STUDIES ON THE SYNTHESIS AND REACTIVITY OF COPPER THIOLATE AND THIOAMIDE COMPLEXES

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ABSTRACT

In response to a clear need for a more systematic approach to the study of the interaction of copper with ligands containing the sulphhydryl group, or in thioamide tautomeric equilibrium with such, cuprous, cupric and mixed valence complexes of ligands containing a thiolate or thioamide moiety have been synthesised and characterised by spectroscopic, magnetic and crystallographic techniques. In certain cases their reactivity in aliphatic and aromatic nitrogen base solvents and nitromethane have been investigated.

Full names for the ligand abbreviations appear at the end of the abstract and ligand structures may be found in Figures at the beginning of the appropriate chapter.

The visible, esr and resonance Raman spectra of the type I, copper protein, azurin from Alcaligenes denitrificans, have been recorded and compared with other type I proteins. Through comparison with the spectral features of a series of cluster complexes $[Cu^{II}_2Cu^{I}_{10}(mmim)_{12}(Y)_4](X)_2$ (where Y = CH_3CN or H_2O, and X = BPh_4, ClO_4, PF_6, CH_3COO or OH), and $[Cu^{II}_6Cu^{I}_8(mea)_{12}Cl]Cl_5.7H_2O$, the so-called "unusual" spectroscopic features of the type I proteins have been re-interpreted as being normal phenomena of a Cu(II)-thiolate interaction coupled with specific geometrical requirements.

Investigation of the mbtH ligand system has led to the reformulation of a number of incorrectly formulated copper complexes as $[Cu(mbtH)_2Cl]$ or [Cu(mbt)] following successful removal of a disulphide contaminant. In support of such, similar cuprous compounds of general formula

$[Cu(LH)_2X]$ (LH = etmbtH, X = Cl, Br, I; LH = mbtH, X = Br, I; LH = mmimH, X = Cl), $[Cu(LH)X].xH_2O$ (LH = mbimH, mpyH, phmtzH, Ph_2PS_2H, X = Cl, Br; LH = mmimH; X = Br) and [Cu(L)] (L = bimet, dimtdz, dipmim etmbt, mpy, phmtz) have been prepared from similar ligand systems. The interaction of a number of these complexes with pyridine led to oxidation of organo-sulphur to sulphate with the production of $[Cu(py)_4SO_4].2H_2O$. This reaction is postulated to occur via two oxidising species $[Cu(py)_2OH)_2]$ or $[Cu(py)_xO]$ depending on whether halides are present or absent in the reaction solutions. Similar sulphato species are seen when quinoline and 3-ethylpyridine are used as solvents. However, compounds of general formula $[Cu(LH)_2X]$ and [Cu(LH)X] yield the complexes $[Cu(3\text{-}Mepy)_3Cl]$ and $[Cu(4\text{-}Mepy)_4Cl_2].H_2O$, from the solvents 3-methyl-pyridine and 4-methylpyridine respectively, which have been structurally characterised by X-ray crystallography.

The cupric and mixed valence complexes $[Cu(ttzH)_3X_2]$ (X = Cl, Br), $[Cu(ttzH)_2Br_2]$, $[Cu^{II}Cu^{I}{}_3(ttz)_5]$, $[Cu^{II}Cu^{I}(mmim)(mmimH)_2Cl_2]$, $[Cu^{II}Cu^{I}(mmimH)_2Cl_3]$, $[Cu(mbim)_2(H_2O)(NH_3)]$, $[Cu(mbim)_2(H_2O)]$, [Cu(dipmim)Cl] and [Cu(etu)OH] have been prepared and characterised by visible, infrared, and esr spectroscopy.

When $[Cu(ttzH)_3Br_2]$ is refluxed in nitromethane, a new cuprous complex [Cu(tztdz)Br] is produced in which modification of the ttzH ligand to produce the new organic moiety tztdz has occurred, confirmed by X-ray crystallography. Similarly the compounds [Cu(tztdz)Cl], $[Cu(tztdz)Cl_2]$ and $[Cu(mimmimz)Cl_2]$ are postulated from the interaction of $[Cu(ttzH)_3Cl_2]$ and $[Cu^{II}Cu^{I}(mmimH)_2Cl_3]$ with nitromethane.

With reference to well-defined literature examples the technique of

esr spectroscopy is shown to discriminate between equatorial donor atom sets of S_4, S_2O_2, S_2N_2, SO_3 and O_4 on the basis of lineshapes and position of fundamental parameters. The new compounds synthesised: $[Cu^{II}Cu^{I}_2(dimetH_2)(dimetH)_3Cl]$, $[Cu^{II}Cu^{I}_3(dimetH_2)_3(dimetH)(ClO_4)_4]$, $[Cu^{II}Cu^{I}_3(dimtolH)_5]$, $[Cu^{II}Cu^{I}_3(dimprolH)_5]$, $[Cu(mpoH_2)(mpoH)(ClO_4)]$, [Cu(phenylglyoxaldtsc)], [Cu(benzildtsc)] . H_2O and [Cu(3-n-heptoxy-2-oxobutyraldehydedtsc)] have been assigned donor sets on the basis of their respective esr signals. Similarly this has been done for a number of unisolatible species produced <u>in situ</u> from interaction of various cupric salts with a number of sulphhydryl and thioamide containing ligands.

Ligand abbreviations

bimetH	-	2-benzimidazoleethanethiol
dimtdzH	-	2,5-dimercapto-1,3,4-thiadiazole
dipmimH	-	4,5-diphenyl-2-mercaptoimidazole
$dimetH_2$	-	1,2-dimercaptoethane
$dimprolH_2$	-	2,3-dimercaptopropanol
$dimtolH_2$	-	3,4-dimercaptotoluene
dtsc	-	dithiosemicarbazide
etmbtH	-	6-ethoxy-2-mercaptobenzothiazole
etuH	-	2-mercaptothiazoline
mbimH	-	2-mercaptobenzimidazole
mbtH	-	2-mercaptobenzothiazole
meaH	-	cysteamine
mimmimz	-	3-(2,1-methylimidazolyl)-2,1-methylimidazoline thione
mmimH	-	2-mercapto-1-methylimidazole
$mpoH_2$	-	2-mercapto-3-pyridinol
$mpyH^2$	-	2-mercaptopyridine
phmtzH	-	2-mercapto-4-phenylthiazole
Ph_2PS_2H	-	diphenylphosphinodithioic acid
py	-	pyridine
ttzH	-	2-mercaptothiazoline
tztdz	-	3-(4,5-dihydro-2-thiazolyl)-2-thiazolidinethione

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