

Complexes of copper(II) with some new thiocarbamide derivatives

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Summary

A new series of thiocarbamides was prepared by the reaction of benzoilthiocyanate with various amines namely 2-aminopyridine (H_2L_I), 3-aminopyridine (H_2L_{II}), 2,3-diaminopyridine (H_2L_{III}), 2,6-diaminopyridine (H_2L_{IV}), *o*-phenylene diamine (H_2L_V), *p*-phenylenediamine (H_2L_{VI}) and ethylene diamine (H_2L_{VII}). The copper(II) complexes of these ligands were isolated and have been characterized by elemental analyses, molar conductivities, magnetic moments and spectral (visible, i.r.) measurements. I.r. spectra show that the ligands behave as dianionic or neutral tetradentates or as monoanionic or neutral bidentates. The $[Cu(HL_I)Cl]_2$ and $Cu(H_2L_{IV})Cl_2$ complexes are diamagnetic and the other complexes have normal magnetic moment at room temperature. Electronic spectral analyses show that $Cu_2(L_{IV})Ac_2$ is planar and the other complexes are tetragonally distorted octahedral. All the complexes are non-electrolytes.

Introduction

Several highly active antithyroid substances contain thiocarbamide moieties, NHCSNH, capable of being oxidized easily, and it has been suggested that interference with thyroxine synthesis results from direct reaction between I_2 and SH (formed by enolization) to form a disulphide^(1–4). Ligands of this type have attracted much attention, and the work presented here describes spectroscopic and ligating properties towards copper(II) of some new thiocarbamides.

Experimental

Preparation of thiocarbamides

The thiocarbamides were prepared according to the method described in the literature⁽⁵⁾.

Preparation and analysis of complexes

The complexes were prepared by mixing equimolar amounts of either the hydrated Cu^{II} chloride or acetate and the thiocarbamide in absolute EtOH or aqueous ethanolic solutions. The mixture was refluxed on a water bath for a time (1–4 h) depending on the thiocarbamide. The products were removed by filtration, washed several times with EtOH and Et_2O , and finally dried in a vacuum desiccator over anhydrous $CaCl_2$.

All measurements were carried out as reported earlier⁽⁶⁾. Molecular weight measurements were made by Rast's method using camphor as a solvent.

Results and discussion

Analytical data are given in Table 1. The molar conductivities in DMSO at 25°C indicate⁽⁷⁾ a nonelectrolytic nature for all complexes. The positions of the most important i.r. bands of each thiocarbamide and its copper complexes are listed in Table 2.

The thiocarbamides can exist in different tautomeric forms, containing keto, thione, enol and thiol groups. However, the important features of the i.r. spectra discussed below provide evidence in favour of the following

Table 1. Analytical and physical data for the Cu^{II} complexes derived from the ligands.

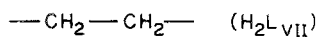
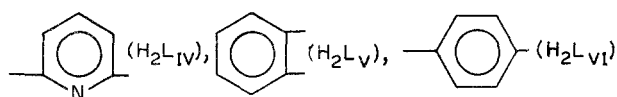
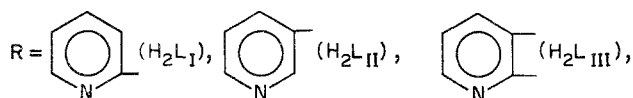
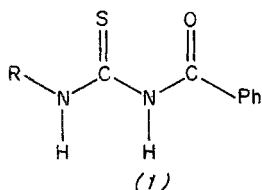
Compound	Colour	M.p. (°C)	Found (Calcd.)%		M	Cl	Ω_m^a (DMF)
			C	H			
$Cu(HL_I)Cl$	yellow	285	43.12 (43.94)	3.22 (3.12)	17.6 (17.9)	9.35 (9.97)	11.3
$Cu(HL_I)Ac$	black	260	42.8 (43.4)	3.86 (4.13)	14.94 (15.31)	–	6.5
$Cu(H_2L_{II})_2Cl_2$	green	210	47.43 (48.11)	3.14 (3.72)	9.43 (9.78)	10.41 (10.92)	8.4
$Cu(HL_{II})Ac \cdot 2H_2O$	grey	214	43.12 (43.42)	3.41 (4.12)	16.47 (15.31)	–	10.2
$Cu(H_2L_{III})Cl_2$	black	220	45.02 (44.09)	3.32 (2.99)	10.48 (11.1)	11.86 (12.39)	12.4
$Cu(H_2L_{IV})Cl_2$	yellow	290	43.42 (44.09)	3.12 (2.99)	11.76 (11.1)	12.65 (12.39)	13.4
$Cu_2(L_{IV})Ac_2$	green	> 300	43.66 (44.11)	3.32 (3.1)	19.13 (18.66)	–	6.5
$Cu(L_V) \cdot 2H_2O$	green	184	51.21 (50.13)	4.12 (3.82)	11.49 (12.05)	–	7.3
$Cu(L_{VI}) \cdot 4H_2O$	green	255	47.88 (46.92)	4.53 (4.29)	11.86 (11.28)	–	11.6
$Cu(L_{VII}) \cdot 2H_2O$	green	200	45.02 (44.66)	4.96 (4.16)	12.11 (13.1)	–	12.2

^a $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$.

Table 2. I.r. spectral bands of ligands and their copper complexes.

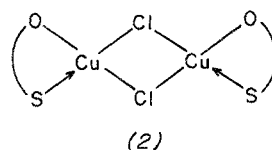
Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}=\text{N}^*)$	$\nu(\text{NH})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}-\text{S})$
(H ₂ L _I)	1685	1250, 690	—	3280	1520	—	—
Cu(HL _I)Cl	—	1230, 680	1620	3120	1530	1220	—
Cu(HL _I)Ac	—	1220, 670	1630	3100	1540	1210	—
(H ₂ L _{II})	1680	1240, 700	—	3180	1510	—	—
Cu(H ₂ L _{II}) ₂ Cl ₂	1670	1230, 670	1610	3140, 3320	1520	1190	—
Cu(H ₂ L _{II})Ac·2H ₂ O	1660	—	1580	3230	1530	—	630
(H ₂ L _{III})	1680	1240, 690	—	3200	1520	—	—
Cu(H ₂ L _{III})Cl ₂	1670	1230	—	3120	1530	—	—
(H ₄ L _{IV})	1680	1240, 700	—	3300, 3320	1520	—	—
Cu(H ₂ L _{IV})Cl ₂	1670	1220	—	3060	1540	—	—
Cu ₂ (L _{IV})Ac ₂	—	1230, 680	1590	3320	1550	1180	—
(H ₂ L _V)	1680	1240, 690	—	3320, 3280, 3130	1515	—	—
Cu(L _V)·2H ₂ O	1670	—	1610	3400	1560	—	625
(H ₂ L _{VI})	1670	1240, 680	—	3340, 3320	1515	—	—
Cu(L _{VI})·4H ₂ O	1670	—	1620	3400	1550	—	630
(H ₂ L _{VII})	1665	1250, 680	—	3410, 3220	1520	—	—
Cu(L _{VII})·2H ₂ O	1660	—	1630	3240	1560	—	640

structural form;

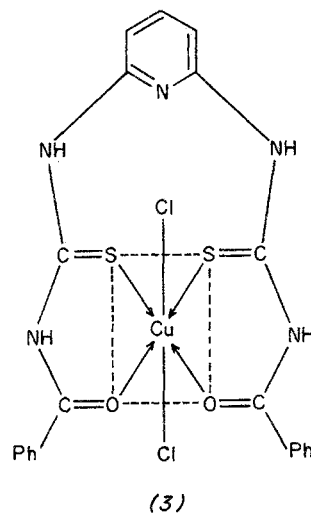


In the region 3410–3050 cm⁻¹ the i.r. spectra of the thiocarbamides show a broad band due to stretching vibrations of the NH groups. The broadness of the bands indicates that both the NH groups are of comparable energy. The strong band at 1670–1685 cm⁻¹ is assigned to $\nu(\text{CO})$, and in the thiocarbamides containing a pyridine ring (L_I–L_{IV}) the band in the region 1640–1595 cm⁻¹ is probably due to the cyclic N=C=N vibration. These compounds have a C=S (thione) group with adjacent protons and this group is likely to undergo enolization⁽⁸⁾. However, the absence of $\nu(\text{S}-\text{H})$ at 2570 cm⁻¹ indicates that these compounds predominantly exist in the thione form in the solid state. The presence of a strong band at 1240–1230 cm⁻¹, tentatively assigned to $\nu(\text{C}=\text{S})$ also supports this assumption. The bands at 1490–1435 cm⁻¹ are assigned to $\nu(-\text{N}-\text{C}=\text{S})$ vibrations⁽¹⁰⁾. Also the bands at 1070, 770 and 650 cm⁻¹ are assigned to $\nu(\text{NCN})$, $\delta(\text{NCO})$ and C=O out of plane bend, respectively. A strong band is observed at 1520 cm⁻¹ which seems to arise from $\nu(\text{C}-\text{N})$ vibration^(11,12) of the thiocarbamides. The band is broad, perhaps due to the mixing with the phenyl ring vibration.

In [Cu(HL_I)Cl]₂ and Cu(HL_I)Ac, the ligand acts as a mononegative bidentate coordinating via the CS and the enolized carbonyl oxygen with the displacement of a hydrogen atom from the latter group as in structure (2). The molecular weight determination (~670), the solubility of the copper chloride complex in pyridine with a simultaneous change in colour to green, and the appearance of a new band at 255 cm⁻¹ due to $\nu_b(\text{Cu}-\text{Cl})$ ⁽¹³⁾ suggests a dimeric nature for these complexes.



In Cu(H₂L_{IV})Cl₂, the ligand behaves as a neutral tetradentate coordinating via the CO and CS in both the ketone and thione forms as in structure (3);



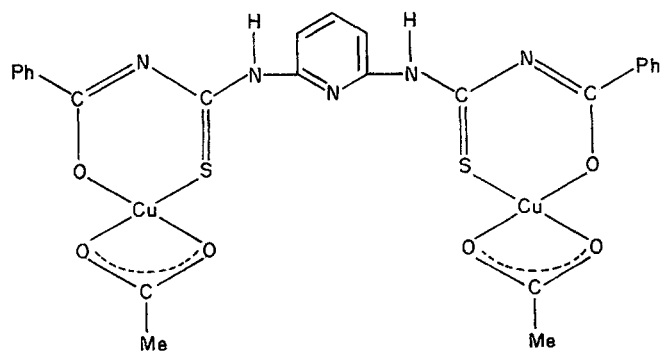
[Cu(HL_I)Cl]₂ and Cu(H₂L_{IV})Cl₂ are new examples of the few copper(II) complexes^(14–16) in which the spin-paramagnetism is completely quenched ($\mu_{\text{eff.}} = \text{zero}$) at room temperature. The copper(II) concentration in the complexes was estimated volumetrically by decomposing them in an atmosphere of nitrogen. Their diamagnetism may be attributed to a super-exchange phenomenon

Table 3. Electronic bands and magnetic moments of the complexes.

Complex	Medium	Electronic bands ($\text{cm}^{-1} \times 10^{-3}$)	μ_{eff} . B.M.	$10D_q$
Cu(HL _I)Cl	DMF	15.857, 19.230, 31.250	Diamagn.	—
Cu(HL _I)Ac	"	20.408	1.98	10.2
Cu(H ₂ L _{III}) ₂ Cl ₂	"	16.4	2.43	8.2
Cu(HL _{II})Ac·2H ₂ O	"	18.7	1.7	8.8
Cu(H ₂ L _{III})Cl ₂	"	17.3, 20.1	1.45	—
Cu(H ₂ L _{IV})Cl ₂	"	17.8	diamagn.	—
Cu ₂ (L _{IV})Ac ₂	"	15.9, 24.4	1.41	—
Cu(L _V)·2H ₂ O	"	13.9, 15.4	1.62	7.48
Cu(L _{VI})·4H ₂ O	"	14.5	1.13	7.3
Cu(L _{VII})·2H ₂ O	"	14.3	1.01	7.1

and/or the higher polarizability^(17,18) of ligand (sulphur donor) which supplies more electron density to copper; the ions consequently interact more strongly, resulting in a diamagnetic complex. The strong spin–spin interaction may take place by overlap of the singly occupied $d_{x^2-y^2}$ orbital on the two cupric ions. In the absence of detailed x-ray work it is difficult to decide between these alternatives. The electronic spectra of these complexes show one or two broad band(s) in the region 14000–19200 cm^{-1} and a charge transfer band near 26500 cm^{-1} . Copper(II) carboxylates which are diamagnetic show three bands at 11000, 13500 and 26000 cm^{-1} ⁽¹⁹⁾. Another diamagnetic copper(II) complex with diazoaminobenzene⁽²⁰⁾ shows two bands at 14900 and 18800 cm^{-1} which are assigned to $d_{xy} \rightarrow d_{z^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ respectively. Tsuchida and coworkers^(21,22) indicated that all the copper complexes in which the paramagnetism is partially or completely quenched, absorb around 26600 cm^{-1} . Khullar *et al.*⁽¹⁵⁾ also reported another diamagnetic copper(II) complex with 2-mercaptobenzothiazole which absorbed at 24400 cm^{-1} . However, the spectra of our complexes (Table 3) show both ligand field and charge transfer bands like the spectra of copper(II) complexes with diazoaminobenzene.

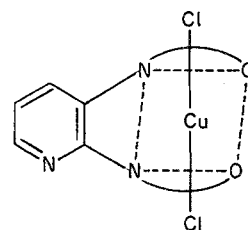
In $\text{Cu}_2(\text{L}_{\text{IV}})\text{Ac}_2$, the ligand acts as a binegative tetradentate coordinating via the CS and the enolized carbonyl oxygen with displacement of hydrogen atoms from the latter group [structure (4)]. The electronic spectrum of this complex exhibits two bands (Table 3). The first is centred at 15873 cm^{-1} and the other, which is more intense, is centred at 24390 cm^{-1} . The band at 24390 cm^{-1} may be assigned to a symmetry-forbidden ligand \rightarrow metal charge transfer band^(23–25), and the one at 15873 cm^{-1} is assigned to the d–d transition corresponding to ${}^2T_{2g} \rightarrow {}^2E_g$; the band position is in agreement with



(4)

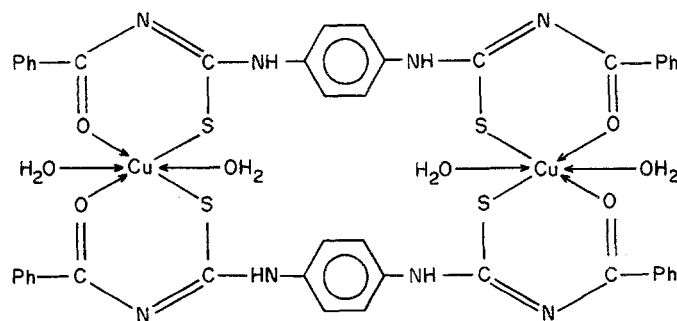
those generally observed for planar copper(II) complexes.

In $\text{Cu}(\text{H}_2\text{L}_{\text{III}})\text{Cl}_2$, the ligand acts as a neutral tetradentate coordinating via the NH and CO as in structure (5). This behaviour is supported by the negative shifts of both $\nu(\text{CO})$ and $\nu(\text{NH})$ groups, and the CS bands remain unaffected, as observed in the i.r. spectrum of the free ligand (Table 2).



(5)

In the complexes $\text{Cu}(\text{L}_{\text{V}})\cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{L}_{\text{VI}})\cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{L}_{\text{VII}})\cdot 2\text{H}_2\text{O}$ the ligands act as binegative tetradentates, coordinating via the CO and the CS in the thiol form with displacement of a hydrogen atom from the latter group. The molecular weight determination suggests a dimeric nature of these complexes as in structure (6).



(6)

The majority of the complexes which are green or blue are tetragonally distorted⁽¹⁹⁾, which appears to be the case for these complexes. The energy level diagram for ligand fields of D_{4h} symmetry would predict three transitions from the ground state; ${}^2A_{1g} \leftarrow {}^2B_{1g}(v_1)$, ${}^2B_{2g} \leftarrow {}^2B_{1g}(v_2)$ and ${}^2E_g \leftarrow {}^2B_{1g}(v_3)$. The splitting of the octahedral 2E_g and ${}^2T_{2g}$ states increases with the tetragonal components of the crystal field. As the energy of the ${}^2A_{1g}$ state increases a situation may arise in which this state is sufficiently close to the ${}^2B_{2g}$ and 2E_g states for the three transitions not be resolved in the spectrum. Thus, from the appearance of a single broad band (Table 3) in the spectra of most of the

complexes studied, it is concluded that all three transitions lie within this one broad envelope^(26–29) and that distortion from the octahedral symmetry is not large. Copper(II) complexes where the geometry is anticipated and known in some cases to be square-planar reinforce this argument⁽³⁰⁾. An approximate value of D_q may be obtained from the following expression:

$$10D_q = \nu_3 - \frac{1}{2}\nu_1 - \frac{1}{3}(\nu_3 - \nu_2)$$

If it is assumed that the splitting of the states due to tetragonal field follows a baricentre rule⁽³¹⁾.

The observed new bands in the complexes at 520–460, 450–380, 350–330 and 320–270 are tentatively assigned to $\nu(\text{Cu—O})$ ⁽³¹⁾, $\nu(\text{Cu—N})$ ⁽³²⁾, $\nu(\text{Cu—S})$ ⁽³¹⁾ and $\nu(\text{Cu—Cl})$ ⁽³³⁾ respectively.

The presence of water within the coordination sphere in the hydrated complexes is supported by the observation of bands in the region 3440–3400, 1640–1610 (sh.) and 960–955 (w) in the spectra of the complexes due to OH stretching, HOH deformation and H₂O rocking⁽³⁴⁾. The water of crystallization was determined from the mass loss observed upon heating the complexes in an oven at 120° C for two hours.

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