Journal of Thermal Analysis, Vol. 35 (1989) 1603–1609

ZINC(II) COMPLEXES OF SALICYLIDENE AMINO ACIDS

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(Received September 27, 1988)

Several zinc(II) complexes of tridentate dibasic salicylidene amino acids have been prepared and characterized. All of them possess dimeric pseudo-octahedral structures, which were established on the basis of thermogravimetric analysis and superimposable infrared spectra of these complexes with those of manganese(II), cobalt(II), nickel(II), and magnesium(II) complexes.

Manganese(II), cobalt(II), nickel(II), and magnesium(II) complexes of salicylideneglycine (salglyH/H_2) (I) have dimeric pseudo-octahedral structures (II) through coordination of water molecules in the trans apical sites [1–4]. The salicylideneleucine Schiff base complex of manganese(II) favoured a four-coordinated anhydro dimeric structure (III) [1]. Bis(salicylideneglycinato)zinc(II) and other related complexes have been synthesized and characterized. Dimeric structures of these complexes have been established by thermogravimetric analyses and superimposable infrared spectra of the related complexes.

Experimental

To a warm solution of salicylaldehyde (0.5 g in 10 ml of ethanol) a hot aqueous solution of glycine (0.3 g in 5 ml of water) was added and the solution refluxed for 30 minutes on a steam bath. To this clear solution an ethanolic solution of zinc(II) acetate (0.75 g in 20 ml of ethanol) was added with stirring, and the resulting solution was refluxed, whereupon white crystals began to separate. After 30 minutes of refluxing the crystals were collected by filtration, triturated with hot

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water to remove any unreacted glycine, washed several times with ethanol, and finally dried over silica gel, yield 0.75 g.

Similar procedures were adopted for the preparation of the other zinc(II) salicylidene amino acid complexes.

Analyses and measurements

The complexes were decomposed by ignition, and zinc was determined as zinc oxide. Nitrogen was determined by the Dumas method, and chloride was determined as silver chloride. Microanalyses of carbon and hydrogen were carried out at CDRI, Lucknow (Table 1). Infrared spectra (Table 2) were run as KBr matrices. Thermogravimetric runs were made in a MOM derivatograph in a stream of air with a heating rate of 5 to 10 deg per minute. For comparative studies with cobalt(II), nickel(II), and manganese(II) complexes identical heating rates were maintained (Fig. 3). In all cases about 10 mg of the finely powdered substances were heated.

Results and discussion

Schiff bases of the salicylideneglycine (I) type containing ONO donor sets react with manganese(II), cobalt(II), nickel(II), and magnesium(II) ions to give dimeric

Table 1 Elemental analysis (%) of zinc(II) complexes of salicylidene amino acids

Complex	Color		Zn	C	H	N	Cl
$[Zn(salgly)(H_2O)_2]_2$	white	found	23.5	38.7	2.6	5.1	—
		calcd.	23.4	38.8	2.5	5.0	—
$[Zn(5Cl\text{-}salgly)(H_2O)_2]_2$	white	found	20.7	34.6	2.2	4.5	11.2
		calcd.	20.8	34.5	2.1	4.4	11.3
$[Zn(5NO_2\text{-}salgly)(H_2O)_2]_2$	white	found	20.2	33.5	2.0	8.5	—
		calcd.	20.1	33.3	1.8	8.6	—
$[Zn(sal\text{-}\alpha\text{-}alan)(H_2O)_2]_2$	white	found	22.4	40.8	3.2	4.8	—
		calcd.	22.3	41.0	3.1	4.7	—
$[Zn(5Cl\text{-}sal\text{-}\alpha\text{-}alan)(H_2O)_2]_2$	white	found	20.1	36.9	2.5	4.4	11.0
		calcd.	20.0	36.7	2.4	4.2	11.1
$[Zn(5NO_2\text{-}sal\text{-}\alpha\text{-}alan)(H_2O)_2]_2$	white	found	19.5	35.7	2.5	8.4	—
		calcd.	19.4	35.5	2.3	8.3	—
$[Zn(salval)(H_2O)_2]_2$	white	found	20.5	45.1	4.1	4.3	—
		calcd.	20.4	44.9	4.0	4.3	—

Abbreviations: $salglyH_2$ = salicylideneglycine; sal-α-alanH_2 = salicylidene-α-alanine; 5Cl-salglyH_2 = 5-chlorosalicylideneglycine; 5Cl-sal-α-alanH_2 = 5-chlorosalicylidene-α-alanine; $5NO_2$-salglyH_2 = 5-nitrosalicylideneglycine; $5NO_2$-sal-α-alanH_2 = 5-nitrosalicylidene-α-alanine; salvalH_2 = salicylidenevaline

Table 2 IR spectral bands of $[M(salgly)(H_2O)_2]_2$ (M = Zn(II), Mn(II), Ni(II), Co(II), or Mg(II))

Complex	ν(cm^{-1})
$[Zn(salgly)(H_2O)_2]_2$	3350–3200 bs, 1650 s, 1610 s, 1550 s, 1480 s, 1450 s, 1400 s, 1340 s, 1310 s, 1200 s, 1145 s, 1135 s, 1080 m, 1045 w, 1000 w, 980 w, 915 m, 815 s, 780 s, 750 w
$[Mn(salgly)(H_2O)_2]_2$	3125 bs, 1645 s, 1600 s, 1548 s, 1470 vs, 1450 s, 1400 s, 1335 s, 1300 s, 1190 vs, 1149 vs, 1130 s, 1060 m, 1041 w, 1010 w, 961 w, 900 w, 854 m, 800 m, 769 w, 759 m, 740 w
$[Ni(salgly)(H_2O)_2]_2 \cdot H_2O$	3200 bs, 1650 vs, 1600 s, 1550 s, 1465 m, 1450 s, 1395 m, 1340 m, 1305 vs, 1205 s, 1155 ms, 1135 s, 1095 ms, 1040 m, 1012 w, 970 w, 948 w, 910 w, 858 w, 792 w, 768 m, 750 ms
$[Co(salgly)(H_2O)_2]_2$	3178 vs, 1644 s, 1600 s, 1545 s, 1470 ms, 1450 s, 1400 s, 1335 ms, 1290 s, 1190s, 1149 s, 1130 s, 1086 m, 1041 w, 1010 w, 958 w, 900 w, 798 m, 770 w, 760 w, 743 w
$[Mg(salgly)(H_2O)_2]_2$	3400–3200 bs, 1660 s, 1600 m, 1540 m, 1475 s, 1445 s, 1410 s, 1340 s, 1303 s, 1198 s, 1155 s, 1132 s, 1085 s, 1042 m, 1020 m, 958 m, 950 w, 905 s, 858 w, 770 s, 760 s, 750 s

bs = broad and strong; vs = very strong; s = strong; ms = medium strong; m = medium; w = weak.

tetraaquabis(salicylideneglycinato)dimetal(II) species with octahedral stereochemistry (II). Other workers have determined the structures and stereochemistry of complexes by physical methods such as measurement of electronic spectra, magnetic susceptibility, and infrared spectra and by thermogravimetric analysis [1–6]. Since zinc(II) offers no special magnetic and electronic properties, we determined the structure of the new zinc(II) complexes by comparing their infrared spectra with those of nickel(II), cobalt(II), manganese(II), and magnesium(II) complexes (Table 2). These spectra are very nearly superimposable (Fig. 2). All these

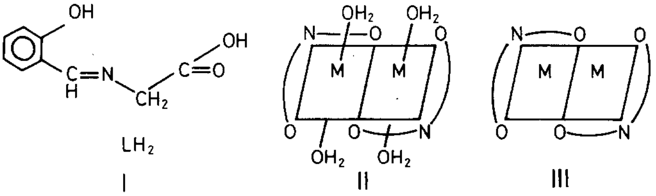

Fig. 1 Salicylideneglycine and its complexes

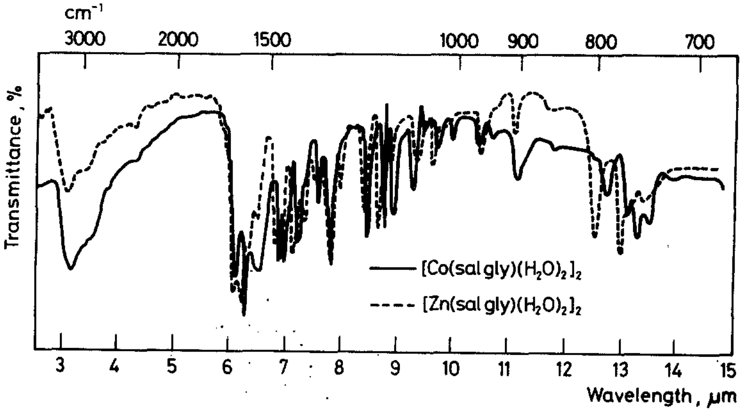

Fig. 2 Infrared spectra of cobalt(II) and zinc(II) complexes of salicylideneglycine

complexes are characterized by a broad strong absorption in the region of 3200–3400 cm^{-1} due to $\nu(H_2O)$ [7]. The strong bands at ~1650 cm^{-1} and 1610 cm^{-1} are assignable to coordinated ν(COO) and ν(C=N) [1, 4–8] while the aromatic C—C bands appear at ~1550 cm^{-1} [8]. The band at 1300 cm^{-1} is evidence of a strong bonding of the metal ion with phenolic oxygen [9]. The presence of coordinated water molecules were confirmed by infrared spectra and were compared with the spectra of nickel(II), cobalt(II), manganese(II), and magnesium(II) complexes. Interestingly, all the infrared spectra are almost superimposable, none of the bands varying by more than 5 to 10 cm^{-1} (Fig. 2, Table 2).

A strong band observed in the region of 1510–1540 cm^{-1} in the spectra of similar type ligands is assigned to the ν(C—O) phenolic stretch [10, 11]. In zinc(II) complexes the band shifts to a higher frequency region, which is attributed to a ring current arising from electron delocalization in the chelate ring. A strong band is also observed at ~1195–1245 cm^{-1}, which is assigned to the ν(C—O) alcoholic stretch [12, 13]. This band is shifted to a lower frequency region, indicating that coordination takes place through the alcoholic oxygen atom of the title ligand.

In the case of cobalt(II) complexes the coordinated water molecules are readily lost at 100–120°, whereas such dehydration does not occur easily at such a low temperature for manganese(II), magnesium(II), and zinc(II) complexes [1–5]. Even on heating the zinc(II) complexes at 140° in a drying pistol for 6–8 hours no such dehydration occurred, indicating that the water molecules in the complexes are tightly bonded. The TG curve of $[Zn(salgly)(H_2O)_2]_2$ showed that all coordinated water molecules were removed at 130–170°, and the residue was zinc oxide [13]. For the $[Zn(sal-\alpha\text{-alan})\,(H_2O)_2]_2$ complex the coordinated water molecules were lost in two steps, indicating the formation of a five-coordinate square pyramidal dimer

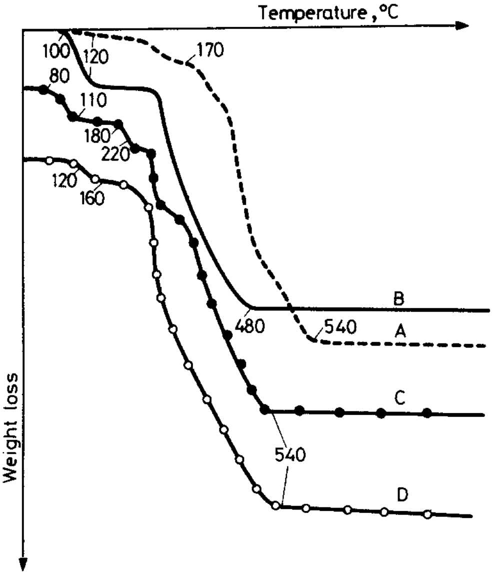

Fig. 3 TG curves of cobalt(II) and zinc(II) complexes. *A* – $[Zn(salgly)(H_2O)_2]_2$; *B* – $[Co(salgly)(H_2O)_2]_2$; *C* – $[Zn(sal\text{-}\alpha\text{-}alan)(H_2O)_2]_2$; *D* – $[Zn(salval)(H_2O)_2]_2$

species, $[Zn(sal-\alpha\text{-}alan)(H_2O)_2]_2$. The TG of $[Co(salgly)(H_2O)_2]_2$ is included in Fig. 3 to support the proposed structure of the zinc(II) complexes.

The mass loss values of all the zinc(II) complexes as well as those of $[Mn(salgly)(H_2O)_2]_2$, $[Mn(5Cl\text{-}sal\text{-}\alpha\text{-}alan)(H_2O)_2]_2$, $[Ni(salgly)(H_2O)_2]_2$, and $[Co(salgly)(H_2O)_2]_2$ are given in Table 3.

$$[Zn(salgly)(H_2O)_2]_2 \xrightarrow[130^\circ-170]{-4H_2O} [Zn(salgly)_2]_2 \xrightarrow[180^\circ-540^\circ]{} ZnO$$

$$[Zn(sal\text{-}\alpha\text{-}alan)(H_2O)_2]_2 \xrightarrow[80^\circ-110]{-2H_2O} [Zn(sal\text{-}\alpha\text{-}alan)(H_2O)]_2 \xrightarrow[180^\circ-220^\circ]{-2H_2O}$$

$$[Zn(sal\text{-}\alpha\text{-}alan)]_2 \xrightarrow[240^\circ-540^\circ]{} ZnO$$

$$[Zn(salval)(H_2O)_2]_2 \xrightarrow[120^\circ-160^\circ]{-2H_2O} [Zn(salval)(H_2O)]_2 \xrightarrow[240-540^\circ]{} ZnO$$

The crystal field stabilization energy (CFSE) of manganese(II) ($3d^5$-system) is zero, and those of nickel(II), cobalt(II), magnesium(II), and zinc(II) are -12 Dq, -8 Dq, 0 Dq, respectively. This indicates that the formation of the dimeric species is not dictated by CFSE, particularly at least for these systems, but

Table 3 TG analysis of zinc(II), manganese(II), nickel(II) and cobalt(II) complexes of salicylidene amino acids

Complex	Loss of water, %				Total loss, %	
	1st step	2nd step	total	calcd.	found	calcd. (ZnO/Mn$_3$O$_4$/Co$_3$O$_4$, ZnO)
[Zn(salgly)(H$_2$O)$_2$]$_2$	12.8 (120°–170 °C)*	—	12.8 (120°–170 °C)*	12.9	70.8 (540 °C)	70.8
[Zn(5Cl-salgly)(H$_2$O)$_2$]$_2$	11.4 (140°–170 °C)	—	11.4	11.4	73.8 (530 °C)	74.0
[Zn(sal-α-alan)(H$_2$O)$_2$]$_2$	6.3 (80°–110 °C)	6.0 (80°–220 °C)	12.3	12.3	72.0 (540 °C)	72.2
[Zn(5Cl-sal-α-alan)(H$_2$O)$_2$]$_2$	10.8 (140°–160 °C)	—	10.8	11.0	75.0 (530 °C)	75.1
[Zn(salval)(H$_2$O)$_2$]$_2$	5.6 (130°–160 °C)	—	5.6	11.2	74.3 (540 °C)	74.6
[Mn(salgly)(H$_2$O)$_2$]$_2$	12.1 (160°–190 °C)	—	12.1	13.9	72.5 (480 °C)	71.6 [67.6)**
[Mn(5Cl-sal-α-alan)(H$_2$O)$_2$]$_2$	6.0 (90°–110 °C)	6.8 (160°–200 °C)	12.8	12.3	76.2 (540 °C)	76.0 [72.6)**
[Ni(salgly)(H$_2$O)$_2$]$_2$	3.1 (60°–100 °C)	13.0 (130°–160 °C)	16.1	16.1	78.5 (500 °C)	78.7
[Co(salgly)(H$_2$O)$_2$]$_2$	13.7 (100°–120 °C)	—	13.7	13.4	68.0 (500 °C)	70.5

* Figures in parentheses indicate the temperature range for the loss of water.

** Figures in brackets indicate values calculated for MnO$_2$.

by the nature of the donor set (e.g., in these cases, ONO types) and more importantly by the size of the metal ions (Mn^{2+} = 0.80 Å, Co^{2+} = 0.72 Å, Ni^{2+} = 0.69 Å, Mg^{2+} = 0.65 Å, Zn^{2+} = 0.74 Å).

The successful synthesis of zinc(II) complexes of salicylidene amino acid ligands further substantiates our earlier assertion that such syntheses are not dictated by CFSE [4].

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The senior author (RKR) expresses his deep gratitude to Prof. R. L. Dutta, Department of Chemistry, Burdwan University, India, for valuable suggestions and discussions during the course of the work. He is also grateful to Dr. R. N. Banerjee of Jadavpur University and Dr. P. Banerjee of the Indian Association for the Cultivation of Science, Calcutta for laboratory and other facilities.

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Zusammenfassung — Einige Zink(II)-komplexe von dreizähligen, dibasischen Salizylidenaminosäuren wurden dargestellt und beschrieben. Alle diese Komplexe besitzen eine pseudooktaedrische Dimerstruktur. Dies wurde mittels thermogravimetrischer Analyse und auf Grund der deckungsgleichen IR-Spektren dieser Komplexe mit denen von Mangan(II)-, Kobalt(II)-, Nickel(II)- und Magnesium(II)-Komplexen festgestellt.

Резюме — Получены и охарактеризованы несколько комплексов цинка с тридентатными двухосновными салицилиденаминокислотами. Все комплексы обладают димерной псевдооктаэдрической структурой, установленной на основе термогравиметрического анализа и сопоставлением ИК спектров этих комплексов с таковыми для двухвалентных марганца, кобальта, никеля и магния.