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Complexes of Copper(I) and Silver(I) with some Thiocarbazide Derivatives

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The preparation and properties of a series of complexes of copper(I) and silver(I) with benzoylthiocarbazide (HBTC), acetylthiocarbazide (HATC) and nicotinoylthiocarbazide (HNTC) are reported. Two types of complexes of copper(I), $Cu(HL)_2Cl, H_2O$ *and CuL, and one of silver(I), AgL, have been prepared and characterized. The structural interpretation of the complexes is based mainly on magnetic measurements and infrared spectra. The complexes are considered to be polymeric with copper(I) and silver(I) exhibiting their usual coordination number four. In the complex* $Cu(HL)_2Cl\,.\,H_2O$*, the ligands act as monodentate, only the sulphur atom being coordinated; in the other complexes the ligands act as terdentate, the coordination occurring through the sulphur, hydrazinic nitrogen and the amido-nitrogen atoms.*

Discussion

Studies of the complexes of copper and silver with different thiocarbonyl ligands such as thiourea,[1] thiosemicarbazide,[2] thiosemicarbazones,[3,4] thiocarbohydrazides,[5] and also N–carbamoyl–N–thiocarbamoylhydrazine[6] have been reported. With thiosemicarbazide and thiocarbohydrazide copper forms complexes in the bivalent state, whereas with the other mentioned ligands copper(II) is reduced to copper(I) which then forms complexes. Some of the ligands act both as neutral[3] and monoacidic[4] and others only as neutral.[1,2,5,6] In most of these complexes copper—both uni- and bi-valent—exhibited coordination number four. However, copper(I) complexes of thiosemicarbazones, CuL have been studied by Bayley *et al.* and have been assigned coordination number two, copper(I) being coordinated with S–atom of one molecule of ligand and the N–atom of the other. With the lastly mentioned ligands[6] coordination occurs only through N–atoms, silver(I) also forms similar complexes with these ligands. Silver(I) complexes with thiosemicarbazide[7] and thiocarbohydrazide,[5] of the type Ag(HL)Cl, have been assigned structures in which the coordination number is again four.

The study of the complexes of copper and silver is now extended to the new ligands, aryl(acyl-)thiocarbazides *viz.* Benzoylthiocarbazide, $C_6H_5CONHNHCSNHNH_2$(HBTC), Acetylthiocarbazide, $CH_3CONHNHCSNHNH_2$(HATC), and Nicotinoylthiocarbazide, $C_6H_4NCONHNHCSNHNH_2$(HNTC), prepared and used previously by us with other metals.[8,9]

Experimental Section

Preparation of the ligands. These are prepared by the general method of Varma.[10]

Preparation of the complexes: Chlorobis[aryl(acyl-)thiocarbazidato]copper(I) monohydrate, $Cu^{I}(HL)_2Cl\,.\,H_2O$. These complexes are prepared by the addition of an ethanolic solution $CuCl_2$ dihydrate to a solution of the ligands in the same solvent (molar ratio of 1:4). The colour of the solution is deep brown at first but gradually becomes colourless on concentration on a water bath with the precipitation of white crystals with slight pale yellow tint. The precipitate is filtered off, washed several times with hot ethanol in order to remove excess reagent, and dried in air.

[Aryl(acyl-)thiocarbazidato]copper(I) Complexes, $Cu^{I}L$. These complexes are prepared by the addition of an ethanolic solution of ligands to an aqueous solution of copper(II) salt (molar ratio of 2:1), followed by the addition of an aqueous solution of sodium bicarbonate with constant stirring. A blue precipitate is formed at first which gradually becomes colourless with simulutaneous liberation of bubbles of gas with an unpleasant odour. The solution containing the precipitate is kept on a water bath for about an hour, cooled, filtered, washed several times with water and finally with hot ethanol, and is dried in air.

[Aryl(acyl-)thiocarbazidato]silver(I) Complexes. $Ag^{I}L$. These complexes are prepared by the addition of an ethanolic solution of the ligands to a solution of silver nitrate in triply distilled water and then following the procedure used in analogous copper(I) complexes.

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Table I. Analytical Data.

Compound	Calculated M%	Calculated N%	Calculated S%	Calculated Cl%	Found M%	Found N%	Found S%	Found Cl%
$Cu(HBTC)_2Cl . H_2O$	11.82	20.85	11.91	6.61	12.08	21.05	11.63	6.51
$Cu(HATC)_2Cl . H_2O$	15.37	27.11	15.49	8.86	15.30	27.05	15.31	9.05
$Cu(HNTC)_2Cl . H_2O$	11.78	25.97	11.87	6.58	11.53	25.82	11.77	6.69
Cu(BTC)	23.30	20.55	11.65	—	23.54	20.70	11.92	—
Ag(BTC)	34.04	17.69	10.09	—	34.07	17.58	10.08	—
	30.16	27.07	15.20	—	30.02	26.95	15.02	—
	42.30	21.97	12.55	—	42.66	22.05	12.40	—
Cu(NTC)	23.21	25.59	11.69	—	23.34	25.68	11.75	—
Ag(NTC)	33.90	22.02	10.06	—	23.92	22.15	10.25	—

Table II. Infrared Spectral Data and Assignments.

Assignments	HBTC	$Cu(HBTC)_2$ Cl . H_2O	Cu(BTC)	Ag(BTC)	HATC	$Cu(HATC)_2$ Cl . H_2O	Cu(ATC)	Ag(ATC)	HNTC	$Cu(HNTC)_2$ Cl . H_2O	Cu(NTC)	Ag(NTC)
OH										3450(wb)		
NH and NH_2 stretch	3310(m)	3480 to		3315(m)	3300(w)	3395(wb)	3350(w)			3260(w)	3245(wb)	3288(w)
	3270(m)	3360(mb)	3280(m)		3270(m)	3275(m)			3200(m)	3195(m)	3195(vw)	3185(vw)
	3120(w)	2185(w)	3130(ms)	3140(ms)	3100(w)	3065(sh)	3240(m)	3230(w)	3120(w)		3090(m)	3112(m)
								3180(w)				
Amide I and NH_2 bend	1630(ms)	1620(s)	1645(ms)	1640(ms)	1640(m)	1625(s)	1645(s)	1645(ms)	1630(ms)	1625(m)	1628(m)	1625(m)
									1600(w)			
Amide II and CN stretch	1533(s)	1545(s)	1530(w)	1535(w)	1570(ms)	1568(ms)	1565(m)	1575(m)	1550(m)	1558(m)	1585(w)	1588(w)
		1505(s)			1510(m)	1500(w)			1505(w)	1500(w)		1568(w)
CS and CN stretch	1320(s)	1315(mb)	1305(w)	1298(m)	1310(s)		1320(m)	1335(w)	1320(s)	1310(w)	1148(wb)	1272(w)
								1310(w)				
Amide III	1230(w)	1235(w)			1270(w)				1220(w)	1222(w)		
					1250(w)	1220(wb)						
NH_2 and NCS bend	1073(s)	1082(w)		1076(m)	1200(w)	1190(w)			1172(w)	1180(w)	1285(w)	1140(wb)
		1050(w)			1100(w)	1155(w)						
NH_2 deformation	1010(ms)	1030(m)	1015(ms)	1045(m)		1075(m)			1115(ms)	1150(m)	1115(w)	1115(vw)
				1018(s)	1030(w)	1025(w)	1030(s)	1040(ms)	1065(ms)	1180(m)	1025(w)	1024(w)
				1005(m)	1010(w)	1005(w)			1020(ms)	1030(ms)	1010(w)	1015(w)
NN stretch	944(s)	970(ms)	970(m)	972(ms)	990(s)	980(ms)	990(m)	990(mb)	990(w)	970(w)	990(m)	995(m)
					910(s)	915(ms)	960(s)	955(ms)	960(m)	965(m)	950(ms)	955(m)
							943(s)	910(w)	915(s)			
NCO, CN and CS stretch	770(s)	775(ms)	758(ms)	760(ms)	760(w)	765(vw)	752(m)	755(m)	790(s)	795(ms)	780(m)	785(m)
	720(s)	720(m)		715(m)	730(s)	725(s)	735(w)		720(s)	715(s)	732(w)	725(sh)
	700(s)						725(w)	722(w)			705(m)	705(m)
	688(ms)	692(s)	682(ms)	690(s)			695(m)	698(w)			680(ms)	690(m)
				686(s)								

s = strong; m = medium; ms = medium strong; w = weak; mb = medium broad; wb = weak broad.

Apparatus and Measurements. I.R. spectra in the region 4000-625 cm^{-1} are run as Nujol mulls on a Perkin-Elmer 221 spectrophotometer. Magnetic behaviour of the complexes is studied on a Gouy Balance. X-ray powder diagrams are taken with a Nonius Guinier Camera.

Results and Discussion

All the copper and silver complexes are white and diamagnetic, so that copper and silver may be considered to have oxidation number one. All the complexes are of very low solubility in water as well as in all common organic solvents—ionising and non-ionising— and conductivity measurements could not be carried out. The low solubility of the complexes may be considered indicative of a polymeric structure. All attempts to obtain cupric complexes of any type have not met with success. Passing of chlorine into the aqueous solution of the copper(I) complexes of both types has no effect upon their colour. X-ray powder patterns of the neutral 1:1 inner chelates of copper(I) and silver(I) are also calculated. From the observed similarities of these patterns, it can be said that the corresponding complexes of each metal are isomorphous.

Infrared Spectra. It has already been mentioned[8,9] that one of the bands in the region 3 μ, *viz.* that at ~3270 cm^{-1}, is assigned to $\nu(NH_2)$[11] and the others are due to ν(NH). In the infrared spectra of the neutral 1:1 metal chelates, it is observed that the ligand bands due to $\nu(NH_2)$ are shifted to lower wave number and thereby indicating that the end nitrogen atom (N^1) is taking part in complex formation. Similar changes are observed with the bands due to ν(NH) and this is perhaps due to the involvement of the nitrogen of one of the NH groups in coordination. It is further seen that the ligand amide II (NH bending) band s also undergo some shift in some cases to higher wave number and amide III bands (NH unsymmetrical stretching) are uniformly absent in all the complexes of this class. The shift in frequency of the amide I (C=C) bands are not indicative of oxygen coordination as in such cases these bands are neither shifted (to lower wave number) nor split on complex formation. It is also seen that the ligand bands at ~770 cm^{-1} assigned as due to δ(NCO) are shifted to lower wave number. This shift, though small in magnitude, probably be attributed to amido nitrogen coordination. It is, therefore, inferred that the second coordination centre is the amido nitrogen (N^4) atom. From the usual characteristic changes[8,9] of both bands at ~1320 cm^{-1} and ~730 cm^{-1} due to ν(CS), the third coordination centre is assumed to be the thioenolic as terdentate. The complexes of this class may therefore be represented tentatively by the polymeric structure (I), with metal exhibiting co-

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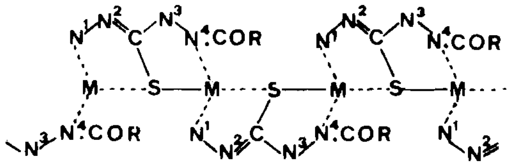
ordination number four.



In the spectra of the complexes of the class Cu(HL$_2$Cl . H$_2$O, the ν(NH) and the ν(NH$_2$) bands in the 3 μ region are either shifted to higher wave number or remain stationary. The amide I, amide II, amide III, and the δ(NCO) bands also remain inaffected. The only bands which are affected on complex formation are those due to ν(CS). As seen from the characteristic changes of both bands due to ν(CS) at ~1320 cm^{-1} and at ~730 cm^{-1}, the coordination centre is, therefore, the thione sulphur atom. It is significant that this form of the ligands predominates in ethanolic solution where complex formation takes place. The ligands are therefore acting as unidentate, similar to thiourea, and thiosemicarbazones towards copper, and the compounds are probably dimeric, similar to CuCl . 2tu and CuCl . 2Hhsc (tu = thiourea, Htsch = thiosemicarbazones), the coordination number of the metal being four.

As all copper complexes are diamagnetic and tetracoordinated, they may be assumed to have tetrahedral stereochemistry.