

# Copper(II) complexes with organic ligands. XVI. Copper(II) *p*-hydroxybenzoate complexes

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Compounds of composition  $\text{Cu}(p\text{-HOB})_2\text{L}_2$  and  $\text{Cu}(p\text{-HOB})_2\text{L}$  (*p*-HOB is *p*-hydroxybenzoate ion) were prepared by reactions of copper(II) *p*-hydroxybenzoate octahydrate or dihydrate with molecular ligands, pyridines, and pyridine-*N*-oxides, in some cases as crystallohydrates. The structure of the prepared compounds is discussed on the basis of the study of their magnetic properties at room temperature and electronic spectra.

From several existing hydrates of copper(II) *p*-hydroxybenzoate [1–3] the octahydrate was investigated in more detail [3, 4] by the study of its magnetic behaviour and e.p.r. spectra. However, only one copper(II) *p*-hydroxybenzoate complex containing *N*-donor ligand has been described till now, its composition being  $\text{Cu}(p\text{-HOB})_2(\text{py})_2$  [2] (py is pyridine). This work deals with reactions of copper(II) *p*-hydroxybenzoate octahydrate (or dihydrate obtained by partial dehydration of octahydrate) with some molecular ligands, pyridines, and pyridine-*N*-oxides in methanolic solutions. Magnetic properties and electronic spectra of the resulting complexes in the solid state were investigated and on this basis their structure is discussed.

## Experimental

### *Chemicals and instruments*

*p*-Hydroxybenzoic acid (99–100%, Schuchardt, München) was recrystallized from hot water. Cu(II) *p*-hydroxybenzoate octahydrate (*I*) was prepared by an analogous way to that described for Cu(II) salicylate tetrahydrate [5]. Dihydrate of Cu(II) *p*-hydroxybenzoate (*II*) was prepared from octahydrate by partial dehydration at  $t \approx 80^\circ\text{C}$  in 5 hours in a thermostat. Methanol, anal. grade, was dried by a molecular sieve (Potasit) and redistilled. Heterocyclic *N*-oxides were prepared and purified as described in [6]. Other chemicals, anal. grade or pure (inland provenience or imported), were purified by usual methods.

### *Reactions of copper(II) p-hydroxybenzoate octahydrate with N-donor ligands of pyridine type*

Reactions were carried out by mixing two methanolic solutions: the first one containing compound (*I*) together with free *p*-hydroxybenzoic acid, the second comprising

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a corresponding *N*-donor molecular ligand (LN). The ligands used were pyridine, isomeric methylpyridines, and dimethylpyridines (2,4-, 3,4-, and 2,6-). The final products crystallized spontaneously from the reaction systems were washed with cooled methanol after isolation and dried freely at room temperature. Solutions of the starting compounds were prepared from *I* (4.8 g;  $10^{-2}$  M) and *p*-hydroxybenzoic acid (0.7 g;  $5 \times 10^{-3}$  M) dissolved in the necessary amount (40 ml) of methanol, and from the corresponding LN ( $3 \times 10^{-2}$  M) dissolved in methanol (10–20 ml). All the isolated products had the composition  $\text{Cu}(p\text{-HOB})_2(\text{LN})_2$ , the complex of 4-methylpyridine in the form of dihydrate.

We did not succeed in isolating the final product under the described conditions only from the reaction system containing 2,6-dimethylpyridine. A greater excess of *p*-hydroxybenzoic acid and LN was necessary in this case (the molar ratio *I*–*p*-HOB–

Table I

Analytical characteristics, electronic spectra, and magnetic properties of copper(II) *p*-hydroxybenzoate complexes

Compound	<i>M</i>	Calculated/ found		Electronic spectra [kK]	Magnetic properties	
		% Cu	% N		$\chi'_M \cdot 10^6$	$\mu_{\text{eff}}$ [B.M.]
$\text{Cu}(p\text{-HOB})_2(\text{py})_2$	495.97	12.81 12.65	5.64 5.66	15.20 sh 18.20	1475	1.84
$\text{Cu}(p\text{-HOB})_2(2\text{-Mepy})_2$	524.03	12.12 11.99	5.34 5.03	16.70	1502	1.85
$\text{Cu}(p\text{-HOB})_2(3\text{-Mepy})_2$	524.03	12.12 12.20	5.34 5.34	14.50	1518	1.86
$\text{Cu}(p\text{-HOB})_2(4\text{-Mepy}) \cdot 2\text{H}_2\text{O}^a$	560.06	11.34 11.22	5.00 4.90	15.40	1498	1.85
$\text{Cu}(p\text{-HOB})_2(2,4\text{-diMepy})_2$	552.08	11.50 11.60	5.07 5.13	15.30 sh 18.20	1510	1.86
$\text{Cu}(p\text{-HOB})_2(3,4\text{-diMepy})_2$	552.08	11.50 11.51	5.07 5.15	14.80	1500	1.85
$\text{Cu}(p\text{-HOB})_2(2,6\text{-diMepy})(\text{MeOH})^b$	476.97	13.32 13.43	2.93 3.08	14.50 27.0 sh	971	1.47
$\text{Cu}(p\text{-HOB})_2(\text{pyox})$	432.87	14.67 14.60	3.23 3.29	14.10 26.7 sh	894	1.41
$\text{Cu}(p\text{-HOB})_2(2\text{-Mepyox})$	446.90	14.21 14.25	3.13 3.15	14.10 26.6 sh	907	1.42
$\text{Cu}(p\text{-HOB})_2(3\text{-Mepyox})$	446.90	14.21 14.05	3.13 3.13	13.90 26.0 sh	893	1.41
$\text{Cu}(p\text{-HOB})_2(4\text{-Mepyox}) \cdot \text{H}_2\text{O}^c$	464.91	13.66 13.65	3.01 2.85	13.90 26.2 sh	1039	1.53

a) Calculated: 55.77% C, 5.04% H;

found: 55.50% C, 5.07% H.

b) Calculated: 55.40% C, 4.86% H;

found: 55.56% C, 4.79% H.

c) Calculated: 51.67% C, 4.12% H;

found: 51.81% C, 4.26% H.

*p*-HOB – *p*-hydroxybenzoate ion; py – pyridine; Me – methyl; sh – shoulder.

—2,6-diMepy = 1 : 1 : 6), and the composition of the final product was then  $\text{Cu}(p\text{-HOB})_2(2,6\text{-diMepy})(\text{MeOH})$ .

The compositions of the isolated complexes were established from the results of chelometric determinations of copper and determinations of nitrogen by the Dumas method. When complexes contained another component besides LN (*i.e.*  $\text{H}_2\text{O}$  or  $\text{MeOH}$ ), carbon and hydrogen were also determined by elemental analysis. The results are listed in Table 1.

### *Reactions of copper(II) *p*-hydroxybenzoate dihydrate with aromatic *N*-oxides*

The reaction systems in methanolic solutions were prepared analogously as in the synthesis of the former group of complexes. Molar ratios of the reacting components  $II-p\text{-HOBH-LNO}$  were from 1 : 1 : 3 to 1 : 1 : 4 (LNO pyridine-*N*-oxide, 2-, 3-, and 4-methylpyridine-*N*-oxide). The final products crystallized spontaneously from the reaction systems were isolated, washed, dried, and then analyzed in the same way as the complexes of the former group. The results are in Table 1.

### *Magnetic and spectral measurements*

Magnetic susceptibilities of the prepared  $\text{Cu(II)}$  *p*-hydroxybenzoate complexes were determined by the Gouy method at room temperature (24–25°C). The powdered preparations were measured at four different intensities of the magnetic field in the range of 3500–8000 Oe. Potassium ferricyanide was used as a calibration standard [7]. The observed values of the molar susceptibilities were corrected for diamagnetism of the individual components using the corresponding Pascal constants [8]. Effective magnetic moments were calculated from the corrected molar susceptibilities  $\chi'_M$  by means of the formula  $\mu_{\text{eff}} = 2.83 [(\chi'_M - N\alpha) T]^{1/2}$ , in which  $N\alpha = 60 \times 10^{-6}$  cgs mol<sup>-1</sup> was inserted for a contribution of the temperature independent paramagnetism of  $\text{Cu}^{2+}$  [9]. The results are shown in Table 1.

Absorption electronic spectra of the complexes in the solid state were measured in the range of wavenumbers  $\bar{\nu} = 28.6\text{--}10.0$  kK ( $\lambda = 350\text{--}1000$  nm) by a recording Perkin–Elmer 450 spectrophotometer. The finely powdered samples in the form of nujol suspensions were put on chromatographic paper Whatman No. 1 to make preparations for measurements. The found positions of the band maxima are seen in Table 1.

### **Results and discussion**

A series of complexes of composition  $\text{Cu}(p\text{-HOB})_2(\text{LN})_2$  was prepared by reactions of copper(II) *p*-hydroxybenzoate octahydrate with *N*-donor molecular ligands of the pyridine type in methanolic solutions. Magnetic moments of these compounds (at room temperature) often exceed the spin-only value for one unpaired electron of the  $3d^9$  configuration of  $\text{Cu}^{2+}$  ion (1.73 B.M.); thus they are in the diapason characteristic of the magnetically diluted mononuclear  $\text{Cu(II)}$  complexes with tetragonal symmetry or with the square-planar structure (Table 1). The expected three bands in the electronic spectra of the complexes  $\text{Cu}(p\text{-HOB})_2(\text{LN})_2$  ( $D_{4h}$  symmetry) corresponding to the transitions  ${}^2E_g$ ,  ${}^2B_{2g}$ ,  ${}^2A_{1g} \leftarrow {}^2B_{1g}$  appeared at the given experimental conditions in the form of one broad absorption band. In two cases (LN = pyridine and 2,4-dimethylpyridine) a marked shoulder on the lower energy side was observed (Table 1). These shoulders can be attributed to the transition  ${}^2A_{1g} \leftarrow {}^2B_{1g}$  since the  ${}^2B_{2g} \leftarrow {}^2B_{1g}$  tran-

sition usually cannot be observed as a separated band in the spectra of the studied complexes because of its low intensity [10, 11].

The maxima of the absorption bands are located on experimental curves in a region characteristic of tetragonally deformed octahedral (or square-planar) Cu(II) complexes containing the chromophore  $[\text{Cu}(\langle \text{O}_2 \rangle \langle \text{N}_2 \rangle)]$  (only the donor atoms in equatorial positions are marked). In accordance with the known properties of the complexes with similar composition, including the magnetic and spectral properties of *e.g.* copper(II) salicylate complexes of  $\text{Cu}(\text{sal})_2(\text{LN})_2$  type [12, 13], we can assume for the  $\text{Cu}(p\text{-HOB})_2(\text{LN})_2$  compound the monodentate coordination of two  $p\text{-HOB}^-$  ions and LN molecules in equatorial positions around  $\text{Cu}^{2+}$ , in the *trans* arrangement. The coordination numbers 5 and 6 may be then complemented by convenient donor O atoms from neighbouring structural units in the crystal structure.

An interesting feature is that 2,6-dimethylpyridine did not build in copper(II) *p*-hydroxybenzoate molecule under the conditions favourable for the successful synthesis of all the others  $\text{Cu}(p\text{-HOB})_2(\text{LN})_2$  complexes. On the other hand, by the reaction of  $\text{Cu}(\text{sal})_2 \cdot 4\text{H}_2\text{O}$  with 2,6-dimethylpyridine in organic solvents, the complex  $\text{Cu}(\text{sal})_2(2,6\text{-diMepy})_2$  was prepared without difficulties [12]. Copper(II) *p*-hydroxybenzoate complex isolated from the reaction system with a greater excess of 2,6-diMepy differs in composition as well as in properties from other  $\text{Cu}(p\text{-HOB})_2(\text{LN})_2$  compound. The complex  $\text{Cu}(p\text{-HOB})_2(2,6\text{-diMepy})_2(\text{MeOH})$  exhibits an anomalously lowered value of its magnetic moment at room temperature,  $\mu_{\text{eff}} = 1.47$  B.M. In its electronic spectrum the unsplit band of the ligand field ( $d-d$  transitions) shows a maximum at  $\bar{\nu} = 14.5$  kK, another absorption band observed as a shoulder at  $\bar{\nu}_{\text{sh}} \approx 27.0$  kK may be, in accordance with the magnetic properties, ascribed to spin-spin interaction. Thus the magnetic and spectral properties of the complex  $\text{Cu}(p\text{-HOB})_2(2,6\text{-diMepy})(\text{MeOH})$  are very similar to those of binuclear Co(II) carboxylate complexes with the bridge structure of the type of copper(II) acetate monohydrate [14].

If such a structure of the discussed copper(II) *p*-hydroxybenzoate complex really exists, then methanol must be bonded as a monodentate molecular ligand in axial (terminal) positions of the binuclear structural unit, and the composition of the complex should be expressed by the formula  $\text{Cu}_2(p\text{-HOB})_4(\text{MeOH})_2 \cdot 2(2,6\text{-diMepy})$ . 2,6-Dimethylpyridine cannot be built in the axial positions for steric reasons [15], in the complexes of copper(II) acetate monohydrate type it can be present only in a secondary sphere (crystallosolvates). Other eventualities that are not in contradiction with the observed magnetic and spectral properties of the discussed complex might be some kinds of polymeric structures in which a superexchange magnetic interaction takes place between  $\text{Cu}^{2+}$  ions [16-18].

For the synthesis of copper(II) *p*-hydroxybenzoate complexes with pyridine-*N*-oxide and its methyl derivatives, octahydrate  $\text{Cu}(p\text{-HOB})_2 \cdot 8\text{H}_2\text{O}$  proved to be inconvenient as a starting compound. However, the corresponding dihydrate obtained by partial dehydration of the octahydrate (at *ca.* 80°C) was suitable, supposing water-free methanol was used as a solvent. The composition of all the isolated compounds is  $\text{Cu}(p\text{-HOB})_2(\text{LNO})$ , the complex of 4-methylpyridine-*N*-oxide in the form of monohydrate. Their magnetic moments are even at room temperature markedly lower than the spin-only value of  $\text{Cu}^{2+}$  ion (Table 1). This corroborates a considerable interaction between the spins of unpaired electrons of the  $\text{Cu}^{2+}$  ions in their structure. The absorption band observed in their electronic spectrum as a shoulder at  $\bar{\nu}_{\text{sh}} = 26-26.7$  kK may also be ascribed to the mentioned interaction. The absorption band of the ligand field is located in its usual position ( $\bar{\nu}_{\text{max}} = 13.9-14.1$  kK) for many binuclear copper(II) carboxylate com-

plexes of the copper(II) acetate monohydrate type. The prepared compounds can be therefore regarded as binuclear Cu(II) complexes, similarly to copper(II) acetate complexes with pyridine-*N*-oxide,  $\text{Cu}(\text{CH}_3\text{COO})_2(\text{pyox})$ , and quinoline-*N*-oxide,  $\text{Cu}(\text{CH}_3\text{COO})_2(\text{quinox})$  [19, 20], or to the complex  $\text{Cu}(\text{sal})_2(\text{quinox})$  [20]. In their structure a pair of  $\text{Cu}^{2+}$  ions is bridged by four bidentate bonded carboxylate ions while molecules of the corresponding heterocyclic *N*-oxide are bonded in axial terminal positions of the structural unit as an *O*-donor monodentate ligand.

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