

THERMAL, SPECTRAL AND MAGNETIC STUDIES ON GLYCINE COMPLEXES OF COBALT(II), NICKEL(II) AND ZINC(II) WITH HYDRAZINE

*B. N. Sivasankar and S. Govindarajan*¹

Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

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Abstract

Hydrazinium metal glycinates $[(N_2H_5)_2M(NH_2CH_2COO)_4]$ and bis(hydrazine)metal glycinates, $[M(NH_2CH_2COO)_2(N_2H_4)_2]$, where $M = Co, Ni$ or Zn have been prepared and characterized by chemical analyses, magnetic moments and vibrational and electronic spectra. The thermal behaviour of these compounds has been studied by thermogravimetry and differential thermal analyses. These complexes decompose with high exothermicity giving metal powder as the final residue. The X-ray powder data of each set of complexes show isomorphism among themselves.

Keywords: bis-hydrazine metal glycinates, complexes, hydrazinium metal glycinates, metal powders, thermal analyses

Introduction

Complexing of transition metals by amino acids has been the subject of study for many years, because of the importance of metal-protein system and the physiological effect of some of these metal compounds. There are a large number of preparation, structural and physical investigations in the area of amino acid complexes of metals and interesting structural features are often observed [1]. Although extensive studies have been done on simple metal glycinates [2-5], the glycino complexes of metal ion with alkali and ammonium ions are scarce [6, 7]. Further, there appears to be no report on the corresponding hydrazine analogue. Also, only few hydrazinium metal carboxylates and metal carboxylate hydrazinates of aliphatic carboxylic acids are known [8-11] which do not include amino acid compounds. Further, the hydrazinecarboxylate anion, NH_2NHCOO^- , forms a variety of crystalline complexes with metal ions,

¹To whom the correspondence should be addressed.

e.g., $M(N_2H_3COO)_2(N_2H_4)_2$ and $N_2H_5[M(N_2H_3COO)_3] \cdot H_2O$, where $M = Mg, Mn, Fe, Co, Ni$ or Zn for which the preparation, structures and thermal properties have been well established [12–15]. However, the corresponding compounds with isoelectronic analogue viz., glycinate, $NH_2CH_2COO^-$, are not known. Hence, attempt has been made to prepare metal hydrazine complexes with glycine and the results obtained are discussed below. As far as we are aware this is the first reported work on the hydrazine derivatives of glycine.

Experimental

All the chemicals used were of analytical grade and the solvents were distilled before use. Hydrazine hydrate (99–100%) was used as such in all the reactions. Metal glycinate hydrates were prepared by the methods as reported earlier [2–5].

Preparation of hydrazinium metal glycinate

Aqueous solution (50 ml) of a mixture of glycine (3 g, 0.04 mol) and hydrazine hydrate (2 ml, 0.04 mol) was added slowly to the aqueous solution (50 ml) of respective metal nitrate hexahydrates [0.01 mol, 2.91 g of $Co(NO_3)_2 \cdot 6H_2O$, 2.91 g of $Ni(NO_3)_2 \cdot 6H_2O$ or 2.97 g of $Zn(NO_3)_2 \cdot 6H_2O$] and the resulting solution was refluxed on a water bath for about 6 h. In the case of nickel the precipitate formed initially was filtered and then the solution was refluxed. The final solution obtained in all the cases was concentrated to 15 ml and allowed to crystallize in a vacuum desiccator over P_2O_5 . The crystals separated after 2–3 days were removed, washed with alcohol and dried over P_2O_5 . The cobalt compound obtained is hygroscopic and hence stored in vacuum desiccator over P_2O_5 . They are soluble in water and insoluble in alcohol and other common organic solvents. In the case of nickel, the precipitate formed prior to refluxion was found to be bis(hydrazine) nickel glycinate.

Preparation of bis(hydrazine) metal glycinate

These complexes were prepared by the reaction of solid metal glycinate hydrates (0.01 mol) and excess hydrazine hydrate (2 ml, 0.04 mol). The reaction was instantaneous and exothermic. The compounds obtained were filtered, washed with alcohol and dried in air. These complexes are stable and insoluble in water and all the organic solvents.

Physico-chemical techniques

The hydrazine content in the complexes was determined volumetrically using a standard KIO_3 solution (0.025 M) under Andrews' conditions [16]. The metal

contents were determined by edta complexometric titrations after decomposing a known amount of compounds with concentrated nitric acid [16]. The molar conductances of the hydrazinium metal glycinates in water (10^{-3} mol) were measured using a Century digital conductivity meter model CC 601 and dip-type cell with a smooth platinum electrode. Room temperature magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constants. Electronic reflectance spectra were recorded on a Shimadzu UV-visible 240A spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 597 using KBr disc in the range $4000\text{--}400\text{ cm}^{-1}$. A DuPont DTA-750 instrument was used to carry out differential thermal analysis and a Perkin-Elmer TGS-2 thermogravimetric system was used for thermogravimetry. The thermal experiments were performed in air under ambient atmosphere with a heating rate of $10\text{ deg}\cdot\text{min}^{-1}$. Platinum cups were used to hold 10–12 mg samples for the analyses. X-ray powder diffraction patterns of the samples were obtained using Philips X-ray diffractometer with vertical goniometer, model PW 1050/70 using $\text{CuK}\alpha$ radiation with nickel filter.

Results and discussion

The reaction of nickel nitrate hexahydrate with equimolar mixture of glycine and hydrazine hydrate in 1:4 ratio resulted in the precipitation of bis(hydrazine) nickel glycinate. The precipitate was removed and the clear solution was evaporated on a water bath to yield the crystals of hydrazinium nickel glycinate. However, the cobalt and zinc nitrate hexahydrates on similar reaction resulted in a clear solution which were evaporated to give the corresponding hydrazinium metal glycinates.

The bis(hydrazine) metal glycinates were prepared by the reaction of metal glycinate hydrates and excess hydrazine hydrate. The composition of the complexes were determined by their chemical analyses, and the results of chemical analyses are summarized in Table 1.

The hydrazinium metal glycinates are water soluble and their molar conductances in water lie in the range $20\text{--}30\text{ ohm}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. These conductance values are in accordance with the non-electrolytic nature of the compounds. The bis(hydrazine) metal glycinate complexes are insoluble in water and also in other common solvents and so their molar conductances could not be measured.

The electronic spectral and magnetic moment values are listed in Table 2. The position of the bands in the spectra of the cobalt and nickel complexes together with their magnetic moments suggest that the metal ions are in an octahedral environment [17, 18].

The infrared spectra of hydrazinium metal glycinates are similar and show bands at 3250 and 1590 cm^{-1} which are due to the N–H stretching and bending vibrations, respectively. The N–N stretching of N_2H_5^+ ion is known to be sensitive to coordination and occurs at $990\text{--}1015\text{ cm}^{-1}$ when coordinated to the

Table 1 Analytical data

Compound	Colour	Yield/ %	M.p./ °C	Metal/ %		Hydrazine/ %		Molar conductance/ Ohm ⁻¹ cm ² ·mole ⁻¹
				Found	Calc.	Found	Calc.	
[(N ₂ H ₅) ₂ Co(NH ₂ CH ₂ COO) ₄]	Pink	85	180(d)	13.6	13.99	15.4	15.22	24
[(N ₂ H ₅) ₂ Ni(NH ₂ CH ₂ COO) ₄]	Blue	60	150(d)	13.5	13.94	15.0	15.22	26
[(N ₂ H ₅) ₂ Zn(NH ₂ CH ₂ COO) ₄]	Colourless	80	150(d)	15.0	15.28	15.2	14.99	25
[Co(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]	Pink	85	90(d)	21.4	21.73	23.8	23.64	—
[Ni(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]	Violet	80(30)*	125(d)	21.1	21.67	23.9	23.66	—
[Zn(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]	Colourless	80	200(d)	23.0	23.55	23.3	23.09	—

* Precipitated during the preparation of hydrazinium complex

d: decompose

Table 2 Magnetic moments and electronic spectral data

Compound	Absorption maxima/cm ⁻¹	Assignments	Magnetic moment/BM
[(N ₂ H ₅) ₂ Co(NH ₂ CH ₂ COO) ₄]	19.452	$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$	4.81
	20.401		
[(N ₂ H ₅) ₂ Ni(NH ₂ CH ₂ COO) ₄]	33.333	Charge transfer	2.95
	17.394	$^3A_{2g} \rightarrow ^3T_{1g}(F)$	
	27.782	$^3A_{2g} \rightarrow ^3T_{1g}(P)$	
	33.333	Charge transfer	
[Co(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]	19.231	$^4T_{2g}(F) \rightarrow ^4T_{1g}(P)$	4.95
	20.404		
[Ni(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]	33.333	Charge transfer	3.13
	17.541	$^3A_{2g} \rightarrow ^3T_{1g}(F)$	
	26.672	$^3A_{2g} \rightarrow ^3T_{1g}(P)$	
	33.333	Charge transfer	

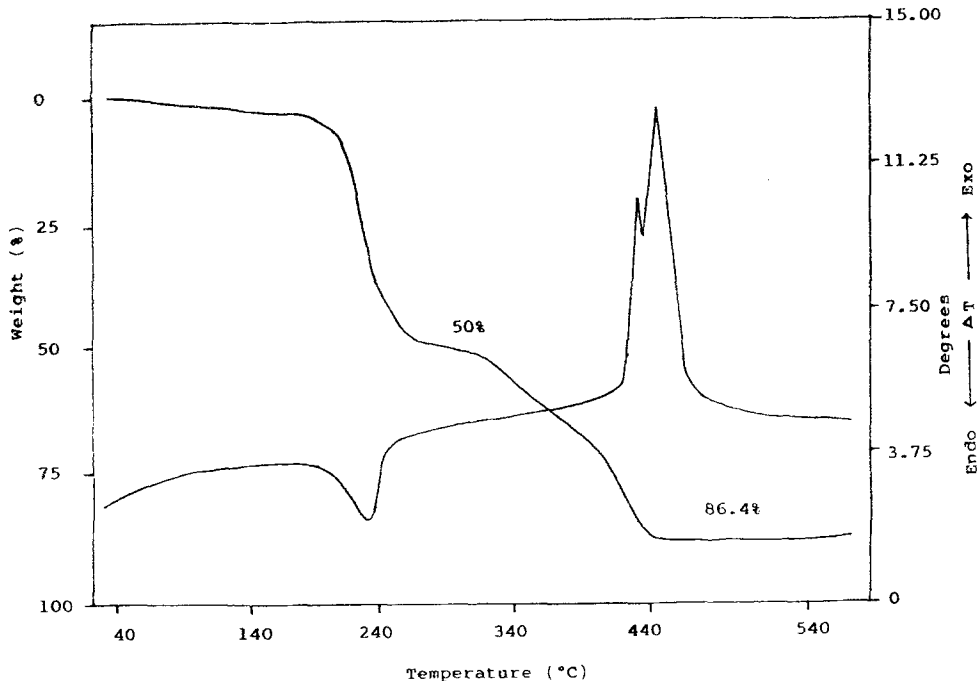


Fig. 1 TG-DTA of $[(N_2H_5)_2Co(NH_2CH_2COO)_4]$

metal ion [19]. These hydrazinium complexes also show band at 1010 cm^{-1} clearly indicating the coordination of hydrazinium ions to the metal ion. The asymmetric and symmetric carbonyl stretching frequencies at 1620 and 1380 cm^{-1} shown by these compounds with the $\Delta\nu$ separation of 240 cm^{-1} suggests the unidentate coordination of carboxylate ions.

The bis(hydrazine) metal glycinate complexes show N-N stretching frequency at 960 cm^{-1} which is ascribable to the bidentate bridging nature of the hydrazine moieties.

In these complexes also, the asymmetric stretching vibration (1600 cm^{-1}) and the $\Delta\nu$ separation (220 cm^{-1}) are assumed to typify a unidentate coordination of the carboxylate ions.

Hydrazinium cobalt and zinc glycinate complexes undergo thermal degradation in two steps giving metal powder as the final residue. The first step is endothermic giving respective metal glycinate as an intermediate which further decomposes exothermically to give the metal powder. However, the nickel compound shows single step exothermic decomposition to give metal powder.

In the case of bis(hydrazine) metal glycinate complexes two step decomposition is observed for cobalt and nickel compounds. The intermediate formed during the degradation in both the cases are respective mono(hydrazine) metal glycinate complexes. This type of mono(hydrazine) intermediates have been already observed in

Table 3 Thermal data

Compound	DTA peak temp./ °C	TG temp. range/ °C	Weight loss/%		Final residue
			Found	Calc.	
[(N ₂ H ₅) ₂ Co(NH ₂ CH ₂ COO) ₄]	230(+)	180-290	50.0	50.86	Co(NH ₂ CH ₂ COO) ₂
	430(-)	290-470	86.4	86.01	Co-metal
	440(-)				
[(N ₂ H ₅) ₂ Ni(NH ₂ CH ₂ COO) ₄]	200(+)	150-475	86.5	86.05	Ni-metal
	410(-)				
	450(-)				
[(N ₂ H ₅) ₂ Zn(NH ₂ CH ₂ COO) ₄]	210(+)	150-270	50.0	50.09	Zn(NH ₂ CH ₂ COO) ₂
	530(-)	270-592	85.2	84.71	Zn-metal
	140(-)	90-190	12.0	11.82	Co(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄)
[Co(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]	205(-)	190-220	79.5	78.26	Co-metal
	150(-)	125-235	12.5	11.83	Ni(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄)
	250(-)	235-250	79.2	78.33	Ni-metal
[Zn(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]	260(-)	240-270	77.4	76.45	Zn-metal

(+) : Endothermic; (-) : Exothermic

Table 4 X-ray powder data (*d*-spacings /Å)

[(N ₂ H ₅) ₂ M(NH ₂ CH ₂ COO) ₄]			[M(NH ₂ CH ₂ COO) ₂ (N ₂ H ₄) ₂]		
Co	Ni	Zn	Co	Ni	Zn
1	2	3	4	5	6
7.38(M)	7.31(M)	7.03(M)	7.15(S)	7.20(S)	7.25(S)
4.10(M)	4.09(S)	4.07(S)	4.07(S)	4.11(S)	4.28(S)
3.80(M)	3.74(M)	3.79(W)	3.58(M)	3.60(W)	3.54(W)
3.50(S)	3.48(S)	3.51(S)	3.38(S)	3.35(S)	3.40(S)
3.33(M)	3.31(S)	3.35(S)	2.78(M)	2.76(S)	2.79(S)
3.24(W)	3.22(M)	3.24(W)	2.60(S)	2.58(S)	2.56(M)
3.03(M)	3.01(W)	3.03(W)	2.53(S)	2.52(S)	2.50(S)
2.94(M)	2.90(W)	2.95(W)	2.20(M)	2.18(S)	2.15(S)
2.81(W)	2.80(M)	2.79(S)	2.02(M)	2.00(M)	1.98(M)
2.65(W)	2.64(M)	2.66(W)	1.94(M)	1.96(M)	1.95(M)
2.58(S)	2.59(S)	2.59(S)	1.83(W)	1.82(W)	1.84(W)
2.51(M)	2.50(M)	2.52(M)	1.79(W)	1.80(W)	1.78(M)
2.48(S)	2.48(S)	2.49(S)	1.70(M)	1.74(W)	1.72(W)
2.29(W)	2.31(M)	2.30(M)	1.65(W)	1.66(W)	1.64(W)
2.18(M)	2.17(W)	2.19(M)	1.48(W)	1.53(W)	1.50(W)

W: weak; M: medium; S: strong

Table 4 Continued

Co	[(N ₂ H ₅) ₂ M(NH ₂ CH ₂ COO) ₄]		
	Ni		Zn
	1	2	3
2.10(W)	2.14(W)	2.16(W)	2.16(W)
2.04(M)	2.02(W)	2.12(W)	2.12(W)
2.00(M)	2.00(W)	2.03(W)	2.03(W)
1.96(S)	1.95(W)	2.01(W)	2.01(W)
1.90(M)	1.91(M)	1.96(M)	1.96(M)
1.84(M)	1.84(W)	1.90(W)	1.90(W)
1.74(M)	1.73(W)	1.84(W)	1.84(W)
1.68(M)	1.67(M)	1.74(W)	1.74(W)
1.64(M)	1.63(W)	1.68(W)	1.68(W)
1.54(M)	1.54(W)	1.63(W)	1.63(W)
1.43(M)	1.44(W)	1.55(W)	1.55(W)
	1.38(W)	1.43(W)	1.43(W)
		1.39(W)	1.39(W)

W: weak; M: medium; S: strong

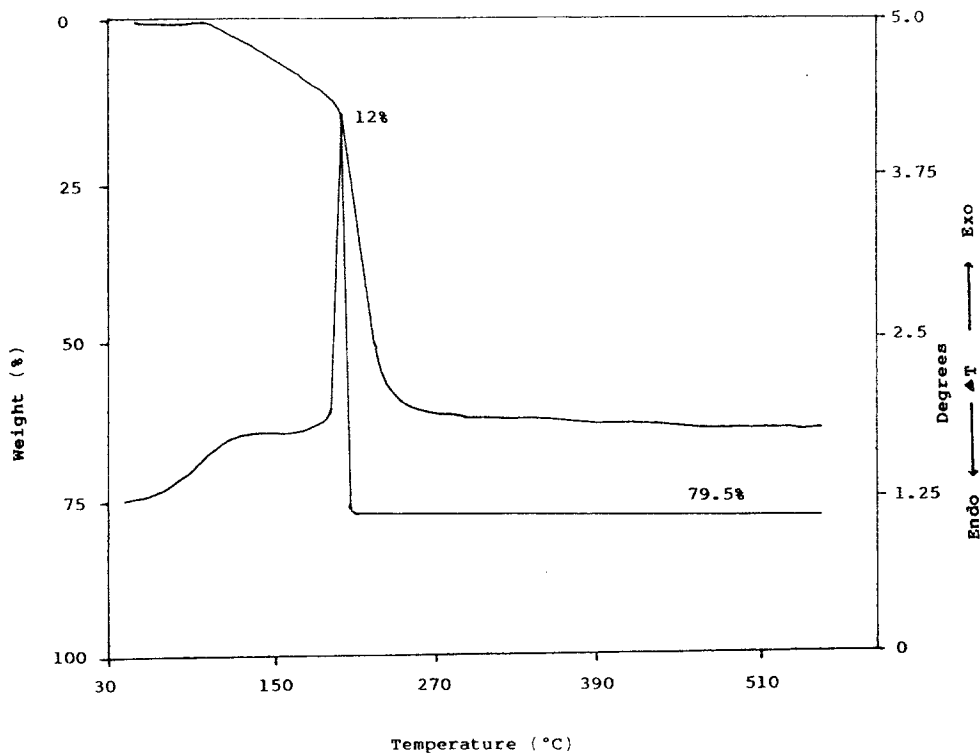


Fig. 2 TG-DTA of $[\text{Co}(\text{NH}_2\text{CH}_2\text{COO})_2(\text{N}_2\text{H}_4)_2]$

number of cases [8–15]. However, the zinc complex decomposes in a single step giving zinc metal as the final product. The actual weight losses reported in Table 3 for the decomposition processes of the compounds compared favourably with the calculated values. The TG and DTA curves of cobalt compounds are given in Figs 1 and 2.

In all the cases the decomposition is exothermic and the end product is the metal powder. The intermediate formed by nickel complex undergo violent decomposition. The interesting feature of the glycinate complexes is their thermal decomposition to give metal powder even in air. A number of hydrazine complexes have been reported to give metal powder only in inert atmosphere [15, 20]. The formation of metal powder in the present case may be due to the high exothermicity of their decomposition, as already observed in the case of tris hydrazine metal carboxylates [21]. The formation of metal powders have been confirmed by their chemical analyses, infrared spectra and X-ray powder diffraction.

The X-ray powder data of hydrazinium metal glycinate show that they are isomorphous. The bis(hydrazine) metal glycinate also show isomorphism

among themselves. The *d*-spacings of these complexes are summarized in Table 4.

Thus, the conductance and magnetic moment data coupled with electronic and infrared spectra reveal that the metal ions in hydrazinium metal glycinate are surrounded by four monodentate glycinate ions and two coordinated hydrazinium cations resulting in the octahedral coordination.

The bis(hydrazine) metal glycinate are expected to have similar structures to that of bis(hydrazine) metal hydrazinecarboxylate, since the isoelectronic glycinate, $\text{NH}_2\text{CH}_2\text{COO}^-$ and hydrazinecarboxylate, $\text{NH}_2\text{NHCOO}^-$ are having the same coordination behaviour. However, in the latter compounds the metal ion is surrounded by two bidentate (chelate) anions and two monodentate hydrazine molecules. Whereas the physico-chemical techniques of the former compounds reveal that the metal ions are having octahedral geometry with two each of unidentate glycinate ions and bridging bidentate hydrazine moieties leading to polymeric structure. The insoluble behaviour of these complexes also indicate their polymeric nature.

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