1600$ cm$^{-1}$. The analysis of the absorption spectra of chlorobromocopper(II) complexes has established that the two new absorption bands have their maxima at 17 000 and 18 850 cm$^{-1}$, and halfwidths 800 and 1000 cm$^{-1}$, respectively. The equilibrium concentrations of chlorobromocopper(II) complexes in the solutions of given compositions as well as their $\varepsilon_{max}$ values were calculated on the basis of the known values of $\varepsilon_{max}$ for [CuCl$_3$AA]$^-$ and [CuBr$_3$AA]$^-$, 2400 and 2320 cm$^2$ mM$^{-1}$, respectively (Table 2).

## Composition of chlorobromocopper(II) complexes

The composition of the complexes formed in the system $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl—LiBr—AA was determined by constructing the isochromatic lines in a Gibbs triangle. Because AA is present in a large excess, its concentration was considered to be constant. From the shape and the position of isochromatic lines one may infer to the number and composition of the mixed complexes formed in solution.

The measurements were carried out at 17 000 and 18 900 cm⁻¹ (Figs. 3 and 4). Maximum absorbance at 18 900 cm⁻¹ corresponds to the solution with a Cu:Cl:Br ratio 1  1.9:1.1 (25% Cu, 47.5% Cl, 27.5% Br). The isochromatic lines constructed at 17 000 cm⁻¹ circumscribe two maxima. One corresponds to the solution with a Cu:Cl:Br ratio 1  1.13:1.96 (24.4% Cu, 27.6% Cl, 48% Br), the other to the solution with a Cu:Cl:Br ratio 1  1.66:1.5 (24% Cu, 40% Cl, 36% Br). Based upon these results we suggest that the complex ion having $\tilde{\nu}_{max}$ at 18 850 cm⁻¹ is composed of Cu, Cl, and Br in the ratio 1:2:1, while the complex ion having $\tilde{\nu}_{max}$ at 17 000 cm⁻¹ in the ratio 1  1  2.



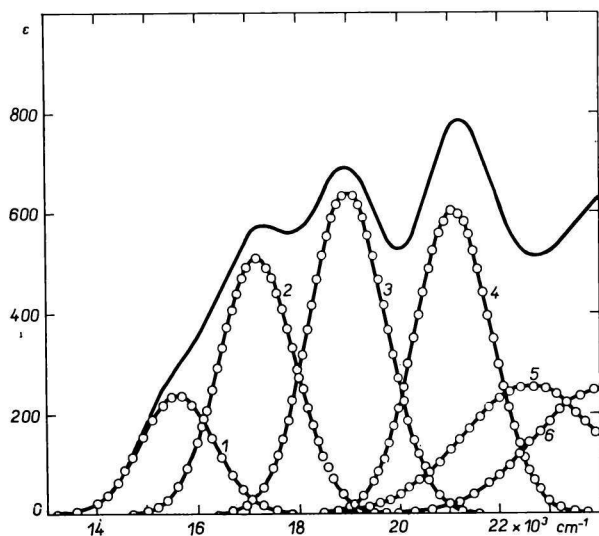*Fig. 2.* Absorption spectrum of the system $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl—LiBr—AA analyzed as Gaussian curves.
$c_{Cu} = 5 \times 10^{-4}$ mol l⁻¹, $c_{Cl} = 10^{-3}$ mol l⁻¹, $c_{Br} = 5 \times 10^{-4}$ mol l⁻¹
*1.* and *5.* absorption bands of $[CuBr_3AA]^-$; *2.* and *6.* absorption bands of $[CuClBr_2AA]$
*3.* absorption band of $[CuCl_2BrAA]^-$; *4.* absorption band of $[CuCl_3AA]^-$

## Discussion

In an analogy to the systems Cu(II)—Cl⁻—AA and Cu(II)—Br⁻—AA [5], in which the complex ions $[CuCl_3AA]^-$ and $[CuBr_3AA]^-$ predominate under certain conditions, it was possible to assume the formation of the complex ions $[CuCl_2BrAA]^-$ and $[CuClBr_2AA]^-$ in the system Cu(II)—Cl⁻—Br⁻—AA. Spectrophotometric study actually confirmed the formation of such mixed chlorobromocopper(II) complexes. The analyses of the absorption spectra clearly showed that a spectrum taken in the visible region is composed of only four
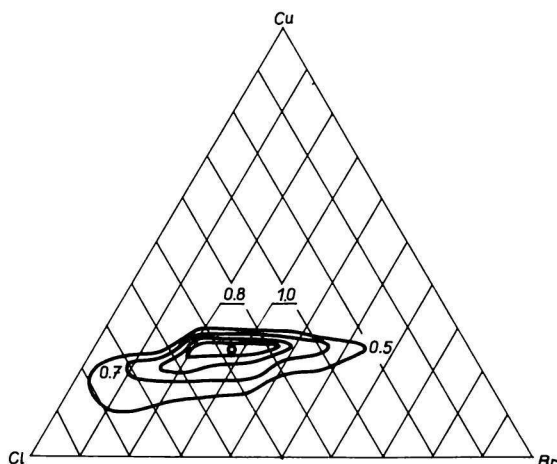
*Fig. 3.* Isochromatic lines of the system $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl—LiBr—AA at 18 900 cm$^{-1}$.
$c_{Cu} + c_{Cl} + c_{Br} = 5 \times 10^{-3}$ mol l$^{-1}$, 1 cm cell.

absorption bands. The existence of an additional mixed complex of the type $[CuCl_xBr_{3-x}AA]^-$ is considered to be less probable. One of the maxima shown in Fig. 4 corresponds to a Cu:Cl:Br ratio $1:1.66:1.5$ and not to the ratio $1:2:1$ as would be expected. This may be due to the fact that the measurements were not done at a wavenumber which corresponds to the maximum absorbance of the complex ion $[CuCl_2BrAA]^-$

The calculation of the values of molar absorptivities of $[CuCl_2BrAA]^-$ at 18 850 cm$^{-1}$ and $[CuClBr_2AA]^-$ at 17 000 cm$^{-1}$ was based on the data obtained by an analysis of the absorption spectra of solutions of different composition maintaining a constant X/Cu ratio of
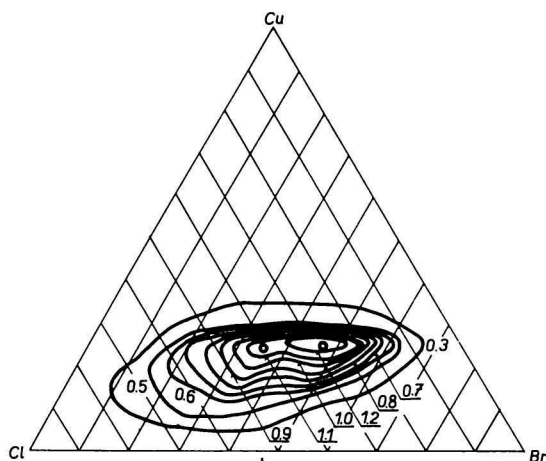


*Fig. 4.* Isochromatic lines of the system $Cu(ClO_4)_2 \cdot 6H_2O$—LiCl—LiBr—AA at 17 000 cm$^{-1}$.
$c_{Cu} + c_{Cl} + c_{Br} = 5 \times 10^{-3}$ mol l$^{-1}$, 1 cm cell.

3 ($X = Cl + Br$). The calculations were carried out under the assumption that all the Cu(II) ions are bound in the complexes $[CuCl_xBr_{3-x}AA]^-$ ($x = 0—3$), which was most probably not fulfilled. If a minute part of Cu(II) bound in the form of $[CuCl_xBr_{4-x}]^{2-}$ is neglected (this is substantiated from the findings of the equilibrium study of the systems Cu(II)—Cl$^-$—AA and Cu(II)—Br$^-$—AA), a certain portion of Cu(II) also can be bound in complexes $[CuX_2AA_2]$, or $[CuXAA_3]^+$ As a result of the redox processes which are not negligible particularly in the systems with a higher content of bromide, a portion of Cu(II) may undergo reduction to Cu(I). Actual values of the equilibrium concentrations of individual complex ions are therefore lower than these calculated by us. From the same reasons, the actual values of molar absorptivities are higher than the calculated ones. This may account for the relatively low value of molar absorptivity of $[CuCl_2BrAA]^-$ at 18 850 cm$^{-1}$ (1360 cm$^2$ mM$^{-1}$) in comparison with $\varepsilon_{max}$ values of other complex species (2320—2400 cm$^2$ mM$^{-1}$). In spite of inaccurate calculations the $\varepsilon_{max}$ values speak clearly for charge-transfer bands.

An increase of the bromide portion in the system produced a slight shift of the values $\bar{v}_{max}$ of the ligand-field bands to the region of higher energies. However, the ligand-field energy of bromine is lower than that of chlorine, so that in the case of identical structures of $[CuCl_3AA]^-$, $[CuCl_2BrAA]^-$, $[CuClBr_2AA]^-$, and $[CuBr_3AA]^-$, a shift in the opposite direction should be observed. The observed phenomenon may be related to a different degree of distortion of the tetrahedron in the given complexes. The tetrahedral distortion is most pronounced in $[CuBr_3AA]^-$ and least in $[CuCl_3AA]^-$ As it has been discussed previously [5], $[CuCl_3AA]^-$ and $[CuBr_3AA]^-$ are formed on a solvolysis of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ which possess a distorted tetrahedral arrangement. The distortion on solvolysis even increases, so that we can speak here either of an extremely distorted tetrahedron or of a deviation from the planary arrangement.

## References

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