

## **SYNTHESIS, SPECTRAL AND THERMAL STUDIES OF *o*-VANILLIN OXIME COMPLEXES OF ZINC(II), CADMIUM(II) AND MERCURY(II)**

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### **Abstract**

Zinc(II), cadmium(II) and mercury(II) complexes of *o*-vanillin oxime have been synthesized and characterized by different physicochemical techniques. All the complexes have been subjected to non-isothermal decomposition studies in nitrogen atmosphere using thermogravimetry. The kinetic parameters for the decomposition of these complexes were evaluated using different methods and comparatively better results were obtained by these different methods. It has also been found that the decomposition processes of all these complexes follow first order kinetics.

**Keywords:** cadmium(II), complexes, mercury(II), *o*-vanillin oxime, spectral and thermal studies, synthesis, zinc(II)

### **Introduction**

In recent years considerable interest has been shown in the coordination chemistry of bivalent transition metals with orthohydroxy oximes [1, 2] because of their applications as analytical reagents in solvent extraction systems [3–4] and in hydrometallurgy [5–7]. However, most of the studies have been concerned with kinetic and equilibrium extraction properties and relatively little work has been reported on the isolation and characterization of the extracted species. In continuation of our work on metal complexes of *o*-vanillin oxime [2], we now report the synthesis, characterization and thermal studies of zinc(II), cadmium(II) and mercury(II) complexes of *o*-vanillin oxime.

### **Experimental**

All chemicals used were of BDH AnalaR grade. The ligand *o*-vanillin oxime(HL) was prepared by the reported method [8]. The structure of HL is shown in Fig. 1. The metal(II) complexes were prepared by refluxing a mixture of metal(II) acetate and HL in the molar ratio of 1:1 (2:1 in the case of zinc(II) complex) in methanol for

about one h in a hot water bath. The crystalline complex formed on cooling was filtered, washed, recrystallized from methanol and dried over  $P_4O_{10}$ . The physico-chemical measurements were made as described previously [2].

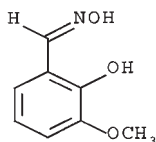


Fig. 1 Structure of *o*-vanilline oxime, HL

## Results and discussion

### Stereochemical investigations

The colours, elemental analyses and stoichiometries of HL and its complexes are given in Table 1. Analytical data of the complexes correspond to  $[Zn(HL)_2(OAc)_2(H_2O)_2]$  and  $[M_2L_2(OAc)_2(H_2O)_2]$  where  $M=Cd$  and  $Hg$ . Zinc(II) complex is soluble in methanol, isopropanol, DMF, DMSO, nitrobenzene and chloroform, while the complexes of cadmium(II) and mercury(II) are insoluble. The molar conductance of zinc(II) complex was measured both in methanol and DMF and the results show it to be a non-electrolyte.

Table 1 Colours and elemental analysis data

Compound	Colour	Elemental analysis data		
		found/(calcd)/%		
		C	H	N
HL	pale yellow	57.9 (57.5)	5.5 (5.4)	8.5 (8.4)
$[Zn(HL)_2(OAc)_2(H_2O)_2]$	pale yellow	44.4 (44.0)	4.8 (4.7)	7.3 (7.1)
$[Cd_2L_2(OAc)_2(H_2O)_2]$	colourless	33.9 (33.7)	3.1 (3.6)	4.2 (3.9)
$[Hg_2L_2(OAc)_2(H_2O)_2]$	yellow	26.2 (26.7)	2.5 (2.8)	3.3 (3.1)

Infrared spectral bands of the ligand and its complexes with the tentative assignments are presented in Table 2. Upon coordination, the intense bands stemming from the stretching and bending vibration modes of the phenolic  $-OH$  disappear indicating the removal of a hydrogen atom, while the sharp band at  $3359\text{ cm}^{-1}$  which is attributed to the stretching vibration of the  $O-H$  bond in the  $N-O-H$  group that is shifted significantly to lower frequencies, indicating coordination of the nitrogen atom [9]. Evidence for this coordination also arises from the small shifts towards lower frequencies of the band at  $1618\text{ cm}^{-1}$  assigned to the  $C=N$  bond. The bands originating from the  $C-O$  stretching vibrations exhibit very small shifts while their intensity is enhanced appreciably. In the region  $400-600\text{ cm}^{-1}$  the bands attributable to  $M-N$  bonds are observed, while bands due to the  $M-O$  is not so distinguishable. The coordination of water to metal in all complexes is indicated by appearance of new bands in the  $3700-3800\text{ cm}^{-1}$  region. The asymmetric

**Table 2** Infrared band assignment of the oxime and its metal complexes\*

Compound	Adsorption maxima/cm <sup>-1</sup>							
	$\nu(\text{=N-OH})$	$\nu(\text{-C=N})$	$\nu(\phi\text{OH})$	$\delta(\phi\text{OH})$	$\nu(\text{C-O})$	$\nu(\text{M-N})$	$\nu_a(\text{COO})$	$\nu_s(\text{COO})$
HL	3359 s	1618 s	1410 s	1250 s	1190 m	–	–	–
[Zn(HL) <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3280 s	1600 s	–	–	1205 sh	550 s	1585 s	1310 s
[Cd <sub>2</sub> L <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3150 s	1595 s	–	–	1195 s	490 s	1603 s	1340 s
[Hg <sub>2</sub> L <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3160 s	1595 s	–	–	1205 s	460 w	1600 s	1295 s

\*s=strong, m=medium, w=weak, sh=shoulder,  $\nu_a$ =asymmetric stretching and  $\nu_s$ =symmetric stretching

and symmetric C–O–O stretching bands, corresponding to unidentate type of acetato ligand are also present in all three complexes [10].

#### *Thermal decomposition studies*

During the past few years, the thermal properties of metal complexes have been investigated extensively as one of the most interesting topics in the field of coordination chemistry [11–14]. Even though a large number of articles have appeared dealing with the applications of thermal analyses to metal complexes, only a little work has been done in the area of their thermal decomposition kinetics [2, 15–25].

**Table 3** Thermal decomposition data

Complex	$T_s$ / K	Decomposition temperature range/ K	Metal residue from TG (theoretical) %
[Zn(HL) <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	703	400–950	11.9 (11.8)
[Cd <sub>2</sub> L <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	683	440–830	32.3 (32.1)
[Hg <sub>2</sub> L <sub>2</sub> (OAc) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	704	400–950	45.6 (45.3)

We have studied the thermal decomposition and kinetics of all these complexes. The general thermal behaviour of these complexes, stability ranges, DTG peak temperatures ( $T_s$ ) and mass loss data are given in Table 3. The theoretical and observed mass losses for the decomposition of all these complexes agree very well. In all cases the residue after the decomposition is found to be the corresponding metal.

It is well known that the basic form of the equation for the kinetic analysis of solid-state non-isothermal decomposition reaction is:

$$\ln g(\alpha) = \ln[A E / q R] + \ln p(x) \quad (1)$$

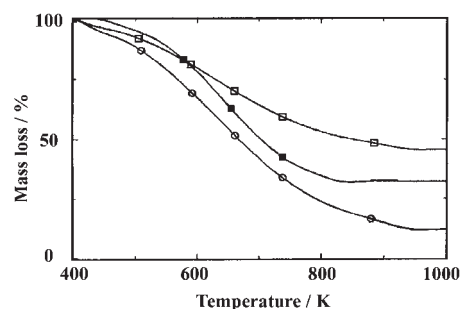
where

$$p(x) = \int_x^{\infty} e^{-x} / x^2$$

and  $x = E/RT$ ,  $A$  is the Arrhenius pre-exponential factor,  $E$  is the activation energy,  $R$  is the gas constant and  $q$  is the heating rate.

Several methods [26–32] are available in the literature for the analysis of a non-isothermal TG trace and for obtaining values of kinetic parameters. Some authors [26–28] are of the opinion that the method based on fitting the reaction model tend to produce unreliable values of Arrhenius parameters. As an alternative they proposed model free methods. However, we obtained better results for model fitting methods, like several other workers [15–18, 24, 25]. In model fitting methods Eq. (1) is utilized in three approaches, viz, integral, differential and approximation. The most accurate among them is the integral method [33–34].

The TG curves for the three complexes are shown in Fig. 2. The instrumental TG curves were redrawn as curves of the fraction decomposed vs. temperature to obtain



**Fig. 2** TG curves of the complexes,  $\circ$  –  $[\text{Zn}(\text{HL})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$ ,  $\blacksquare$  –  $[\text{Cd}_2\text{L}_2(\text{OAc})_2(\text{H}_2\text{O})_2]$  and  $\square$  –  $[\text{Hg}_2\text{L}_2(\text{OAc})_2(\text{H}_2\text{O})_2]$

primary  $\alpha$ - $T$  data. The kinetic analyses of  $\alpha$ - $T$  data using various solid-state mechanistic equations [23] shows that the F1 (first order) mechanism gives the best linear fit (with a maximum value of  $r$ ) in all cases. Accordingly  $E$  was calculated from the slope and  $A$  was calculated from the intercept value as described in an earlier work [35]. The kinetic parameters were also evaluated using Coats-Redfern [29], Freeman-Carroll [30] and Horowitz-Metzger [31] equations.

**Table 4** Kinetic data obtained from the general approach (GM) and Coats-Redfern (CR), Freeman-Carroll (FC) and Horowitz-Metzger (HM) methods

Complex	Method	$E/$ $\text{kJ mol}^{-1}$	$\ln A/$ $\text{s}^{-1}$	$-\Delta S/$ $\text{J K}^{-1} \text{mol}^{-1}$	$r$
$[\text{Zn}(\text{HL})_2(\text{OAc})_2(\text{H}_2\text{O})_2]$	GM	23.84	1.56	239.10	-0.9999
	CR	18.51	0.15	250.81	-0.9987
	FC	23.31	1.82	236.92	-0.9996
	HM	31.98	2.92	227.78	0.9083
$[\text{Cd}_2\text{L}_2(\text{OAc})_2(\text{H}_2\text{O})_2]$	GM	36.53	2.83	228.29	-0.9999
	CR	31.25	3.07	226.29	-0.9997
	FC	34.87	3.94	219.06	-0.9992
	HM	45.13	5.78	203.76	0.9956
$[\text{Hg}_2\text{L}_2(\text{OAc})_2(\text{H}_2\text{O})_2]$	GM	23.14	1.54	239.21	-0.9999
	CR	17.84	0.12	251.02	-0.9988
	FC	20.56	1.72	237.72	-0.9976
	HM	31.31	2.78	228.91	0.9906

The kinetic parameters for the general approach, and Coats-Redfern, Freeman-Carroll and Horowitz-Metzger methods are given in Table 4. The satisfactory values of  $r$  ( $\approx 1$ ) in all cases indicate good agreement with the experimental data. The values of kinetic parameters obtained from these four approaches are reasonable and in good

agreement to some extent. A close examination of the results reveals that these complexes show similar thermal behavior that is as expected given their similar structures.

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## References

- 1 M. E. Keeney, K. Osseo-Asare and K. A. Woods, *Coord. Chem. Rev.*, 59 (1984) 141.
- 2 M. R. P. Kurup, E. Lukose and K. Muraleedharan, *J. Therm. Anal. Cal.*, 59 (2000) 915.
- 3 A. Chakravorty, *Coord. Chem. Rev.*, 13 (1974) 1.
- 4 R. B. Singh, B. S. Garg and R. P. Singh, *Talanta*, 26 (1979) 425.
- 5 A. W. Ashbrook, *Coord. Chem. Rev.*, 16 (1975) 285.
- 6 J. S. Preston, *J. Inorg. Nucl. Chem.*, 37 (1975) 1235.
- 7 J. M. Pratt and R. I. Tilley, *Hydrometallurgy*, 5 (1979) 29.
- 8 A. I. Vogel, *A. Text Book of Practical Organic Chemistry*, 3rd Ed., Longmans, London 1973.
- 9 M. L. Kantouri and Hartophylles, *Polyhedron*, 7 (1992) 789.
- 10 B. S. Garg, M. R. P. Kurup, S. K. Jain and Y. K. Bhoon, *Transition Met. Chem.*, 13 (1988) 309.
- 11 J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand.*, 70 A (1966) 487.
- 12 A. V. Nikolaev, V. A. Logvinenko, V. M. Gorbachov and L. I. Myachina in I. Buzas (Ed.), *Thermal Analysis*, Vol. I, Hydon & Sons, London 1975.
- 13 J. O. Hill and R. J. Magee, *Rev. Inorg. Chem.*, 3 (1981) 141.
- 14 S. K. Sengupta and S. Kumar, *Thermochim. Acta*, 72 (1984) 349.
- 15 P. M. Madhusudhanam, P. N. K. Nambissan and C. G. R. Nair, *Thermochim. Acta*, 9 (1974) 149.
- 16 P. M. Madhusudhanam, K. K. M. Yusuff and C. G. R. Nair, *J. Thermal Anal.*, 8 (1975) 31.
- 17 V. Indira and G. Parameswaran, *J. Thermal Anal.*, 32 (1987) 1151.
- 18 K. Krishnan, K. N. Ninan and P. M. Madhusudhanam, *Thermochim. Acta*, 125 (1988) 111.
- 19 K. K. Aravindakshan and K. Muraleedharan, *J. Thermal Anal.*, 37 (1991) 791.
- 20 K. K. Aravindakshan and K. Muraleedharan, *Thermochim. Acta*, 159 (1990) 101.
- 21 R. L. Bohn in H. G. McAdie (Ed.), *Proc. First Toronto Symposium on Thermal Analysis*, Chemical Institute of Canada, 1983.
- 22 K. K. Aravindakshan and K. Muraleedharan, *J. Thermal Anal.*, 37 (1991) 803.
- 23 K. K. Aravindakshan and K. Muraleedharan, *Reactivity of Solids*, 8 (1990) 91.
- 24 R. L. Reed, L. Weber and B. S. Gottfried, *Ind. Eng. Chem. Fundament.*, 4 (1965) 38.
- 25 N. Saravanan and K. K. M. Yusuff, *React. Kinet. Catal. Lett.*, 55 (1995) 407.
- 26 J. H. Flynn and L. A. Wall, *Polym. Lett.*, 4 (1966) 323.
- 27 T. Ozava, *Bull. Chem. Soc. Jpn.*, 38 (1965) 1881.
- 28 J. Šesták and G. Berggren, *Thermochim. Acta*, 3 (1971) 1.
- 29 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.
- 30 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.
- 31 H. Horowitz and G. Metzger, *Anal. Chem.*, 35 (1963) 1464.
- 32 S. R. Dharwadkar and M. D. Karkhanavala, *Thermal Analysis*, Vol. II, Proc. 2nd ICTA, MA, Academic Press, New York 1969, p. 1049.
- 33 J. Šesták, V. Satava and W. W. Wendlandt, *Thermochim. Acta*, 7 (1973) 333.
- 34 J. Šesták, *Talanta*, 13 (1966) 567.
- 35 M. P. Kannan, K. Muraleedharan and T. Gangadevi, *Thermochim. Acta*, 186 (1991) 265.