

**A NEW ROUTE TO COPPER(II)  $\mu_4$ -OXO COMPLEXES  $\text{Cu}_4\text{OHal}_6\text{L}_4$** 

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A novel procedure is suggested for the preparation of tetranuclear copper(II)  $\mu_4$ -oxo complexes  $\text{Cu}_4\text{OHal}_6\text{L}_4$  with N-heterocycles as ligands, consisting of the oxidation of piperidine or morpholine complexes of copper(I) halides with organic polyhalo compounds in the presence of water. The reaction proceeds readily even at room temperature giving the product in a high yield (up to 88%).

Compounds of  $\text{Cu}_4\text{OCl}_6\text{L}_4$  type have been mentioned first by Bertrand and Kelley<sup>1</sup>, who prepared the complex with triphenylphosphine oxide (TPPO) by refluxing  $\text{CuCl}_2 \cdot \text{TPPO}$  in methyl isobutyl ketone. Many complexes of this kind have been described since then; they were usually obtained as by-products from reaction systems containing copper halides, amines and alcohols<sup>2-7</sup>, or isolated during the crystallization of other copper complexes from polar solvents<sup>1,8</sup>. A number of these compounds arose from the synthesis of  $\text{Cu}_4\text{OHal}_6(\text{CH}_3\text{OH})_4$  from copper(II) chloride and oxide (3 : 1) in methanol followed by replacement of methanol by other ligands<sup>9,10</sup>.

In this paper, a new route to complexes of this kind is described, consisting of the oxidation of piperidine or morpholine complexes of copper(I) halides with organic polyhalo compounds in the presence of water. In contrast to the previous procedures where the halogen for the building of the  $\text{Cu}_4\text{OCl}_6$  skeleton was always of inorganic nature, this is the first case where the complex formation proceeds with the participation of a halogen split off from a C—Hal bond.

**EXPERIMENTAL****Chemicals**

Copper(I) chloride and bromide were obtained by reduction of copper(II) sulphate with sulphur dioxide<sup>11</sup>. Acetonitrile (Croft Laboratories) was purified following the procedure by O'Donnell and coworkers<sup>12</sup>, and absolutized by allowing it to stand with an A5 molecular sieve. Piperidine (Lachema, Brno) was dried with a molecular sieve and rectified. Methyl trichloroacetate was prepared by esterification of trichloroacetic acid (Fluka) with methanol. Chloroform and dichloromethane (both Lachema, Brno) were washed twice with sulphuric acid and water and

rectified. Tetrachloromethane (Lachema, Brno), morpholine, tetrabromomethane and methyl dichloroacetate (all Fluka) were used as received.

### Analytical Methods

Electronic spectra of the compounds in dichloromethane solutions were scanned on a Specord UV-VIS spectrophotometer over the region of 240–770 nm, infrared spectra of KBr discs were run on a Specord 75 IR instrument (both Carl Zeiss, Jena). Gas chromatographic analyses were performed on a 3 m × 3 mm column packed with 3% Silicone OV-17 on Gas-Chrom Q at 70–140°C using a TC detector.

### Procedure

6 mmol of copper(I) chloride or bromide was dissolved at room temperature in 10 ml of anhydrous acetonitrile in a 30 ml flask fitted with a septum and a magnetic stirrer. The flask was flushed with nitrogen (15 min), 1.5 mmol of water in 6 mmol of amine (piperidine or morpholine) was injected through the septum, and after 15 min, 3 mmol of the corresponding polyhalo compound was added. Upon this procedure, the reaction mixture turned dark and in several minutes, heated up by 5–10°C and crystals of the complex started to separate. After the reaction (in 15–60 min) the product was filtered out by suction, washed with 10 ml of ether, and dried in air.

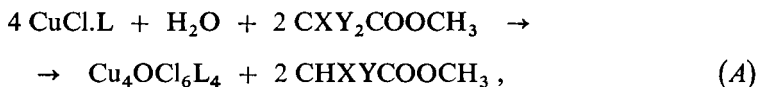
$\text{Cu}_4\text{OCl}_6(\text{Pip})_4$ , brown crystals, m.p. 172–173°C (ref.<sup>4</sup> 170–171°C). For  $\text{C}_{20}\text{H}_{44}\text{N}_4\text{OCu}_4\text{Cl}_6$  (823.5) calculated: 30.86% Cu, 25.84% Cl, 29.14% C, 5.34% H, 6.80% N; found: 30.01% Cu, 25.57% Cl, 28.71% C, 5.34% H, 6.70% N.

$\text{Cu}_4\text{OBr}_6(\text{Pip})_4$ , brown crystals, m.p. 140–142°C (ref.<sup>4</sup> 139–140°C). For  $\text{C}_{20}\text{H}_{44}\text{N}_4\text{OCu}_4\text{Br}_6$  (1090.3) calculated: 23.31% Cu, 43.98% Br, 22.03% C, 4.07% H, 5.14% N; found: 23.01% Cu, 46.00% Br, 22.02% C, 4.04% H, 4.87% N.

$\text{Cu}_4\text{OCl}_6(\text{Morph})_4 \cdot 2 \text{CH}_3\text{CN}$ , brown crystals, m.p. 164–166°C (ref.<sup>4</sup> 164°C). For  $\text{C}_{20}\text{H}_{38}\text{N}_6 \cdot \text{O}_5\text{Cu}_4\text{Cl}_6$  (913.4) calculated: 27.83% Cu, 23.29% Cl, 26.28% C, 4.60% H, 9.20% N; found: 27.94% Cu, 23.59% Cl, 24.18% C, 4.61% H, 7.59% N.

## RESULTS

The complex compounds  $\text{Cu}_4\text{OCl}_6\text{L}_4$  with piperidine or morpholine ligands were synthesized by allowing alkyl tri- or dichloroacetates and water to act on complexes of copper(I) chloride with the corresponding amine in acetonitrile solution according to the reaction



where L is piperidine or morpholine, X is Cl or H, and Y is Cl. The identity of the compounds prepared was confirmed by elemental analysis and by comparison of their melting temperatures and electronic and infrared spectra with published data<sup>4</sup>. The dichloroacetates or monochloroacetates forming during the reaction were identified by gas chromatography.

It was found that reaction (A) is not specific to polychloroacetates only; other polyhalo compounds such as tetrahalomethanes can be employed for the synthesis as well, the yields, however, are then considerably lower (Table I) and moreover, the product obtained with tetrachloromethane contains another, unidentified component.

The coordination of some types of amine ligands to copper(I) chloride or bromide allows in this case for a rapid oxidation of copper(I) by organic compounds from which their halogen is easily eliminated, similarly as coordination of ligands facilitates the oxidation of copper(I) by oxygen<sup>2</sup>. It is interesting that in this reaction, water acts, on the one hand, as an oxygen donor for the formation of the  $\text{Cu}_4\text{OHal}_6$  skeleton, as observed recently for the formation of complexes from copper(II) halides<sup>3,7,9</sup>, and on the other hand, provides hydrogen for the selective reduction of the polyhalo compound.

The route described can be occasionally convenient for obtaining  $\text{Cu}_4\text{OHal}_6\text{L}_4$  complexes. It should be, however, stressed that the reaction might also find application in the selective hydrogenolysis of some polyhalo compounds that otherwise is accomplished under much severer reaction conditions (145–150°C, 3–5 h) using 2-propanol in the presence of iron pentacarbonyl<sup>13</sup> or dichlorotris(triphenylphosphine)ruthenium(II) (ref.<sup>14</sup>).

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TABLE I

Conditions of preparation and band positions in the electronic and infrared spectra of  $\text{Cu}_4\text{OHal}_6\text{L}_4$  complexes with piperidine (Pip) or morpholine (Morph) ligands

Complex	Oxidant	Reaction time min	Yield %	Electronic spectrum nm	Infrared spectrum $\text{cm}^{-1}$
$\text{Cu}_4\text{OCl}_6(\text{Pip})_4$	$\text{CCl}_3\text{COOCH}_3$	30	83	280, 435 <sup>a</sup> , 741	575, 3 195
	$\text{CHCl}_2\text{COOCH}_3$	60	65	—	—
	$\text{CCl}_4$	30	15	—	—
$\text{Cu}_4\text{OBr}_6(\text{Pip})_4$	$\text{CB}_4$	30	25	328, 397 <sup>a</sup> , 750	530, 3 200 <sup>a</sup>
$\text{Cu}_4\text{OCl}_6(\text{Morph})_4 \cdot 2 \text{CH}_3\text{CN}$	$\text{CCl}_3\text{COOCH}_3$	15	88	272, 435 <sup>a</sup> , 741	580, 3 198

<sup>a</sup> Low intensity.

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