

Institute of General Chemistry of the University of Rome and Institute of Physical Chemistry  
of the University of Frankfurt am Main

## Properties and Electronic Structure of Tetrahalogenocuprate (II)-Complexes

By

CLAUDIO FURLANI and GIORGIO MORPURGO

Several salts containing the complex anions  $[CuCl_4]^-$  or  $[CuBr_4]^-$  have been prepared, and their spectra have been measured and interpreted in terms of ligand-field theory. They exhibit a  $d-d$  band with  $\tilde{\nu}_{max}$  about 8—9000  $cm^{-1}$ , and several well defined charge-transfer bands in the visible and near ultraviolet spectral range. Several experimental facts, supported by theoretical considerations, indicate that the structure of the  $[CuX_4]^-$  anions is not a truly tetrahedral, but a flattened tetrahedral one, of symmetry  $D_{2d}$ . Details on the course of the endothermic solvolysis reactions which occur in polar organic solvents, and on the probable nature of the solvolysis products are reported and discussed.

Plusieurs sels des anions complexes  $[CuCl_4]^{2-}$  et  $[CuBr_4]^{2-}$  ont été préparés et leurs spectres mesurés et interprétés dans le cadre de la théorie du champ des ligands.

Ils montrent une bande  $d \rightarrow d$  avec  $\tilde{\nu}_{max}$  dans la région de 8000 à 9000  $cm^{-1}$  et plusieurs bandes bien définies du type «transfert de charges» dans le visible et l'ultraviolet proche. Plusieurs résultats expérimentaux, soutenus par des considérations théoriques, indiquent que la structure des ions  $[CuX_4]^{2-}$  n'est pas celle d'un tétraèdre véritable mais celle d'un tétraèdre déformé, de symétrie  $D_{2d}$ . Des détails sur le cours des réactions endothermiques de solvolyse, qui ont lieu dans les solvants organiques polaires et sur la nature probable des produits de la solvolyse sont rapportés et discutés.

Mehrere Salze der komplexen Anionen  $[CuCl_4]^{2-}$  und  $[CuBr_4]^{2-}$  wurden dargestellt, ihre Spektren gemessen und ligandenfeldtheoretisch interpretiert. Die Spektren zeigen eine  $d \rightarrow d$ -Bande mit  $\tilde{\nu}_{max}$  im Gebiet von 8000 bis 9000  $cm^{-1}$  und mehrere wohldefinierte Elektronenüberführungsbanden im sichtbaren und nahen ultravioletten Spektralbereich. Mehrere experimentelle Befunde, die von theoretischen Überlegungen unterstützt werden, deuten darauf hin, daß die  $[CuX_4]^{2-}$ -Anionen nicht rein tetraedrisch gebaut sind, sondern längs einer zweizähligen Achse gestauchte Tetraeder der Symmetrie  $D_{2d}$  darstellen.

Einzelheiten über den Verlauf der endothermen Solvolysereaktionen in polaren organischen Lösungsmitteln und über die wahrscheinlichen Solvolysprodukte werden mitgeteilt und diskutiert.

The existence of halogenocomplexes of Cu(II) has been reported for a long time by several authors [5, 9, 29, 30, 2], and spectroscopic evidence for it has been claimed [8, 1, 11, 28, 27]. The present work was undertaken in order to obtain better knowledge of the electronic structure and of related properties of complexes where halide ions are the sole ligands, i.e. pseudotetrahedral tetrahalogenocuprates (II); actually, although halide ions can act as ligands in mixed complexes of copper with octahedral or square planar coordination environment, it seems doubtful that under these symmetries they can occupy all coordination positions, except in very distorted octahedral forms in solid  $CuBr_2$  [21] or  $CuCl_2$  [33, 10] or in infinite chains of distorted planar units in solid  $CsCuCl_3$  [32]; there are, on the

contrary, many examples of mixed coordination of  $Cu^{++}$  through both halide and oxygen ligands (e.g. planar  $[Cu(H_2O)_2Cl_2]$  units in the equatorial plane of  $[Cu(H_2O)_2Cl_aCl_b]_2$ ) are contained in solid  $CuCl_2 \cdot 2H_2O$  [20] and in  $K_2CuCl_4 \cdot 2H_2O$  [23]), but the only ascertained cases of discrete coordination units containing only copper and halide are those of solid  $Cs_2CuCl_4$  [11, 22] and of tetrahalogenocuprates(II) of the type  $R_2CuX_4$  with complex cations  $R^+$  [15], which have been prepared recently by GILL and NYHOLM [16]. In mixed complexes, also the effect of the presence of halide ions in the coordination sphere has been investigated [8, 28, 27], but, as to complexes containing  $[CuX_4]^-$  anions, only a few preliminary data are available from the literature [11, 22, 16, 19], and they are sometimes not completely clear: so e.g. GILL and NYHOLM [16] reported for  $[CuBr_4]^-$  two charge transfer bands with maxima at 643 and at 433  $m\mu$ , which SCHNEIDER [31] found also in solutions containing  $[Cu^{++}]$  and  $[Br^-]$  in ratio 1:3, and cannot therefore be due to a tetrahalogenocomplex (they are actually due to solvolysis products of  $[CuBr_4]^-$ , as will be discussed below; see also Fig. 2). To clarify this situation, we undertook a systematic study of the electronic spectra and structure of tetrahalogenocuprate(II) complex anions, both in the solid state and in solution.

Tetrahalogenocuprates(II)  $R_2Cu^{II}X_4$ , where  $R =$  an onium cation, and  $X = Cl^-$  or  $Br^-$ , have been prepared for the first time by GILL and NYHOLM [16], with  $R = [As(C_6H_5)_3CH_3]^+$ . In the course of the present work we prepared several new salts corresponding to the same general formula, which are listed below, under "Experimental part" (we were however unable to prepare the tetrachlorocomplex with tetraphenylarsonium cations, which give only a brown trichlorocuprate (II)). The chloro-complexes are egg-yellow, and the bromo-complexes are dark violet, almost black; such a striking difference in colour is due to the position of the charge transfer bands in their visible spectra (as we shall discuss in detail below, d-d transitions, i.e. transitions localized mainly on the central ion of the complex, fall into the near infrared region, and do not therefore contribute to the visible colour of the substances, whereas charge transfer bands occur at relatively low frequencies, and determine the visible part of the spectrum). All complex salts of the formula  $R_2Cu^{II}X_4$  are crystalline substances which resemble in several respects tetrahedral tetrahalogenometallates(II) of other bivalent transition metals of the first row, e.g.  $[NiCl_4]^-$  [4, 12, 17] or  $[MnCl_4]^-$  [26, 13, 7], but differ markedly from them in other aspects. Among the analogies, one can mention the way of preparation (mixing of stoichiometric amounts of  $CuX_2$  and of  $RX$  leads usually at once to precipitation of the corresponding complex salt), the ready decomposition by water (however,  $[CuCl_4]^-$  and  $[CuBr_4]^-$  can exist to a limited extent, and in equilibrium with other complex forms, in concentrated aqueous chloride [30, 2] or bromide [28] solutions; such possibility of existence also in aqueous solutions is almost unique in the series of tetrahedral tetrahalogenocomplexes of transition metals of the first row, and is shared only by  $Co^{II}$  [24, 6]). The salt character and consequently the solubility in polar organic solvents like  $CH_3NO_2$ ,  $CH_3CN$  and dimethylformamide and the behaviour in solution as strong 1:2 electrolytes, the non-existence of solid salts with non-complex cations (the only known exception being till now  $Cs_2CuCl_4$  [11, 22]), and the high absorption intensity of the bands of the electronic spectrum are also common

features of the other tetrahalogenometallates(II) mentioned above. The high intensity of absorption is a consequence of the breakdown of the Laporte selection rule, since in tetrahedral complexes there is no longer a centre of symmetry, and the electronic states have therefore no longer definite parities. On the other hand, there are some other properties which place tetrahalogenocuprates(II) in a special position among tetrahalogenometallates(II) of the transition metals: dissimilarities include (i) differences in chemical behaviour, e.g. tetrahalogenocuprates(II) are much more stable in alcoholic solutions than the corresponding tetrahedral complexes of  $Ni^{II}$ ,  $Mn^{II}$  or  $Fe^{II}$ , but are much less stable in dimethylformamide; solvolysis does not only lead to octahedral complex species, but primarily to tetraordinated, probably distorted planar, solvated species; (ii) spectral behaviour, since  $[CuX_4]^-$  anions display an absorption band with a maximum at frequencies too high to be compatible with reasonable values of the tetrahedral splitting factor  $\Delta_{tet}$ ; (see below, "Theoretical interpretation"). All such dissimilarities are probably a consequence of a difference in the structure of the complex unit  $[CuX_4]^-$ : unlike tetrahedral halogenocomplexes of other transition metals of the first row, which are either perfectly tetrahedral ( $Co^{II}$ ,  $Mn^{II}$ ,  $V^{III}$  [15]) or only very slightly or undetectably distorted ( $Fe^{II}$  and  $Ni^{II}$  [15, 12]), the complex anions  $[CuCl_4]^-$  and  $[CuBr_4]^-$  are certainly strongly distorted; as will be discussed in more detail in the theoretical part, experimental data at our disposal, and especially the spectrochemical ones, are in favour of a flattened tetrahedral structure of symmetry  $D_{2d}$ . It is to be recalled that in the only compound of this type for which a complete structure determination has been carried out until now, namely  $Cs_2CuCl_4$  [22], such a flattened tetrahedral shape of the  $[CuCl_4]^-$  anions has been actually demonstrated by X-rays (the angles  $Cl-Cu-Cl$  turned out to be  $104 \pm 3^\circ$  and  $120 \pm 3^\circ$ , respectively [22]), and, although there is no direct proof that the same structure is preserved also in the solid salts  $R_2CuX_4$ , with  $R$  = an onium cation, and in the  $[CuX_4]^-$  anions in solution, it seems nevertheless quite reasonable to assume that the structure of the complex is of the same type in the latter cases, too.

### Spectroscopic Measurements: Experimental Results

We measured the spectra of the complexes under investigation both in the solid state (as reflection spectra of the powdered crystals, and in some cases also in nujol or hexachlorobutadiene mulls) and in solution. It turned out that the spectra have exactly the same shape in the solid state and in solutions in  $CH_3NO_2$  or in  $CH_3CN$ , provided the concentration of the solid salt in solution is not too low or an excess of the corresponding free halide is present (in other solvents, and also in nitromethane or acetonitrile at low concentrations without excess  $[X^-]$  added, the form of the spectrum is altered; see below). This identity proves that solution spectra measured under the conditions mentioned above are actually due to the  $[CuX_4]^-$  anions; since of course solution spectra are more reproducible and more exactly quantitative than the spectra of the solids, from this on the term "spectra of the tetrahalogenocuprate anions" will refer to spectra measured in solutions in  $CH_3NO_2$  or in  $CH_3CN$  in presence of a substantial excess of free halide ions.

The spectra of  $[CuCl_4]^-$  and of  $[CuBr_4]^-$  are reported in Fig. 1; both consist of a broad, asymmetric band of medium intensity ( $\log \epsilon \sim 2$ ) in the near infrared region, which can be identified as the d-d band of the central ion, i.e. an electronic transition mainly localized on  $Cu^{II}$ , and of a system of at least three more intense bands in the visible and ultraviolet region, which can be assigned to a charge-transfer mechanism operating from the halide ions to the  $Cu^{++}$  ions. All four bands are shifted towards lower frequency values in the bromocomplex than in the chlorocomplex; for the ligand-field band, this is a consequence of the position of  $Br^-$  after  $Cl^-$  in the spectrochemical series, and for the charge-transfer bands it can be more simply explained as a consequence of the lower electron affinity of bromine. It is interesting to note that the relatively low frequency of the first charge-transfer band of  $[CuBr_4]^-$  ( $16500\text{ cm}^{-1}$ ) should allow photochemical decomposition to take place easily, and actually SCHNEIDER [31] reported formation of bromine from  $Cu^{++}$  and  $Br^-$  in acetonitrile solutions, although such decomposition is not so ready as to require special precautions to be taken during spectrophotometric measurements in order to avoid massive decomposition. (A much easier decomposition should be

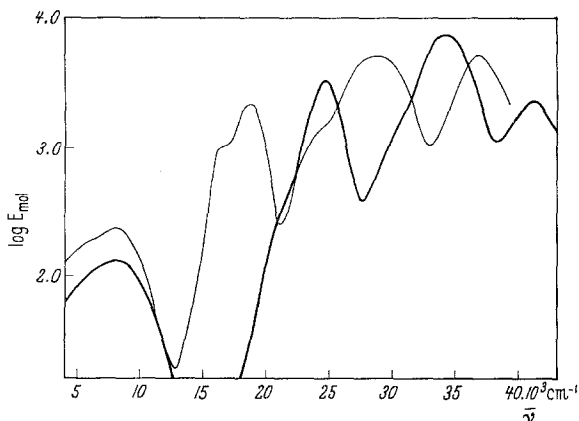


Fig. 1. Molar absorption spectra of  $[CuX_4]^-$  anions in acetonitrile solutions; data taken from measurements on  $[C_6H_5CH_2N(CH_3)_2]_2 [CuCl_4]^-$  and  $[(C_2H_5)_4N]_2 [CuBr_4]^-$  in the concentration range  $10^{-3}$  to  $10^{-2}$  M in presence of an at least 20-fold excess of the corresponding substituted ammonium halide

—  $[CuCl_4]^-$ ; - - -  $[CuBr_4]^-$

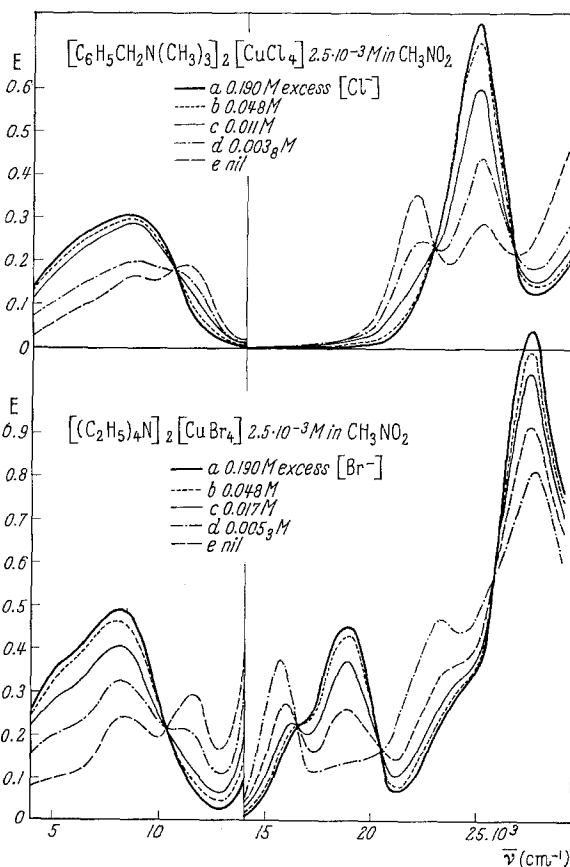


Fig. 2. Effect of halide ions on the spectra of  $[CuX_4]^-$  in nitromethane at room temperature; spectra were measured up to  $14000\text{ cm}^{-1}$  in 1-cm absorption cells (left), then in 1-mm cells (right)

expected for a  $Cu^{++}$ -iodide complex, and indeed such a complex is incapable of stable existence and decomposes spontaneously, giving  $Cu^+$  and iodine.)

Tetrachlorocuprate(II) and tetrabromocuprate(II) salts are not perfectly stable, even in solutions in  $CH_3NO_2$  or in  $CH_3CN$ : whereas at relatively high concentrations ( $> 0,01$  M) their absorption spectra have exactly the same aspect as in Fig. 1, at low concentrations and if no excess halide is present, solvolytic decomposition occurs, which is accompanied by significant spectral changes: the visible colour of the tetrachlorocomplex turns from light yellow to brown-yellow, and that of the tetrabromocomplex from violet to deep green, while the absorption

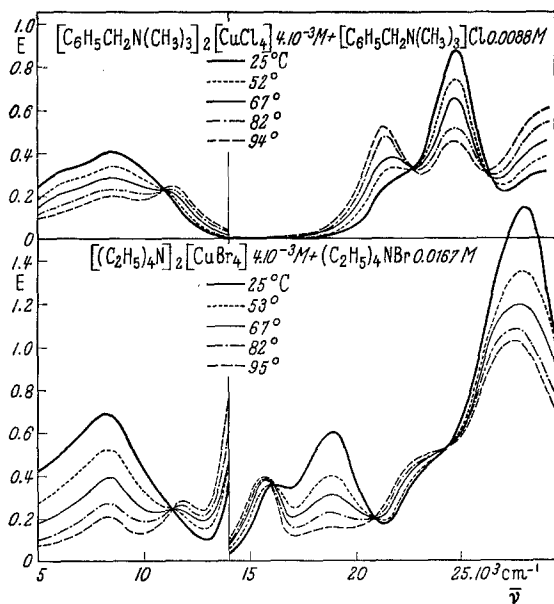


Fig. 3. Temperature effect on the absorption spectra of  $[CuX_4]^{2-}$  anions in nitromethane, in presence of a not very high excess of free halide ions; spectra were measured in 1-cm absorption cells from 5000 to  $14000\text{ cm}^{-1}$ , and in 1-mm cells from  $14000\text{ cm}^{-1}$  onwards

whereas some of our data seem to indicate also presence of dihalide species of type  $[CuX_2L_2]$  ( $L = \text{solvent molecule}$ )\*\*. We think that under our experimental

\* Charge-transfer bands at  $633, 430$  and  $362\text{ m}\mu$  ( $643, 433$  and  $369\text{ m}\mu$  in ref. [16]) in the spectrum of the solvolyzed bromocomplex, and at  $456$  ( $435$  in ref. [16]) and  $360\text{ m}\mu$  in the spectrum of the solvolyzed chlorocomplex have been erroneously attributed by GILL and NYHOLM [16] to the tetrahalogenated species, instead of the true values of  $526$  and  $345$ , respectively  $400$  and  $290\text{ m}\mu$ .

\*\* Assuming that there is only one predominant solvolysis product, and that the concentrations of the tetrahalogenated species and of the solvolysis product can be inferred from the heights of the absorption peaks at  $21900$  and  $25000\text{ cm}^{-1}$  (chlorocomplexes) or at  $15800$  and  $19000\text{ cm}^{-1}$  (bromocomplexes), we attempted an estimate of the equilibrium constant of the solvolysis reaction; it turned out that the ratio of the concentrations of the solvolyzed to that of the tetrahalogenated species was roughly proportional to the inverse square of the free halide concentration, and therefore the reaction seemed to occur with removal of two halide ions from each complex molecule, the approximate values of the apparent equilibrium con-

spectra exhibit profound variations, as is shown in Fig. 2 (curves marked "nil")\*. The extent to which decomposition occurs decreases if excess halide ions are added to the solutions, and solvolysis can be completely prevented even at very low complex concentrations by a large excess of halide ions (see Fig. 2). Our measurements provide us little information about the composition of the solvolysis products, although there is no doubt that they are still  $Cu^{II}$ -halide complexes, containing however less than  $4X^-$  per metal ion. SCHNEIDER [31] reported experimental evidence in favour of  $[CuBr_3]^-$  species in dilute acetonitrile solutions containing a low ratio of  $[Br]^-$  to  $[Cu^{++}]$ ,

conditions both the trihalide and the dihalide species can exist in solution, and although there is no definite and direct evidence for the tetracoordination of the central copper (II) ions in the solvolyzed species, we think it is reasonable to assume it; actually, the high intensity of the d—d band also in the solvolyzed complex seems to exclude an octahedral structure. It is to be noted that, unlike other tetrahalogenometallates of transition metals of the first row, which give, after decomposition under analogous conditions, either a precipitate of metal

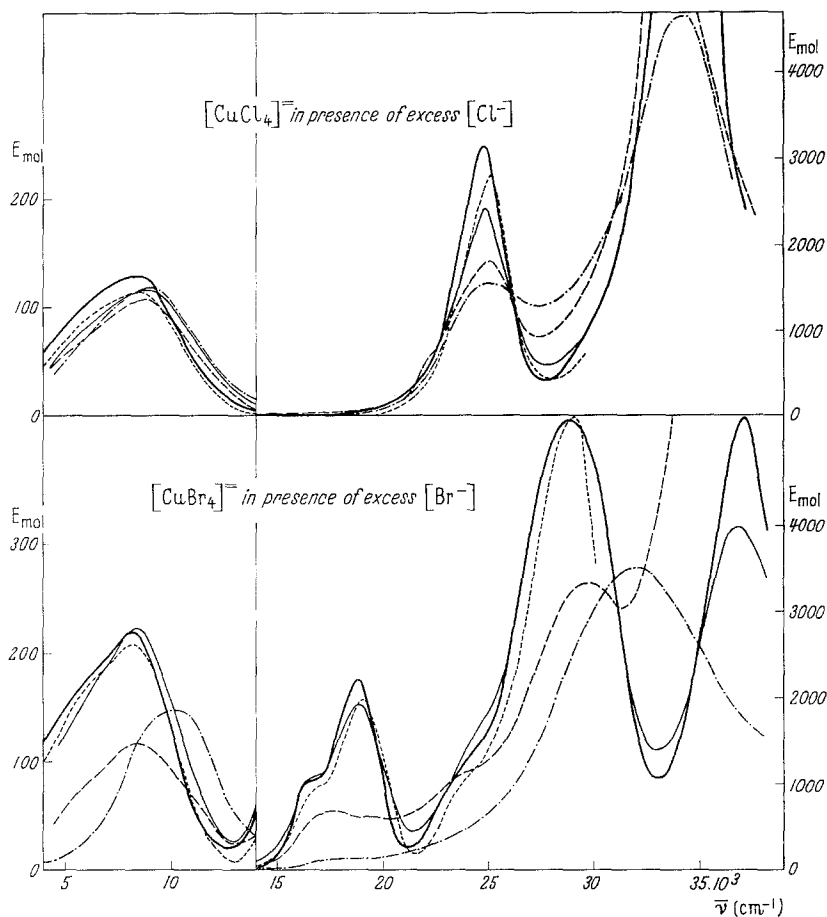


Fig. 4. Solvent effect upon the spectra of  $[CuX_4]^{2-}$ , in presence of a large excess of the corresponding halide ions; ..... nitromethane; — acetonitrile; - - - - dimethylformamide; - · - · - dimethylsulphoxide; ——— abs. ethyl alcohol; (see Table for the composition of the solutions)

halide (e.g.  $[NiCl_4]^{2-}$  in  $CH_3NO_2$  [12]) or octahedrally coordinated species (e.g.  $[NiX_4]^{2-}$  or  $[MnX_4]^{2-}$  in dimethylformamide [4, 12, 17, 13, 7]), tetrahalogenocuprates(II) give soluble, probably distorted square planar solvolysis products.

constants being  $\frac{[CuX_2L_2][X^-]^2}{[CuX_4]^{2-}} = (2,4 \pm 0,5) \cdot 10^{-4}$  for the bromocomplex, and  $(0,4, \pm 0,1) \cdot 10^{-4}$  for the chlorocomplex, both in  $CH_3NO_2$  at 25° C. However, it has not been investigated whether and how strongly these apparent values of equilibrium constants depend on the presence of possible traces of impurities (e.g. water) in the solvent employed.

Table. A survey of the main features of the spectra of pseudotetrahedral  $[CuX_4]^-$  anions and of related species —  $\bar{\nu}_{max}$  in  $kK$ 

Absorbing species	Solvent	d-d band		1st charge transfer band		2nd charge transfer band		3rd charge transfer band		Range of concn. of copper species	Concn. of added halide (mol/l)	Visible colour of solutions	
		$\bar{\nu}_{max}$	log $\epsilon$	$\bar{\nu}_{max}$	log $\epsilon$	$\bar{\nu}_{max}$	log $\epsilon$	$\bar{\nu}_{max}$	log $\epsilon$				
$[CuCl_4]^-$ " " " " "	$CH_3NO_2$ $CH_3CN$	8,5	2,08	25,0	3,46	—	—	—	—	$5.10^{-4}$ — $5.10^{-2}$	0,10	yellow	
		8,4 (5,8)	2,09	24,8	3,50	34,2 <sub>5</sub>	3,86	41,2	3,37	3,37	$5.10^{-4}$ — $5.10^{-2}$	0,05	yellow
	$CiCH_2CN$	8,6 (5,9)	2,11	—	—	—	—	—	—	—	1.— $8.10^{-3}$	0,2—0,3	yellow
		8,9	2,07	25,0	3,20	34,0	3,68	—	—	—	1.— $6.10^{-3}$	0,10	yellow
	"	DMSO	8,5	2,03	24,9	3,25	33,7	3,76	—	—	$1.10^{-3}$ — $1.10^{-2}$	0,05	yellow
		EtOH	8,7	2,06	24,7	3,41	34,4	3,81	41,6	3,36	1.— $6.10^{-3}$	0,83	yellow
"	Ref. spectrum	8,6	—	24,4	—	—	—	—	—	—	—	yellow	
$[CuBr_4]^-$ " " " " "	$CH_3NO_2$ $CH_3CN$	8,15	2,33	19,0 (16,6)	3,34 (3,0)	29,0 (23,5)	3,72 (3,06)	—	—	$5.10^{-4}$ — $5.10^{-2}$	0,10	violet	
		8,1	2,35	18,8 (16,6)	3,33 (3,0)	28,9 (23,5)	3,72 (3,08)	36,9	3,73	3,73	$1.10^{-3}$ — $1.10^{-2}$	0,18	violet
	"	DMSO	10,4 (9,4)	2,16	18,2	2,10	31,8	3,54	—	—	1.— $6.10^{-3}$	0,10	brown-violet
		DMF	8,3	2,08	17,6 (19,2)	2,80 (2,76)	29,0 (23,5)	3,53 (3,06)	—	—	1.— $8.10^{-3}$	0,10	red-brown
	"	EtOH	8,3 (6,0)	2,36	18,9 (16,5)	3,28 (3,0)	28,9 (23,5)	3,70 (3,15)	36,6	3,60	$1.10^{-3}$ — $1.10^{-2}$	1,0	violet
		Ref. spectrum	8,2	—	18,7 (16,3)	—	—	—	—	—	—	—	violet-black
$[CuCl_nL_{4-n}]^-$ $[CuBr_nL_{4-n}]^-$	$CH_3NO_2$ $CH_3NO_2$	11,0	1,8 <sub>8</sub>	21,9	3,16	—	—	—	—	$2.10^{-3}$	none	orange	
		11,6	2,0	15,8	3,14	23,2 (27,8 <sup>?</sup> )	3,23 (3,5 <sup>?</sup> )	—	—	—	$2.10^{-3}$	none	green

Table (Continued)

$CuCl_2$	$CH_3CN$ **, **	11,6 8,3 (5,6)	1,9 2,10	21,9 24,8	2,76 3,51	32,4 34,0	3,61 ~4	(37,8) 41,2	(3,32) 3,37	$1.10^{-3}$ — $1.10^{-2}$ $6.10^{-3}$	none 0,05	brown-yellow yellow
"	"	"	"	"	"	"	"	"	"	"	"	"
"	EtOH	11,2	1,90	—	—	32,0	~4	—	—	$1.-6.10^{-3}$	none	pale green
"	"	9,7	2,07	25,3	3,20	34,6	~4	41,6	3,36	$6.10^{-3}$	1,0	yellow
$CuBr_2$	$CH_3CN$ **, **	11,2	1,93	15,9	2,72	(23,5)	3,0	36,9	~4	$1.-6.10^{-3}$	none	green
"	"	8,0	2,34	19,0	3,32	(28,0)	(3,35)	36,8	3,72	$2.-6.10^{-3}$	0,10	violet
"	EtOH	(5,5)	2,27	(16,6)	(3,02)	29,1	3,76	(39,0)	(3,18)	$1.-4.10^{-3}$	none	dark yellow
"	"	11,1	2,29	—	—	32,3	3,51	—	—	"	"	"
"	"	8,3 <sub>5</sub>	2,29	18,7 (16,7)	3,11 (2,93)	(25,5) 29,1	(3,0) (3,04)	36,2	3,54	$4.10^{-3}$	0,50	violet

DMSO = Dimethylsulphoxide

DMF = Dimethylformamide

 \*  $[CuX_4]^-$  is probably solvolyzed

 \*\* Solution prepared from  $CuX_2$ , but probably containing  $[CuX_4]^-$ 

Parenthesis denotes shoulder

Another striking difference is that, whereas solvolysis of other tetrahalogenometallates is usually exothermic, the true tetrahedral species being favoured at high temperatures in solution, with copper the opposite situation occurs: the overall reaction  $[CuX_4]^- \rightarrow [CuX_nL_{4-n}]$  is endothermic, and the equilibrium is shifted towards right at high temperatures, as is shown in Fig. 3.

We attempted also the use of other solvents, like dimethylsulphoxide or dimethylformamide, but they proved in general to be less satisfactory, since they cause more rapid and profound decomposition of the tetrahalogenocuprate(II) anions, even in presence of a large excess of free halides, with the possible exception of  $[CuCl_4]^-$  in dimethylsulphoxide (without excess halide, decomposition is in these cases almost complete and leads to octahedrally solvated species). The form of the spectra in different solvents, in presence of excess halide, is shown in Fig. 4, and Table summarizes the main features of the measured spectra. In alcoholic solution there is again a difference with respect to tetrahedral halogenocomplexes of other transition metals, since tetrahalogenocuprates(II) are much more stable in alcohol than e.g. tetrahalogenonickelates(II) [12] or tetrahalogenomanganates(II) [13], and, if a large excess of free halide is added, their formation can be quantitative (see Fig. 4 and 6). We measured also a few spectra in monochloroacetonitrile, which is more transparent in the near infrared range



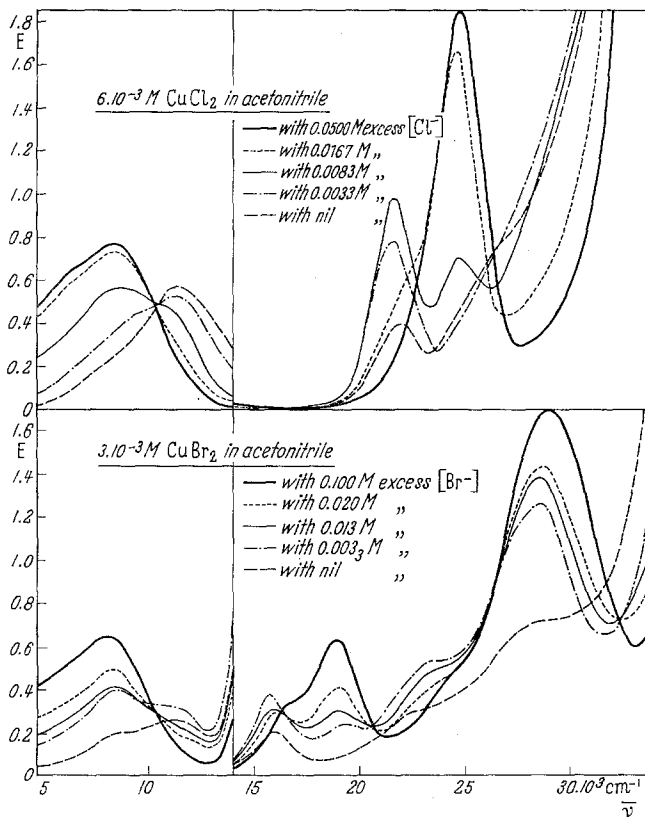


Fig. 5. Absorption spectra of anhydrous copper(II) halides in acetonitrile without and with excess halide ( $C_6H_5CH_2N(CH_3)_3 Cl$  or  $(C_2H_5)_4 NBr$ ); spectra were measured in 1-cm absorption cells from 5000 to 14000  $cm^{-1}$  (left), then in 1-mm cells (right)

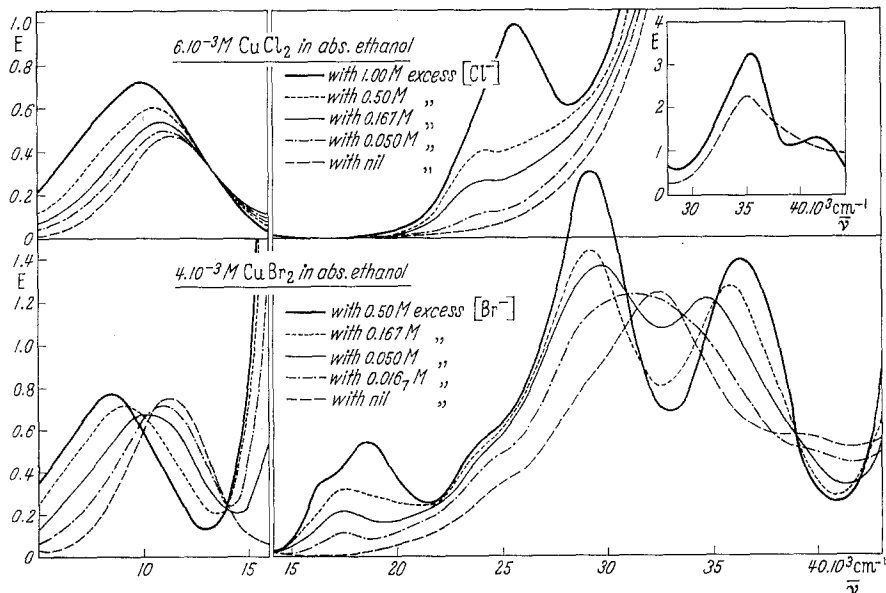


Fig. 6. Absorption spectra of anhydrous copper(II) halides in absolute ethanol without and with excess halides ( $LiCl$  or  $(C_2H_5)_4 NBr$ ); spectra were measured in 1-cm absorption cells from 5000 to 16000  $cm^{-1}$ , and in 1-mm cells from 14000  $cm^{-1}$  onwards

than most other suitable solvents [14]; the results were quite similar to those obtained in  $CH_3CN$ , but enabled us to observe more accurately the long-wave descent of the ligandfield band of  $[CuCl_4]^-$ ; however, we could not use  $CICH_2CN$  to measure the spectrum of  $[CuBr_4]^-$ , since it exchanges its halogen, although not very rapidly.

In order to confirm the existence of the species  $[CuX_2L_2]$ , we measured also the spectra of solutions of  $CuCl_2$  or  $CuBr_2$  in  $CH_3CN$  or  $CH_3NO_2$ , although we could not obtain by this way the desired complete evidence. The spectra are similar to, but not identical with, those typical of the solvolyzed  $[CuX_4]^-$  species (see Fig. 5 and 6), thus indicating the possibility of further removal of halide ions from the environment of  $Cu^{++}$ ; additional complications arise from the possible occurrence of the redox reaction  $Cu^{++} + Br^- \rightarrow Cu^+ + \frac{1}{2} Br_2$ ; however, addition of a slight excess of free halide to an acetonitrile solution, to give a ratio  $[Cu^{++}]$ : total  $[X^-]$  in the range 2,2—3,0, is sufficient to bring the absorption spectrum to the form we attributed to  $[CuX_nL_{4-n}]$  (see Fig. 2, curves marked "nil"). It appears therefore reasonable to assume that  $[CuX_2L_2]$  and  $[CuX_3L]^-$  can actually exist, at least in part, also in nonaqueous solutions of  $CuCl_2$  or  $CuBr_2$ , although they are possibly not perfectly stable towards further solvolysis. In dilute alcoholic solutions,  $Cu^{++}$  is probably present in form of pseudo-octahedral species (see Fig. 6), but on addition of increasing amounts of excess halide, the spectrum evolves towards the forms which are characteristic of  $[CuX_nL_{4-n}]$ , and finally of the tetrahalogenated species  $[CuX_4]^-$ .

### Spectroscopic Measurements: Theoretical Interpretation

There is little doubt that the observed frequency of the near-infrared band in the spectra of tetrahalogenocuprates(II) cannot be explained by ligand-field considerations on the assumption of a purely tetrahedral symmetry, in which case a much lower frequency value should be expected: although  $\Delta$  for hexacoordinated pseudo-octahedral  $Cu(II)$  complexes is not exactly known (literature estimates range from 6300 [18] to 12000  $cm^{-1}$  [3, 25] for  $[Cu(H_2O)_6]^{++}$ ), it is evident that  $|\Delta|$  in a purely tetrahedral ligand field should not exceed 5000  $cm^{-1}$ , and probably should be of the order of 3—4000  $cm^{-1}$ , whereas the observed maximum frequency is about 8—9000  $cm^{-1}$ . Furthermore, the observed d—d band is very broad and

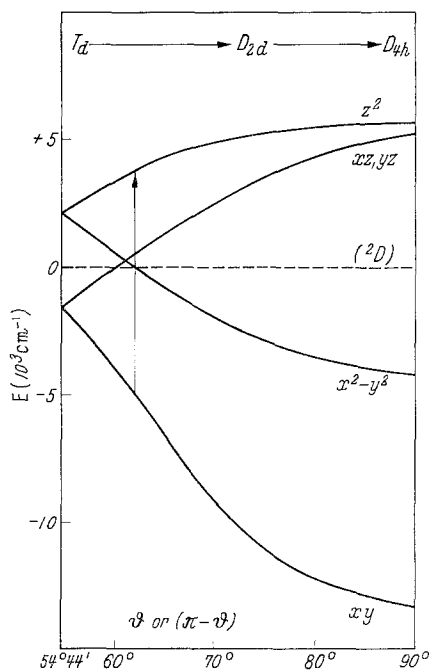


Fig. 7. Calculated term system of the configuration  $(3d)^9$  of  $Cu^{++}$  in a pseudotetrahedral (flattened) complex  $[CuX_4]^{2-}$  of symmetry  $D_{2d}$ , assuming four equivalent point-charge ligands, as a function of the  $\vartheta$  values of the ligands; the polar axis is taken coincident with the  $S_4$  axis and the  $\varphi$ -coordinates of the four ligands are  $\pi/4$ ,  $3\pi/4$ , and  $5\pi/4$  and  $7\pi/4$ . Assumed parameter values:  $f = 2,10$ ;  $R = 1,96 \text{ \AA} = 3,70 \text{ a.u.}$ ;  $G(2) = 0,1664 \text{ a.u.}$ ;  $G(4) = 0,0592 \text{ a.u.}$ ;  $A_{octahedral} = 8100 \text{ cm}^{-1}$ . Energy levels are classified according to the one-electron eigenfunctions of the  $3d$  hole

strongly asymmetric, and probably contains under its envelope more than one transition (a hidden maximum lies around  $6000\text{ cm}^{-1}$ ), whereas under symmetry  $T_d$  only one transition, namely from  ${}^2T_2$  to  ${}^2E$  of  $(3d)^9$  ( $T_d$ ) of  $\text{Cu}^{++}$ , is expected. All these facts point to a strongly distorted tetrahedral structure, probably corresponding to a flattened tetrahedron of symmetry  $D_{2d}$ , intermediate between those of a planar square and of a true tetrahedron. This conclusion is supported not only by the analogy with the ascertained structure of  $[\text{CuCl}_4]^-$  in  $\text{Cs}_2\text{CuCl}_4$  [22],

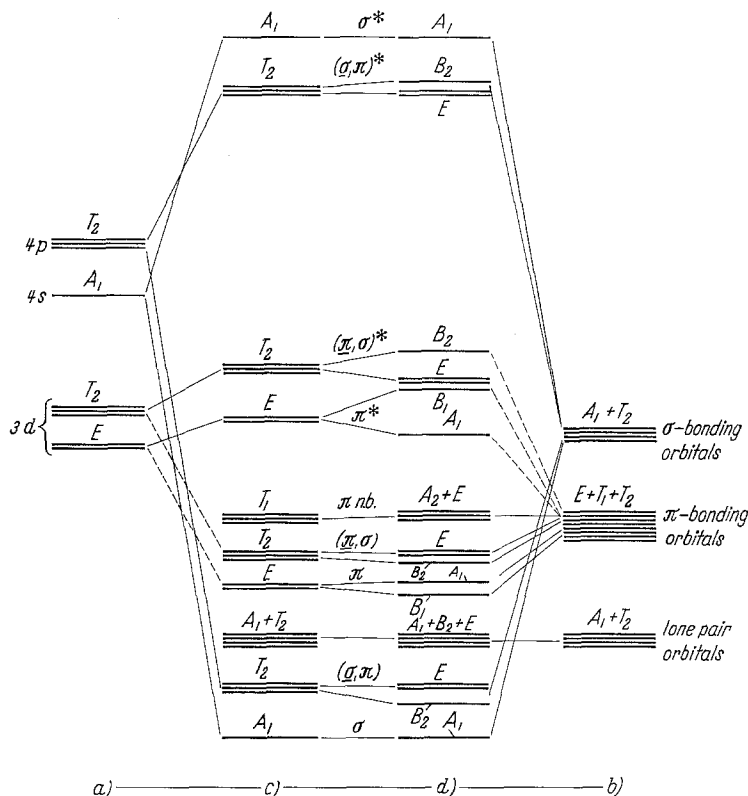


Fig. 8. Schematic ordering of the M.O.s in a complex  $[\text{CuX}_4]^-$ , assuming either tetrahedral ( $T_d$ ) or distorted tetrahedral ( $D_{2d}$ ) symmetry: a) metal orbitals under an electrostatic perturbation of symmetry  $T_d$ ; b) ligand orbitals under the same perturbation; c) M.O.s ( $T_d$ ); d) M.O.s ( $D_{2d}$ )

but also by theoretical considerations: we calculated the term system of the configuration  $(3d)^9$  according to a point charge model for an increasingly flattened tetrahedral structure, and, as the results reported in Fig. 7 show, progressive flattening of the tetrahedral structure results in increased splitting of both the ground and the excited tetrahedral level, and in a marked shift towards higher frequencies of the highest expected d-d transition; notwithstanding the limitations of a point charge model, the qualitative picture given by Fig. 7 is certainly correct, and it appears that a transition frequency of the order of the experimental frequency ( $\bar{\nu}_{max} \sim 8-9000\text{ cm}^{-1}$ ) would be consistent with a  $\text{Cl}-\text{Cu}-\text{Cl}$  angle (smaller value) narrowed by about  $8^\circ$  with respect to the tetrahedral value.

Crystal-field theory does not provide us much evidence about the interpretation of the more intense visible and ultraviolet bands in the spectra of  $[CuCl_4]^-$  and  $[CuBr_4]^-$ ; assuming however that the order of the M.O.s in the complex corresponds to the qualitative picture of Fig. 8, the three observed charge transfer bands could be tentatively accounted for as transitions from the  $\pi$ -nonbonding orbitals ( $A_2 + E$ ) and the  $\pi$ -bonding orbitals ( $B_2 + E$ ) and ( $A_1 + B_1$ ) ( $D_{2d}$ ), which are, in an electrostatic picture, formed mainly by orbitals of the ligands, to the first partly free one-electron orbital, i.e. to  $T_2$  ( $T_d$ ) or to  $B_2$  ( $D_{2d}$ ), which should be mainly metal orbitals.

We have still less evidence as to the structure and interpretation of the spectra of the solvolyzed species, which we formulated as  $[CuX_nL_{4-n}]$ . The most significant experimental facts on passing from  $[CuX_4]^-$  to  $[CuX_nL_{4-n}]$  are that the ligand-field band moves to higher frequencies, but retains its relatively high intensity, whereas the charge transfer bands move to lower frequencies. We are of the opinion that it should be possible to draw from these facts the conclusion that on solvolysis the complex species retain essentially their geometric configuration, only slightly changing towards a more planar conformation. Such an explanation would account for both the blue shift of the ligand-field band as a consequence of more pronounced tetragonality of the solvolyzed complex (see Fig. 2 and Table), and the red shift of the charge transfer bands; the latter shift could be interpreted as a consequence of smaller overall electrostatic repulsion between the ligands (now representing two negative charges and two dipoles instead of four negative charges) and the metal electrons in their 3d orbitals.

### Experimental Part

*Preparation of the complexes.* Precipitation of the complex salts  $R_2CuX_4$  usually takes place spontaneously on mixing alcoholic solutions of  $CuX_2$  and of  $RX$  in stoichiometric amounts; the only observed exceptions were  $[(n-Bu)_4N]_2[CuBr_4]$ , which is too soluble and requires vacuum removal of the solvent before crystallizing, and  $[Ph_4As][CuCl_3]$ , which, despite all attempts, was always obtained as a trichloro and not as a tetrachlorocomplex. Recrystallization is easily accomplished with satisfactory results from ethanol in presence of excess halide, or from nitromethane or acetonitrile. We thus prepared

bis-tetramethylammonium tetrachlorocuprate(II)  $[(CH_3)_4N]_2[CuCl_4]$ , golden yellow leaflets

(analysis: C 27,45%, H 7,20%, N 7,76%, Cu 18,03%, Cl 39,65%);

$C_8H_{24}N_2CuCl_4$  requires C 27,19%, H 6,84%, N 7,91%, Cu 17,97%, Cl 40,08%;

bis-trimethylbenzylammonium tetrachlorocuprate(II)  $[C_6H_5CH_2N(CH_3)_3]_2[CuCl_4]$ , yellow leaflets

(analysis: C 47,69%, H 6,30%, N 5,30%, Cu 12,50%, Cl 27,77%);

$C_{20}H_{42}N_2CuCl_4$  requires C 47,50%, H 6,38%, N 5,49%, Cu 12,58%, Cl 28,05%);

bis-tetraethylammonium tetrabromocuprate(II)  $[(C_2H_5)_4N]_2[CuBr_4]$ , very dark violet needles

(analysis: C 30,40%, H 6,26%, N 4,33%, Cu 10,02%, Br 48,94%);

$C_{16}H_{40}N_2CuBr_4$  requires C 29,86%, H 6,27%, N 4,32%, Cu 9,88%, Br 49,67%);

bis-tetra-n-butylanionium tetrabromocuprate(II)  $[(C_4H_9)_4N]_2[CuBr_4]$ , very dark violet crusts

(analysis: C 45,09%, H 8,17%, N 3,24%, Cu 7,19%, Br 35,14%);

$C_{32}H_{72}N_2CuBr_4$  requires C 44,29%, H 8,37%, N 3,23%, Cu 7,32%, Br 35,93%);

bis-tetramethylammonium tetrabromocuprate(II)  $[(CH_3)_4N]_2[CuBr_4]$ , very dark violet needles

(analysis: C 18,02%, H 4,65%, N 5,05%, Cu 12,02%, Br 59,45%);

$C_8H_{21}N_2CuBr_4$  requires  $C$  18,10%,  $H$  4,55%,  $N$  5,27%,  $Cu$  11,95%,  $Br$  60,14%), and tetraphenylarsonium trichlorocuprate(II)  $[(C_6H_5)_4As][CuCl_3]$ , brown prismatic crystals

(analysis:  $C$  51,90%,  $H$  3,64%,  $Cu$  10,73%,  $Cl$  18,25%;

$C_{24}H_{20}AsCuCl_3$  requires  $C$  52,10%,  $H$  3,64%,  $Cu$  11,49%,  $Cl$  19,21%).

*Properties of the complexes.* All tetrahalogenocomplexes we prepared are air-stable substances, which can be hydrolytically decomposed, but are in general only moderately hygroscopic. They are soluble in polar organic solvents, where they behave as 1:2 electrolytes (molar conductivities are of the order of 250 in nitromethane or 130 in acetonitrile). They are all paramagnetic, and have a magnetic moment (uncorrected for Curie temperature) of about  $1,95 \pm 0,05$  B.M., in agreement with previous reports by GILL and NYHOLM [15, 16]. Their solutions in polar organic solvents are not unconditionally stable: on the contrary, they can easily undergo decomposition, their colour turning from yellow to orange for the chlorocomplexes, and from violet through grey-blue to green for the bromocomplexes; such changes, which we have interpreted as due to solvolysis reactions, take place on dilution of the solutions (but can be then prevented by addition of a sufficient excess of free halide ions) or on heating; in the latter case, the temperature range at which the colour change occurs is the higher the larger the excess of halide ions present, but anyway the colour change is practically complete at the boiling temperature of the solutions, whatever the excess of halide present. Such spectral changes are exemplified in Fig. 3, where, however, reported data are not exactly quantitative, since measured absorbance values are reported there as such, without any correction for the thermal coefficient of cell thickness and for concentration changes due to thermal dilatation of the solutions.

*Spectrophotometric measurements* were performed with a Beckman DK2 instrument, in silica cells of 1 cm or of 1 mm thickness. Solvents were made accurately anhydrous according to usual techniques [12, 13], although small traces of water had no significant effect on the shape and the intensity of the spectra. Reference solutions contained stoichiometrically equivalent amounts of onium halides  $RX$ , in order to match exactly the absorption due to the excess halides added, if present, and to the cations of the complex salts. For the particular care and special devices used in measurements at low frequencies ( $\lesssim 5000$   $cm^{-1}$ ), see ref. [14].

The Lambert-Beer law is obeyed rather exactly by the bands of  $[CuCl_4]^-$  in nonaqueous solvents, provided an excess of  $[Cl^-]$  is present, over a wide range of concentrations. For  $[CuBr_4]^-$  however, even in presence of excess  $[Br^-]$ , the ratio  $E/C_{mol}$  for both the d-d band and the charge transfer bands is not perfectly constant, but decreases slightly towards low concentrations; this behaviour is probably to be connected to the easier decomposability of the tetrabromoanions. Without excess halide, much more marked deviations from Lambert-Beer law occur for both tetrachloro- and tetrabromocuprate(II) complexes: the ratio  $E/C_{mol}$  decreases rapidly at the absorption maxima of the  $[CuX_4]^-$  species with decreasing concentration, whereas an increasing absorption takes place at the maxima of the solvolyzed species (see e.g. Fig. 2). No significant difference was detected among the spectra of the same complex anion with different cations.

*Acknowledgment.* The present work was carried out under a program of physico-chemical investigations on metal complexes, executed jointly by the Institute of General Chemistry of the University of Rome and the Institute of Physical Chemistry of the University of Frankfurt am Main, and sponsored by the Scientific Office of the NATO, whose financial support is here gratefully acknowledged.

### Literature References

- [1] BALLHAUSEN, C. J.: *Mat.-fys. Medd. Dan. Vid. Selsk.* **29**, no. 4 (1954).
- [2] BJERRUM, J.: *Mat.-fys. Medd. Dan. Vid. Selsk.* **22**, no. 18 (1946).
- [3] —, C. J. BALLHAUSEN and C. K. JØRGENSEN: *Acta chem. Scand.* **8**, 1275 (1954).
- [4] BUFFAGNI, S., and T. M. DUNN: *Nature* **188**, 937 (1960).
- [5] CHROBAK, L.: *Z. Krist.* **88**, 35 (1934).
- [6] COTTON, F. A., D. M. L. GOODGAME and M. GOODGAME: *J. Am. chem. Soc.* **83**, 4690 (1961).
- [7] — — — *J. Am. chem. Soc.* **84**, 167 (1962).
- [8] DESESA, M. A., and L. B. ROGERS: *Anal. chim. Acta* **6**, 534 (1952).

- [9] DOEHLEMANN, E., and H. FROMHERZ: *Z. physik. Chem. A* **171**, 371 (1934).
- [10] FEITKNECHT, W., A. LUDI and H. R. OSVALD: Proc. 7th Int. Conf. on Coordination Chemistry, Stockholm 1962, paper 1B6, page 24.
- [11] FEISENFELD, G.: Proc. Roy. Soc. London A **236**, 506 (1956).
- [12] FURLANI, C., and G. MORPURGO: *Z. physik. Chem. (Frankfurt)* **28**, 93 (1961).
- [13] —, and A. FURLANI: *J. inorg. nucl. Chem.* **19**, 51 (1961).
- [14] —, C., E. CERVONE and V. VALENTI: *J. inorg. nucl. Chem.* 1962 (in press).
- [15] GILL, N. S., R. S. NYHOLM and P. PAULING: *Nature* **182**, 168 (1958).
- [16] — — *J. chem. Soc. (London)* **1959**, 3997.
- [17] GOODGAME, D. M. L., M. GOODGAME and F. A. COTTON: *J. Am. chem. Soc.* **83**, 4161 (1961).
- [18] GRIFFITH, J. S.: *The theory of transition-metal ions*, p. 301. Cambridge: University Press 1961.
- [19] GRUEN, D. M., and R. L. MCBETH: *Nature* **194**, 468 (1962).
- [20] HARKER, D.: *Z. Krist. A* **93**, 136 (1936).
- [21] HELMHOLZ, L.: *J. Am. chem. Soc.* **69**, 886 (1947).
- [22] —, and R. F. KRUEH: *J. Am. chem. Soc.* **74**, 1176 (1952).
- [23] HENDRICKS, S. B., and R. G. DICKINSON: *J. Am. chem. Soc.* **49**, 2149 (1927).
- [24] HOLM, R., and F. A. COTTON: *J. Am. chem. Soc.* **80**, 5658 (1958).
- [25] HOLMES, O. G., and D. S. McCLURE: *J. chem. Physics* **26**, 1686 (1957).
- [26] JØRGENSEN, C. K.: *Acta chem. Scand.* **11**, 53 (1957); see also references [16] and [4].
- [27] KÖNIG, E., and H. L. SCHLÄFER: *Z. physik. Chem. (Frankfurt)* **26**, 371 (1960).
- [28] KOSOWER, E. M., R. L. MARTIN and V. W. MELOCHE: *J. Am. chem. Soc.* **79**, 1509 (1957).
- [29] MELLOR, D. P.: *Chem. Reviews* **33**, 137 (1943).
- [30] MOELLER, T.: *J. physic. Chem.* **48**, 111 (1944).
- [31] SCHNEIDER, W.: Proc. 7th Int. Conf. on Coordination Chemistry, Stockholm 1962, paper 1B7, page 27.
- [32] WELLS, A. F.: *J. chem. Soc. (London)* **1947**, 1662.
- [33] — *J. chem. Soc. (London)* **1947**, 1670.

(Received July 4, 1962)