

The Preparation and Characterisation of Some Solid Copper Dioxygen Complexes

GÁBOR SPEIER*, ZOLTÁN TYEKLÁR

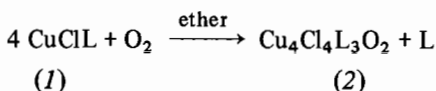
Department of Organic Chemistry of the Veszprém University of Chemical Engineering, 8201 Veszprém, Hungary and ANTAL ROCKENBAUER

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, 1525 Budapest, P.O. Box 17, Hungary

Received January 25, 1982

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



- 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

*Author to whom all correspondence should be addressed
[†]Satisfactory elemental analyses were obtained.

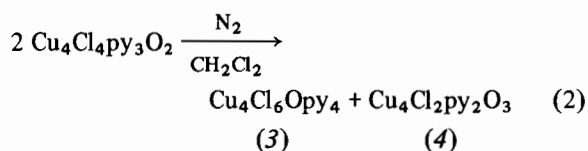
TABLE I. The Properties of $\text{Cu}_4\text{Cl}_4\text{L}_3\text{O}_2$ Complexes.

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

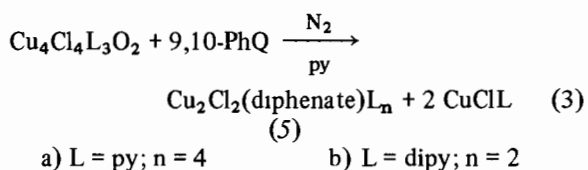
^aTemperature of O₂-loss. ^bReaction time. ^c μ_{eff} per 4Cu atom. ^dThe ν_{Cu} ¹⁸O values in brackets.

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 $\nu_{\text{Cu–O}}$ absorptions were assigned using (2a–d) prepared with ¹⁸O₂. 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 preceded 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 H₂O₂ 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.



Adding *o*-phenylenediamine to a pyridine solution of (2a) (2.1), *cis,cis*-mucononitrile and CuClpy₃ were obtained. The oxygenolysis of 9,10-phenanthrenequinone (9,10-PhQ) by (2a) and (2d) resulted in well-defined diphenato copper(II) complexes (5a, 5b) and CuClL, also according to eqn. (3).



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 O₂-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 H₂O₂ [13].

Acknowledgement

We thank Professor L. Markó for helpful discussion.

References

- 1 A. D. Zuberbuhler in 'Metal Ions in Biological Systems', ed. H. Sigel, Marcel Dekker, New York, 1976, p 325.
- 2 H. Praliaud, Y. Kodratoff and M. W. Mathieu, *Spectrochim. Acta*, **30A**, 1389 (1974); G. Goudurier, H. Praliaud and M. V. Mathieu, *Spectrochim. Acta*, **30A**, 1399 (1974).
- 3 A. S. Hay, H. S. Blanchard, G. F. Endres and J. W. Eustance, *J. Am. Chem. Soc.*, **81**, 6336 (1966); H. Finkbeiner, A. S. Hay, H. S. Blanchard and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).
- 4 S. Arcus, J. L. Wilkinson, C. Mealli, T. S. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 7564 (1974).
- 5 H. Gampp and A. D. Zuberbuhler, *Chimia*, **32**, 54 (1978).
- 6 C. E. Kramer, G. Davies, R. B. Davis and R. W. Slaven, *J. Chem. Soc., Chem. Commun.* 606 (1975); I. Bodek and G. Dabies, *Inorg. Chim. Acta*, **27**, 213 (1978); *Inorg. Chem.*, **17**, 1814 (1978).
- 7 G. Davies, M. F. El-Shazly, M. W. Rupich, M. R. Churchill and F. J. Rotella, *J. Chem. Soc., Chem. Commun.*, 1045 (1978).
- 8 H. C. Meinders, F. Van Bolhuis and G. Challa, *J. Mol. Catal.*, **5**, 225 (1979).
- 9 M. G. Simmons and L. J. Wilson, *J. Chem. Soc., Chem. Commun.*, 634 (1978).
- 10 M. M. Rogic and T. R. Demmin, *J. Am. Chem. Soc.*, **100**, 5472 (1978).
- 11 C. Jallabert, C. Lapinte and H. Riviere, *J. Mol. Catal.*, **7**, 127 (1980).
- 12 G. Speier and Z. Tyeklár, *React. Kinet. Catal. Lett.*, **15**, 91 (1980).
- 13 G. Speier and Z. Tyeklár, *J. Chem. Soc., Perkin Transactions*, **2**, 1176 (1981).