

# Copper(II) complexes with triphenylphosphine oxide. I. Preparation and properties of $\text{Cu}(\text{OPPh}_3)_4\text{X}_2 \cdot 2\text{H}_2\text{O}$

D. MAKÁŇOVÁ, G. ONDREJOVIČ, M. MELNÍK, and J. GAŽO

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

Received 14 July 1975

Accepted for publication 20 November 1975

The preparation and some properties of  $\text{Cu}(\text{OPPh}_3)_4\text{X}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{OPPh}_3 =$  triphenylphosphine oxide;  $\text{X} = \text{Cl}, \text{Br}$ ) complexes are described. Thermal properties of these complexes as well as their infrared, electronic, e.p.r. spectra and magnetic properties were studied.

Obtained results indicate that the  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complex contains chromophore  $[\text{CuO}_4\text{Cl}_2]$  with oxygen atoms in equatorial positions and chlorine atoms in axial positions of distorted tetragonal bipyramide. In  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$  we assume that oxygen atoms of triphenylphosphine oxide are shifted from equatorial plane with indication of a distorted tetrahedron. Water in both complexes is bonded by hydrogen bonds.

В работе описан способ приготовления и некоторые свойства комплексов  $\text{Cu}(\text{OPPh}_3)_4\text{X}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}$ ). Исследованы термическая устойчивость этих комплексов, их ИК спектры, электронные спектры поглощения, ЭПР спектры и магнитные свойства.

Полученные результаты говорят о том, что комплекс  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  содержит хромофор  $[\text{CuO}_4\text{Cl}_2]$  с атомами кислорода в экваториальных положениях и атомами хлора в аксиальных положениях искаженной тетрагональной бипирамиды. В  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$  наблюдается отклонение от экваториальной плоскости атомов кислорода трифенилфосфиноксида с признаками искаженного тетраэдра. Молекулы воды в этих комплексах присоединены водородными связями.

Reaction of  $\text{CuCl}_2$  with  $\text{PPh}_3$  in molar ratio 1:1 and 1:4 in acetone gives rise to  $\text{Cu}(\text{I})$  complexes with  $\text{PPh}_3$  and after a longer standing of the reaction solutions also to  $\text{Cu}(\text{OPPh}_3)_2\text{Cl}_2$ ,  $\text{Cu}_4\text{OCl}_6(\text{OPPh}_3)_4$ , and  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , which were separated chromatographically on a column of  $\text{Al}_2\text{O}_3$  [1]. When the conditions of formation of  $\text{OPPh}_3$ , which is necessary for formation of  $\text{Cu}(\text{II})$  complexes with  $\text{OPPh}_3$ , were studied it was found that the oxidation-reduction decomposition of unstable chlorotriphenylphosphine complexes of  $\text{Cu}(\text{II})$  produces chlorine which reacts with excess  $\text{PPh}_3$  to give  $\text{Ph}_3\text{PCl}_2$  [2]. The  $\text{OPPh}_3$  formed by solvolysis of  $\text{Ph}_3\text{PCl}_2$  reacts with  $\text{Cu}(\text{II})$  to give triphenylphosphine oxide complexes.

The subject of our interest are the complexes  $\text{Cu}(\text{OPPh}_3)_4\text{X}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}$ ), which were for the first time prepared in our laboratory. They are formed not only at

oxidation-reduction decomposition of the Cu(II) complexes with PPh<sub>3</sub>, but also by a direct synthesis of CuX<sub>2</sub> and OPPh<sub>3</sub> under certain conditions. These complexes are interesting from several aspects. There is an unusually large number of ligands with possibility of coordination per one central atom. Therefore certain peculiarities can be expected in their structure which should be reflected also in chemical properties. The experiments show that by the decomposition of these complexes it is possible to prepare not only all known halocopper(II) complexes with triphenylphosphine oxide ligand, but also two thus far not described substances [3].

This paper deals with the preparation and study of some properties of Cu(OPPh<sub>3</sub>)<sub>4</sub>X<sub>2</sub>·2H<sub>2</sub>O complexes.

## Experimental

### *Chemicals, analytical methods, and equipments*

CuCl<sub>2</sub> was prepared by thermal dehydration of hydrate in the flow of HCl. CuBr<sub>2</sub> was prepared by reaction of hydrobromic acid with copper(II) hydroxide carbonate. Triphenylphosphine oxide was prepared by the standard method [4]. Water in the complexes was substituted by D<sub>2</sub>O by standing of pulverized hydrates over D<sub>2</sub>O in a desiccator.

The copper content was determined complexometrically using murexide as an indicator while chlorides and bromides content was determined argentometrically with potentiometric indication of the titration end-point. Carbon and hydrogen contents were determined by standard methods of elemental analysis.

The melting points were determined using a Kofler block and the infrared spectra of Nujol suspensions of samples were recorded on Perkin—Elmer 225 and UR-10 instruments. The electronic spectra of Nujol suspensions of samples on chromatographic paper were measured with a Perkin—Elmer 450 instrument. Thermal records were obtained using Derivatograph OD-102. Magnetic susceptibilities were measured by the Gouy method in the temperature range 90—350 K on a Newport Instrument Ltd. device. CuSO<sub>4</sub>·5H<sub>2</sub>O [5] was used as a standard. Diamagnetic corrections were calculated using Pascal constants [6] and magnetic moment values were calculated according to the relation

$$\mu_{\text{eff}} = 798.1 (\chi_{\text{M}} T)^{1/2}.$$

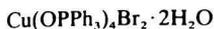
The e.p.r. spectra of the polycrystalline samples were recorded on a Varian E 3 spectrometer at microwave frequency 9300 MHz.

### *Preparation of the complexes*

#### Cu(OPPh<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>·2H<sub>2</sub>O

Anhydrous CuCl<sub>2</sub> (10.45 g; 0.078 mole) was dissolved in ethanol (25 ml) and to this solution acetone (175 ml) was added. The solution was mixed with a saturated solution of OPPh<sub>3</sub> in acetone containing 105.5 g OPPh<sub>3</sub> (0.355 mole) at 20°C. The volume of resulting red-brown solution was reduced to a half by evaporation and then distilled water (3.5 ml; 0.19 mole) was added. In the course of 48 hrs blue crystals crystallized at room temperature and these were washed with ethanol and dried *in vacuo*. Melting point was found to be 142°C.

For Cu(OPPh<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (1283.53) calculated: 4.95% Cu, 5.52% Cl, 67.37% C, 5.02% H; found: 4.76% Cu, 5.46% Cl, 67.10% C, 5.03% H.



$\text{CuBr}_2$  (14.03 g; 0.063 mole) was dissolved in ethanol (775 ml) and to the solution distilled water (2.85 ml; 0.158 mole) was added. The solution was mixed with ethanol solution of  $\text{OPPh}_3$ , prepared by dissolving  $\text{OPPh}_3$  (80 g; 0.284 mole) in ethanol (118 ml). In the course of 3 days at room temperature green crystals crystallized from the solution and these were washed with ethanol and dried *in vacuo*. Melting point 138°C.

For  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$  (1372.44) calculated: 4.63% Cu, 11.64% Br, 63.01% C, 4.70% H; found: 4.59% Cu, 11.71% Br, 62.93% C, 4.75% H.

Both complexes dissolve in ethanol, acetone, chloroform, acetonitrile, and acrylonitrile. They are insoluble in water, toluene, and carbon tetrachloride and decompose in benzene and diethyl ether.

## Results and discussion

### Preparation of the complexes

The complexes  $\text{Cu}(\text{OPPh}_3)_4\text{X}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) can be prepared by two procedures. The first is the reaction of  $\text{CuX}_2$  with  $\text{PPh}_3$  in a suitable nonaqueous solvent. This procedure uses  $\text{Ph}_3\text{PX}_2$  which is formed due to a mutual influence of ligands and oxidation-reduction process. Solvolysis of  $\text{Ph}_3\text{PX}_2$  produces  $\text{OPPh}_3$ , required for the formation of complexes. Disadvantage of this procedure is that besides the described complexes also other triphenylphosphine oxide complexes of  $\text{Cu}(\text{II})$  are formed (depending on molar ratio of  $\text{Cu}(\text{II})$  and  $\text{PPh}_3$ ) which can be separated chromatographically on a column of  $\text{Al}_2\text{O}_3$ . In this way we have prepared  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  [1] and it can be assumed that analogous bromide can be also prepared by this method.

The second procedure is a direct synthesis of  $\text{CuX}_2$  with  $\text{OPPh}_3$  in the presence of water in a suitable solvent. This method is simpler and less time-consuming than the first one.

### Thermal decomposition

The course of thermal decomposition is practically the same for both complexes studied. The record of thermal decomposition of  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$  is shown in Fig. 1. Both complexes are practically stable up to 85°C. When temperature is increased further, a gradual colour change takes place, the bromide complex turning from original green to red-brown and the chloride complex from blue to orange. At temperatures 100°C for the bromide and 114°C for the chloride complex endothermic change occurs accompanied by a 2.5% loss of weight for the bromide and 2.8% for the chloride complexes, which corresponds practically to the loss of two water molecules. Another endothermic change takes place at ~145°C for the bromide and at 155°C for the chloride complex, this time without loss of weight.

From these data as well as from the results presented in [1] it follows that by thermal dehydration of the  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complexes it is not possible to prepare nonaqueous compounds with composition  $\text{Cu}(\text{OPPh}_3)_4\text{X}_2$ . Dehydration leading to a loss of two water molecules is in both cases accompanied by liberation of two  $\text{OPPh}_3$  molecules and  $\text{Cu}(\text{OPPh}_3)_2\text{X}_2$  results.

### Infrared spectra

Three wavenumber regions were studied. Stretching vibrations of the OH group of a water molecule were observed as a broad absorption band at 3000—3400  $\text{cm}^{-1}$ . Such broad

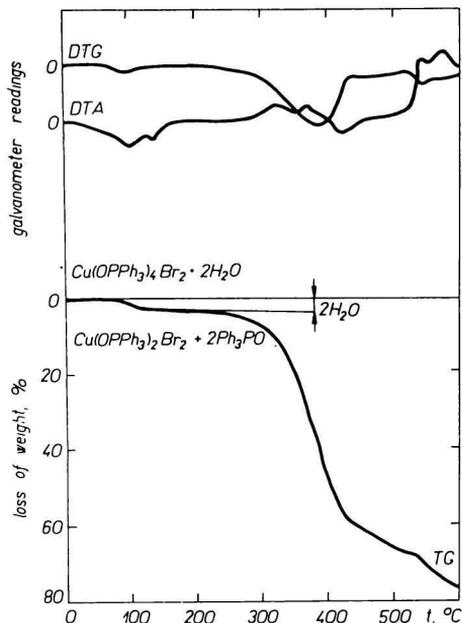


Fig. 1. Thermogram of  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$ .

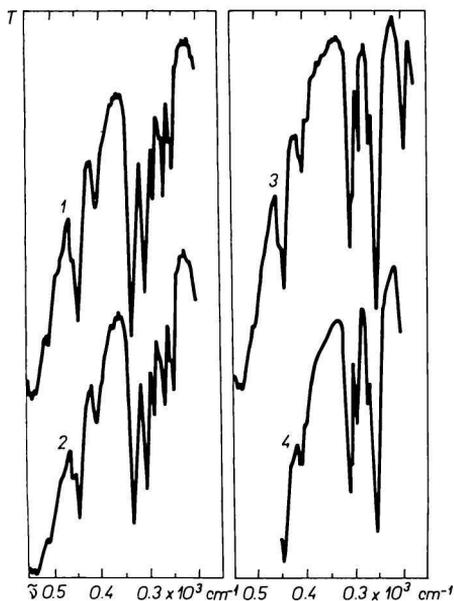


Fig. 2. The infrared spectra in  $200\text{--}550\text{ cm}^{-1}$  region.

1.  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ;
2.  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{D}_2\text{O}$ ;
3.  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$ ;
4.  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{D}_2\text{O}$ .

absorption bands indicate that the OH group interacts with other atoms *via* hydrogen bonds [7]. Possible interacting atoms are oxygen and chlorine or bromine. When water in the complexes is replaced by  $\text{D}_2\text{O}$  as can be expected [8] broad absorption bands  $\tilde{\nu}(\text{OH})$  at  $3000\text{--}3400\text{ cm}^{-1}$  disappear and new bands corresponding to stretching vibrations of O—D group appear at about  $2350\text{ cm}^{-1}$ . Presented data together with the fact that dehydration of the complexes is accompanied by a more drastic decomposition to  $\text{Cu}(\text{OPPh}_3)_2\text{X}_2$  and  $\text{OPPh}_3$  indicate that the water molecules and their interactions *via* hydrogen bonds are important for existence of the structure of complexes.

Wavenumber region  $1100\text{--}1200\text{ cm}^{-1}$  gives the information on the coordination of  $\text{OPPh}_3$  on central atom. The coordination is usually manifested by a shift of P—O stretching vibrations of triphenylphosphine oxide to lower wavenumbers [9]. For pure  $\text{OPPh}_3$  the P—O stretching vibration is observed at  $1191\text{ cm}^{-1}$ . In both complexes studied the position of  $\tilde{\nu}(\text{P—O})$  bands is changed very little if compared to pure  $\text{OPPh}_3$  ( $1193\text{ cm}^{-1}$  for  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $1190\text{ cm}^{-1}$  for the analogous bromide). The fact that the coordination of ligand practically does not influence the wavenumber of P—O stretching vibrations can be explained by symmetry of the structure of the complex [1, 10] and also by a contribution of the hydrogen-bond interactions of water molecules with other atoms. In the infrared spectra of both complexes a band corresponding to the bending vibration of water at about  $1630\text{ cm}^{-1}$  was not observed. This is a further evidence for a strong bonding of water molecules in the structure of the complexes by hydrogen bonds.

The far infrared spectra of complexes are shown in Fig. 2. The far infrared spectra

of  $D_2O$  hydrates do not show any observable differences. Comparing the spectra of  $Cu(OPPh_3)_4X_2 \cdot 2H_2O$  with those of  $Cu(OPPh_3)_4X_2 \cdot 2D_2O$  it is evident that substitution of  $H_2O$  by  $D_2O$  is not accompanied by a shift of bands to lower wavenumbers. Thus the far infrared spectra indicate that water molecules are not coordinated with central atom and they are apparently bonded in the complexes by hydrogen bonds.

Positions of the  $\tilde{\nu}(Cu-O)$  bands ( $442$  and  $443\text{ cm}^{-1}$ , respectively) clearly suggest the coordination of  $OPPh_3$  through oxygen donor atom. The bands at  $331\text{ cm}^{-1}$  ( $\tilde{\nu}(Cu-Cl)$ ) and  $250\text{ cm}^{-1}$  ( $\tilde{\nu}(Cu-Br)$ ) suggest the presence of monofunctionally bonded X with chlorine atoms occupying apparently the terminal positions [11, 12].

### Electronic spectra

The electronic spectra of  $Cu(OPPh_3)_4X_2 \cdot 2H_2O$  ( $X = Cl, Br$ ) complexes were measured in Nujol mull in the region  $8-30 \times 10^3\text{ cm}^{-1}$ . The spectra of both complexes are analogous in the region above  $13 \times 10^3\text{ cm}^{-1}$ . The electronic spectrum of  $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$  (Fig. 3) in

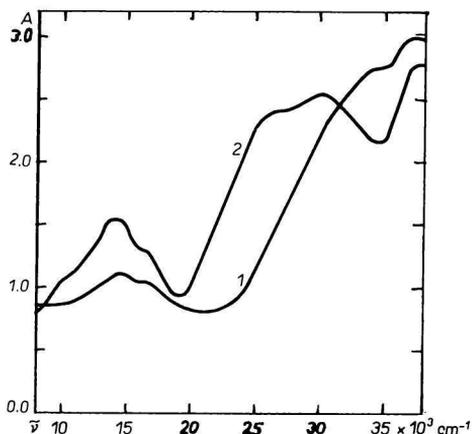


Fig. 3. The electronic spectra.  
1.  $Cu(OPPh_3)_4Cl_2 \cdot 2H_2O$ ;  
2.  $Cu(OPPh_3)_4Br_2 \cdot 2H_2O$ .

visible region shows a band at  $14.4 \times 10^3\text{ cm}^{-1}$  and a shoulder at  $17.4 \times 10^3\text{ cm}^{-1}$ . In the u.v. region another shoulder at  $34.0 \times 10^3\text{ cm}^{-1}$  and a band at  $37.4 \times 10^3\text{ cm}^{-1}$  appear, which are apparently connected with charge transfer from the ligands to the central atom. The band and shoulder in the visible region can be assigned to the following  $d-d$  transitions of  $Cu(II)$  atom



The electronic spectrum of  $Cu(OPPh_3)_4Br_2 \cdot 2H_2O$  complex shows a band at  $14.2 \times 10^3\text{ cm}^{-1}$  and shoulders at  $10.0 \times 10^3\text{ cm}^{-1}$  and  $17.0 \times 10^3\text{ cm}^{-1}$ , which are assigned to  $d-d$  transitions of  $Cu(II)$  atom. In the u.v. region the charge-transfer bands at  $26.0 \times 10^3\text{ cm}^{-1}$ ,  $30.0 \times 10^3\text{ cm}^{-1}$ , and  $37.5 \times 10^3\text{ cm}^{-1}$  were observed.

*The e.p.r. spectra*

The e.p.r. spectrum of the chloride complex is typically axial with hyperfine splitting in axial direction (Table 1). The form of spectrum together with the values  $g_{\parallel} > g_{\perp}$  and simultaneously  $g > 2.04$  suggest the presence of the  $d_{x^2-y^2}$  ground state in mononuclear units with effective spin  $S = 1/2$ . While the e.p.r. spectrum of the chloride complex is axial with hyperfine splitting only in axial direction, the bromide complex exhibits this splitting also in the equatorial plane.

*Magnetic properties*

The study of the temperature dependence of magnetic properties of  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$  shows (Tables 2 and 3) that with decreasing temperature the

Table 1

Data calculated from e.p.r. spectra of  $\text{Cu}(\text{OPPh}_3)_4\text{X}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{X}=\text{Cl}, \text{Br}$ ) complexes

Complex	$g_{\perp}$	$g_{\parallel}$	$g_{\text{av}}$	$A_{\perp} \cdot 10^{-4}$	$A_{\parallel} \cdot 10^{-4}$
$\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	2.06	2.26	2.13	30	120
$\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$	2.08	2.38	2.21		85

Table 2

Magnetic data on  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$   
( $\Delta = 9.009 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1}$ )

$T$ K	$\chi_m \cdot 10^{-9}$ $\text{m}^3 \text{ kg}^{-1}$	$\chi_m^{\text{exp}} \cdot 10^{-8}$ $\text{m}^3 \text{ mol}^{-1}$	$\chi_m^{\text{calc}} \cdot 10^{-8}$ $\text{m}^3 \text{ mol}^{-1}$	$\mu_{\text{eff}}$ B.M. ( $\pm 0.02$ )
100	39.06	5.914	5.979	1.94
126	28.76	4.592	4.331	1.92
138.5	25.25	4.140	3.988	1.91
151	21.98	3.723	3.722	1.89
164	19.22	3.367	3.183	1.88
178	17.33	3.125	3.102	1.88
191	14.82	2.803	2.870	1.85
205.5	12.94	2.561	2.657	1.83
216.5	11.68	2.400	2.512	1.82
229	10.30	2.223	2.358	1.80
245.5	9.29	2.094	2.184	1.81
259.5	8.42	1.981	2.058	1.81
272.5	7.66	1.883	1.962	1.81
285	6.91	1.787	1.866	1.80
293.5	7.03	1.804	1.813	1.83
310	6.40	1.723	1.708	1.84
325	5.52	1.610	1.569	1.83
339	5.02	1.545	1.555	1.83

Table 3

Magnetic data on  $\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$   
 $(\Delta = 9.29 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1})$

$T$ K	$\chi_m \cdot 10^{-9}$ $\text{m}^3 \text{ kg}^{-1}$	$\chi_m^{\text{exp}} \cdot 10^{-8}$ $\text{m}^3 \text{ mol}^{-1}$	$\chi_m^{\text{calc}} \cdot 10^{-9}$ $\text{m}^3 \text{ mol}^{-1}$	$\mu_{\text{eff}}$ B.M. ( $\pm 0.02$ )
89.5	56.52	8.687	8.774	2.22
114	41.19	6.584	6.569	2.19
127	35.79	5.842	5.796	2.17
140.5	30.52	5.118	5.164	2.14
155	27.13	4.652	4.626	2.14
168.5	24.24	4.255	4.214	2.14
193.5	19.59	3.617	3.618	2.11
208	17.33	3.308	3.344	2.09
220	16.33	3.170	3.147	2.11
234.5	15.07	2.998	2.938	2.12
248.5	13.94	2.842	2.763	2.12
262	12.68	2.670	2.609	2.11
274	11.30	2.408	2.486	2.08
285	10.42	2.360	2.376	2.07
295	9.67	2.256	2.298	2.06

Table 4

Parameters obtained from magnetic measurements

Complex	$T$ K	$\chi_K \cdot 10^6$	$\chi_M \cdot 10^6$	$\mu_{\text{eff}}$ B.M.	$C$	$\Theta$
$\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	293.5	0.56	1436	1.83	0.40	+16
$\text{Cu}(\text{OPPh}_3)_4\text{Br}_2 \cdot 2\text{H}_2\text{O}$	295	0.77	1796	2.06	0.51	+16.5

values of magnetic moments moderately increase, both complexes being magnetically diluted Cu(II) complexes. In both cases the observed temperature dependence of molar susceptibility obeys the Curie—Weiss law

$$\chi_m' = \alpha C / (T - \Theta).$$

The parameters are presented in Table 4. The values of Weiss constant indicate the presence of some ferromagnetic interaction which is practically the same for both complexes.

On the basis of the experimental data it is possible to assume the presence of  $[-\text{CuO}_4-\text{Cl}_2-]$  chromophore with a nondegenerate ground state in  $\text{Cu}(\text{OPPh}_3)_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  complex. In the environment of Cu(II) atom there are four  $\text{OPPh}_3$  molecules in equatorial plane, remaining two positions on longer coordinates being occupied by two chlorine atoms with a simultaneous formation of distorted tetragonal bipyramide in axial direction. Two water molecules as shown by the infrared spectra are bonded in the crystal lattice by hydrogen bonds.

From the magnitude of magnetic moment and the magnetic properties of the bromide complex as well as from the electronic spectra structural differences can be expected for bromide complex in comparison with the chloride complex. The higher value of magnetic moment  $\mu_{\text{eff}} = 2.06$  B.M. for the bromide complex compared to  $\mu_{\text{eff}} = 1.83$  B.M. for the chloride complex indicates tetrahedral structure, further evidence for this structure being the band at  $10.0 \times 10^3 \text{ cm}^{-1}$  in the electronic spectrum. On the other hand, the similarity of the electronic spectra of both complexes in the region above  $13.0 \times 10^3 \text{ cm}^{-1}$  as well as the band at  $250 \text{ cm}^{-1}$  assigned to Cu—Br stretch indicate the presence of  $[\text{CuO}_4\text{X}_2]$  (X = Cl, Br) chromophore. On the basis of data obtained we assume that in the bromide complex the oxygen atoms of triphenylphosphine oxide do not lie in the same plane, but they are shifted from it with indication of distorted tetrahedron which could be connected also with the effect of steric factors.

*Acknowledgements.* The authors express their gratitude to Dr M. Livař for recording the electronic spectra and to Dr J. Baxa and O. Lakatošová for the infrared spectra. Thanks are also expressed to I. Lieblová and J. Viskupičová for experimental assistance.

### References

1. Makáňová, D., Ondrejovič, G., and Gažo, J., *Chem. Zvesti* **27**, 4 (1973).
2. Makáňová, D., Ondrejovič, G., Valigura, D., and Gažo, J., *Chem. Zvesti* **28**, 604 (1974).
3. Makáňová, D., Ondrejovič, G., and Gažo, J., *Chem. Zvesti* **30**, 81 (1976).
4. Vanino, L., *Handbuch der präparativen Chemie, II. Organischer Teil*, p. 723. F. Enke, Stuttgart, 1937.
5. Figgis, B. N. and Nyholm, R. S., *J. Chem. Soc.* **1959**, 331.
6. Earnshaw, A., *Introduction to Magnetochemistry*, pp. 6—8. Academic Press, London, 1968.
7. Roland, G. and Duyckaerts, G., *Spectrochim. Acta* **22**, 793 (1966).
8. Beattie, I. R., Gilson, T. R., and Ozin, G. A., *J. Chem. Soc. (A)* **1969**, 534.
9. Goodgame, D. M. L. and Cotton, F. A., *J. Chem. Soc.* **1961**, 2298.
10. Bertrand, J. A. and Kelley, J. A., *J. Amer. Chem. Soc.* **88**, 4746 (1966).
11. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd Edition, p. 214. Wiley, New York, 1970.
12. Karayannis, N. M., Mikulski, C. M., Pytlewski, L. L., and Labes, M. M., *Inorg. Chem.* **9**, 582 (1970).

Translated by K. Sarka