THERMAL ANALYSIS OF 2-OXOCYCLOPENTANEDITHIOCARBOXYL-ATO COMPLEXES OF IRON(III), COPPER(II) AND ZINC(II) CONTAINING PYRIDINE OR MORPHOLINE AS THE SECOND LIGAND

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A series of ternary complexes of the types $M_2L_2'L_2''$; $ML_2'L_2''$ (*M*=Fe, Cu, Zn; L'=2-oxocyclopentane dithiocarboxylate; L''=pyridine, morpholine) and $CuL_2'H_2O$ was prepared afresh. Except the iron complex, all are dimer and complexation is through the dithio moiety of the ligand L'. Their thermal decomposition was carried out in air at heating rate 10°C min^{-1} and it revealed that the dehydration of the aqua complex follows the same path as the carboxylates and the pyridine complexes have the tendency to follow one-step decomposition. The copper complexes are less thermally stable. The overall thermal stability of the 2-oxocyclopentanedithiocarboxylato complexes of the three metals with the volatile ligands was found to be in the order: $(CuLmorph)_2<CuL_2H_2O<(CuLpy)_2<(ZnLmorph)_2<(ZnLpy)_2<FeL_2py_2$. The thermogravimetric properties of the complexes have been studied and the data were subjected to kinetic analysis. The values of *n*, *E*, *A* and $\Delta S^{\#}$ have been approximated and compared. Any formation of bridged structure is not indicated in the first step case.

Keywords: *dehydration, kinetic parameters, morpholine, non-isothermal decomposition, 2-oxocyclopentanedithiocarboxylate, pyridine*

Introduction

Sulfur has been an interesting element particularly for the varieties of its compounds and varieties of bonding it is involved in [1]. It has a prominent bioinorganic chemistry and a large number of enzymes and other proteins such as the iron sulfur proteins exhibit fantastic properties involving the sulfur atoms in them [2, 3]. It is an important element forming chains [4] and more interestingly, bridges in polymers and in varieties of composite materials, giving rise to strength and resistance to aging. Iron and many other elements also form many significant nanomaterials during nanotisation [5–10]. Cyclic organic compounds having sulfur outside the ring have attracted researchers for a long time. 2-oxocyclopentane dithiocarboxylic acid [11] is one such compound in which the element is attached to a non-aromatic ring.

The relationship between the structure and thermolysis of organometallic compound and also the investigation of the influence of metal and ligand nature on the process of thermal decomposition are of certain interest. Therefore, many authors have investigated metal and ligand nature in organometallic compounds of several central atoms and also examined their thermal and other properties [12–29]. Coordination chemistry of common metals such as copper, iron and zinc involving this molecule seems to have escaped proper attention of workers so far. A series of ternary complexes of the types $M_2L_2'L_2''$; $ML_2'L_2''$ (*M*=Fe, Cu or Zn; L'=2-oxocyclopentane dithiocarboxylate; L''=pyridine, morpholine) and $CuL_2'H_2O$ has been chosen for the present work to find out the bonding and any relationship of the presence of the volatile ligands with thermal stability of the complex. Except the iron complex, all are dimers and complexation is through the dithio moiety of the ligand L'. Thermal analysis could throw light on the relative stabilities of complexes involving such cyclic compounds and metals. Attempt has been made to get an idea of relative thermal stabilities of the thiocarboxylates and lactates [30] (carboxylate). It has been observed that aqua complex follows the same path as the carboxylates [30–38] and the pyridine complexes have the tendency to follow one-step decomposition. The copper complexes are less thermally stable.

Experimental

Synthesis of the complexes

2-oxocyclopentanedithiocarboxylic acid was prepared by the method of Takeshima *et al.* [11]. Substitution reaction of cyclopentanone and carbon

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disulfide was carried out in presence of aqueous alkali to get the acid. 60 g of KOH pellets were dissolved in 60 mL of cold water in a beaker to which 10 mL of cyclopentane (BDH) and 9 mL of carbon disulfide (BDH) were added slowly one after another. The beaker was kept in ice bath. It was followed by stirring till the colour changed to yellow and then dark brown. Using a separating funnel, the mixture was washed twice with benzene to remove the excess of carbon disulfide. Each time, the lower dark layer was taken. It was poured slowly and cautiously into a mixture of 100 mL of conc. HCl, 400 mL of H_2O and about 500 g of ice with stirring. A reddish brown precipitate appeared which was filtered on pump, washed with water and dried. The compound was recrystallised using minimum quantity of hot rectified spirit and dried. Shining deep red crystals with yellowish tint, were obtained (*m.p.* 90°C). Molar ratios (1:1/1:2) of the respective metal chlorides and the ketone were taken for complexation. These were dissolved separately in minimum quantity of hot rectified spirit. The ligand solution was added slowly with constant stirring to the salt solution. In case of the pyridino/morpholino complex, the base was added drop wise in appropriate molar ratio with shaking until new precipitate appeared. It was followed by dilution with cold water except in cases of the iron and the zinc complexes. In case of the iron complex, the washing was done by ether after filtration on pump.

Methods

The stoichiometry of the dried complex was established using routine elemental analysis and molecular mass determination (Table 1). Magnetic susceptibility measurements were made on a Gouy's balance. Electronic spectra were recorded on a Beckman DU6 spectrophotometer. IR spectra of the freshly prepared samples were also recorded on a Perkin Elmer Spectrophotometer 577 over a range of 4000–200 cm^{-1} using KBr-supporting disc.

Thermal analysis of the freshly prepared compound was carried out by crushing and pouring it loosely into the sample holder of a Stanton-Redcroft TG 750 thermobalance and dispersing it well. Sample size was kept at 4–8 mg to minimize the impact of heat and mass-transfer phenomena and the TG curves were recorded keeping dry air as the purge gas and heating rate was programmed at 10°C min^{-1}. The residues were analyzed for percentage of the metal by dissolving as usual.

Results and discussion

The copper complex, $CuL_2'H_2O$ exhibits an anomalous magnetic moment of 1.34 B.M. which is apparently on account of dimerisation of the compound in the solid-state. The other copper complexes having bases are diamagnetic and result from auto-reduction of copper(II) to copper(I) on addition of bases. The iron complex is diamagnetic and is a dimer. The charge transfer bands in the spectra have been found to be obscuring the normal *d–d* bands. In case of the copper(II) complex, charge transfer bands at 40000, 32790 and 24100 cm^{-1} may be attributed to $\sigma \rightarrow d_x2_{-y}2$, $\pi \rightarrow d_x2_{-y}2$ and $\pi(n) \rightarrow d_x2_{-y}2$ absorptions of the organic constituents [39]. Electronic transitions of iron(III) complexes may be assigned to interligand transitions (43480 cm^{-1}) and to metal to ligand or ligand to metal charge transfers (26670 cm^{-1}).

Table 1 Results of elemental analysis [found (calcd)%] and basic physical properties of the complexes

| Composition | Colour | Solubility | | | | M | C | H | N | S | Mol. mass |
		Abs. alcohol	Ether	Chloroform	Acetone						
FeL₂py₂	Brown	s(yellowish green soln)	sp	ns	ph	10.53 (10.49)	49.72 (49.62)	4.65 (4.51)	5.32 (5.62)	24.21 (24.06)	533.1
(CuLpy)₂	Dark brown	p	p	p	p	21.21 (21.06)	43.5 (43.78)	3.83 (3.98)	4.42 (4.64)	21.4 (21.22)	602.4
(CuLmorph)₂	Dark brown	p	p	p	p	20.42 (20.51)	38.8 (38.77)	5.02 (5.16)	4.33 (4.52)	20.75 (20.67)	620.3
CuL₂H₂O	Brown	pw	p	sw	sp	15.67 (15.89)	35.86 (36.04)	4.1 (4.0)	–	31.89 (32.04)	400.28
(ZnLpy)₂	Yellowish brown	p	ns	s	s	21.22 (21.54)	43.53 (43.49)	4.02 (3.95)	4.47 (4.61)	21.2 (21.08)	604.70
(ZnLmorph)₂	Brown	p	p	p	p	21.12 (20.99)	38.62 (38.53)	5.2 (5.13)	4.42 (4.49)	20.7 (20.55)	622.09

(s=soluble; sw=soluble on warming; p=partly soluble; pw=partly soluble on warming; sp=sparingly soluble; ph=partly soluble when hot; ns=not soluble)

The carbonyl frequency remains unaltered on chelation and this eliminates the possibility of the involvement of the group in coordination [40]. The C=S frequency drops in each case indicating bonding through the sulfur. The vibrational frequency earlier reported [11] at 1700 cm^{-1} has been found at 1660 cm^{-1}. A new peak at 3410 cm^{-1} may be due to the lattice water. The doublets in the range 400–320 cm^{-1} appear in complexes exhibiting coordination through the sulfur. The peaks at 2480

Table 2 Kinetic parameters of thermal decomposition of the complexes (E in kJ mol^{-1}, A in s^{-1} and $\Delta S^{\#}$ in J K^{-1} mol^{-1})

Composition	Decomposition step	Kinetic parameter	F–C	C–R	F–S–W
FeL$_2$py$_2$	1st	E	57.4	44.03	42.54
		A	$3.49 \cdot 10^6$	$6.25 \cdot 10^1$	$1.13 \cdot 10^2$
		n	3.3	1	–
		$\Delta S^{\#}$	86.89	–4.02	0.90
	2nd	E	43.6	37.35	36.54
		A	$4.42 \cdot 10^2$	$0.127 \cdot 10^2$	$1.2 \cdot 10^2$
		n	4.1	2	–
		$\Delta S^{\#}$	9.03	–39.63	–20.98
(CuLpy)$_2$		E	49.04	21.7	29.83
		A	$3.26 \cdot 10^3$	$2.0 \cdot 10^3$	$1.76 \cdot 10^4$
		n	4.1	1	–
		$\Delta S^{\#}$	26.80	–72.85	35.73
(CuLmorph)$_2$	1st	E	52.89	24.4	25.1
		A	$4.4 \cdot 10^5$	$5.24 \cdot 10^4$	$2.33 \cdot 10^2$
		n	5	1	–
		$\Delta S^{\#}$	70.31	–43.13	–30.7
	2nd	E	38.28	48.86	42.55
		A	$1 \cdot 10^2$	$1.91 \cdot 10^2$	$4.45 \cdot 10^3$
		n	2	2	–
		$\Delta S^{\#}$	–2.39	–16.23	–9.19
CuL$_2$H$_2$O	1st	E	194.77	44.03	44.27
		A	$1.84 \cdot 10^{25}$	$1.498 \cdot 10^3$	$2.99 \cdot 10^3$
		n	6.1	0	–
		$\Delta S^{\#}$	449.70	23.74	29.48
	2nd	E	105.27	93.7	95.76
		A	$3.06 \cdot 10^6$	$4.4 \cdot 10^4$	$8.68 \cdot 10^4$
		n	1.1	2	–
		$\Delta S^{\#}$	82.84	47.56	53.21
(ZnLpy)$_2$		E	90.54	20.42	29.43
		A	$4.05 \cdot 10^6$	$4.09 \cdot 10^2$	$5.02 \cdot 10^2$
		n	3.5	2	–
		$\Delta S^{\#}$	86.24	–66.84	–63.71
(ZnLmorph)$_2$	1st	E	97.61	43.54	44.57
		A	$1.64 \cdot 10^{11}$	$1.9 \cdot 10^2$	$1.54 \cdot 10^2$
		n	5.1	1	–
		$\Delta S^{\#}$	176.13	–14.04	3.33
	2nd	E	95.73	88.19	91.6
		A	$2.22 \cdot 10^6$	$5.86 \cdot 10^4$	$4.36 \cdot 10^5$
		n	2	2	–
		$\Delta S^{\#}$	81.08	50.85	67.55

and 1660 cm^{-1} have been assigned to ν_{SH} and $\nu_{C=O}$, respectively. The former frequency disappears completely. The peaks at 2960 cm^{-1}(ν_{-CH_2-asym}); 1460, 1450 cm^{-1} (δ_{-CH_2-}) and cyclic ring vibrations; 1120 cm^{-1} (C–C–C stretching vibrations; δ_{C-H} overtones) and at 1075 cm^{-1} (combination band of $\nu_{C=O}$ and in plane C–H bending; shifts up to 1085 cm^{-1}) remain mostly unaltered. The peaks at 2910 cm^{-1}($\nu_{sym(-CH_2-)}$ changes up to 2940 cm^{-1}); 1660 cm^{-1} ($\nu_{C=O}$; shifts up to 1670 cm^{-1}); 1581 cm^{-1} ($\nu_{C=O}$ and cyclic ring vibrations; shifts up to 1570 cm^{-1}); 1540 cm^{-1} (cyclic ring vibrations; shifts up to 1530 cm^{-1}); 1250 cm^{-1} ($\nu_{C=S}$; $\nu_{C=O}$; splits to 1285 and 1230 cm^{-1} after elimination of $\nu_{-C=S}$ bands) and 1025 cm^{-1} ($\nu_{C=S}$; $\nu_{C=O}$; $\nu_{C(=S)-S-H}$;$\nu_{C=O}$ asym.; splits in range 1020–1005 cm^{-1}); a new peak ca. 945 cm^{-1} (coordinated water appearing only in complex); 996 cm^{-1} ($\nu_{-C=S}$; $\nu_{C=O}$; $\nu_{C=S\ asy}$; δ_{C-SH}; splitting to respective vibrations on elimination of $\nu_{C=S}$ in complexes); the absence of the peak at 800 cm^{-1} ($\nu_{C=S\ sym}$) in complexes after elimination of $\nu_{C=S}$ bands and the new peaks in the said range of 400–320 cm^{-1} indicate linkage through the two sulfur atoms of the –C(=S)–S group.

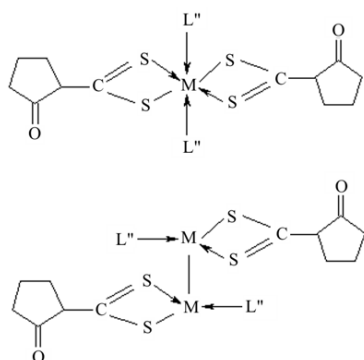The structures that were proposed on the basis of these discussions are given in Fig. 1.

Fig. 1 Bonding of complexes

The pyridino ternary complexes of copper and zinc decompose in one step (Fig. 2). In other such complexes, the base has a tendency to escape early followed by a brief stabilization after which the second step starts. The copper complexes start to decompose early. The morpholino complex is stable up to 75°C and CuL$'_2$H$_2$O, up to 90°C. The iron complex is quite stable up to 140°C and this could well be suggested as an alternative mode for quantitative estimation of iron. The zinc complexes are stable up to ca. 120°C. CuL$'_2$H$_2$O shows similarity in the decomposition pattern with that of the carboxylates. The α–T plot of none of these steps shows any period of induction hence no physisorption or surface nucleation is indicated [41]. The thermogravimetric data were subjected
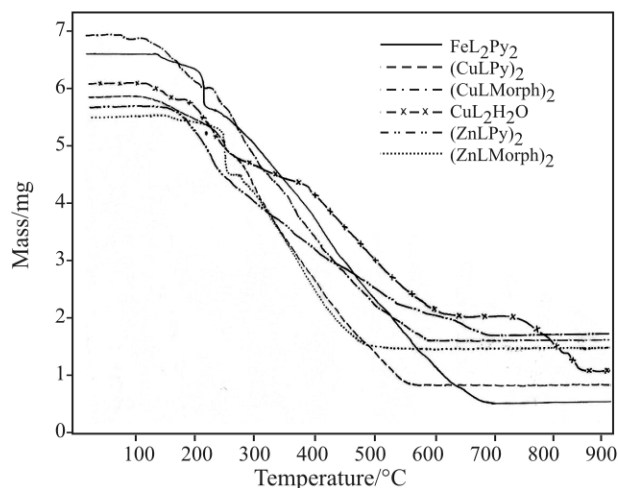

Fig. 2 TG curves of the complexes

to kinetic analysis using the Freeman–Carroll [42]; Coats–Redfern [43] and Fuoss–Salyer–Wilson [44] methods. The values of n, E, A and $\Delta S^{\#}$ as approximated for the different steps are given in Table 2. The results from the latter two methods are in good agreement with each other and could be accepted.

Conclusions

The following conclusions are drawn from the study:

- The overall thermal stability of the 2-oxocyclopentanedithiocarboxylato complexes of the three metals with the volatile ligands was found to be in the order:

$$(CuLmorph)_2 < CuL_2H_2O < (CuLpy)_2 < (ZnLmorph)_2 < (ZnLpy)_2 < FeL_2py_2$$

- CuL$'_2$H$_2$O shows similarity in the decomposition pattern with that of the carboxylates.
- The other copper complexes having bases are diamagnetic and result from autoreduction of copper(II) to copper(I) on addition of bases.
- The iron complex is diamagnetic and is a dimer.
- The values of entropy of activation of all the steps of all the compounds except the first step of the iron complex, the morpholino zinc complex and the second step of the morpholino copper complex have large magnitude which may be assigned to possible rearrangements among various degrees of freedom leading to a more ordered structure of the transition states.

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