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The Preparation and Characterisation of Some Solid Copper Dioxygen Complexes

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There are many reports dealing with the addition of molecular oxygen to cuprous salts [1]. However, there has not been very much information on the structure of the entity or entities formed [2–12]. It appears that three complexes have been isolated [5, 7, 8]. Two structures were established by X-ray crystallography (tetranuclear-hexa-μ-chloro, μ^4-oxo with N-pyrrolidone [7] and binuclear-di-μ-hydroxo with tetramethylethylenediamine as ligand [8]. A dimeric oxo bridged cupric complex with dimethylsulfoxide as ligand was also isolated [5]). Complexes with di-μ-oxo structure have been also suggested [4, 9].

We have found that the CuClL complexes (*1a–d*) suspended in ether take up dioxygen at 25 °C in an irreversible reaction to yield brownish powders of the complexes (*2a–c*) and a green substance of (*2d*) in nearly 100% yield[‡]. However, complexes with

$$\underset{(1)}{4\ \mathrm{CuClL}} + \mathrm{O_2} \xrightarrow{\text{ether}} \underset{(2)}{\mathrm{Cu_4Cl_4L_3O_2}} + \mathrm{L}$$

L = a) pyridine
  b) 4-picoline
  c) 2,4-lutidine
  d) 2,2′-dipyridyl

o-phenanthroline, 4-cyanopyridine, and 4-benzoylpyridine were not oxidized in several days. They are only stable in the solid state and are very sensitive toward moisture. The spectral and magnetic data of (*2a–d*) are given in Table I. In the solid state they are paramagnetic: in dichloromethane (*2a*) shows enhanced paramagnetism of μ_{eff} 3.32 B.M./4Cu indicating some decomposition. The compounds are E.S.R. inactive (even at low temperature) in the solid form, showing weak signals of mononuclear Cu(II) impurities in less than 0.1% by (*2a–c*) and below 1% by (*2d*). The reflectance spectra of (*2a–d*) have ligand–metal charge transfer bands and a band due to d–d* transition at 725–769 nm. In the IR spectra the ν_{Cu-O} absorptions were assigned using (*2a–d*) prepared with $^{18}O_2$. All attempts to find the ν_{O_2} band in the IR and laser Raman spectra failed, due to decomposition in the laser beam. By controlled thermolysis of (*2a–d*), molecular oxygen was set free (at temperatures shown in Table I) which was preceeded or followed by the ligands (*2a–c*), resulting in residues of CuCl and CuCl(dipy) of (*2d*) respectively. No oxidation of the ligands was observed. The presence of a peroxo group was indicated by chemical evidence (positive test for H_2O_2 on acidification).

Attempts to crystallize (*2a–d*) and measure their molecular weights have been unsuccessful due to decomposition according to eqn. (2) with the formation of (*3*) [3] and (*4*) in 76 and 98% yield.

$$2\ \mathrm{Cu_4Cl_4py_3O_2} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{N_2}} \underset{(3)}{\mathrm{Cu_4Cl_6Opy_4}} + \underset{(4)}{\mathrm{Cu_4Cl_2py_2O_3}} \qquad (2)$$

Adding *o*-phenylenediamine to a pyridine solution of (*2a*) (2.1), *cis,cis*-mucon準onitrile and CuClpy$_3$ were obtained. The oxygenolysis of 9,10-phenanthrenequinimine (9,10-PhQ) by (*2a*) and (*2d*) resulted in well-defined diphenato copper(II) complexes (*5a*, *5b*) and CuClL, also according to eqn. (3).

$$\mathrm{Cu_4Cl_4L_3O_2} + 9{,}10\text{-PhQ} \xrightarrow[\mathrm{py}]{\mathrm{N_2}} \underset{(5)}{\mathrm{Cu_2Cl_2(diphenate)L_n}} + 2\ \mathrm{CuClL} \qquad (3)$$

a) L = py; n = 4 b) L = dipy; n = 2

TABLE I. The Properties of $Cu_4Cl_4L_3O_2$ Complexes.

	M.p./°C[a]	t/h[b]	μ_{eff}/B.M.[c]	ν_{CuO}/cm^{-1} [d]	Reflectance spectra/nm			
2a	268	5	2.76	572(545)	313	270	435	725
2b	255	11	2.63	572(545)	313	328	370	769
2c	173	19	2.12	562(535)	313	351	377	735
2d	236	17	2.69	558(530)	317	357		735

[a] Temperature of O_2-loss. [b] Reaction time. [c] μ_{eff} per 4Cu atom. [d] The $\nu_{Cu}{}^{18}O$ values in brackets.

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[‡] Satisfactory elemental analyses were obtained.

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From the results we assume that (*2a–d*) are at least tetranuclear species having two Cu(I) and two Cu(II) atoms, which are bridged by a peroxide ligand. Since paramagnetism of (*2*) does not arise from unpaired electrons on the oxygen but from the Cu(II) entities with apparent ESR inactivity, they show typical Type 3 copper(II) behaviour. The thermolysis data suggest that in (*2*) the oxygen–oxygen bond remains uncleaved and the O_2-uptake is under certain conditions reversible. The oxygenolysis of 9,10-phenanthrenequinone by (*2a*) and (*2d*) may proceed through a nucleophilic attack of the peroxide ligand of (*2*) on the quinone, as found recently in a similar reaction of 3,5-di-*t*-butyl-*o*-benzoquinone with H_2O_2 [13].

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