*Inorganica Chimica Acta*, *145* (1988) 167–169

# The Synthesis of Copper(II) Complexes of 2-[(2-Mercaptophenyl)iminomethyl]phenols by the Electrochemical Cleavage of a Disulphide Bond

R. BASTIDA, M. R. BERMEJO, M. S. LOURO,
J. ROMERO, A. SOUSA*

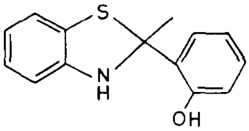
*Departamento de Quimica Inorganica, Universidad de Santiago, Santiago de Compostela, Spain*

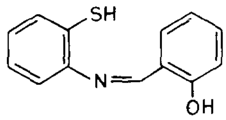
and D. E. FENTON*

*Department of Chemistry, The University, Sheffield S3 7HF, U.K.*

(Received December, 4, 1987)

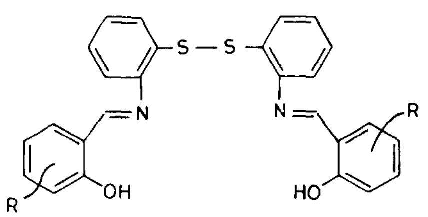
The presence of an anionic suphur atom, from cysteine, in the low symmetry type I copper sites of copper-bearing metalloproteins such as plastocyanin and azurin [1] has stimulated interest in the synthesis of copper complexes derived from ligands bearing such a sulphur atom [2]. The direct synthesis of Schiff bases, which might act as potential model systems for type I sites can be problematic due to the formation of benzothiazolines; for example the reaction of 2-aminothiophenol and salicylaldehyde has been reported to yield 2-(2-hydroxyphenyl)benzothiazoline (I) [3] as well as the terdentate Schiff base 2-[(2-mercaptophenyl)iminomethyl]phenol (II; $H_2$mim) [4]. Such syntheses may be directed towards the Schiff base by the presence of metal template ions [5] but often in the presence of copper(II) the thiol can be oxidised to the corresponding disulphide with accompanying reduction of the copper(II) [6].


I


II

In order to overcome these difficulties we have utilised an electrochemical reductive cleavage of the disulphide bond present in preformed Schiff bases such as **III**. These compounds are readily prepared by the reaction of the required salicylaldehyde and 2,2′-dithiobenzenamine in ethanol.

In a typical experiment a solution of **III** in acetonitrile together with a few mg of $[Me_4N][ClO_4]$, added as a supporting electrolyte, was placed into a cell containing a platinum wire cathode and an anode derived from copper foil suspended from a platinum wire [7]. Nitrogen was bubbled through the cell to maintain an inert atmosphere and also to act as an agitator during the electrolysis. A precipitate of the complex, e.g. Cu(mim), appeared within one hour and at the completion of the reaction the complex was collected, washed with acetonitrile and ether and dried *in vacuo*. The experimental conditions are given in Table I. Analytical data for the complexes are given in Table II. The electrochemical efficiency, defined as the amount of metal dissolved per Faraday of charge, was found to be 1.0 ± 0.1 mol $F^{-1}$. It can be reasonably postulated that the formation of Cu(I) at the anode is followed by oxidation to Cu(II) in the solution.


R = H, 3-$OC_2H_5$, 5-$OCH_3$, 4,6-$(OCH_3)_2$

$(L_2H_2)$

III

The green complexes were characterised by elemental analysis, IR and visible spectroscopy. The absence of bands in the IR attributable to $\nu_{OH}$ and $\nu_{SH}$ indicate full deprotonation of the ligand on complexation. The complex derived from salicylaldehyde was shown to be identical with that prepared by the conventional routes used by Muto [4] and by Ison and Kokot [8], for which spectral parameters were reported by Addison *et al.* [9] and by Fee *et al.* [10]. Magnetic studies suggest that the complex is at least dimeric and possibly polymeric in the solid state [8, 10]; this is a consequence of the copper atoms in the monomer unit being coordinatively unsaturated in the tricoordinate environment made available by the terdentate ligand.

The introduction of nitrogenous Lewis bases [L = pyridine(pyr), 2,2′-bipyridine(bipy) and 1,10-phenanthroline(phen)] into the electrochemical cell led to the isolation of the corresponding adducts Cu(mim)·L. The monohydrate Cu(min)·$H_2O$ has previously been reported and is proposed as being a square-planar complex from visible spectroscopic studies [11]; an impure pyridinate was found en route to the isolation of a dimethylsulphoxide adduct Cu(mim)·dmso [8]. Cu(mim) has also been shown to be monomeric in dimethylformamide solution [9]. It is not unreasonable to propose from the visible spectrum that the monoligated pyridine complexes

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*Authors to whom correspondence should be addressed.

0020-1693/88/$3.50

TABLE I. Experimental Conditions for the Synthesis of CuL and CuLL′

| R | L′ | $L_2H_2$ (g)[a] | L′ | Initial voltage (V)[b] | Time of reaction (h) | Metal dissolved (mg) | $E_f$ | Yield (%)[c] |
|---|---|---|---|---|---|---|---|---|
| H | | 0.30 | | 10 | 1 | 26 | 1.1 | 72 |
| H | pyr | 0.20 | 3 ml | 10 | 1 | 25 | 1.0 | 70 |
| H | bipy | 0.15 | 0.1 g | 15 | 1 | 26 | 1.1 | 80 |
| H | phen | 0.15 | 0.15 g | 10 | 1 | 28 | 1.1 | 85 |
| 3-$OC_2H_5$ | | 0.25 | | 15 | 1.5 | 36 | 1.0 | 75 |
| 3-$OC_2H_5$ | phen | 0.25 | 0.35 g | 10 | 2 | 48 | 1.0 | 78 |
| 5-$OCH_3$ | | 0.20 | | 8 | 2 | 45 | 0.95 | 82 |
| 5-$OCH_3$ | bipy | 0.20 | 0.15 g | 10 | 2 | 47 | 1.0 | 79 |
| 5-$OCH_3$ | phen | 0.20 | 0.15 g | 6 | 1.5 | 34 | 0.97 | 76 |
| 4,6-$(OCH_3)_2$ | pyr | 0.20 | 2 ml | 6 | 2 | 46 | 0.97 | 43 |
| 4,6-$(OCH_3)_2$ | phen | 0.20 | 0.15 g | 9 | 2 | 48 | 1.0 | 72 |

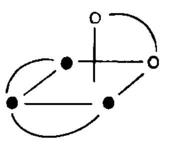
[a] In 50 ml of $CH_3CN$. [b] Voltage to produce a current of 10 ma. [c] Based on the amount of metal dissolved.

TABLE II. Analytical Data for the Complexes CuL and CuLL′

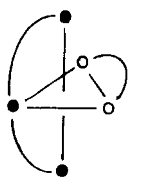
| R | L′ | Compound | Melting point (°C) | Analysis: found (calc.) (%) | | |
|---|---|---|---|---|---|---|
| | | | | C | N | H |
| H | | $CuC_{13}H_9NOS$ | 320 | 52.9(53.0) | 5.1(4.8) | 3.1(3.1) |
| H | pyr | $CuC_{18}H_{14}N_2OS$ | 315 | 58.7(58.5) | 7.4(7.6) | 3.8(3.8) |
| H | bipy | $CuC_{23}H_{17}N_3OS$ | | 59.8(61.8) | 8.9(9.4) | 3.6(3.8) |
| H | phen | $CuC_{25}H_{17}N_3OS$ | 266 | 63.5(63.7) | 8.8(9.2) | 3.5(3.6) |
| 3-$OC_2H_5$ | | $CuC_{15}H_{13}NO_2S$ | 252 | 53.3(53.9) | 4.3(4.2) | 3.8(3.8) |
| 3-$OC_2H_5$ | pyr | $CuC_{20}H_{18}N_2O_2S$ | | 58.6(58.1) | 6.3(6.8) | 4.1(4.8) |
| 3-$OC_2H_5$ | phen | $CuC_{27}H_{21}N_3O_2S$ | 229 | 62.9(62.9) | 8.0(8.1) | 4.4(4.1) |
| 5-$OCH_3$ | | $CuC_{14}H_{11}NO_2S$ | 265 | 51.9(52.4) | 4.5(4.4) | 3.6(3.5) |
| 5-$OCH_3$ | bipy | $CuC_{24}H_{19}N_3O_2S$ | 215 | 59.0(59.1) | 8.5(8.8) | 4.0(4.4) |
| 5-$OCH_3$ | phen | $CuC_{26}H_{19}N_3O_2S$ | 253 | 59.6(60.3) | 8.0(8.4) | 3.6(3.8) |
| 4,6-$(OCH_3)_2$ | pyr | $CuC_{20}H_{12}N_2O_3S$ | 295 | 50.4(50.8) | 6.0(6.5) | 3.8(4.2) |
| 4,6-$(OCH_3)_2$ | phen | $CuC_{27}H_{15}N_3O_3S$ | 264 | 60.1(61.1) | 8.1(7.9) | 4.0(4.0) |

are square coplanar in nature (e.g. the diffuse reflectance spectrum of CuL·pyr (R = H) has bands at 620 and 530 nm). Solution studies concerning the stability of ternary mixed ligand complexes derived from Cu(mim) in the presence of bipy and phen indicated the availability of 1:1:1 complexes [12]; this was corroborated by the isolation of Cu(mim)·bipy·1.5$H_2O$ by conventional synthetic procedures [9].

Steric constraints imposed by the relatively rigid tridentate ligand restrict the number of likely coordination environments to two (**IV** and **V**). The meridional positions will be occupied by the terdentate ligand in the square pyramid and the equatorial positions will be occupied by the bidentate ligand in the trigonal bipyramid. EPR studies indicate that the bipy adduct has an essentially square pyramidal geometry with an axial bipy [9]. The visible spectra support such a proposal for the complexes of the same type isolated herein, for example CuL·bipy (R = 5-$OCH_3$) has bands at 615 and 500 nm and CuL·phen (R = 3-$OC_2H_5$) has bands at 600 and 515 nm in the diffuse reflectance spectra).



**IV**



**V**

It is noted that the successful employment of the electrochemical cleavage of the disulphide bond leading to the preparation of copper(II) complexes of terdentate ligands such as **IV** offers a facile general entry into the synthesis of thiol-derived complexes. Further work is in progress to establish this generality.

## Acknowledgements

We thank the British Council and the Xunta de Galicia for support of our collaboration.

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