

## **THERMOGRAVIMETRIC STUDIES ON SOME Cu(II) AMINE COMPLEXES**

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Thermogravimetric analysis of solid state bis-Cu(II) amine complexes  $\text{CuL}_2\text{X}_2$ , where  $X = \text{Cl}^-$  or  $\text{NO}_3^-$  and  $L =$  ethylenediamine (en), tetramethylethylenediamine (tmn), *o*-phenylenediamine (opd) and 2,2' bipyridyl (bpy), has been carried out and the kinetic parameters have been determined by fitting the observed mass losses corresponding to various steps using the Coats and Redfern equation. These studies show that the activation energies of these complexes decrease on changing the ligand in the order:  $\text{bpy} > \text{opd} > \text{en} > \text{tmn}$ . This trend can be attributed to the rigidity of the N—C—C—N skeleton in the bpy and opd ligands and steric crowding at the nitrogens in the tmn ligand. The majority of the decomposition steps were found to be composite in nature and frequently involved fractional groups expelled from the complexes. From the observation of  $E_a > \Delta H$ , the thermal decomposition process of these complexes appears to be governed by the "nucleation and growth" mechanism.

Our studies on the temperature dependence of the electrical conductivity of some solid state bis Cu(II) amine complexes  $\text{CuL}_2\text{X}_2$  where  $X = \text{Cl}^-$  or  $\text{NO}_3^-$  and  $L =$  ethylenediamine (en), tetramethylethylenediamine (tmn), *o*-phenylenediamine (opd) and 2,2' bipyridyl (bpy), exhibited a number of discontinuities in various temperature intervals which are indicative of structural phase changes and/or thermal decomposition. Though the literature on such coordination complexes is quite extensive [1], except for some complexes of  $\text{Cu(II)SO}_4$  [2], very little is known about their thermal stability. Therefore, in order to understand the reasons for the above-mentioned discontinuities in the electrical conductivity at various temperatures, the thermal properties of the complexes were studied.

### **Experimental**

The above-mentioned Cu(II) amine complexes were prepared by treating aqueous alcoholic solutions of  $\text{CuX}_2$  ( $X = \text{Cl}^-$  or  $\text{NO}_3^-$ ) and the appropriate ligands  $L$  (en, tmn, opd, bpy) in the stoichiometric ratio of 1:2 by following procedures similar to those reported in the literature [3]. The complexes were characterised by elemental microanalysis (C, H, N), estimation of Cu [4] and

chlorine by ion-exchange chromatography [4] and also by infrared and electronic spectra. Thermogravimetric (TG) analysis was carried out on a home-made thermobalance in air atmosphere at a constant heating rate of 3 deg/min up to about 800° using about 60–70 mg of sample in a quartz crucible.

## Results and discussion

### *Elemental and spectral analysis*

The elemental and spectral analysis showed that the bis-en complex of Cu(II) chloride was a monohydrate and the bis-tmn complex of Cu(II) nitrate was a trihydrate while other complexes were anhydrous; the molecular (empirical) formulae of the complexes were (I)— $\text{Cu(en)}_2(\text{NO}_3)_2$ , (II)— $\text{Cu(tmn)}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , (III)— $\text{Cu(opd)}_2(\text{NO}_3)_2$ , (IV)— $\text{Cu(bpy)}_2(\text{NO}_3)_2$ , (V)— $\text{Cu(en)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  and (VI)— $\text{Cu(bpy)}_2\text{Cl}_2$ . The infrared and electronic spectral data of the complexes were in good agreement with the reported [5] data on similar complexes and were indicative of an octahedral structure with the four N-atoms from the two ligand molecules having a square planar arrangement about the central Cu-atom.

### *Thermal analysis*

The TG curve for  $\text{Cu(en)}_2(\text{NO}_3)_2$  consisted of a single step in the range 220–250° corresponding to simultaneous loss of both the ligand (en) molecules and anions ( $\text{NO}_3^-$ ) leaving behind CuO as the residue (Fig. 1). This sudden loss of the fragments due to an explosion-type reaction appears to be responsible for the somewhat larger difference between the observed and calculated % mass losses. The decomposition of  $\text{Cu(tmn)}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  takes place in two steps; the first step over the range 100–120° corresponding to fractional loss of the crystal water ( $\sim 2.25 \text{ H}_2\text{O}$  molecules) is followed by loss of the remaining 0.75  $\text{H}_2\text{O}$  together with both the ligand molecules (tmn) and  $\text{N}_2\text{O}_5$ , the final residue again being CuO. The decomposition of  $\text{Cu(opd)}_2(\text{NO}_3)_2$  proceeds in two steps; the first one around 190° corresponding to loss of both ligand molecules (opd) is followed by loss of  $\text{N}_2\text{O}_5$  over the range 270–370° leaving behind CuO. The dissociation of  $\text{Cu(bpy)}_2(\text{NO}_3)_2$  also takes place in two steps; the first one between 280 and 300° corresponds to the loss of both ligand molecules (bpy) together with 0.55  $\text{N}_2\text{O}_5$  which is followed by the next step in the range 320–410° with loss of 0.45  $\text{N}_2\text{O}_5$ , again resulting in CuO as the final residue. The common feature of all these Cu(II) nitrate complexes is that their dissociation is preceded by liquefaction and this appears to be a general feature of other compounds containing nitrate groups. The TG curve of  $\text{Cu(bpy)}_2\text{Cl}_2$  also

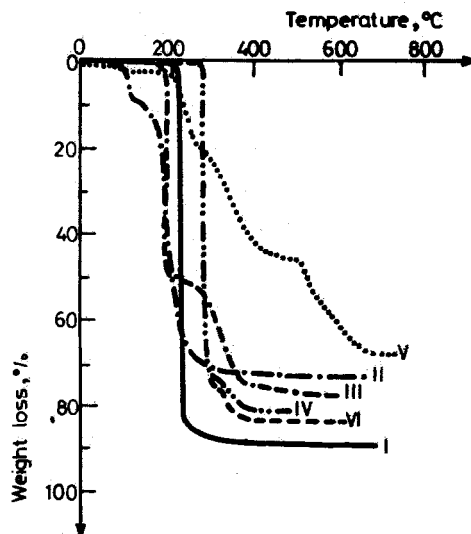


Fig. 1 TG curves for Cu(II)-amine complexes. I:  $\text{Cu(en)}_2(\text{NO}_3)_2$ , II:  $\text{Cu(tmn)}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , III:  $\text{Cu(opd)}_2(\text{NO}_3)_2$ , IV:  $\text{Cu(bpy)}_2(\text{NO}_3)_2$ , V:  $\text{Cu(en)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ , VI:  $\text{Cu(bpy)}_2\text{Cl}_2$

consisted of two steps; the first one like in the case of  $\text{Cu(bpy)}_2(\text{NO}_3)_2$  over  $280\text{--}300^\circ$  corresponding to loss of both ligand molecules (bpy) together with loss of  $0.3 \text{ Cl}_2$  and the second one over  $330\text{--}420^\circ$  with loss of the remaining  $0.7 \text{ Cl}_2$  ultimately resulting in  $\text{CuO}$  as the residue. The TG curve of  $\text{Cu(en)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  was somewhat more complicated showing four steps: the first step over  $90\text{--}100^\circ$  corresponding to a fractional loss of crystal water ( $0.35 \text{ H}_2\text{O}$ ), followed by the second step over  $220\text{--}280^\circ$  with loss of the remaining crystal water ( $0.65 \text{ H}_2\text{O}$ ) together with one ligand molecule (en), the third step over  $300\text{--}440^\circ$  resulting in loss of the second ligand molecule (en) and finally the last step over  $510\text{--}640^\circ$  with loss of both the anions ( $2\text{Cl}^-$ ) ultimately resulting in  $\text{CuO}$  as in all other cases. This complex also showed liquefaction prior to the first step of dissociation. The apparent liquefaction of  $\text{Cu(en)}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  and  $\text{Cu(tmn)}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  preceding the first decomposition steps is attributable to the presence of water of crystallisation.

The kinetic parameters, viz., the order of reaction ( $n$ ), activation energy ( $E_a/\text{kJ mol}^{-1}$ ), the frequency factor ( $A$ ) and the rate constant ( $k$ ) corresponding to each of the observed steps of decomposition in the TG curves were deduced by fitting the observed degree of decomposition ( $\alpha$ ) related to each step to the Coats and Redfern equation [6]. The kinetic parameters so obtained corresponding to various decomposition steps of all the complexes are included in Table 1.

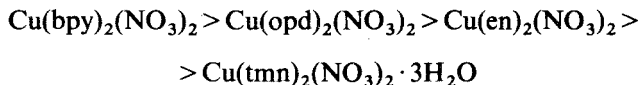
Thermal decompositions of systems involving metal nitrates and nitrites are

Table 1 Data of thermal decomposition and kinetic parameters

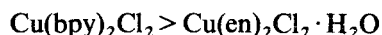
Complex	Step	Temp. range, °C	Mass loss, %		Probable composition of		$n$	$E_a$ /kJ mol <sup>-1</sup>	$k$ (T/K)
			obs.	calc.	expelled group	residue			
I Cu(en) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	1	220-250	84.5	(79.3)	2 en + N <sub>2</sub> O <sub>5</sub>	CuO	0.75	573	0.94 (506)
	1	100-120	8.5	(8.5)	2.25 H <sub>2</sub> O	Cu(tmn) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 0.75H <sub>2</sub> O	2.0	427	0.69 (385)
II Cu(tmn) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> · 3H <sub>2</sub> O	2	150-360	72.3	(74.6)	2 tmn + N <sub>2</sub> O <sub>5</sub> + 0.75 H <sub>2</sub> O	CuO	2.0	161	0.25 (483)
	1	190-210	51.0	(53.5)	2 opd	Cu(NO <sub>3</sub> ) <sub>2</sub>	0.75	628	1.17 (476)
III Cu(opd) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	2	270-370	24.0	(26.7)	N <sub>2</sub> O <sub>5</sub>	CuO	2.5	144	2.40 (607)
	1	280-300	73.0	(74.3)	2 bpy + 0.55 N <sub>2</sub> O <sub>5</sub>	CuN <sub>0.9</sub> O <sub>3.25</sub>	0.75	995	0.58 (566)
IV Cu(bpy) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	2	320-410	8.2	(9.7)	0.45 N <sub>2</sub> O <sub>5</sub>	CuO	2.5	571	0.96 (621)
	1	90-100	2.3	(2.3)	0.35 H <sub>2</sub> O	Cu(en) <sub>2</sub> Cl <sub>2</sub> · 0.65 H <sub>2</sub> O	2.0	615	5.89 (371)
V Cu(en) <sub>2</sub> Cl <sub>2</sub> · H <sub>2</sub> O	2	220-280	24.0	(26.3)	0.65 H <sub>2</sub> O + en	Cu(en) <sub>2</sub> Cl <sub>2</sub>	2.0	312	0.56 (526)
	3	300-440	21.0	(22.0)	en	CuCl <sub>2</sub>	1.75	218	0.20 (853)
VI Cu(bpy) <sub>2</sub> Cl <sub>2</sub>	4	510-640	22.0	(26.0)	Cl <sub>2</sub>	CuO	1.75	218	0.20 (853)
	1	280-300	74.8	(74.6)	2 bpy + 0.3 Cl <sub>2</sub>	CuCl <sub>1.4</sub>	0.75	900	0.91 (566)
	2	330-420	8.0	(11.1)	0.7 Cl <sub>2</sub>	CuO	2.0	128	0.10 (618)

found to be complicated by the occurrence of interactions between the evolved oxides of nitrogen and a possibility of phase transition altering the behaviour of the original reactant [7]. The present studies also indicate such complexity as experienced in the attempt to fit the observed % mass losses to the calculated ones requiring assumptions of composite steps as indicated under "probable composition of expelled group" in Table 1. This implies that the majority of the decomposition products are frequently fractional groups being lost from the complex. The order of reaction ( $n$ ) corresponding to the best straight line graphs range from 0.75 to 2.5. Though the concept of "order of a reacton" is not well defined for solid state thermal decompositions, they can be taken to correspond approximately to the dimensionality of the growth process in the thermal decomposition. Thus, the cases of  $n \leq 1$ ,  $1 < n \leq 2$  and  $2 < n \leq 3$  can be taken to imply the nucleation and growth processes to be approximately one-, two- and three-dimensional, respectively. Because of the composite nature of the steps the calculated activation energies and the rate constants are to be considered as averages for the products involved in the steps. In spite of these limitations, they indicate some general trends as follows.

Within the group of the  $\text{Cu}(\text{NO}_3)_2$  complexes containing different ligands, the activation energies are found to decrease in the order:



Similarly within the group of Cu(II) chloride complexes the activation energies are found to decrease as



If the magnitude of activation energy is considered as a measure of stability, then the above trends imply that the complexes of cyclic ligands such as bpy and opd are stronger than those of open chain ligands such as en and tmn. The greater stability of bpy and opd complexes may be ascribed to the rigidity of their N—C—N skeletons. Furthermore, the higher stability of a bpy complex than that of an opd complex may be due to the stronger coordinating ability of the ring-nitrogens of the former. Similarly, the lowest stability of a tmn complex might be due to the steric crowding at the coordinating N due to two methyl groups. A comparison of the results for en complexes of Cu(II) chloride and Cu(II) nitrate and similarly those for the bpy complexes of Cu(II) chloride and Cu(II) nitrate show that they follow quite different courses of reaction and the related kinetic parameters also vary considerably. This is consistent with the general observation that, "changing the anion has a pronounced effect on the thermal stability of a complex" [1, 8]. For all these complexes, the activation energies for the steps involving loss of ligand

molecules are all found to be higher than the reported enthalpies in solution [1]. Though the thermodynamic quantities for reactions in solutions and solid state cannot be compared directly, the observation that  $\Delta H < E_a$  can be taken to imply that the decomposition rate is governed by the "nucleation and growth" mechanism [9].

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**Zusammenfassung** — Kupfer(II)-bisaminkomplexe der Formel  $\text{CuL}_2\text{X}_2$  mit  $X = \text{Cl}^-$  oder  $\text{NO}_3^-$  und  $L =$  Äthylendiamin (en), Tetramethyläthylendiamin (tmn), *o*-Phenylendiamin (opd) und 2,2'-Bipyridyl (bpy) wurden thermogravimetrisch untersucht und die kinetischen Parameter aus den gemessenen, zu den entsprechenden Schritten gehörenden Masseverlustwerten unter Anwendung der Gleichung von Coats und Redfern bestimmt. Es ergab sich, daß die Aktivierungsenergie dieser Komplexe entsprechend folgender Ligandenreihe abnimmt:  $\text{bpy} > \text{opd} > \text{en} > \text{tmn}$ . Dies kann bei den bpy und opd Liganden auf die Starrheit des N—C—N Fragmentes und im Falle der tmn Liganden auf eine räumliche Überfülltheit am Stickstoffatom zurückgeführt werden. Die Mehrzahl der Zersetzungsschritte sind komplexer Natur und haben häufig aus den Komplexen stammende Teilgruppen zum Ergebnis. Aufgrund der Beobachtung  $E_a > \Delta H$  scheint der thermische Zersetzungsvorgang dieser Komplexe durch einen „Keimbildungs- und -wachstums“ mechanismus bestimmt zu werden.

**Резюме** — Проведен термогравиметрический анализ твердых бис-(амино)медь(II) комплексов общей формулы  $\text{CuL}_2\text{X}_2$ , где  $X =$  хлорид или нитрат, а  $L =$  этилендиамин (en), тетраметилэтилендиамин (tmn), *o*-фенилендиамин (opd) и 2,2-бипиридил (bpy). С помощью уравнения Коутса—Рэдферна были определены кинетические параметры реакций разложения. Проведенные

исследования показали, что энергии активации этих комплексов уменьшаются в ряду лигандов в следующем порядке  $brp > opd > ep > imn$ . Такой порядок может быть обусловлен жесткостью скелетного звена  $N-C-C-N$  в бипиридине и *o*-фенилендиамине и стерическими препятствиями при атомах азота в тетраметилендиаминах. Установлено, что основные стадии разложения носят сложный характер и часто включают отдельные группы, выделяющиеся из комплексов. Исходя из значений  $E_a$  и  $\Delta H$ , можно сделать заключение, что процесс термического разложения подчиняется механизму «образования и роста центров кристаллизации».