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THERMAL, SPECTRAL, ESR AND MAGNETIC STUDIES OF SOME COPPER(II) THIOSEMICARBAZONE COMPLEXES

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ABSTRACT

Copper(II) forms 1 : 1 dimeric complexes with the thiosemicarbazones of salicylaldehyde, 5-bromo-salicylaldehyde, 2-hydroxy-1-naphthaldehyde and vanillin. All the complexes are found to be non-electrolytes in nitrobenzene and square planar structures are assigned to them based on electronic, ESR and room-temperature magnetic measurements. IR studies reveal that the complexes are formed by the replacement of the hydrogen atom of the SH group by Cu^{II}, with N and S coordinating to the metal. Thermal studies indicate that the decomposition takes place in two stages. Interpretation and mathematical analysis of these data and evaluation of the order of reaction, and of the energy and entropy of activation, based on Coats–Redfern, Horowitz–Metzger and MacCallum–Tanner methods, are also given. On the basis of our findings the relative thermal stabilities of the Cu^{II} chelates can be given as $[Cu(VTSC)Cl]_2 < [Cu(NTSC)Cl]_2 \approx [Cu(BrSTSC)Cl]_2 < [Cu(STSC)Cl]_2$.

INTRODUCTION

Metal complexes of thiosemicarbazone have been known for their pharmacological applications [1]. Significant antitubercular [2], fungicidal [3] and antiviral [4] activities have been reported for thiosemicarbazones and their derivatives. Their activity has frequently been thought to be due to their ability to chelate trace metals. In continuation of our earlier work on transition metal complexes of thiosemicarbazones [5–7] we report here the preparation of copper(II) complexes of salicylaldehyde thiosemicarbazone (STSC), 5-bromo-salicylaldehyde thiosemicarbazone (Br-STSC), 2-hydroxy-1-naphthaldehyde thiosemicarbazone (NTSC) and vanillin thiosemicarbazone (VTSC). The complexes were characterized by thermal, spectral, ESR and magnetic studies.

EXPERIMENTAL

Materials and methods

The aromatic aldehyde thiosemicarbazones were prepared according to the procedures described in the literature [8].

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General methods for preparing the complexes

A methanolic solution of Cu^{II} was added dropwise to a hot solution of the ligand in methanol (1 : 1 ratio). The separated complex was filtered off, washed with methanol and dried in a desiccator.

Physical measurements

The molar conductance of the complexes in nitrobenzene at a concentration of $\sim 10^{-4}$ M was measured with a Toshniwal conductivity bridge having a cell constant of 0.7. The thermal characterization of the complexes was carried out using a DuPont 990 modular thermal analyser system, in conjunction with a 951 thermogravimetric analyser, in air and at a heating rate of 20° min^{-1}. IR spectra of the ligands and the complexes in KBr were recorded on a Beckmann IR-12 IR spectrophotometer in the 4000–200 cm^{-1} region. The electronic spectra in methanol were obtained with a Pye Unicam SP 1800 UV spectrophotometer and the ESR spectra in pyridine were recorded using a Varian E-4 band spectrometer. The values of $\bar{g}$ were measured relative to Coppiger's radical. The magnetic measurements were taken at room temperature on a Gouy balance using $[HgCo(NCS)_4)]$ as a calibration standard.

RESULTS AND DISCUSSION

All the complexes are found to be coloured. They are insoluble in water and are soluble in alcohols, ketones, DMF etc. The analytical data given in Table 1 show copper to ligand ratios of 1 : 1 and the presence of one chlorine atom in the complexes. The complexes are found to be stable in air.

Nitrobenzene solutions of the complexes have low conductance values in the range of 0–6 indicating a non-electrolytic nature.

THERMOGRAVIMETRIC ANALYSIS

The thermal behaviour of the above chelates was studied in detail. The TG traces exhibit a two stage decomposition pattern. The decomposition temperature ranges in DTA and DTG for the four Cu^{II} chelates are given in Table 2. Data from independent pyrolysis experiments are also included in this table. These complexes may contain lattice water as is shown by a small change in the TG curve below 100 °C. The mass-loss data at the end of the first stage for each complex indicates that the Cl atom and the thiosemicarbazide molecule are detached from the metal chelates and the second stage corresponds to the loss of the hydroxy-aldehyde part. The final pyrolysis products, in all four complexes, correspond to the oxide.

TABLE 1

Analytical data, molar conductance and magnetic moments of the Cu^{II} complexes

	Metal oxide (%)	Carbon (%)	Hydrogen (%)	Chlorine (%)	Nitrogen (%)	Molar conductance ($V\ cm^2$)	μ_{eff} (B.M.)
$[Cu(STSC)Cl]_2$	26.54 (25.64)	29.98 (29.18)	3.96 (3.98)	9.95 (10.77)	12.67 (12.75)	4.2	1.2
$[Cu(Br–STSC)Cl]_2$	25.0 (25.16)	28.87 (27.09)	2.98 (2.84)	11.76 (12.16)	11.71 (11.84)	0	1.10
$[Cu(NTSC)Cl]_2$	23.0 (23.12)	40.49 (41.99)	2.56 (2.6)	10.43 (10.32)	12.43 (12.64)	3.5	1.12
$[Cu(VTSC)Cl]_2$	24.89 (24.67)	32.92 (33.45)	3.93 (3.43)	10.96 (10.97)	11.79 (13.00)	5.6	1.09

(Theoretical values are given in parentheses.)

TABLE 2

Thermal decomposition data

Substance	Stage	Peak temperature in DTG (°C)	Temperature range in DTG (°C)	Peak temperature in DTA (°C)	% loss of mass		From pyrolysis
					from TG	theoretical	
$[Cu(STSC)Cl]_2$	I	260	150–300	270 w	40	41.97	72.9
	II	490	300–750	512 s	72.8	72.87	
$[Cu(BrSTSC)Cl]_2$	I	230	100–350	237 m	34	33.06	79.5
	II	560	350–700	555 s	80.4	78.63	
$[Cu(NTSC)Cl]_2$	I	430	100–500	419 m	34	35.91	78.8
	II	570	500–750	602 s	80	76.79	
$[Cu(VTSC)Cl]_2$	I	290	50–325	361 m	36	38.08	75.9
	II	515	325–700	505 s	76.8	75.38	

An examination of the decomposition temperature of these chelates indicates that the $[Cu(STSC)Cl]_2$ chelate is the most stable. Inspection of the data in Table 2 reveals that the introduction of a bromine atom or benzene ring decreases the thermal stability. The lower thermal stability of $[Cu(BrSTSC)Cl]_2$ and $[Cu(NTSC)Cl]_2$ may be attributed to the electron-withdrawing effect of a bromine or phenyl ring leading to a reduction in electron density at the reactive centre. $[Cu(VTSC)Cl]_2$ is also less stable than the $[Cu(STSC)Cl]_2$ complex and this can be explained in terms of hydrogen bonding, involving the methoxy group of the vanillin molecule, which in turn leads to a decreased electron density at the reactive centre.

Thermal decomposition kinetics

Kinetic parameters, viz. activation energy, $E^{\star}$, pre-exponential factor A, and order parameters n, for the thermal decomposition of the four copper(II) complexes were evaluated from the TG data. The fractional decomposition α for the relevant temperature was calculated from the TG curves. Using a computer, the best fit value of n was determined for the decomposition of the four complexes, and it was found to be 1 for both stages in all the cases. Using this value of n, the kinetic parameters were calculated from the following three non-mechanistic integral equations.

Coats–Redfern equation [9]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\phi E^{\star}}\left(1-\frac{2RT}{E^{\star}}\right)\right] - \frac{E^{\star}}{RT} \qquad (1)$$

MacCallum–Tanner equation [10]

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \log\frac{AE^{\star}}{\phi R} - 0.483E^{\star 0.435} - \frac{(0.449+0.217E^{\star})10^3}{T} \qquad (2)$$

Horowitz–Metzger equation [11]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\frac{ART_s^2}{\phi E^{\star}} - \frac{E^{\star}}{RT_s} + \frac{\theta E^{\star}}{RT_s^2} \qquad (3)$$

The left-hand side of the above equations was plotted against reciprocal absolute temperature $(1/T)$ for eqs. (1) and (2) and against $\theta = (T - T_s)$ for eqn. (3). From the slope and intercept, $E^{\star}$ and A were calculated, and their values are reported in Table 3. It can be seen that the values of $E^{\star}$ and A from the three equations are nearly the same. It is also found that, the

TABLE 3

Kinetic parameters for the thermal decomposition of Cu^{II} complexes using three equations

Sample	Stage	Coats–Redfern			MacCallum–Tanner			Horowitz–Metzger		
		E^*	A	ΔS	E^*	A	ΔS	E^*	A	ΔS
$[Cu(STSC)Cl]_2$	I	120.66	2.117×10^{11}	−32.94	99.90	3.411×10^{12}	−9.819	125.49	2.078×10^{12}	−13.94
	II	344.68	1.742×10^{23}	192.31	347.68	4.765×10^{26}	258.15	306.75	4.700×10^{22}	181.41
$[Cu(BrSTSC)Cl]_2$	I	60.11	4.054×10^{5}	−141.99	60.65	4.706×10^{8}	−83.28	64.99	3.442×10^{6}	−124.19
	II	92.04	4.85×10^{5}	−144.69	105.15	1.180×10^{9}	−79.82	130.28	6.604×10^{7}	−103.81
$[Cu(NTSC)Cl]_2$	I	19.95	9.363	−233.58	24.80	1.916×10^{-1}	−265.94	33.07	4.592×10^{1}	−220.35
	II	159.76	8.369×10^{8}	−82.78	122.12	1.183×10^{10}	−60.75	168.7	1.602×10^{10}	−58.32
$[Cu(VTSC)Cl]_2$	I	37.70	5.928×10^{6}	−120.609	33.61	1.951×10^{4}	−133.79	50.74	1.215×10^{6}	−168.16
	II	69.81	8.457×10^{3}	−117.92	74.89	1.075×10^{4}	−170.45	82.10	8.738×10^{4}	−158.49

greater the thermal stability of a compound, the larger the activation energy for decomposition.

IR spectra

The IR spectra of the ligands and the complexes were examined in detail. The characteristic IR bands are given in Table 4. The strong bands in the spectra between 3520 and 3270 cm^{-1} may be assigned to ν NH_2 and ν NH [12]. The strong band around 3150 cm^{-1} in the spectrum of the ligands may be due to ν OH. The low frequency shift of this band compared to normal OH vibration bands at 3480 cm^{-1} may be due to hydrogen bonding [13]. The fact that these two bands due to ν NH and ν OH are retained almost at the same position, excludes any possible participation of the oxygen of the phenolic group or the nitrogen of the NH_2 group in coordination. The shifting of the band at 1620 cm^{-1} (ν C = N) to lower wavenumbers in the complexes indicates the participation of N^3 in coordination [14]. The bands near 3500 and 1600 cm^{-1} (antisymmetric and symmetric OH stretching and HOH bending) [13] indicates the presence of lattice water. The absence of bands in the region 2650–2500 cm^{-1} in the free ligand indicates that it exists in the thioketo form in the solid state. However, during the complex formation it might exist in the enol form. This is indicated by the absence of the band due to ν C = S of the ligand in the complexes and the appearance of a new band on complexation around 660 cm^{-1} which can be attributed to ν C–S. The bands appearing around 550 cm^{-1} in the spectrum of the complexes may be assigned to M–N stretching frequencies [15].

ESR and electronic spectra

The d–d bands of Cu^{II} complexes for which a square planar structure has been proposed [16–18] occur in the range 14000–18000 cm^{-1}, and when a planar structure is distorted to a tetrahedral configuration, the frequency of

TABLE 4

Characteristic bands (cm^{-1}) of Cu^{II} complexes

Sample	ν OH	ν C–N*	ν C–N	ν C–S	ν M–N
STSC	3200 s	1620 s	760 s	—	—
$[Cu(STSC)Cl]_2$	3200 s	1610 s	—	660 m	540 s
BrSTSC	3180 s	1610 s	800 s	—	—
$[Cu(BrSTSC)Cl]_2$	3180 s	1600 s	—	660 m	520 m
NTSC	3200 s	1610 s	775 s	—	—
$[Cu(NTSC)Cl]_2$	3200 s	1600 s	—	680 m	560 m
VTSC	3150 s	1600 s	780 s	—	—
$[Cu(VTSC)Cl]_2$	3150 s	1580 s	—	680 m	550 m

TABLE 5

ESR, optical absorption and bonding parameters of complexes

Complexes	$g_{\parallel}$	$g_{\perp}$	$^2B_{1g} \rightarrow {}^2B_{2g}$ $E_{\parallel}$ (cm^{-1})	$^2B_{1g} \rightarrow {}^2E_g$ $E_{\perp}$ (cm^{-1})	$k_{\parallel}$	$k_{\perp}^2$
$[Cu(STSC)Cl]_2$	2.097	2.049	16393	25006	0.24	0.75
$[Cu(BrSTSC)Cl]_2$	2.103	2.053	17241	23530	0.27	0.75
$[Cu(NTSC)Cl]_2$	2.097	2.049	16666	24390	0.25	0.73
$[Cu(VTSC)Cl]_2$	2.099	2.056	16666	24390	0.25	0.82

this band is diminished. The electronic spectra of these Cu^{II} complexes showed absorption maxima at ~ 16000 cm^{-1}, so square planar structures can be assigned to them. The bands observed around 16000 cm^{-1} are attributed to $^2B_{1g} \rightarrow {}^2B_{2g}$ and the bands in the 23000–25000 cm^{-1} region are assigned to $^2B_{1g} \rightarrow {}^2E_g$ transition.

ESR spectra are helpful for determining the structure of the complex molecules in solutions. The freshly prepared toluene or CCl_4 solutions of these adducts do not have any ESR spectra because of the existence of the dimeric molecule in these solutions, whereas the strong four-line ESR spectra characteristic of monomeric Cu^{II} complexes are observed for solutions of these molecules in polar solvents. Interaction of the unpaired electron with one ^{14}N nucleus of nitrogen coordinated to the Cu^{II} ion gives rise to superhyperfine structure, readily observed for the fourth peak (high field) of Cu hyperfine lines.

The ESR spectra of copper–thiosemicarbazone complexes are found to be similar and give only approximate g values. The spin Hamiltonian constants ($g_{\parallel}$ and $g_{\perp}$) are given in Table 5. The optical and ESR data can be correlated and the orbital reduction parameters $k_{\parallel}^2$ and $k_{\perp}^2$ calculated. These are presented in the table along with the ESR and optical data.

The $g_{\parallel}$ values are almost the same for all four complexes, indicating that the type of bonding is the same in all cases. Kivelson and Neiman have shown that $g_{\parallel}$ is a moderately sensitive function for indicating covalency [19]. The small g values (< 2.3) indicate strong interaction between the ligand and the copper(II) ion which in turn reveals the covalent character of the bonding [20].

Massacesi et al. [21] reported that $g_{\parallel}$ is 2.3–2.4 for Cu–O bonds; 2.2–2.3 for Cu–N bonds and mixed Cu–N and Cu–O systems and 2.1–2.2 for Cu–S bonds. For the present Cu–thiosemicarbazone complexes $g_{\parallel}$ is 2.09–2.1, in conformity with the presence of Cu–S and N bonds in these chelates.

Hathaway [22] pointed out that for pure σ bonding $k_{\parallel} \approx k_{\perp} \approx 0.77$, for in-plane π bonding $k_{\parallel} < k_{\perp}$ and for out-of-plane π bonding $k_{\parallel} > k_{\perp}$. In all the present complexes $k_{\parallel} < k_{\perp}$ which suggests that in these chelates in-plane π bonding is present.

Magnetic moments

The values of magnetic moments (μ_{eff}) for the Cu^{II} complexes are given in Table 1. It shows a low value compared with the spin-only value (1.73 B.M.). This suggests a binuclear configuration, facilitating antiferromagnetic exchange [23].

The elemental analysis of the present complexes and the thermogravimetric results show that the stoichiometry is 1 : 1 in all the complexes. As shown in Table 1, all magnetic moments are low compared with the spin-only value. The magnetic moment values of Cu-thiosemicarbazone complexes and the data obtained from ESR and optical absorption studies indicate square-planar geometry for all these chelates.

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