A General Route to Thiolato Ligands via t-Butyl Sulphides

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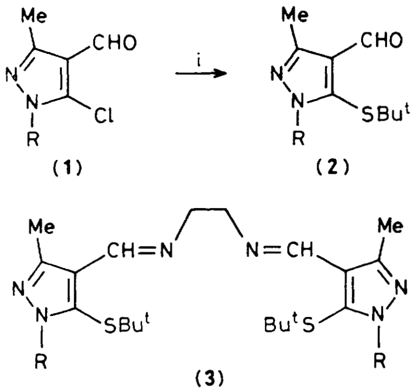
It is demonstrated that t-butyl sulphides are versatile intermediates in the preparation of new mono- and binucleating thiolato ligands; the properties of some copper complexes of such ligands are discussed.

The characterization of Cu^{II} sites in metalloenzymes depends to some extent on the preparation and design of Cu^{II} complexes which mimic aspects of the chemical and physical properties of the protein Cu^{II} sites. Therefore it is useful to prepare and characterize monomeric and dimeric copper(II) thiolate systems which are reasonable models of the ligand environment in type I and type III copper proteins,[1] and the 'visible' Cu_A in cytochrome *c* oxidase.[2]

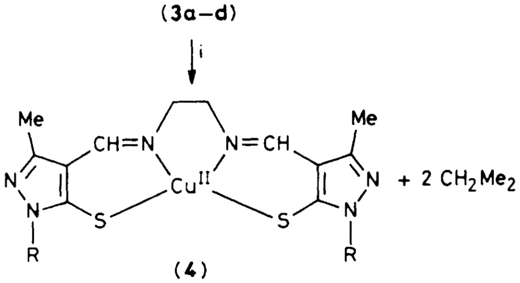
Although metal complexes of mercaptoimines and thioxoimines are known,[3,4] the preparation of such compounds is often impeded by the instability of β-mercaptoaldehydes in general as well as the formation of unwanted condensation and oxidation products.[5,6] We have recently demonstrated[7] that a t-butyl group can be used to protect the thiol group[8] in β-mercaptoaldehydes, and furthermore that t-butyl sulphides are conveniently prepared from the 2-methyl-2-propanethiolato anion and halogen substituted heterocycles.

In the present work we have used the 4-formylpyrazole-5-



a; R = Me
b; R = Ph
c; R = p-$NO_2C_6H_4$
d; R = 2-pyridyl

Scheme 1. i, $NaSCMe_3$.



a; R = Me
b; R = Ph
c; R = p-$NO_2C_6H_4$
d; R = 2-pyridyl-H^+

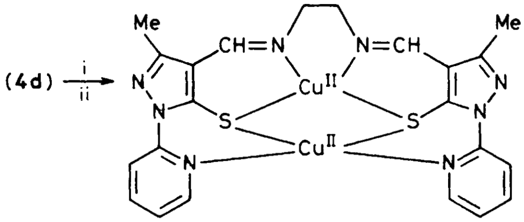
Scheme 2. i, Cu^{2+}.

thione[9] ring as an example and hence the 5-chloro-4-formyl-3-methyl-1-substituted pyrazole (**1**)[10] as the starting material (Scheme 1).† The resulting t-butyl sulphides (**2**) or (**3**) were all stable colourless crystalline compounds† soluble in non-polar solvents. The di-imines (**3**) were prepared in nearly quantitative yields by the reaction of the aldehydes (**2**) with 1,2-diaminoethane in absolute ethanol.

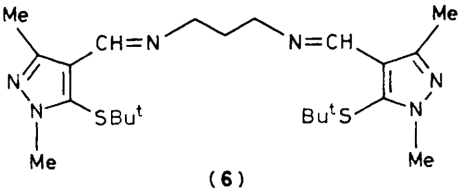
It is known that strong acids as well as Lewis acids will cleave t-butyl sulphides. Metal ions such as copper(II) may also function as Lewis acids; thus when a di-imine such as (**3b**) (1 mmol) was heated (40 °C) with copper(II) acetate (1 mmol) in methanol (50 ml) for 20 min, isobutene was evolved and a maroon red copper(II) complex (**4**) was precipitated[11] in 80% yield, analytically pure after one recrystallization from 2-methoxyethanol (Scheme 2). When the di-imine (**3d**) was treated with copper(II) chloride, isobutene was again evolved and the acid form of the 1 : 1 complex (**4d**) was formed. Treatment of complex (**4d**) with triethylamine and a further equivalent of copper(II) chloride in methoxyethanol resulted in the formation of the binuclear complex (**5**) (Scheme 3).

In order to investigate a copper complex with tetrahedral distortion the complex (**7**) was prepared from compound (**6**).

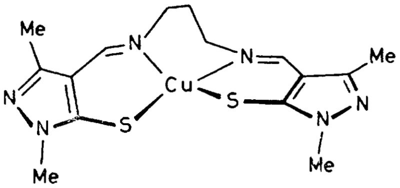
In contrast to the maroon coloured complexes (**4a**—**d**) complex (**7**) was nearly black. The copper(II) complexes (**4a**—



Scheme 3. i, NEt_3; ii, Cu^{2+}.



(**6**)



(**7**)

c) are all very stable compounds; heating at the m.p. did not lead to decomposition. Thus the mass spectra could be carried out at the m.p. of each compound with the molecular ion as the base peak. No low molecular weight fragments were lost from M^+, while other large peaks in the mass spectrum still contained the copper(II) ion.

The co-ordination sphere for complex (**4**) is similar to those of the Schiff base complexes of o-mercaptobenzylideamine and 1-phenyl-3-iminomethylpyridine-2(1H)-thione,[3,12] and the stereochemistry‡ is undoubtedly *cis*-planar as found for the analogous hydroxoimine complexes. It can be seen that all the complexes described here [(**4a**—**d**), (**5**), (**7**)] contain two thiolate[13] groups.

The visible–u.v. spectra of complexes (**4a**—**d**) (in dimethylformamide) show a weak d–d band in the region 800—830 nm (ϵ = 100), the position of which is dependent upon the substituent R. The trend is opposite to that expected from the inductive properties of the substituent R. However this variation fits the expected variation of a $^2A_1 \rightarrow {}^2B_2$ (D_{2d}) transition in a CuL_4 chromophore, distorted more (**4b**) or less (**4a**) from planar geometry. In addition the spectra show bands at 500—520 nm and 430—440 nm of medium intensity (ϵ = 500—2000). These bands are assigned as $Cu^{II} \leftarrow RS$ (σ and π) ligand to metal change transfer (L.M.C.T.) bands.[1]

The spectrum of the binuclear complex (**5**) does not show any strong deviation from this pattern. Preliminary e.s.r. and magnetic susceptibility measurements suggest a weak antiferromagnetic coupling, in contrast to copper type III behaviour.

The visible–u.v. spectrum of complex (**6**) does not show any ligand field bands below 900 nm and is dominated by intense (ϵ = 1200 and 3000) bands at 580 and 487 nm. We assign

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† All new compounds gave satisfactory analytical and spectroscopic data.

‡ In analogy to the 1-phenyl-3-iminomethylpyridine-2(1H)-thione copper(II) complexes (ref. 3).

these bands to the $Cu^{II} \leftarrow RS_{\sigma}$ L.M.C.T. transitions which are strongly red shifted owing to the distortion of the CuS_2N_2 chromophore towards tetrahedral[14] geometry.

Thus, it is suggested that complex (**7**) simulates copper type I behaviour. In a future paper we will describe in detail the e.s.r. and magnetic properties of these and similar complexes.

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