

A thermal analysis study of some transition-metal dithizonates

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Abstract

Solid dithizonates of Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II), have been prepared. Thermogravimetry (TG), derivative thermogravimetry (DTG), differential scanning calorimetry (DSC), X-ray diffraction powder patterns and elemental analysis have been used to characterize and study the thermal stability and thermal decomposition of these compounds. © 1998 Elsevier Science B.V.

Keywords: Transition metal; Dithizonate; Thermal decomposition

1. Introduction

The aqueous solution chemistry of dithizone (diphenylthiocarbazone) has been extensively studied since the introduction of these compounds as a reagent for the determination of heavy metals. Studies of the solid-state compounds have been reported by Harding [1], who derived the crystal structure of the mercury dithizone complex by X-ray diffraction. Bryan and Knoff [2] reported the preliminary results of an X-ray diffraction study of keto cupric dithizonate. The structure of keto nickel dithizonate was determined from three-dimensional single crystal X-ray data by Laing and Sommerville [3]. Mawby and Irving [4] described the crystal structure of keto zinc(II) dithizonate and its relevance to the stabilities of its *o*- and *p*-methyl derivatives. Dyfverman [5] described the infrared spectra of a number of metal dithizonates. Pariaud and Archinard [6] reported the preparation and ther-

mogravimetric studies of silver, lead, zinc and copper dithizonates and the TG curves recorded in a Chevenard thermobalance showed explosive decomposition for these compounds. No reference has been found to the application of TG and DSC in the study of iron(II), cobalt(II), nickel(II) and cadmium(II) dithizonates.

In this study, bivalent iron, cobalt, nickel, copper, zinc, cadmium and lead dithizonates are prepared and investigated by complexometry, TG, DTG, DSC and X-ray diffraction powder patterns.

2. Experimental

Aqueous solutions of the metal were prepared by dissolving the chloride (Co), nitrate (Cd, Pb) or sulphate (Fe, Cu, Ni, Zn). The solid state complexes were prepared by mixing solutions of the corresponding metal ions in excess with a dithizone solution of 0.05% (w/v) in ketone, to effect total precipitation of metal dithizonate. The precipitates were washed with distilled water to eliminate chloride, nitrate or

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sulphate ions, filtered and dried and stored in a desiccator over anhydrous calcium chloride.

The metal contents of the complexes were determined by complexometric titration with standard EDTA solution [7], after samples had been heated in a digestion apparatus with concentrated nitric acid and 30% hydrogen peroxide added dropwise or concentrated sulphuric acid and perchloric acid for the zinc compound. Metal contents were also determined from the TG curves. The dithionite and water contents of the cobalt compound were determined from the TG curves and confirmed by carbon, nitrogen, sulphur and hydrogen microanalytical determinations.

The TG and DTG curves were recorded on a Perkin–Elmer TGS-2, thermogravimetric system with an air flow of 5 ml min⁻¹, a heating rate of 20°C min⁻¹ and a platinum crucible. The DSC curves were obtained using a Mettler TA-4000 thermoanalyser system with air flow rate of 150 ml min⁻¹, and a

heating rate of 20°C min⁻¹, and aluminium crucibles with perforated covers.

X-ray powder patterns were obtained with an HGZ 4/B horizontal diffractometer (GDR) equipped with a proportional counter and pulse height discriminator. The Bragg–Brentano arrangement was adopted using CoK_α (λ=1.78897 Å) and a setting of 38 KV and 20 mA.

Carbon, nitrogen, sulphur and hydrogen were determined by microanalytical procedures using CE Instruments, EA 1110 CHNS-0 apparatus.

3. Results and discussion

Table 1 presents the analytical and thermoanalytical (TG) data and Table 2 the elemental analysis results for the prepared compounds from which the general formula M(HDz)₂; Co(HDz)₂·H₂O and CuDz

Table 1
Analytical and thermoanalytical TG results

Compound	Metal (%)			Dz or Hdz ^a (%)		Water (%)		Residue
	theor	TG	EDTA	theor	TG	theor	TG	
Fe(HDz) ₂	9.86	10.4	9.95	85.91	85.1	–	–	Fe ₂ O ₃
Co(HDz) ₂ ·H ₂ O	10.03	9.58	9.26	83.27	83.7	3.07	3.2	CoO
Ni(HDz) ₂	10.31	10.1	10.19	86.88	87.0	–	–	NiO
CuDz	19.99	20.8	20.48	74.98	73.6	–	–	CuO
Zn(HDz) ₂	11.35	11.6	11.29	85.87	85.5	–	–	ZnO
Cd(HDz) ₂	18.04	17.5	17.63	79.39	80.0	–	–	CdO
Pb(HDz) ₂	28.86	30.2	28.07	68.17	66.4	–	–	Pb ₃ O ₄

^a Dz or Dhz, dithionite.

Table 2
Elemental analysis (E.A.) results

Compound ^a	N (%)		C (%)		H (%)		S (%)	
	theor	E.A.	theor	E.A.	theor	E.A.	theor	E.A.
Fe(HDz) ₂	19.78	19.57	55.12	55.10	3.92	3.75	11.32	11.45
Co(HDz) ₂ ·H ₂ O	19.07	18.90	53.14	54.84	4.13	4.11	10.91	9.05
Ni(HDz) ₂	19.68	19.34	54.84	54.03	3.90	3.86	11.26	10.53
CuDz	17.63	18.36	49.12	51.61	3.18	3.59	10.09	12.26
Zn(HDz) ₂	19.46	20.09	54.21	56.13	3.86	4.01	11.13	12.83
Cd(HDz) ₂	17.99	18.05	50.12	50.89	3.57	3.65	10.29	11.48
Pb(HDz) ₂	15.61	15.18	43.50	42.85	3.10	3.03	8.93	10.53

^a Dz or Hdz, dithionite.

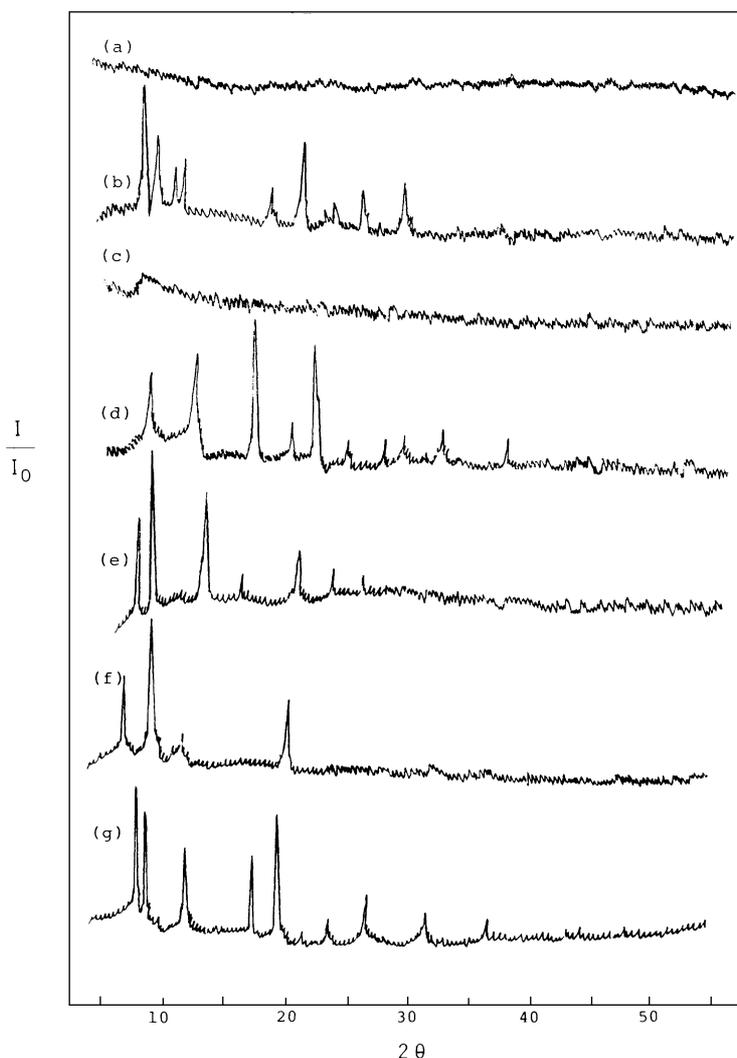


Fig. 1. X-ray powder diffraction patterns of: (a) $\text{Fe}(\text{HDz})_2$; (b) $\text{Co}(\text{HDz})_2 \cdot \text{H}_2\text{O}$; (c) $\text{Ni}(\text{HDz})_2$; (d) CuDz ; (e) $\text{Zn}(\text{HDz})_2$; (f) $\text{Cd}(\text{HDz})_2$; and (g) $\text{Pb}(\text{HDz})_2$.

can be established, where M is (Fe(II), Ni(II), Zn(II), Cd(II) or Pb(II), and HDz or Dz the dithizonate.

Although the same procedure has been adopted in the preparation of these complexes, the dithizonate ligand in the copper complex was in the 'enol' form, whereas for the other metals, the keto form of dithizonate was present. All complexes were obtained in the anhydrous form, except for cobalt dithizonate which had hydration water.

The X-ray powder patterns, Fig. 1 show that the cobalt, copper, zinc, cadmium and lead complexes

have a crystalline structure, and for the iron and nickel complexes the diffraction patterns indicate an amorphous structure.

The TG and DTG curves are shown in Fig. 2. These show mass losses in two, three or four steps for iron and cobalt dithizonates. The first mass loss begins with a slow process, followed by a fast process, without evidence of combustion (explosion) during thermal decomposition.

A great similarity is also observed in the TG and DTG curves of the other dithizonates (Fig. 2(c–g)),

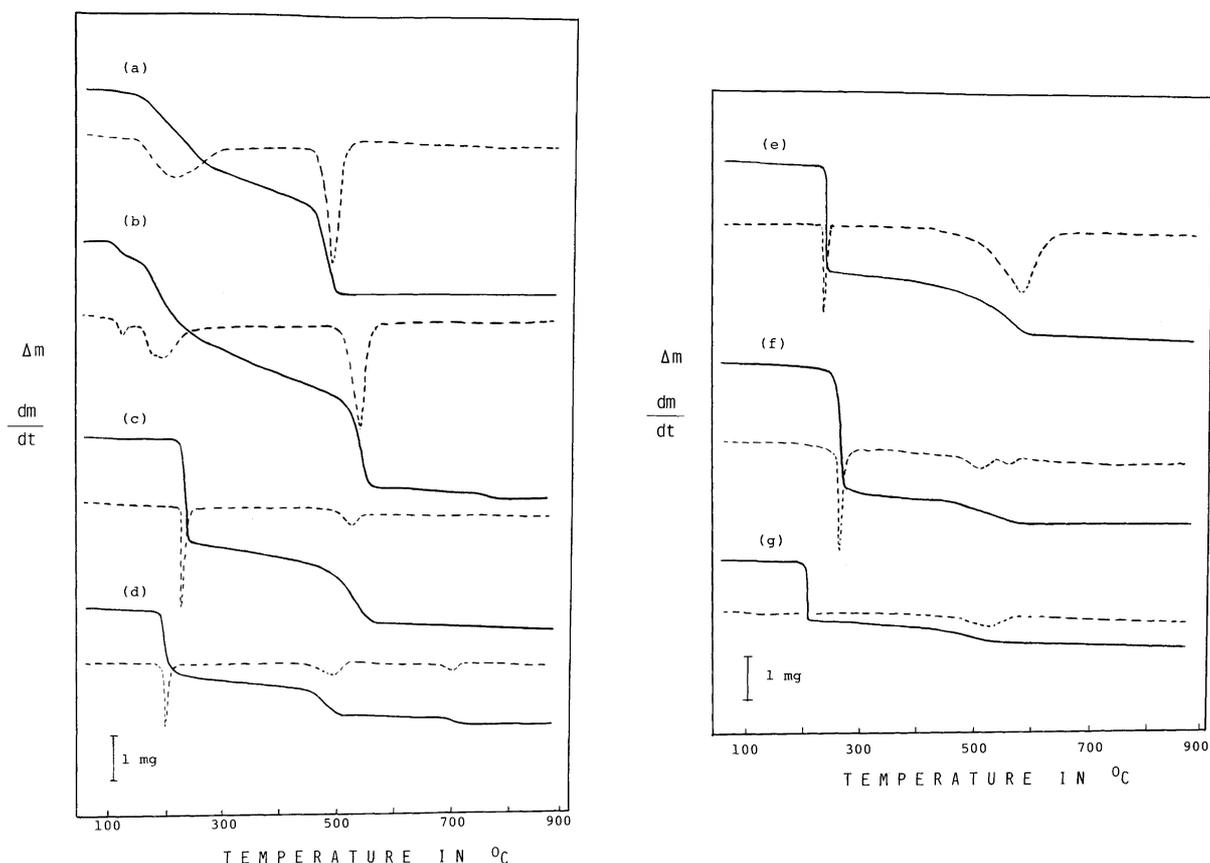


Fig. 2. TG and DTG curves of: (a) $\text{Fe}(\text{HDz})_2$ (4.64 mg); (b) $\text{Co}(\text{HDz})_2 \cdot \text{H}_2\text{O}$ (5.75 mg); (c) $\text{Ni}(\text{HDz})_2$ (4.25 mg); (d) CuDz (2.99 mg); (e) $\text{Zn}(\text{HDz})_2$ (3.80 mg); (f) $\text{Cd}(\text{HDz})_2$ (4.00 mg); and (g) $\text{Pb}(\text{HDz})_2$ (2.41 mg).

where the first mass loss begins with a very fast process due to combustion (explosion) and is followed by a slow process.

For the iron complex, the TG and DTG curves (Fig. 2(a)) show that thermal decomposition occurs in two consecutive steps between 115° and 510°C. In the first step, up to 320°C, the mass loss corresponds to 36.6% and the second step, which begins with a slow process followed by a fast mass loss, corresponds to 48.5% and the formation of iron oxide, Fe_2O_3 .

For the cobalt compound, the TG and DTG curves (Fig. 2(b)) show mass losses in four steps between 100° and 800°C. The first mass loss observed up to 135°C is due to the dehydration with loss of $1\text{H}_2\text{O}$ (theor, 3.07%; TG, 3.1%). The second and third steps, observed between 135° and 320°C and 320–580°C, show the same behaviour of the iron compound, the

mass losses correspond to 29.9 and 49.6%, respectively, with the formation of CoO_2 and a small quantity of carbonaceous residue. The last step, between 690° and 850°C, is assigned to the pyrolysis of carbonaceous residue and reduction of $\text{Co}(\text{IV})$ to $\text{Co}(\text{II})$ with the formation of cobalt oxide, CoO as final residue (theor, 2.72%; TG, 4.3%).

In the nickel, copper, zinc, cadmium and lead dithizonates, the TG and DTG curves Fig. 2(c–g) show mass losses in two steps, except for the copper complex which shows three steps. The first mass loss that occurs through a very fast process at 210° (Ni), 175° (Cu), 220° (Zn), 230° (Cd) and 190° (Pb) is due to the combustion (explosion) of the sample with loss of 46.7, 40.1, 52.6, 62.5 and 49.8%, respectively. The second step observed up to 570° (Ni), 520° (Cu) and 600°C (Zn, Cd, Pb) with loss of 41.2, 31.4, 33.2, 17.0

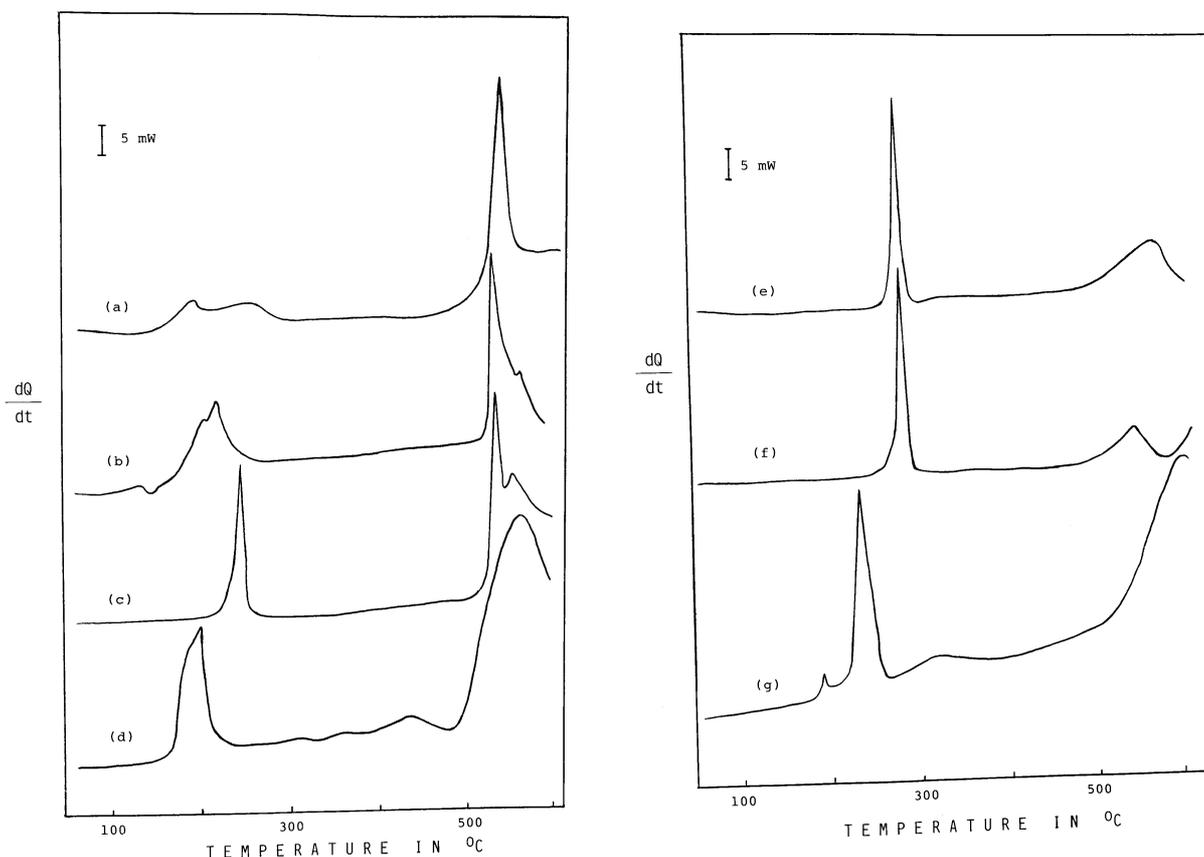


Fig. 3. DSC curves of: (a) $\text{Fe}(\text{HDz})_2$; (b) $\text{Co}(\text{HDz})_2 \cdot \text{H}_2\text{O}$; (c) $\text{Ni}(\text{HDz})_2$; (d) CuDz ; (e) $\text{Zn}(\text{HDz})_2$; (f) $\text{Cd}(\text{HDz})_2$; and (g) $\text{Pb}(\text{HDz})_2$.

and 17.0%, respectively, is ascribed to the final thermal decomposition of these complexes with the formation of NiO , ZnO , CdO , PbO_2 and CuO . Only for the copper complex, the oxide is accompanied by a small quantity of carbonaceous residue, the pyrolysis of which occurs between 680° and 730°C .

The thermal decomposition temperature and the form of the TG curves of the zinc and lead dithizonates are in agreement with the studies of Pariaud and Archinard [6], but in disagreement for the copper compound. This disagreement is related to the ligand structure in these complexes.

In previous experiments, when a sample of 10 mg of the complex was heated at a rate of $20^\circ\text{C min}^{-1}$ in a furnace in a platinum crucible, explosion with projection of materials were observed for the compounds, where the TG curves show a very fast mass loss in the first step. The same behaviour was also observed in the

TG curves, for these compounds with a sample mass of 7 mg, where the oscillation in the thermobalance system was recorded during the first step of mass loss.

The DSC curves are shown in Fig. 3. These curves show exothermic peaks up to 600°C , all of which are in accord with the mass losses observed in the TG and DTG curves. For the cobalt compound, one endothermic peak due to dehydration is observed at 140°C and is in agreement with the TG and DTG data.

For the iron and cobalt dithizonates (Fig. 2(a and b)), the exotherm between 140° and 290°C (Fe), and the broad exothermic peak at 210°C (Co) are attributed to the oxidative thermal decomposition of the organic matter, and correspond with the first and second steps of the TG and DTG curves of the iron and cobalt compounds, respectively. The sharp exothermic peaks at 525° (Fe) and 520°C (Co) are ascribed to the final pyrolysis of the carbonaceous

material resulting from the thermal decomposition process.

For the nickel, copper, zinc, cadmium and lead dithizonates (Fig. 3(c–g)), the sharp exothermic peaks at 240°, 195°, 270°, 280° and 230°C, respectively, are attributed to combustion and are in agreement with the TG and DTG data. The small exothermic peak at 190°C observed only for the lead compound, is due to a crystalline transition that precedes the combustion. The exotherm in the 500–600°C range, with a sharp peak at 530°C followed by small peak at 545°C in the nickel compound, is attributed to the final pyrolysis of the carbonaceous residue. For the other compounds, the sequence of a small exotherm above 300°C with a broad exothermic peak at 550°C (Cu), the broad exothermic peaks at 570°C (Zn) and 540°C (Cd), and the exotherm between 280° and above 600°C (Pb) are ascribed to the final oxidation of the carbonaceous materials resulting from the combustion process.

4. Conclusion

The X-ray powder patterns verified that these complexes have a crystalline structure, except for the iron and nickel compounds that indicate an amorphous structure. The TG, DTG, DSC, complexometry and

elemental-analysis data establish the stoichiometry of these complexes in the solid state and provide some indication of the thermal stabilities and the decomposition products. The TG, DTG and DSC analyses of these complexes revealed that the combustion temperature depends on the identity of the metal ion present and no combustion was observed for the iron and cobalt complexes.

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References

- [1] M.M. Harding, *J. Chem. Soc.* (1958) 4136.
- [2] R.F. Bryan, P.M. Knoff, *Proc. Chem. Soc.* (1961) 203.
- [3] M. Laing, P. Sommerville, *J. Chem. Soc. (A)* (1971) 1247.
- [4] A. Mawby, H.M.N.H. Irving, *Anal. Chim. Acta* 55 (1971) 269.
- [5] A. Dyfverman, *Acta Chem. Scand.* 17 (1963) 1609.
- [6] J.C. Pariaud, P. Archinard, *Recueil* 71 (1952) 634.
- [7] C.N. Oliveira, M. Ionashiro, C.A.F. Graner, *Ecl. Quim.* 10 (1985) 7.