

Metal Complexes of Sulphur-Nitrogen Chelating Agents: Part XIII†—Synthesis & Characterization of Copper(II) Complexes with Some Monoprotic Tridentate Ligands

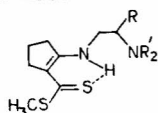
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Copper(II) complexes of the types CuL^{1-3}X ($\text{X} = \text{Cl}, \text{Br}$), $[\text{Cu}_2\text{L}_2^{1-2}](\text{NO}_3)_2$, $\text{Cu}_2\text{L}^{1-3}\text{Cl}_3$ and $[\text{Cu}(\text{HL}^1)(\text{H}_2\text{O})][\text{CuCl}_4]$ have been synthesized from the tridentate ligands methyl 2-amino(β -ethylamino)cyclopent-1-en-dithiocarboxylate (HL^1), methyl 2-amino(β -isopropylamino)cyclopent-1-en-dithiocarboxylate (HL^2) and methyl 2-amino(β -[N,N-diethyl]ethylamino)cyclopent-1-en-dithiocarboxylate (HL^3). All these compounds have been characterized. The compounds $[\text{Cu}_2\text{L}_2](\text{NO}_3)_2$ and Cu_2LCl_3 are strongly antiferromagnetic. In solution both Cu_2LCl_3 and $[\text{Cu}(\text{HL}^1)(\text{H}_2\text{O})][\text{CuCl}_4]$ undergo solvolytic decomposition. The EPR spectra have provided evidence for strong in-plane σ -bonding and out-of-plane π -bonding in the compounds $\text{CuL}^{1-3}\text{Cl}$.

Current interest in the coordination chemistry of sulphur-nitrogen ligands has addressed¹⁻⁴ to the design and synthesis of copper(II) complexes that would mimic the type-1 copper in blue copper proteins. As part of our studies⁵⁻¹² on sulphur-nitrogen bonded metal complexes using 2-aminocyclopent-1-en-dithiocarboxylic acid and its derivatives we have recently introduced the ligands HL^{1-3} and have reported reactivities of their palladium(II) complexes¹³ and thermodynamics of nucleophilic substitution of nickel(II) complexes¹⁴. The present study has been undertaken to explore the chemistry of the copper(II) complexes of HL^{1-3} , especially to see whether stable Cu(II)-SR bond is formed.



$\text{R} = \text{R}' = \text{H}$; HL^1
 $\text{R} = \text{CH}_3$, $\text{R}' = \text{H}$; HL^2
 $\text{R} = \text{H}$, $\text{R}' = \text{C}_2\text{H}_5$; HL^3

Materials and Methods

All the chemicals used were reagent grade. The preparation of the ligands has been described earlier¹³. The equipments used for physical measurements were those reported recently^{15,16}.

Preparation of the metal complexes:

CuLX ($\text{L} = \text{L}^{1-3}$; $\text{X} = \text{Cl}, \text{Br}$)

A solution of the copper(II) halide (4 mmol) in methanol (25 ml) was added dropwise with stirring to a

solution of the ligand (4 mmol) in methanol (60 ml). During addition a bluish-grey compound began to separate. The reaction mixture was stirred for 2 hr, the solid compound filtered off, washed several times with methanol and benzene, and finally dried *in vacuo*. Due to poor solubility the compounds CuL^{1-2}X could not be recrystallized; however, CuL^3X being fairly soluble were recrystallized from chloroform.

$[\text{Cu}_2\text{L}_2](\text{NO}_3)_2$ ($\text{L} = \text{L}^{1-2}$)

These green-coloured compounds were obtained in the same way as described above.

$\text{Cu}_2\text{L}^{1-3}\text{Cl}_3$

To a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) in methanol (10 ml) was added with stirring a solution of the ligand (1 mmol) in methanol (10 ml). During addition a red-coloured compound formed which was filtered immediately after the addition was complete. The compound was washed thoroughly with methanol and benzene, and dried *in vacuo*. Due to solvolytic decomposition the compound could not be recrystallized.

$[\text{Cu}(\text{HL}^1)(\text{H}_2\text{O})][\text{CuCl}_4]$

A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2 mmol) and LiCl (12 mmol) dissolved in methanol (10 ml) was added to a solution of the ligand (1 mmol) in methanol (20 ml). The solution was stirred for 40 hr during which a brown coloured compound deposited slowly. The product was collected by filtration, washed with methanol and dried *in vacuo*.

Results and Discussion

The reaction between stoichiometric amounts of

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Table 1—Analytical, Magnetic and Conductivity Data for the Complexes

Compound	Found (Calc) %				μ_{eff} (B.M.)	Λ_{M} ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
	C	H	N	Cu		
CuL ¹ Cl	34.2(34.4)	4.9(4.8)	9.0 (8.9)	20.1(20.2)	1.98	15
CuL ¹ Br	—	—	7.7 (7.8)	17.6(17.7)	2.12	18
CuL ² Cl	—	—	8.4 (8.5)	19.2(19.4)	1.83	20
CuL ² Br	32.0(32.2)	4.5(4.6)	7.4 (7.5)	16.9(17.1)	1.76	20
CuL ³ Cl	42.4(42.2)	6.1(6.2)	7.5 (7.6)	17.0(17.2)	1.87	18
CuL ³ Br	—	—	6.9 (6.7)	15.2(15.3)	1.83	22
CuL ¹ (NO ₃)	31.5(31.7)	4.3(4.4)	12.4(12.3)	18.5(18.7)	0.98	65
CuL ² (NO ₃)	—	—	11.6(11.9)	18.2(17.9)	1.02	70
Cu ₂ L ¹ Cl ₃	24.4(24.1)	3.6(3.3)	6.1 (6.2)	28.5(28.3)	0.76	—
Cu ₂ L ² Cl ₃	—	—	6.3 (6.0)	27.8(27.5)	0.81	—
Cu ₂ L ³ Cl ₃	—	—	5.4 (5.5)	24.9(25.2)	0.85	—
Cu ₂ (HL ¹)(H ₂ O)Cl ₄	21.8(21.5)	3.8(3.6)	5.8 (5.6)	25.0(25.2)	1.78	—

*At 300 K. ^b In DMF.

copper(II) halides and the ligands results in the formation of the compounds of composition CuLX (Table 1). A similar reaction with copper(II) nitrate yields CuL(NO₃) (L = L¹⁻²), but with HL³ no such compound could be prepared. When the ligand is treated with copper(II) chloride in the molar ratio of 1:2, compounds of composition Cu₂LCl₃ are obtained. These compounds on treatment with excess of ligand transform to the species CuLX. From a slow reaction involving [CuCl₄]²⁻ and HL¹ a compound which analyzed for Cu₂(HL)(H₂O)Cl₄ was obtained.

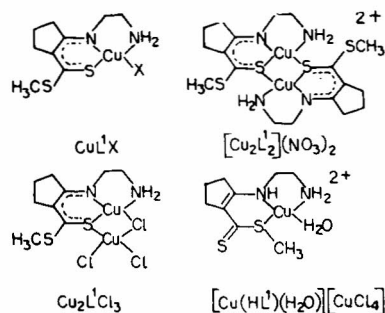
Electrical conductivity measurements (Table 1) show that while CuLX are nonelectrolytes, CuL(NO₃) behave as 1:1 electrolytes. Extensive solvolysis occurs in the case of Cu₂LCl₃ and Cu₂(HL)(H₂O)Cl₄ in N,N-dimethylformamide (DMF) as the conductivity values show strong concentration dependence.

Room temperature magnetic moments (Table 1) for CuLX lie in the normal range (1.8-2.1 B.M.), but subnormal moments (*ca.* 1 B.M.) observed for CuL(NO₃) clearly indicate that they are dimeric compounds. Strong antiferromagnetic interaction exists also between the two copper(II) centers of Cu₂LCl₃. However, the normal moment observed for copper(II) in Cu₂(HL)(H₂O)Cl₄ probably indicates the absence of Cu—Cl—Cu bridge.

Infrared spectral features of the copper(II) complexes are quite similar to those observed for the palladium(II)¹³ and nickel(II)¹⁴ complexes of these ligands. The complexes of HL¹ and HL² exhibit $\nu_{\text{N-H}}$ and $\nu_{\text{as N-H}}$ in the range 3300-3100 cm⁻¹. Considerable delocalization of double bonds in the chelate rings of CuLX, CuL(NO₃) and Cu₂LCl₃ is evident from the appearance of bands due to $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{N}+\text{C}-\text{C})$ around 1570 and 1460 cm⁻¹ respectively. The compound Cu₂(HL¹)(H₂O)Cl₄ exhibits a broad band due to the water molecule at

3600-3400 cm⁻¹, and a strong band due to $\nu(\text{C}=\text{S})$ ¹⁷ at 1130 cm⁻¹ which are absent in other compounds. A comparison of the spectra for CuLX and CuL(NO₃) reveal the presence of a strong band at 1380 cm⁻¹ and a medium one at 830 cm⁻¹ in the latter type of compounds which may be considered as due to ionic nitrate¹⁸. Thus on the basis of conductivity, magnetic and IR data the nitrate bearing compounds should be formulated as [Cu₂L₂](NO₃)₂. In the range 600-300 cm⁻¹ several new bands that are absent in the free ligands have been observed in the complexes. Two vibrations at 550 ± 10 and 500 ± 10 cm⁻¹ appear to be due to $\nu\text{Cu}-\text{N}$ ^{19,20} and another vibration at 380 ± 10 cm⁻¹ seems to be due to $\nu\text{Cu}-\text{S}$ ^{21,22}. Finally the compounds containing chloride ions probably display $\nu\text{Cu}-\text{Cl}$ at 280-330 cm⁻¹.

The difference in structures of CuLX and [Cu₂L₂](NO₃)₂ has been further established from their powder diffraction data. The *d*-spacings of CuL¹Cl and CuL¹Br are quite similar, but are at variance with [Cu₂L₂](NO₃)₂[†]. On the basis of the information available we propose the following structures for the compounds under consideration.



In the case of [Cu(HL¹)(H₂O)][CuCl₄] one may consider the possibility of metal binding through

[†] Powder diffraction data are available on request.

Table 2—EPR and Electronic Spectral Data for the Compounds $\text{CuL}^1\text{--}^3\text{Cl}$

Compound	$g_{\perp}$	$g_{\parallel}$	$E_{d_{x^2-y^2} \rightarrow E_{d_{yz, xz}}}$ (cm^{-1})	$E_{d_{x^2-y^2} \rightarrow E_{d_{xy}}}$ (cm^{-1})	$\alpha^2\beta^2$	$\alpha^2\gamma^2$
CuL^1Cl	2.031	2.128	17,820	23,100	0.34	0.36
CuL^2Cl	2.026	2.123	17,120	22,730	0.32	0.33
CuL^3Cl	2.037	2.148	17,700	21,740	0.40	0.45

thione sulphur. However, consideration of the fact that thioether sulphur acts as a better donor than thione²³ favours the bonding proposed above.

The electronic spectra of the complexes of the type CuLX exhibit two absorption bands around 18,000 and 22,000 cm^{-1} which may be considered as due to $^2\text{B}_{1g} \rightarrow ^2\text{E}_g$ and $^2\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ transitions respectively of D_{4h} symmetry (see EPR spectra). A strong band observed in these compounds in the region 25,000–26,000 cm^{-1} appears to be due to $\sigma(\text{S}) \rightarrow \text{Cu}$ charge transfer transition. Other higher energy bands are due to internal ligand transitions. The complexes $[\text{Cu}_2\text{L}_2](\text{NO}_3)_2$ show a single $d-d$ band at 17,500 cm^{-1} . The spectra of Cu_2LCl_3 and $[\text{Cu}(\text{HL}^1)(\text{H}_2\text{O})][\text{CuCl}_4]$ in their DMF solutions changed with time and therefore were of little value for fuller characterization.

The axial EPR spectra for polycrystalline CuLCl recorded at 77K do not show any hyperfine splitting. The g -values (Table 2) lie in the range expected for tetragonal copper(II) complexes in D_{4h} symmetry with the unpaired electron in $d_{x^2-y^2}$ ground state. In copper(II) complexes of D_{4h} symmetry the g -tensors are approximately related²⁴ as

$$g_{\parallel} = 2.0023 - \frac{8\xi\alpha^2\beta^2}{E_{xy} - E_{x^2-y^2}}$$

$$g_{\perp} = 2.0023 - \frac{2\xi\alpha^2\gamma^2}{E_{yz, zx} - E_{x^2-y^2}}$$

where ξ is the spin-orbit coupling constant for Cu^{2+} ion (-830 cm^{-1}), and α , β , γ are the parameters representing in-plane σ - and π -bonding and out-of-plane π -bonding respectively. A value of $\alpha^2\beta^2 = \alpha^2\gamma^2 = 1$ would indicate complete ionic character, while a value of 0.25 for these parameters would indicate complete covalent bonding. The estimated values of $\alpha^2\beta^2$ and $\alpha^2\gamma^2$ for the complexes (Table 2) indicate strong in-plane σ - and π -bonding, as well as strong out-of-plane π -bonding. It may be noted that the values for CuL^3Cl are greater than those for CuL^1Cl and CuL^2Cl . This would mean relatively weaker σ -bonding and stronger π -bonding in CuL^1Cl or CuL^2Cl . This is rather expected because the Et_2N moiety of HL^3 serves as a stronger σ -donor than the NH_2 group in HL^1 and HL^2 . Similar observation concerning π -delocalization effect has been made with

the complexes PdLX and NiLX from their ^1H NMR spectra^{13,14}.

The compounds CuLX are of particular interest to us with regard to the generation of CuN_2S_2 core of blue copper proteins. Preliminary studies have shown that the halide ion can be substituted by a thioether ligand by carrying out the reaction in the presence of stoichiometric amount of silver perchlorate. The lack of formation of $[\text{Cu}_2\text{L}_2](\text{NO}_3)_2$ shows that the diethylamino group can exert considerable steric influence, a feature that can be exploited in combination with a sterically crowded thioether to form tetrahedral species. Detailed studies are underway and will be reported later.

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