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Preparation and thermal decomposition of solid state cobalt, nickel, copper and zinc chelates of ethylenediaminetetraacetic acid

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Abstract

Solid state chelates of general formula $H_2[M(EDTA)] \cdot nH_2O$, where M is Co, Ni, Cu or Zn, and EDTA is ethylenediaminetetraacetate, were prepared. Thermogravimetry–derivative thermogravimetry (TG–DTG), differential thermal analysis (DTA) and complexometry were used to characterize and to study the thermal stability and thermal decomposition of these compounds.

INTRODUCTION

Since the isolation of chelates of lanthanum, neodymium and yttrium with EDTA by Brintzinger and co-workers [1, 2], several chelates of this ligand with various metals in the solid state have been reported. Moeller et al. [3] described the nature of solid state chelates of the type H[Ln(EDTA)] and their sodium salts by using infrared spectroscopy, DTA, X-ray diffraction and light rotation measurements, in an attempt to characterize these compounds. Sawyer and Paulsen [4] investigated the properties and infrared spectra of EDTA chelates with several divalent ions. Wendlandt and co-workers [5–7] have published more complete studies of the thermal properties of a number of EDTA complexes. Kolat and Powell [8] extended Moeller's work and investigated a series of lanthanide chelates using several techniques, including TG, to study the dehydration of these compounds [8]. Charles [9] investigated the thermal properties of some solid neodymium complexes derived from ethylenediaminetetraacetic acid by TG and DTA. Bhat and Krishna Iyer [10] described the thermal decomposition of EDTA complexes of Ca, Ba, Co, Cu, Ni, Bi, Sb and Dy in the solid state using TG techniques in air and nitrogen atmosphere.

In this study, solid state chelates of Co, Ni, Cu and Zn with EDTA were

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prepared and investigated by complexometry, TG and DTA in atmospheres of air, N_2 and CO_2; this represents an extension of part of the work of Bhat and Krishna Iyer.

EXPERIMENTAL

Ethylenediaminotetraacetic acid (EDTA) chelates of cobalt, nickel, copper and zinc were obtained by slow addition, with stirring, of stoichiometric quantities of the respective metal carbonate to EDTA solution. The partially dissolved mixture was heated to 60°C to facilitate evolution of CO_2. After cooling, the solution was allowed to evaporate at ambient temperature and pressure over anhydrous calcium chloride until constant weight.

The metal content of the Co, Ni, Cu and Zn chelates was determined by ignition to the oxide followed by complexometric titrations with a standard EDTA solution [11]. The water and EDTA contents were determined from the curves.

TG curves were recorded on a Perkin-Elmer TGS-2 thermogravimetric system; samples of about 7 mg were placed in alumina crucibles and heated at 20°C min^{-1} in N_2 (flow ≈20 ml min^{-1}), CO_2 (flow ≈10 ml min^{-1}) and air atmospheres (flow ≈5 ml min^{-1}) at ambient pressure.

DTA curves were recorded on Perkin-Elmer DTA-1700 equipment; α-Al_2O_3 was used as reference material. Samples of about 7 mg were placed in alumina crucibles and heated at 20°C min^{-1}, under the same conditions as the TG curves.

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical data of the prepared compounds of general formulae $H_2[M(EDTA)] \cdot nH_2O$, where M is Co, Ni, Cu or Zn, and $n = 1$ (Cu), $n = 2$ (Co, Zn) and $n = 2.5$ (Ni).

The TG–DTG curves of these compounds are shown in Fig. 1. The TG curves show mass losses in steps characteristic of each compound. The thermal decompositions depend on the atmosphere used.

Cobalt complex

The TG–DTG curves, Fig. 1 (curves a, b, c) show mass losses in four, five and three steps in N_2, CO_2 and air atmosphere, respectively.

For N_2 atmosphere, the first mass loss up to 190°C is due to dehydration, with loss of $2H_2O$ (TG, 9.55%; calc., 9.36%). The second step, between 260 and 400°C, is assigned to the loss of $4CH_2$ and $1H_2O$ (TG, 19.10%; calc., 19.25%). The third step takes place between 400 and 480°C, with the loss of 2(NCOO) (TG, 30.01%; calc., 30.12%). The last step, between 480 and

TABLE 1

Analytical and thermoanalytical results

Compound	Atm.	H_2 EDTA in %		Water in %		Final TG residue	Residue in %		Metal in %	
		Calc.	TG	Calc.	TG		Calc.	TG	Calc.	EDTA
$H_2[Co(EDTA)] \cdot 2H_2O$	N_2	75.35	74.34	9.36	9.55	Co	15.30	15.42	–	–
	CO_2	75.72	74.72	9.36	9.78	Co	15.30	15.50	–	–
	Air	69.12	68.02	9.36	9.82	Co_2O_3	21.53	22.15	15.30	15.07
$H_2[Ni(EDTA)] \cdot 2.5H_2O$	N_2	69.61	69.35	11.43	11.10	NiO	18.96	19.56	–	–
	CO_2	69.61	69.13	11.43	11.40	NiO	18.96	19.46	–	–
	Air	69.61	70.82	11.43	11.33	NiO	18.96	18.56	15.02	14.90
$H_2[Cu(EDTA)] \cdot H_2O$	N_2	78.06	>73.35	4.85	5.24	Cu	17.09	<22.16	–	–
	CO_2	78.06	77.91	4.85	4.74	Cu	17.09	17.34	–	–
	Air	73.76	73.07	4.85	4.74	CuO	21.39	22.19	17.09	16.92
$H_2[Zn(EDTA)] \cdot 2H_2O$	N_2	69.93	69.83	9.20	8.80	ZnO	20.78	20.77	–	–
	CO_2	69.93	>69.26	9.20	9.00	ZnO	20.78	<23.48	–	–
	Air	69.93	70.12	9.20	9.28	ZnO	20.78	20.42	16.69	16.70

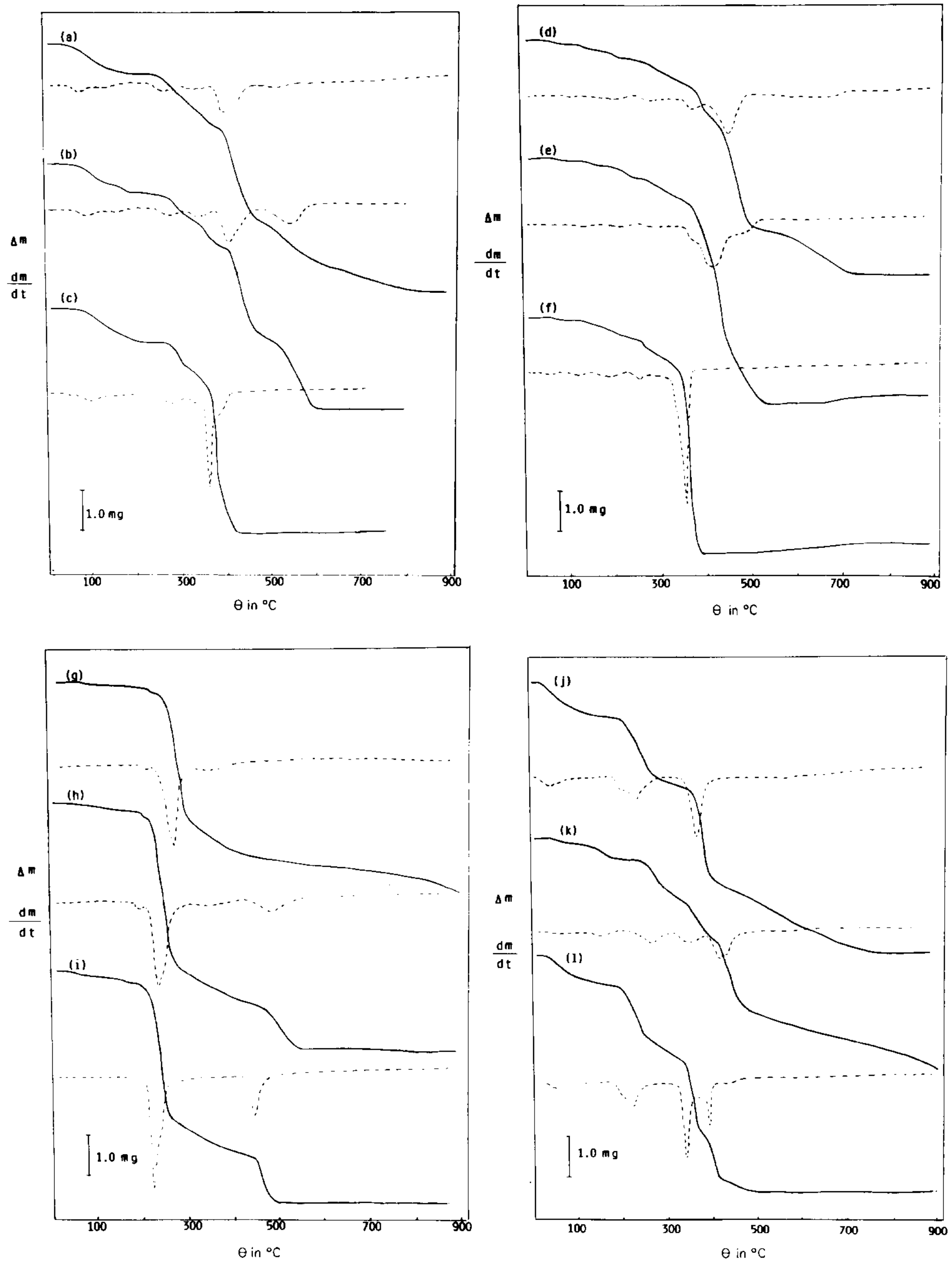

Fig. 1. TG–DTG curves of the cobalt complex $H_2[Co(EDTA)] \cdot 2H_2O$: (a) N_2 atmosphere (7.33 mg); (b) CO_2 atmosphere (7.16 mg); (c) air atmosphere (7.13 mg); (d) N_2 atmosphere (7.21 mg); (e) CO_2 atmosphere (7.45 mg); (f) air atmosphere (7.06 mg); (g) N_2 atmosphere (6.68 mg); (h) CO_2 atmosphere (7.38 mg); (i) air atmosphere (7.39 mg); (j) N_2 atmosphere (8.52 mg); (e) CO_2 atmosphere (7.58 mg) and (f) air atmosphere (7.54 mg). Heating rate, 20°C min^{-1}; alumina crucible.

900°C, is due to the final thermal decomposition with formation of metal as residue (TG, 25.23%; calc., 25.98%).

For CO_2 atmosphere, the first mass loss up to 190°C is due to the loss of $2H_2O$ (TG, 9.78%; calc., 9.36%). The second mass loss, 260–330°C, is assigned to the loss of $1CH_2$ and $1H_2O$ (TG, 8.38%; calc., 8.32%), and the third step, between 330 and 400°C, to the loss of $3CH_2$ (TG, 10.47%; calc., 10.93%). The fourth step, between 400 and 460°C, is ascribed to the loss of 2(NCOO) (TG, 30.03%; calc., 30.12%). The last step, between 460 and 610°C, is due to the final thermal decomposition with formation of metal as residue (TG, 25.84%; calc., 25.98%).

For air atmosphere, the first mass loss up to 180°C is due to the loss of $2H_2O$ (TG, 9.82%; calc., 9.36%). The second step, between 260 and 370°C, is a slow process assigned to the loss of $4CH_2$ and $1H_2O$ (TG; 18.93%; calc., 19.25%). The last step, between 370 and 420°C, is ascribed to the final pyrolysis with formation of Co_2O_3 as residue (TG, 49.09%; calc., 49.87%).

The interpretation of the thermal decomposition results for the anhydrous compound, in N_2 and air atmosphere, are in disagreement with the results reported by Bhat and Krishna Iyer [10]. The TG curves in air atmosphere are in agreement with the behaviour reported by Morris et al. [7] where a weight gain was not observed.

Nickel complex

The TG–DTG curves, Fig. 1 (curves d, e, f), show mass losses in four steps in N_2, and two steps in CO_2 and air atmospheres.

For N_2 atmosphere, the mass loss up to 320°C is due to the loss of $2.5H_2O$ (TG, 11.10%; calc., 11.43%). The thermal decomposition of the anhydrous compound between 320 and 420°C (second step) is ascribed to the loss of $3CH_2$ and $1H_2O$ (TG, 15.26%; calc., 15.26%) and the third step, between 420 and 520°C, to the loss of CH_2, NCH_2CO and NCH_2COO (TG, 36.75%; calc., 36.07%). The last step (520–750°C) is due to the final thermal decomposition of the compound with formation of NiO as residue (TG, 17.34%; calc., 18.28%).

For CO_2 atmosphere, the mass loss up to 320°C is due to the loss of $2.5H_2O$ (TG, 11.40%; calc., 11.43%). After the dehydration, the thermal decomposition of the anhydrous compound occurs in one step between 320 and 550°C, with formation of a mixture of metal and oxide, which is subsequently converted to the oxide, NiO, as shown by the mass gain observed in the TG curves after 650°C.

For air atmosphere, the mass loss up to 300°C is due to the loss of $2.5H_2O$ (TG, 11.33%; calc., 11.43%). The thermal decomposition of the anhydrous compound occurs in one step between 300 and 390°C with formation of a mixture of metal and oxide, which is subsequently converted to the oxide, NiO, as shown by the TG curves after 550°C.

These results are also in disagreement with the data reported by Bhat and Krishna Iyer [10], even in the aspect of the TG curves in nitrogen and air atmospheres.

Copper complex

The TG–DTG curves, Fig. 1 (curves g, h, i) shows mass losses in three steps in all the atmospheres used. The water of hydration is lost through a slow process, indicating that it is probably co-ordinated to the metal, as already observed by Bhat and Krishna Iyer [10].

For N_2 atmosphere, the mass loss up to 230°C is due to dehydration (TG, 5.24%; calc., 4.85%). The second step, between 230 and 400°C, is ascribed to the thermal decomposition of the anhydrous compound with losses of $2(HOOCCH_2–N–CH_2–CH_2)$ (TG, 54.64%; calc., 54.39%). For the last step, in which the final thermal decomposition of the other two carboxyl groups occurs, the TG–DTG curves show that the final mass loss takes place above 900°C (TG, 18.71%; calc., 19.37%).

For CO_2 atmosphere, the mass loss up to 210°C is due to the dehydration (TG, 4.78%; calc., 4.85%). The second step (210–350°C) is ascribed to the loss of $2(HOOCCH_2–N–CH_2–CH_2)$ (TG, 54.88%; calc., 54.39%). The last step (350–560°C) is assigned to the loss of the other two carboxyl groups with formation of metal as residue (TG, 23.04%; calc., 23.67%).

For air atmosphere, the mass loss up to 210°C is due to the dehydration (TG, 4.74%; calc., 4.85%). The second step (210–290°C) is ascribed to the loss of $2(HOOCCH_2–N–CH_2–CH_2)$, (TG, 46.68%; calc., 46.85%). The last step, between 290 and 510°C, is assigned to the loss of the other two carboxyl groups with formation of the oxide CuO as residue (TG, 18.94%; calc., 19.37%).

The thermal decomposition of the copper complex, in all the atmospheres used, and the calculation based on the mass loss observed in the TG curves suggest the elimination of two carboxyl groups in the last step; this is in disagreement with the interpretation reported by Bhat and Krishna Iyer [10]. In this work, when samples heated up to 400°C were analysed for carbon, hydrogen and nitrogen, nitrogen was not found.

Zinc complex

The TG–DTG curves, Fig. 1 (curves j, k, l) show mass losses in four steps in N_2 and in five steps in CO_2 and air atmospheres.

For N_2 atmosphere, the first mass loss up to 150°C is due to the loss of $2H_2O$ (TG, 8.80%; calc., 9.20%). The second mass loss, between 150 and 290°C, is ascribed to the loss of $4CH_2$ and $1H_2O$ (TG, 18.78%; calc., 18.93%) and the third step (290–460°C) to the loss of CH_2NCOO and NCO (TG, 29.34%; calc., 29.12%). The last step, between 460 and 800°C, is assigned to the final thermal decomposition with formation of ZnO as residue (TG, 21.71%; calc., 21.97%).

For CO_2 atmosphere, the first mass loss up to 190°C is due to the loss of $2H_2O$ (TG, 9.00%; calc., 9.20%). The second step, between 220 and 320°C, is ascribed to the loss of $2CH_2$ and $1H_2O$ (TG, 11.87%; calc., 11.78%) and the third step (320–400°C) to the loss of $2CH_2$ and CO (TG, 14.51%; calc., 14.32%). The fourth step, between 400 and 470°C, is assigned to the loss of CH_2–N–COO–N (TG, 21.77% calc., 12.97%) and the last step, between 470°C and >900°C, to the final thermal decomposition (TG, 21.11%; calc., 21.97%).

For air atmosphere, the first mass loss up to 150°C is due to the loss of $2H_2O$ (TG, 9.28%; calc., 9.20%). The second step, between 150 and 260°C, is ascribed to the loss of $4CH_2$ and $1H_2O$ (TG, 19.23%; calc., 18.93%) and the third step (260–380°C) to the loss of NCOO and NCO (TG, 25.86%; calc., 25.54%). The fourth step, between 380 and 400°C, is assigned to the loss of CH_2 and CH_2COO (TG, 18.40%; calc., 18.57%) and the last step (400–510°C) to the loss of CO with formation of ZnO residue (TG, 6.63%; calc., 7.15%).

Figure 2 shows the DTA curves of the prepared compounds in N_2, CO_2 and air atmospheres.

Cobalt complex

The DTA curve in N_2 atmosphere, Fig. 2, curve a, shows endothermic and exothermic peaks. The endothermic peak at 140°C and the shoulder at 190°C are ascribed to the dehydration. The endothermic peaks at 250, 390 and 490°C, and the exothermic peak at 680°C are attributed to the thermal decomposition of the anhydrous compound, all in correspondence with the mass losses observed in the TG curves.

For CO_2 atmosphere, Fig. 2, curve b, the DTA curve shows only endothermic peaks. The peak at 200°C is ascribed to the dehydration, and the peaks at 310, 450 and 520°C are attributed to the thermal decomposition of the anhydrous compound.

For air atmosphere, Fig. 2, curve c, the endothermic peaks at 150 and 210°C are ascribed to the dehydration. The endothermic peak at 290°C, followed by broad exotherm between 300 and 620°C with the peak at 450°C, are ascribed to the thermal decomposition. The last endothermic peak at 920°C is attributed to the reduction reaction of Co_2O_3 to Co_3O_4.

Nickel complex

The DTA curve in N_2 atmosphere, Fig. 2, curve d, shows only endothermic peaks. The peaks at 80, 120, 200 and 220°C are ascribed to the

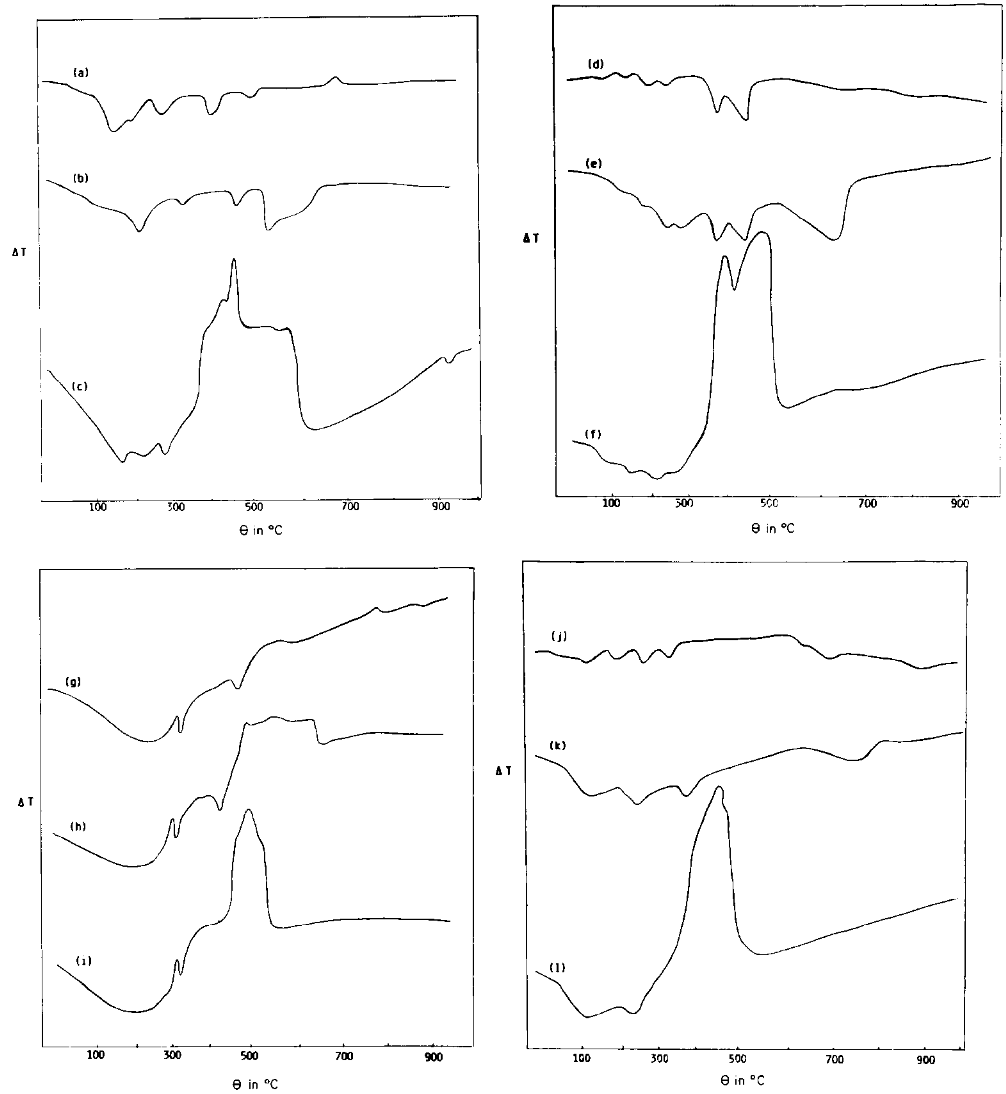

Fig. 2. DTA curves of the cobalt complex, $H_2[Co(EDTA)] \cdot 2H_2O$: (a) N_2 atmosphere; (b) CO_2 atmosphere; (c) air atmosphere; (d) N_2 atmosphere; (e) CO_2 atmosphere; (f) air atmosphere; (g) N_2 atmosphere; (h) CO_2 atmosphere; (i) air atmosphere; (j) N_2 atmosphere; (k) CO_2 atmosphere and (l) air atmosphere. Heating rate, 20°C min^{-1}; sample ≈7 mg; alumina crucible and α-Al_2O_3 as reference material.

dehydration that takes place in consecutive steps. The peaks at 380 and 480°C are assigned to the partial thermal decomposition of the anhydrous compound and, in correspondence with the mass losses observed in the TG curves (550–850°C), are attributed to the final thermal decomposition of the compound.

For CO_2 atmosphere, Fig. 2, curve e, once more, only endothermic peaks are observed. The peaks due to dehydration occur in the same temperature range as was observed in N_2 atmosphere. The peaks at 380, 440 and 630°C are attributed to the thermal decomposition of the anhydrous compound. No exothermic peak is observed in the DTA curve, although the corresponding TG curve shows a mass gain after 650°C, attributed to the oxidation reaction of the mixture of metal and oxide to NiO.

For air atmosphere, Fig. 2, curve f, evidence of endothermic peaks at 90, 140 and 210°C are ascribed to the dehydration. The broad exotherm between 300 and 520°C, with two peaks, is attributed to the pyrolysis of the anhydrous compound. The broad exotherm between 520 and 700°C is attributed to the oxidation reaction of the mixture of metal and oxide to NiO.

Copper complex

The DTA curves in N_2, CO_2 and air atmosphere, Fig. 2, curves g, h and i, respectively, show a broad endotherm between 100 and 290°C characteristic of a slow dehydration; this is in agreement with the TG data.

The endothermic peak at 320°C in N_2 and air atmosphere, and at 310°C in CO_2 atmosphere, is probably due to the structural rearrangement that occurs after the dehydration. No fusion process was observed in samples heated up to 400°C: this is in disagreement with the result reported by Bhat and Krishna Iyer [10].

For N_2 atmosphere, the endothermic peak at 480°C followed by a small broad exotherm between 500 and 590°C, and the peaks at 780°C (exo) and 880°C (endo), are attributed to the thermal decomposition of the compound.

For CO_2 atmosphere, the thermal decomposition shows an endothermic peak at 420°C followed by a broad exotherm between 450 and 650°C.

For air atmosphere, only a broad exotherm with a peak at 495°C is observed in the thermal decomposition of the compound.

Zinc complex

The DTA curve in N_2 atmosphere, Fig. 2, curve j, shows only endothermic peaks. The first peak at 120°C is attributed to the dehydration. The peaks at 190, 260 and 330°C are ascribed to the partial thermal decomposition of the anhydrous compound and are in correspondence with the second and third mass losses observed in the TG curves. The broad endotherm between 600 and 950°C, with evidence of two peaks at 700 and 900°C, is assigned to the final thermal decomposition of the compound.

For CO_2 atmosphere, Fig. 2, curve k, the DTA curve also shows only endothermic peaks. The first peak at 120°C is attributed to the dehydration and the peaks at 250, 390 and 740°C are attributed to the thermal decomposition of the anhydrous compound.

For air atmosphere, the endothermic peak at 100°C is ascribed to the dehydration. The endothermic peak at 220°C, followed by a broad exotherm between 220 and 560°C with the peak at 460°C, are attributed to the thermal decomposition of the anhydrous compound.

CONCLUSIONS

The results of the present work have provided information about the thermal decomposition of the cobalt, nickel and copper complexes. Our results in nitrogen and air atmosphere are in disagreement with those already described in the literature.

In addition, the thermal decomposition of these compounds in CO_2 atmosphere has been described. Moreover, the thermal decompositions of the zinc complexes have been reported for the first time.

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