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Reactions of Copper Chelates Derived from 2-Aminobenzenethiol

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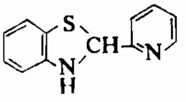
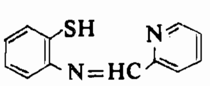
The reactions of copper(II) chloride with some ligands derived from 2-aminobenzenethiol have been investigated. 2,2'-Pyridylmethylthioaniline (N–S–N) and N-*2-methylthiophenyl-2'-pyridylmethyleneimine (N–N–SMe) yield the complexes $CuCl_2$(N–S–N) and $CuCl_2$(N–N–SMe), respectively, which probably contain five-coordinate copper. The complex $CuCl_2$(N–N–SMe) can also be prepared by the reaction of: (i) 2-methylthioaniline (N–SMe) with copper(II) chloride and pyridine-2-aldehyde; (ii) pyridine-2-aldehyde with $CuCl_2$(N–SMe). 2-(2-Pyridyl)benzothiazoline rearranges in the presence of copper chloride to yield the copper complex, CuCl(N–N–S), of the tautomeric Schiff base,* N-*2-mercaptophenyl-2'-pyridylmethyleneimine (N–N–SH).*

Introduction

We have previously reported some reactions of metal chelates of sulphur ligands. These reactions include: (i) *S*-dealkylation of coordinated thioethers,[1-5] (ii) the metal-ion induced rearrangement of 2-(2-pyridyl)benzothiazoline (I) to yield metal complexes of the tautomeric Schiff base *N*-2-mercaptophenyl-2'-pyridylmethyleneimine (II; N–N–SH),[6] and (iii) reactions of nickel chelates of 2-aminobenzenethiol (III) and its derivatives.[7] We now report some reactions of copper chelates derived from (III).


(I)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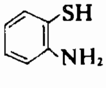
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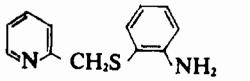
Results and Discussion

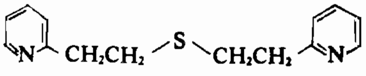
Copper(II) chloride reacts with 2(2'-pyridylmethylthio)aniline (IV; N—S—N) in alcohol to yield the complex $CuCl_2$(N–S–N), which is virtually a non-electrolyte in nitrobenzene (Λ_{2000}, 1.1 ohm^{-1}cm^{2}mole^{-1} at 25°). This compound has a normal magnetic moment (Table I). Its infrared spectrum displays strong bands at 3080 cm^{-1} ($_{\nu}$N—H) and 1560 cm^{-1} ($_{\delta}$N—H); these bands are characteristic of a coordinated amine. The related ligand, 2,2'-bis(2-pyridyl)-diethyl sulphide (V; pds) also forms a similar complex $CuCl_2$(pds).[8] It is most likely that both ligands (IV) and (V) behave as tridentates in these complexes.

Table I. Magnetic Data for Copper(II) Complees

Compound	Colour	M.p.	χ'_M [a]	μ B.M.	T(°K)
$CuCl_2$(N—SMe) [5]	green	112°	1380	1.81	295
$CuCl_2$(N—S—N)	dark green	130	1430	1.85	298
$CuCl_2$(N—N—SMe)	green	188	1460	1.85	293
CuCl(N—N—S)	dark grey	174	1440	1.86	297

[a] Corrected for diamagnetism.


(IV)


(V)

The various possible stereochemical arrangements of tridentate ligands have been discussed.[9] It is sufficient to note here that the ligand (IV; N—S—N) will be bent at the sulphur donor atom and thus cannot occupy three coordination positions in the one plane. In contrast, the Schiff base (II) and its *S*-methylated derivative, *viz.*, *N*-2-methylthiophenyl-2'-pyridylmethyleneimine (VI; N—N—SMe) have the donor atoms in conjugation and thus these ligands are planar. In this respect the ligand (VI) is similar to 2,2',2''-terpyridyl (terpy) which reacts with copper(II) chloride to form the five-coordinate complex $CuCl_2$(terpy).[10] Copper(II) chloride reacts with (VI) to yield green crystals of $CuCl_2$(N—N—SMe), which has a small conductivity in nitromethane (Λ_{1000} = 4.4 ohm^{-1}cm^{2}mole^{-1} at 25°). Although this compound and the copper complex of (IV) are formally

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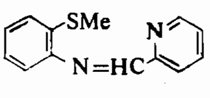
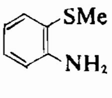
[1] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, *19*, 1391 (1966).
[2] L. F. Lindoy, S .E. Livingstone, and T. N. Lockyer, *Nature*, *211*, 519 (1966).
[3] S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Letters*, *3*, 35 (1967).
[4] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, *6*, 652 (1967).
[5] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, *20*, 471 (1967).
[6] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, *1*, 365 (1967).
[7] L. F. Lindoy and S. E. Livingstone, *Inorg. Chem.*, *7*, ... (1968) (in the press).
[8] E. Uhlig, B. Borek, and H. Glänzer, *Z. anorg. Chem.*, *348*, 189 (1966); E. Uhlig and G. Heinrich, *Z. anorg. Chem.*, *328*, 127 (1964).
[9] H. A. Goodwin, "Design and Stereochemistry of Multidentate Chelating Agents", ch. 4 in "Chelating Agents and Metal Chelates" (Eds. F.P. Dwyer and D. P. Mellor), Academic Press, New York, p. 143 (1964).
[10] C. M. Harris, T. N. Lockyer, and N. C. Stephenson, *Austral. J. Chem.*, *19*, 1741 (1966).

five-coordinate, they may be chloro-bridged and six-coordinate. However, these complexes are not sufficiently soluble for a molecular weight determination. Their diffuse reflectance spectra display a maximum at 13,300 cm^{-1} (750 mμ) and resemble the spectra of the five-coordinate complexes discussed by Sacconi and Bertini.[11] Consequently these complexes probably are five-coordinate, since copper form five-coordinate complexes with a variety of tridentate ligands.[12,13]



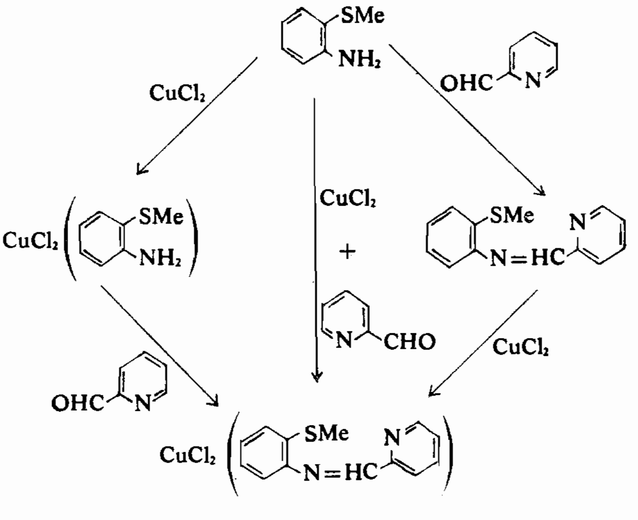
(VI)



(VII)

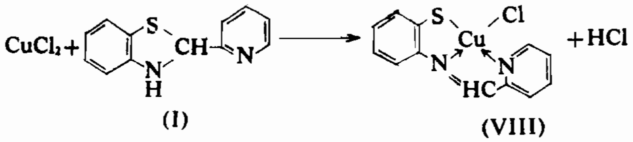
Copper(II) chloride reacts with 2-methylthioaniline (VII; N–SMe) and pyridine-2-aldehyde to yield the Schiff base complex, CuCl$_2$(N–N–SMe). This complex can also be obtained from the reaction of a solution of dichloro-2-methylthioaniline-copper(II), CuCl$_2$(N–SMe), with pyridine-2-aldehyde. The various methods of preparation of CuCl$_2$(N–N–SMe) are illustrated in Scheme I.

The infrared spectrum of CuCl$_2$(N–SMe) shows a strong broad envelope of bands centred at 3140 cm^{-1}; these bands are due to the stretching modes of the coordinated amine. The deformation modes appear as a medium to strong band at 1545 cm^{-1}. The products from the various preparations of CuCl$_2$(N–N–SMe) have identical infrared spectra and the absence of the amine bands found in CuCl$_2$(N–SMe) confirms that the Schiff base condensation has occurred.



Scheme I.

A solution of 2-(2-pyridyl)benzothiazoline (I) reacts with copper(II) chloride under nitrogen to give dark grey crystals of CuCl(N–N–S). The dark colour of this compound suggests that the metal-ion induced rearrangement shown in Scheme II has occurred. The infrared spectrum is quite similar to that of the analogous nickel complex[7] and contains no bands in the N–H stretching region.



Scheme II.

The copper complex (VIII) dissolves in nitromethane to yield a purple solution. Its conductivity (Λ_{1500}, 17 ohm^{-1}cm^{2}mole^{-1} at 25°) indicates a slight dissociation in this solvent and its magnetic moment is normal for copper(II).

The metal-ion induced rearrangement of 2-(2-pyridyl)benzothiazoline (I) has been observed to occur in the presence of zinc(II),[6] cadmium(II),[6] nickel(II),[7] molybdenum(III),[14] and copper(II) (this paper). It is very likely that this rearrangement proceeds via the cleavage of the –S–CH$<$ bond of the benzothiazoline ring. *S*-Dealkylation reactions of a number of metal chelates of aryl-alkyl thioethers have been reported an discussed.[1-5,15] It is possible that both these types of reaction are related, since each involves the cleavage of a carbon-sulphur bond in the presence of a metal ion and in each the final product is a metal chelate of a thiol ligand.

Experimental Section

Analyses. All complexes were dried *in vacuo* over phosphorus pentoxide before analysis. Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales. Sulphur was determined by the Australian Microanalytical Service, Melbourne.

Dichloro-2-(2-pyridyl)methylthioanalinecopper(II). The addition of a solution of 2-(2-pyridyl)methylthioaniline[7] (0.6 g) in alcohol (10 ml) to copper chloride (0.5 g) in alcohol (25 ml) yielded fine mid-green crystals of the *complex*; yield 0.6 g (Found: C, 40.6; H, 3.5; Cu, 18.0; N, 7.6; S, 9.0. $C_{12}H_{12}Cl_2CuN_2S$ requires C, 41.1; H, 3.45; Cu, 18.1; N, 8.0; S, 9.1%).

*Dichloro-*N*-2-methylthiophenyl-2′-pyridylmethylene-iminecopper(II).* *Preparation 1.* *N*-2-Methylthio phenyl-2′-pyridylmethyleneimine[7] (1 g) in alcohol (50 ml) was slowly added to copper chloride dihydrate (1.4 g) in alcohol (50 ml). The solution was stirred at room temperature for 15 min; green crystals of the *complex* deposited; yield 1.2 g (Found: C, 43.0; H, 3.3; Cl, 20.0; Cu, 17.8; N, 7.8; S, 8.7. $C_{13}H_{12}Cl_2CuN_2S$ requires C, 43.0; H, 3.3; Cl, 19.55; Cu, 17.5; N, 7.7; S, 8.8%).

Preparation 2. Preparation 1 was repeated except that formation of the ligand (1 g) was allowed to

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(11) L. Sacconi and I. Bertini, *Inorg. Chem.*, *5*, 1520 (1966).

(12) E. L. Muetterties and R. A. Schunn, *Quart. Revs.*, *20*, 245 (1966).

(13) D. St. C. Black, *Austral. J. Chem.*, *21*, 803 (1963).

(14) L. F. Lindoy, S. E. Livingstone, and T. N. Locker, *Austral. J. Chem.*, *18*, 1549 (1965).

(15) L. Sacconi and G. P. Speroni, *Inorg. Chem.*, *7*, 295 (1968).

occur in the presence of the copper chloride solution (*i.e.* alcohol solutions of pyridine-2-aldehyde and 2-methylthioaniline were mixed in the correct proportion and the resulting solution was immediately added to the copper chloride solution); yield 1.2 g (Found: C, 42.7; H, 3.3; N, 7.4).

Preparation 3. Dichloro-2-methylthioanilinecopper-(II) (0.6 g) was finely ground and added to methanol (200 ml) containing pyridine-2-aldehyde (0.3 g). This suspension was shaken at room temperature for 3 hr, treated with charcoal, and then filtered. The green filtrate was concentrated under reduced pressure to a small volume, whereupon the compound deposited as green crystals; yield 0.4 g (Found: C, 42.8; H, 3.5; N, 7.3).

Chloro(N-*2-thiophenyl-2′-pyridylmethyleneimine*)-*copper(II)*. 2-(2-Pyridyl)benzothiazoline[6] (0.43 g) in alcohol (100 ml) was heated at the reflux under nitrogen. To this refluxing solution copper chloride dihydrate (0.48 g) in alcohol (100 ml) was added during 30 min to give a purple solution from which dark grey crystals of the *complex* deposited; yield 0.5 g (Found: C, 45.7; H, 3.05; N, 8.5. $C_{12}H_9Cl$-CuN_2S requires C, 46.15; H, 2.9; N, 9.0%).