

## COPPER (I) COMPLEXES WITH PHOSPHINE AND OXINE

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Some new copper (I) complexes containing mixed ligands and bearing the general formula  $[\text{CuX}(\text{PPh}_3)(\text{HOx})]_2$  (where  $\text{PPh}_3$  = triphenylphosphine and  $\text{HOx}$  = 8-hydroxyquinoline, and  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$  and  $\text{SCN}^-$ ) have been studied and appear to have dimer and distorted tetrahedral structures having anion bridging.

## INTRODUCTION

A number of workers have prepared copper (I) halide [1-3] nitrate [4], and thiocyanate [5] complexes with triphenylphosphine, bearing the formula  $\text{CuSCN}(\text{PPh}_3)_2$ . Structurally they are considered bridged dimers. The mixed ligand complexes of the type  $\text{CuNO}_3(\text{PPh}_3)(\text{BiL})$  have been reported [6] where  $\text{BiL}$  is 1,10-phenanthroline or 2,2'-biquinoly.

The complexes of copper (I) containing mixed ligands are reported here. The ligands introduced are triphenylphosphine ( $\text{PPh}_3$ ) and 8-hydroxyquinoline ( $\text{HOx}$ ). The metal to be tried is copper; anions under consideration are  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ , or  $\text{SCN}^-$ . The general formula for the complexes has been proposed on the basis of elemental analysis (Table 1) and spectral studies (Table 2). They are considered to contain tetrahedrally coordinated copper (I)

with bridging anions.

## RESULTS AND DISCUSSION

It is evident from the spectral data that copper is coordinated tetrahedrally; the magnetic susceptibility measurements proved these compounds to be diamagnetic and showed the position of the metal atom. The IR spectra of these complexes may be conveniently assigned to three groups; triphenylphosphine, 8-hydroxyquinoline and bridge forming anions having a distorted tetrahedral structure on each of the copper atoms. Molecular models indicate that a *trans* configuration would be favoured over the *cis*. They are sparingly soluble in common organic solvents to the extent that solution spectra and conductivity data could not be obtained. This property suggests that ionic species are unlikely.

Table 1. Elemental analysis, melting point and state of the complexes.

Compound	C (%)	H (%)	N (%)	X (%)	P (%)	Cu (%)	M.p.	Colour
$[\text{CuCl}(\text{PPh}_3)(\text{HOx})]_2 \cdot \text{H}_2\text{O}$	61.70 (61.83)	4.61 (4.58)	2.58 (2.67)	6.51 (6.76)	5.73 (5.91)	11.78 (12.12)	220 d	Pale green
$[\text{CuBr}(\text{PPh}_3)(\text{HOx})]_2 \cdot \text{H}_2\text{O}$	56.90 (57.00)	4.38 (4.22)	2.15 (2.46)	13.90 (14.06)	5.10 (5.45)	10.90 (11.18)	258	Cream
$[\text{CuI}(\text{PPh}_3)(\text{HOx})]_2 \cdot \text{H}_2\text{O}$	53.21 (53.43)	3.82 (3.79)	2.01 (2.31)	20.58 (20.92)	4.08 (5.10)	10.11 (10.48)	261	Pale yellow
$[\text{CuNO}_3(\text{PPh}_3)(\text{HOx})]_2$	60.34 (60.84)	4.01 (4.32)	5.01 (5.25)	— —	5.71 (5.81)	11.78 (11.93)	210 d	Yellow
$[\text{CuSCN}(\text{PPh}_3)(\text{HOx})]_2$	63.09 (63.56)	4.14 (4.16)	5.14 (5.29)	5.19 (6.06)	5.70 (5.86)	11.70 (12.02)	222	Pale yellow

Calculated values are given in parenthesis.

Table 2. IR absorption spectra in  $\text{cm}^{-1}$ .

$[\text{CuCl}(\text{PPh}_3)(\text{HOx})]_2 \cdot \text{H}_2\text{O}$	3448, 1583s, 1508s, 1486s, 1494s, 1384s, 1334s, 1125s, 1108m, 1042m, 1005s, 883s, 825m, 806s, 782s, 748s, and 704s.
$[\text{CuBr}(\text{PPh}_3)(\text{HOx})]_2 \cdot \text{H}_2\text{O}$	3443b, 1584s, 1507s, 1484db,s, 1442s, 1386s, 1334s, 1124s, 1040s, 1014m, 882m, 802m, 782m, 756s & 706s.
$[\text{CuI}(\text{PPh}_3)(\text{HOx})]_2 \cdot \text{H}_2\text{O}$	3438b, 1536s, 1500s, 1483s, 1438s, 1386s, 1334m, 1280db, 1124s, 1105s, 1040s, 1014m, 883m, 826m, 782s, 747s and 702s.
$[\text{CuNO}_3(\text{PPh}_3)(\text{HOx})]_2$	2090m, 1570s, 1485s, 1438-55trp, 1391s, 1284m, 1260b, 1104s, 1036s, 887m, 842s, 805s, 782s, 755b and 707-717 db.
$[\text{CuSCN}(\text{PPh}_3)(\text{HOx})]_2$	2108s, 1588db,s, 1505s, 1484s, 1440s, 1391s, 1335m, 1292m, 1200m, 1175m, 1110s, 1045s, 1018s, 845m, 825s, 811s, 781m, 748-60trp, and 710-715db,s.

The IR absorption spectra in the region 1104 – 1125  $\text{cm}^{-1}$  of the complexes prepared in this laboratory and with the assigned formula  $[\text{CuX}(\text{PPh}_3)(\text{HOx})]_2$  indicate that phosphorus atom is coordinated to copper as discussed by Deacons and Green [7], and the shifts to higher energies with the increase in intensity supports the assumption that both the phosphine groups are coordinated. The absorption in the region 695–705  $\text{cm}^{-1}$  attributed to out-of-plane ring deformations, is observed in the region 704–708  $\text{cm}^{-1}$  in our complexes. The absorption at 745  $\text{cm}^{-1}$  has been assigned to the degeneracy of the three benzene rings [8, 9] in triphenylphosphine, is consistent with absorption in the region 747–756  $\text{cm}^{-1}$  in the complexes synthesized; the shifting in the band position may be attributed to phosphine coordination.

The peaks in the IR spectrum of 8-hydroxyquinoline at 1504 and 1580  $\text{cm}^{-1}$ , are generally assigned to C=C and C=N stretching vibrations. Our complexes show the slight shifting of the peak position of the former one at around 1490  $\text{cm}^{-1}$ , whereas the latter occurs at the same position with an increase in intensity. In metal chelates a band in the region 850–870  $\text{cm}^{-1}$  is assigned possibly to the C=O bond or to a M–O stretching frequency [10]. This band is absent in our complexes indicating the presence of free oxine.

In case of nitrate complex, there may be two possible structures to be considered, tricoordinate monomer and a nitrate bridged dimer. It is observed that the presence of coordinated bidentate group is consistent with the peak

recorded at 1284  $\text{cm}^{-1}$  [11]. The second one is further supported on the basis of IR spectrum of  $\text{CuNO}_3(\text{PPh}_3)_2$ . X-ray crystallographic study of  $\text{CuNO}_3(\text{PPh}_3)_2$  has shown tetrahedrally coordinated copper (I) with a bidentate nitrate group [6].

The IR spectrum shows strong absorptions in the thiocyanate C–N region at 2108  $\text{cm}^{-1}$ . Band at this energy suggests sulphur-bonded groups as determined by Mitchell and Williams [12]. It is expected that N-bonding of Cu(I) may facilitate the  $\pi$ -acceptor behaviour of triphenylphosphine and may favour s-coordination. The spectrum of  $[\text{CuSCN}(\text{PPh}_3)(\text{HOx})]_2$  presents a strong band at lower frequency than the value required for a bridging thiocyanato group as stated in case of  $(\text{NH}_4)[\text{Cd}(\text{NCS})_4] \cdot 2\text{H}_2\text{O}$  [13], it may be due to the presence of two ligands having a large difference in basicity and in  $\pi$ -bonding ability towards the copper (I) atoms. Similar results were obtained by Toeindiskoetler and Solomon [14] during the course of examining several complexes of N-heterocyclic amines with copper (I) and copper (II) thiocyanates. On the basis of the above observations the probable structures assigned to the complex is a distorted tetrahedrally dimer which is further supported by magnetic susceptibility measurements showing it to be diamagnetic and the symmetry calculations show that the metal has  $C_{2h}$  symmetry.

#### EXPERIMENTAL

1.  $[\text{CuX}(\text{PPh}_3)(\text{HOx})]_2 \cdot \text{H}_2\text{O}$  (X=  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ )

was prepared by stirring under reflux equimolar quantities of 8-hydroxyquinoline and tetrakis (triphenylphosphine) Cu(I) [5] in benzene for 4–5 hr. The first crystallized material was discarded due to complete elimination of triphenylphosphine. The mother liquor after several crystallizations gave the crystalline product of above formula and was found stable in air.

2.  $[\text{CuNO}_3(\text{PPh}_3)(\text{HOx})]_2$  was obtained by stirring under reflux equimolar ratio of 8-hydroxyquinoline and di- $\mu$ -nitrate-bis- (triphenylphosphine) copper (I) [5] in ethanol for 5 hr. The resulting solution gave pale yellow crystals at room temperature.

3.  $[\text{CuSCN}(\text{PPh}_3)(\text{HOx})]_2$ . The procedure adopted was the same as mentioned above, except that chloroform was used, in place of ethanol.

IR spectra were recorded in KBr discs using a Unicam SP 200G spectrophotometer. Phosphorous estimation was done spectrophotometrically by Heteropoly Blue method using a Unicam SP 500 spectrophotometer.

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