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Tris-hydrazine metal glycinates and glycolates: preparation, spectral and thermal studies

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Abstract

Tris-hydrazine metal glycinates and glycolates of formula $M(XCH_2COO)_2(N_2H_4)_3$, where X is NH_2 or OH, respectively, and M is Mn, Co, Ni, Zn or Cd, have been prepared and characterized by analytical, magnetic, and electronic and infrared spectral studies. Magnetic moment and electronic spectral data show that all the complexes are spin-free octahedra. Infrared spectra reveal the bridging bidentate coordination of the hydrazine molecules. These compounds undergo violent thermal decomposition in a single step to give the respective metal powders as the final residue. The X-ray powder diffraction patterns indicate that the complexes are isomorphous, not only within but also between the series.

Keywords: Co-ordination; Decomposition; DTA; Glycinate; Glycolate; IRS; Isomorph; TG; Tris-hydrazine compound; XRD

1. Introduction

Hydrazine complexes of metal(II) salts are of two main types. The more common of these is the type containing bridging bidentate hydrazine. This is well established in compounds of the type $M(N_2H_4)_2X_2$ [1-10], where M is Mn, Fe, Co, Ni, Cu, Zn or Cd and X is Cl, Br, I, NCS, NO_3, ClO_4 or N_3. The bis-hydrazine complexes have also been studied with carboxylate anions such as formate, acetate and oxalate, and their thermal properties have been discussed [11-16]. The other type of hydrazine

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complex contains unidentate hydrazine, as found in octahedral $Co(N_2H_4)_6Cl_2$ [17] and in $M(N_2H_3COO)_2(N_2H_4)_2$, where M is Mn, Fe, Co, Ni and Zn [18]. In no case so far has hydrazine been found to be bidentate (chelate) to the same metal atom.

Some tris-hydrazine complexes were prepared earlier [3], but these interesting compounds have received little attention since that time. Only the nickel(II) compounds, $Ni(N_2H_4)_3X_2$ where X is Cl, Br, NO_3, $0.5SO_4$ and BF_4, have been studied further [19,20] although no information on the crystal structure of any of these compounds is available. Apart from the sulphate complexes, the tris-hydrazine complexes are characteristically unstable in air being liable to sudden and spontaneous decomposition with smoke evolution. They are, thus, considerably less stable both thermally and in air than the corresponding bis-hydrazine complexes.

Although both bis- and tris-hydrazine complexes are known with a variety of inorganic anions, only bis-hydrazine complexes are known with organic anions, namely, formate, acetate and oxalate. Among the carboxylates, the acetate complexes have been thoroughly studied. However, there is no report on the hydrazine complexes of substituted acetic acid. We were not only able to prepare the hydrazine metal complexes of substituted acetic acid, namely, glycine and glycolic acid, but also obtained their tris-hydrazine complexes. The results are reported below.

2. Experimental

2.1. Preparation of tris-hydrazine metal glycinates

To an aqueous solution of metal nitrate hydrates (0.01 mol dm^{-3}), for example, $Mn(NO_3)_2 \cdot 4H_2O$ (2.51 g, 0.01 mol dm^{-3}), an aqueous solution containing both glycine (1.5 g, 0.02 mol dm^{-3}) and hydrazine hydrate (2 ml, 0.04 mol dm^{-3}) was added slowly with stirring. The pH of the solution was found to be between 9 and 10. The basicity of the solution facilitates the precipitation of tris-hydrazine metal glycinate complexes, namely, $M(NH_2CH_2COO)_2(N_2H_4)_3$ where M is Mn, Co, Ni, Zn or Cd. The crystalline precipitate formed after 3-4 h was filtered, washed with alcohol and dried over P_2O_5.

2.2. Preparation of tris-hydrazine metal glycolates

These compounds were prepared by the same method as described above by substituting glycolic acid (1.52 g, 0.02 mol dm^{-3}) for glycine.

The hydrazine content in the complexes was determined volumetrically using a standard KIO_3 solution (0.025 mol dm^{-3}) under Andrew's conditions [21]. The metal content was determined by EDTA complexometric titrations after decomposing a known amount of the compound with concentrated nitric acid [21]. Room-temperature magnetic moments were determined by Gouy's method using $Hg[Co(CNS)_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constants. Electronic spectra were recorded on a Shimadzu UV–VIS 240A spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer, using KBr discs, in the range 4000–200 cm^{-1}. A Du Pont DTA 750 instrument was used for the differential thermal analysis and a Perkin-Elmer TGS 2 thermogravimetric system for the thermogravimetry. TG and DTA experiments were performed in air with a heating rate of 10°C min^{-1} using platinum cups as sample holders. X-ray powder diffraction patterns of the samples were obtained using a Philips X-ray diffractometer model PW 1050/70 and Cu Kα radiation.

3. Results and discussion

The tris-hydrazine metal glycinate and glycolate complexes were prepared by mixing an aqueous solution containing respectively carboxylic acid and hydrazine hydrate (1:2 ratio) with an aqueous solution of metal nitrate, in 2:1 ratio. The complexes are stable in air, except the manganese and cobalt compounds which decompose on long standing in air; therefore they are stored in a vacuum desiccator containing P_2O_5. Also, the manganese and cobalt complexes decompose in water while all the other complexes are insoluble in water. All the complexes are insoluble in alcohol and most organic solvents. The corresponding iron and copper complexes could not be prepared due to the precipitation of iron as hydroxide and the ease of reduction of copper salt to copper metal, respectively. The results of chemical analyses are in good agreement with the proposed formula, $M(XCH_2COO)_2(N_2H_4)_3$ where X is NH_2 or OH, and M is Mn, Co, Ni, Zn or Cd. octahedral type [22].

Table 1
Chemical analysis and magnetic moment data

Compound	Colour	Metal/%		Hydrazine/%		Yield/ %	Magnetic moment/BM
		Found	Calcd.	Found	Cald.		
$Mn(NH_2CH_2COO)_2(N_2H_4)_3$	Colourless	18.00	18.36	32.00	32.14	85	6.02
$Co(NH_2CH_2COO)_2(N_2H_4)_3$	Pink	19.00	19.44	32.00	31.71	90	4.82
$Ni(NH_2CH_2COO)_2(N_2H_4)_3$	Violet	19.00	19.38	31.50	31.74	90	3.02
$Zn(NH_2CH_2COO)_2(N_2H_4)_3$	Colourless	21.00	21.11	31.00	31.05	85	Diamagnetic
$Cd(NH_2CH_2COO)_2(N_2H_4)_3$	Colourless	31.00	31.51	26.50	26.96	80	Diamagnetic
$Mn(HOCH_2COO)_2(N_2H_4)_3$	Colourless	18.10	18.24	31.80	31.93	80	5.79
$Co(HOCH_2COO)_2(N_2H_4)_3$	Pink	18.90	19.31	31.70	31.51	90	4.85
$Ni(HOCH_2COO)_2(N_2H_4)_3$	Violet	19.00	19.25	31.20	31.53	90	3.37
$Zn(HOCH_2COO)_2(N_2H_4)_3$	Colourless	20.50	20.97	30.50	30.85	85	Diamagnetic
$Cd(HOCH_2COO)_2(N_2H_4)_3$	Colourless	31.00	31.54	26.50	26.81	85	Diamagnetic

3.1. Magnetic susceptibility measurements

The magnetic moment values of the manganese, cobalt and nickel complexes are given in Table 1. These values indicate that the metal ions are of high-spin. As expected, the zinc and cadmium compounds are diamagnetic.

3.2. Electronic spectra

The electronic spectrum of tris-hydrazine cobalt glycinate shows two bands at 19 230 and 21 230 cm^{-1} and these bands are assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. For tris-hydrazine cobalt glycolate, this transition is seen at 19 230 and 21 050 cm^{-1}.

The tris-hydrazine nickel glycinate complex shows two bands at 18 250 and 27 780 cm^{-1}. These bands are ascribable to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively. These transitions for the corresponding tris-hydrazine nickel glycolate complex appear at 18 180 and 27 620 cm^{-1}, respectively. These spectral results are in accordance with the octahedrally coordinated Co(II) and Ni(II) compounds [23]. The electronic spectra of these complexes are virtually identical to that of $[M(en)_3]^{2+}$ [19] indicating a ligand field of six nitrogen atoms from the three hydrazine molecules around the metal ion. However, very little change occurs in the spectra on changing the anion, thus implying little or no ligand field contribution from the anion. Thus, the electronic spectra of the tris-hydrazine complexes are not inconsistent with the formation of complexes as adducts, for example $MX_2(N_2H_4)_2 \cdot N_2H_4$, i.e. one hydrazine molecule uncoordinated, or as containing both unidentate and bidentate hydrazine.

3.3. Infrared spectra

The most direct evidence for formulating these compounds as containing only bridging hydrazine molecules comes from the infrared spectra. If the hydrazine molecule is monodentate, then the N–N stretching frequency appears at 940–920 cm^{-1}, while the N–N stretching frequency of bridged hydrazine moieties lies in the region 980–950 cm^{-1}, as reported earlier [24]. If both kinds of hydrazine are present, then splitting or two bands are expected in the region 980–920 cm^{-1}. However, all the tris-hydrazine complexes prepared in the present work show a very sharp, single band at 970 cm^{-1}, indicating the presence of only bridged hydrazine molecules. Thus, it is concluded that the glycinate or glycolate anions are not coordinated to the metal ion and are present only outside the coordination sphere, as reported earlier [25]. The observed carbonyl stretching frequency at 1590 cm^{-1} in these complexes also confirms the presence of ionic nature in both the glycinate and glycolate anions [26].

3.4. Thermal decomposition

Evidence that all three hydrazine molecules are coordinated is provided by the surprising thermal stability of these complexes. No decomposition occurs upon heating at lower temperatures up to 200°C. Above this temperature, depending on the metal ion, these complexes undergo violent, single-step exothermic decomposition with the complete breakdown of the complexes without prior evolution of hydrazine. The final decomposition residue is the metal powder in all cases, as evident from thermogravimetry. The TG and DTA results of these complexes are summarized in Table 2, and the thermograms of the glycinate and glycolate complexes of nickel are shown in Fig. 1 as representative examples.

Table 2
Thermal analysis data

Compound	Thermogravimetry			DTA peak temp./°C	Final residue
	Temp. range/°C	Weight loss/%			
		Found	Calcd.		
$Mn(NH_2CH_2COO)_2(N_2H_4)_3$	200–250	82.00	81.64	240 (exo)	Mn
$Co(NH_2CH_2COO)_2(N_2H_4)_3$	200–240	81.50	80.56	235 (exo)	Co
$Ni(NH_2CH_2COO)_2(N_2H_4)_3$	230–250	81.00	80.62	240 (exo)	Ni
$Zn(NH_2CH_2COO)_2(N_2H_4)_3$	200–280	80.00	78.89	265 (exo)	Zn
$Cd(NH_2CH_2COO)_2(N_2H_4)_3$	240-275	69.80	68.49	260 (exo)	Cd
$Mn(HOCH_2COO)_2(N_2H_4)_3$	200–250	82.50	81.76	240 (exo)	Mn
$Co(HOCH_2COO)_2(N_2H_4)_3$	240–260	82.00	80.69	240 (exo)	Co
$Ni(HOCH_2COO)_2(N_2H_4)_3$	250–275	82.00	80.75	260 (exo)	Ni
$Zn(HOCH_2COO)_2(N_2H_4)_3$	250–270	80.00	79.03	265 (exo)	Zn
$Cd(HOCH_2COO)_2(N_2H_4)_3$	250–275	70.00	68.66	265 (exo)	Cd

3.5. X-ray powder diffraction

The isomorphism among the tris-hydrazine metal glycinates is shown by their similar X-ray powder patterns. The diffraction patterns of the tris-hydrazine metal glycolates are also identical, indicating their structural similarity. Also, it is interesting to note that both series of compounds are isomorphous not only among themselves but also between them. This clearly shows that the anions do not affect the overall structure and are only present outside the coordination sphere, maintaining the electro-neutrality of the compound. The '*d*' spacings of all the complexes are summarized in Table 3.

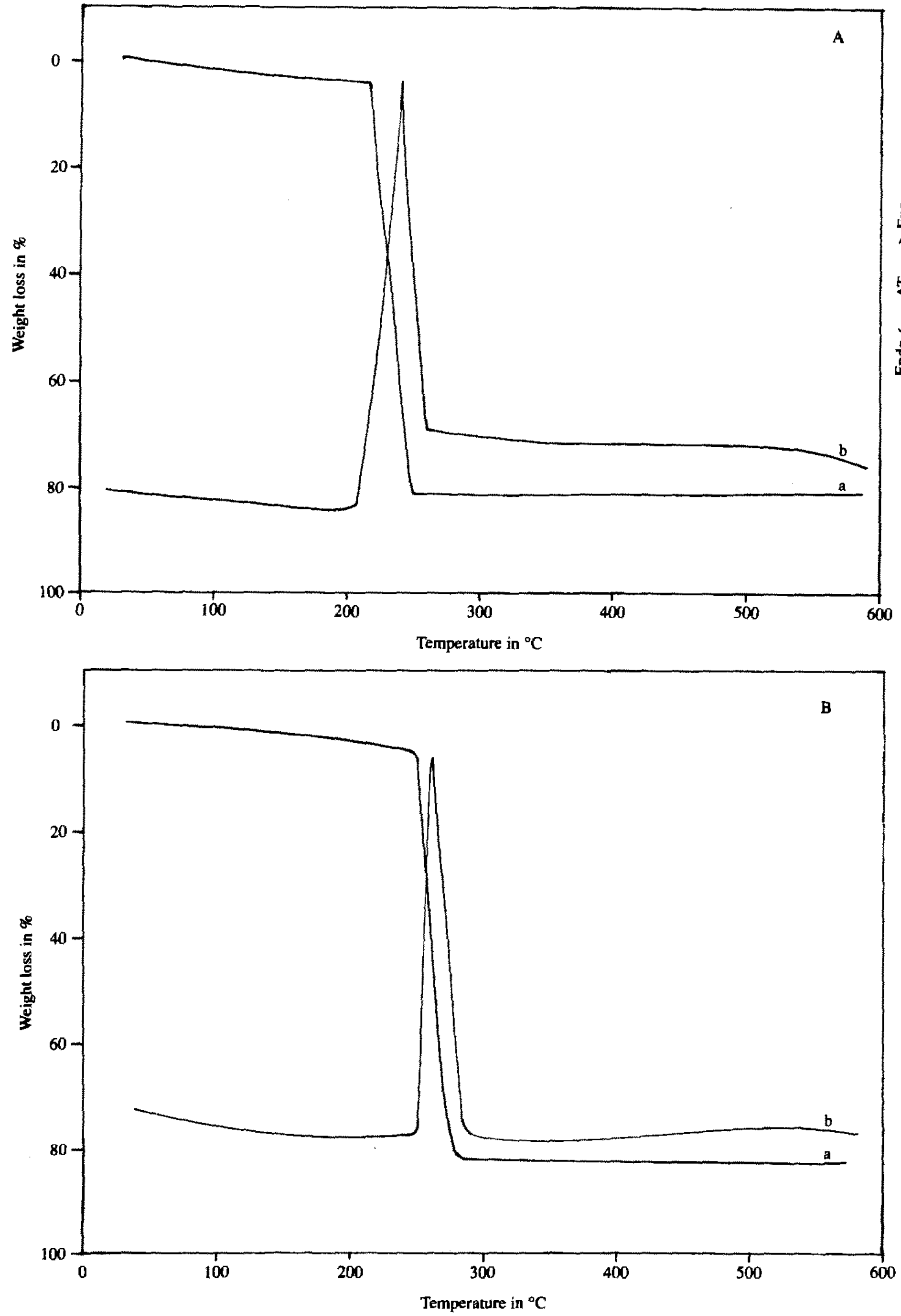

Fig. 1. A. TG (curve a) and DTA (curve b) of $Ni(NH_2CH_2COO)_2(N_2H_4)_3$. B. TG (curve a) and DTA (curve b) of $Ni(HOCH_2COO)_2(N_2H_4)_3$.

Table 3
d Values of $M(H_2NCH_2COO)_2(N_2H_4)_3$ and $M(HOCH_2COO)_2(N_2H_4)_3$ in Å [a]

$M(H_2NCH_2COO)_2(N_2H_4)_3$					$M(HOCH_2COO)_2(N_2H_4)_3$				
Mn	Co	Ni	Zn	Cd	Mn	Co	Ni	Zn	Cd
6.86 (80)	6.91 (75)	6.96 (86)	7.03 (100)	7.06 (96)	7.08 (64)	7.03 (64)	7.03 (70)	7.08 (53)	7.08 (58)
6.38 (34)	–	6.41 (40)	–	6.39 (58)	–	6.34 (20)	–	–	6.41 (60)
5.54 (22)	5.57 (28)	5.53 (24)	–	5.56 (30)	5.61 (28)	5.57 (42)	5.75 (30)	5.87 (74)	5.75 (65)
4.10 (100)	4.08 (100)	4.06 (100)	4.08 (62)	4.10 (100)	4.06 (100)	4.06 (100)	4.11 (100)	4.08 (100)	4.10 (100)
3.97 (38)	3.99 (41)	3.95 (32)	3.95 (45)	3.90 (42)	3.95 (20)	3.93 (24)	3.92 (18)	3.99 (45)	3.97 (40)
3.55 (30)	3.52 (20)	3.54 (11)	3.53 (12)	3.56 (13)	3.55 (12)	3.56 (18)	3.53 (20)	3.53 (16)	3.53 (18)
3.48 (18)	3.49 (24)	3.45 (22)	3.44 (20)	3.47 (25)	3.45 (16)	3.48 (14)	3.47 (17)	3.44 (18)	3.48 (22)
3.34 (14)	3.35 (20)	3.36 (18)	3.35 (45)	3.38 (21)	3.35 (91)	3.34 (98)	3.36 (75)	3.36 (36)	3.38 (47)
2.88 (46)	2.86 (64)	2.85 (59)	2.84 (54)	2.87 (70)	2.85 (42)	2.86 (50)	2.87 (60)	2.88 (26)	2.86 (21)
2.81 (20)	2.80 (24)	2.81 (20)	2.80 (46)	2.80 (22)	2.82 (35)	2.78 (60)	2.81 (43)	2.82 (67)	2.82 (52)
2.65 (42)	2.67 (40)	2.69 (41)	2.64 (10)	2.69 (45)	2.65 (18)	2.68 (21)	2.68 (18)	2.66 (31)	2.67 (18)
2.58 (18)	2.57 (15)	2.58 (9)	2.59 (30)	2.57 (11)	2.59 (52)	2.58 (71)	2.59 (65)	2.59 (39)	2.58 (24)
2.37 (14)	2.36 (12)	2.37 (10)	2.36 (12)	2.38 (11)	2.37 (18)	2.37 (21)	2.36 (19)	2.36 (9)	2.38 (16)
2.23 (14)	2.22 (18)	2.23 (13)	2.22 (18)	2.24 (22)	2.23 (12)	2.24 (18)	2.23 (14)	2.23 (10)	2.23 (15)
2.19 (10)	2.20 (12)	2.20 (9)	2.19 (38)	2.17 (8)	2.18 (34)	2.19 (34)	2.19 (40)	2.20 (32)	2.19 (34)
1.96 (20)	1.97 (26)	1.96 (25)	1.97 (29)	1.98 (30)	1.97 (38)	1.96 (43)	1.98 (28)	2.01 (16)	2.00 (24)
1.81 (10)	1.80 (9)	1.81 (8)	1.80 (5)	1.79 (9)	1.80 (18)	1.81 (21)	1.80 (24)	1.80 (9)	1.80 (18)
1.78 (11)	1.77 (7)	1.79 (7)	1.77 (5)	1.78 (6)	1.77 (12)	1.78 (20)	1.79 (18)	1.78 (11)	1.78 (15)
1.63 (9)	1.64 (9)	1.64 (8)	1.63 (5)	1.64 (5)	1.63 (14)	1.62 (24)	1.63 (20)	1.63 (5)	1.64 (8)
1.56 (7)	1.56 (8)	1.55 (6)	1.56 (9)	1.55 (8)	1.55 (14)	1.55 (29)	1.55 (18)	1.56 (9)	1.56 (6)

[a] The values given in parentheses indicate the relative intensities.

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