

# Trimellitate complexes of divalent transition metals with hydrazinium cation

## Thermal and spectroscopic studies

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**Abstract** New dihydrazinium divalent transition metal trimellitate hydrates of empirical formula  $(\text{N}_2\text{H}_5)_2\text{M}(\text{Htm})_2 \cdot n\text{H}_2\text{O}$ , where  $n = 1$  for  $\text{M} = \text{Co}$  or  $\text{Ni}$ , and  $n = 2$  for  $\text{M} = \text{Mn}$ ,  $\text{Zn}$ , or  $\text{Cd}$  ( $\text{H}_3\text{tml} = \text{trimellitic acid}$ ), and mono-hydrazinium cadmium trimellitate,  $[(\text{N}_2\text{H}_5)\text{Cd}(\text{Htm})_{1.5} \cdot 2\text{H}_2\text{O}]$  have been prepared and characterized by physico-chemical methods. Electronic spectroscopic, and magnetic moment data suggest that  $\text{Co}$  and  $\text{Ni}$  complexes adopt an octahedral geometry. The IR spectra confirm the presence of monodentate carboxylate anion ( $\Delta\nu = \nu_{\text{asy}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-) > 190 \text{ cm}^{-1}$ ) and coordinated  $\text{N}_2\text{H}_5^+$  ion ( $\nu_{\text{N-N}} 1015 - 990 \text{ cm}^{-1}$ ) in all the complexes. All the complexes undergo endothermic decomposition eliminating  $\text{CO}_2$  in the temperature region  $200\text{--}250 \text{ }^\circ\text{C}$ , followed by exothermic decomposition (in the range of  $500\text{--}570 \text{ }^\circ\text{C}$ ) of organic moiety to give the respective metal carbonate as the end products except nickel and cobalt complexes, which leave respective metal oxides. X-ray powder diffraction patterns reveal that  $\text{Ni}$  and  $\text{Co}$  complexes are isomorphous as are those of,  $\text{Zn}(\text{II})$  and  $\text{Cd}(\text{II})$  of the type,  $(\text{N}_2\text{H}_5)_2\text{M}(\text{Htm})_2 \cdot 2\text{H}_2\text{O}$ .

**Keywords** Chemical synthesis · Inorganic compounds · Thermogravimetric analysis (TGA) · X-ray diffraction

## Introduction

Benzene-1,2,4-tricarboxylic acid, commonly referred to as trimellitic acid, due to the presence of a pair of adjacent carboxylic acid groups as in phthalic acid with an additional carboxylic acid group in it, possesses a good ligating ability. Its dianionic behavior seems to resemble the coordinating nature of phthalates and terephthalates. The complexation of lanthanides with trimellitic acid has been studied potentiometrically and calorimetrically [1] and in terms of basicity, the statistical effect of unbound carboxylate groups and steric factors [2]. The stereochemistry of the trimellitate anion shows that it functions as a bidentate ligand with adjacent carboxylate groups in lanthanide complexes. Trimellitates of  $\text{Sc}(\text{III})$  and  $\text{Cu}(\text{II})$  have also been prepared and characterized by thermal studies [3, 4]. Scandium trimellitate,  $\text{Sc}(\text{tml}) \cdot 4\text{H}_2\text{O}$ , undergoes decomposition to give  $\text{Sc}_2\text{O}_3$  and  $\text{C}$  as final products. Copper trimellitate pentahydrate,  $\text{Cu}_3(\text{tml})_2 \cdot 5\text{H}_2\text{O}$ , decomposes in two steps giving  $\text{CuO}$  as the final product. The burning of organic anion is accompanied by a strong exothermic effect.

Hydrazine, the simplest diamine even after getting protonated as  $\text{N}_2\text{H}_5^+$  evinces its coordinating ability. A variety of complexes containing coordinated and uncoordinated hydrazinium moieties, such as hydrazinium metal oxalate [5, 6], malonate [7], and phthalate [8] have been studied. Thermal reactivity of metal carboxylates with hydrazine is of increasing interest, since they serve as precursors to fine-particle oxide materials and metal carbonates [5–16]. Though a very few simple metal complexes of trimellitate have been reported, yet, a detailed study of trimellitic acid complexes of transition metals with hydrazinium cation with special emphasis on its thermal reactivity has not been attempted so far. In this paper, we report for the first time the synthesis, spectroscopic, and

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thermal studies on divalent transition metal complexes of trimellitic acid with hydrazine.

## Experimental

Preparation of  $(\text{N}_2\text{H}_5)_2\text{M}(\text{Htm})_2 \cdot n\text{H}_2\text{O}$  where  $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}, \text{and Cd}$

To an aqueous solution of trimellitic acid (0.428 g, 2 mmol in 40 mL distilled water), hydrazine hydrate of 99–100% purity (0.2 g, 4 mmol) was added and heated over hot water bath at 80 °C, for about 15 min. Then to the clear solution obtained at pH 3.5, was added with vigorous stirring, the respective metal nitrate hydrate (1 mmol, e.g., 0.292 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ). The solution was then reduced to half of its volume by heating over boiling water bath and allowed to stand at room temperature. Slowly flake like crystals of the complex appeared after a couple of days and settled down. They were filtered, washed with alcohol and ether, and air-dried. The same final product was obtained when the above experimental procedure was pursued at room temperature; however, the products were obtained after 4 days.

Preparation of  $(\text{N}_2\text{H}_5)\text{Cd}(\text{Htm})_{1.5} \cdot 2\text{H}_2\text{O}$

The above procedure was followed taking trimellitic acid, hydrazine hydrate (99–100% pure), and cadmium nitrate in the molar ratio, 2:4:1 at room temperature. The solution was left undisturbed without heating. Slowly a crystalline precipitate was formed after 1 day and settled down. It was filtered, washed with alcohol and ether, and air-dried.

### Physicochemical techniques

The stoichiometry of the complexes was fixed by chemical analysis [17]. Hydrazine content was determined by

titrating against standard  $\text{KIO}_3$  ( $0.025 \text{ mol dm}^{-3}$ ) under Andrews conditions. Metal contents were determined by titrating with EDTA ( $0.01 \text{ mol dm}^{-3}$ ) after decomposing the complexes with conc.  $\text{HNO}_3$ . The elements were determined by microelemental analysis. Electronic spectra in the UV–visible region were obtained using a Hitachi Perkin Elmer 20/200 recording spectrophotometer by dispersing the solid samples in Nujol. IR spectral data of the complexes were recorded as KBr pellets using a Perkin Elmer 597 spectrometer. The magnetic susceptibility of the complexes was measured (298 K) using a vibrating sample magnetometer (VSM E.G&G model 155) in the magnetic field from 2 to 10 KG and appropriate corrections were also made. The X-ray diffractograms of the complexes were recorded using a Philips X ray diffractometer (model p N 1050/70) employing  $\text{Cu K}_\alpha$  radiation with a nickel filter. The simultaneous TG–DTA experiments were carried out in air, using STA 1500 thermal analyzer at the heating rate of 10 °C per min. Platinum cups were employed as sample holders and alumina as reference. The temperature was ambient to 700 °C.

## Results and discussion

The results of chemical analysis of the complexes are given in Table 1 and are best fit with the proposed compositions viz.,  $(\text{N}_2\text{H}_5)_2\text{M}(\text{Htm})_2 \cdot n\text{H}_2\text{O}$ , where  $\text{M} = \text{Co}$  and  $\text{Ni}$ ,  $n = 1$ ;  $\text{M} = \text{Mn}, \text{Zn}$  or  $\text{Cd}$ ,  $n = 2$ , and  $(\text{N}_2\text{H}_5)\text{Cd}(\text{Htm})_{1.5} \cdot 2\text{H}_2\text{O}$ . The complexes are isolated as solids, air stable and are insensitive to light. All the complexes are insoluble in water and most of the organic solvents like alcohol, chloroform, and acetone. While Co and Ni complexes are monohydrated, rest of the complexes are dihydrated. Cadmium forms two different products with trimellitic acid in the same ratio, but with different experimental condition. The dihydrazinium compound of cadmium was obtained

**Table 1** Analytical, elemental and IR data of trimellitate complexes

Complex (color)	Found (calculated)/%						IR data/ $\text{cm}^{-1}$			
	Carbon	Hydrogen	Nitrogen	Hydrazine	Metal		$\nu_{\text{COO}}$ (asym)	$\nu_{\text{COO}}$ (sym)	$\nu_{\text{CO}}$ (free COOH)	$\nu_{\text{N-N}}$
$(\text{N}_2\text{H}_5)_2\text{Co}(\text{Htm})_2 \cdot \text{H}_2\text{O}$ (pink)	38.56 (38.64)	3.48 (3.58)	9.90 (10.02)	11.5 (11.40)	10.3 (10.54)		1607	1373	1685	1008
$(\text{N}_2\text{H}_5)_2\text{Ni}(\text{Htm})_2 \cdot \text{H}_2\text{O}$ (green)	38.42 (38.66)	3.79 (3.58)	9.98 (10.02)	11.6 (11.5)	10.4 (10.50)		1607	1373	1685	1016
$(\text{N}_2\text{H}_5)_2\text{Zn}(\text{Htm})_2 \cdot 2\text{H}_2\text{O}$ (dirty white)	36.93 (37.03)	3.81 (3.77)	9.21 (9.60)	10.6 (10.97)	11.3 (11.20)		1607	1371	1697	993
$(\text{N}_2\text{H}_5)_2\text{Cd}(\text{Htm})_2 \cdot 2\text{H}_2\text{O}$ (dull white)	34.01 (34.26)	3.62 (3.48)	8.75 (8.89)	9.9 (10.15)	17.6 (17.83)		1620	1373	1697	987
$(\text{N}_2\text{H}_5)_2\text{Mn}(\text{Htm})_2 \cdot 2\text{H}_2\text{O}$ (pale brown)	37.52 (37.70)	3.81 (3.84)	9.72 (9.77)	10.9 (11.17)	9.8 (9.59)		1560	1369	1695	989
$(\text{N}_2\text{H}_5)\text{Cd}(\text{Htm})_{1.5} \cdot 2\text{H}_2\text{O}$ (dull white)	32.54 (32.83)	3.01 (3.04)	5.59 (5.67)	6.5 (6.49)	23.5 (2278)		1607	1369	1694	987

from the hot concentrated solution, whereas monohydrazinium compound isolated without concentrating the solution.

### Electronic spectra and magnetic moment

The electronic spectrum shows absorptions at  $14985\text{ cm}^{-1}$ ,  $29410\text{ cm}^{-1}$  for nickel complex which are assigned to the transitions,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ ;  ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$  and that for cobalt complex, shows  $\lambda_{\text{max}}$  at  $14490\text{ cm}^{-1}$ ,  $22220\text{ cm}^{-1}$  which are assigned to  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ ;  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ . The absorption maxima at  $37040\text{ cm}^{-1}$  for nickel and  $34480\text{ cm}^{-1}$  for cobalt are charge transfer bands. These are characteristic of octahedral coordination around Ni(II) and Co(II) [18]. The magnetic moments of cobalt and nickel complexes were found to be 5.1 and 3.1 BM, respectively, which corresponds to high spin octahedral geometry [19].

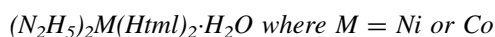
### IR spectra

The IR spectra of all complexes are summarized in Table 1. The absorption bands in the range  $1015\text{--}990\text{ cm}^{-1}$  for N–N stretching establish the presence of coordinated  $N_2H_5^+$ . They also show the absorption bands at  $3300\text{--}3280\text{ cm}^{-1}$  owing to N–H stretching [20, 21]. The presence of bands at  $1607\text{ cm}^{-1}$  and at  $1370\text{ cm}^{-1}$  in the spectra assigned to asymmetric and symmetric stretching of C=O of carboxylates and the difference between the above two,  $200\text{ cm}^{-1}$ , supports the monodentate [22] coordination of the carboxylate groups. The acid behaves as dianion in the complexes showing strong absorptions at

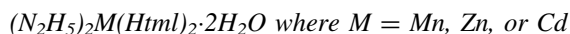
$1697\text{--}1685\text{ cm}^{-1}$  in their spectra, which are characteristic of free carboxyl groups [23].

### Thermal analysis

Simultaneous TG–DTA data have been presented in Table 2. The compositions of the intermediates and the final products are those, which best fit with the observed mass losses in the TG studies. Thermogravimetric results are in good agreement with the corresponding DTA data. The TG–DTA curves of prepared complexes are given in Fig. 1.



The DTA curves of these complexes show two peaks corresponding to a two step decomposition of the complexes as shown by TG. The first endothermic peak at  $235\text{ }^\circ\text{C}$  (Ni) and  $230\text{ }^\circ\text{C}$  (Co) is assigned to simultaneous decarboxylation of two free COOH groups and dehydration in the complexes. The second peak is an exothermic peak at  $480\text{ }^\circ\text{C}$  (Ni) and  $500\text{ }^\circ\text{C}$  (Co) indicating the complete decomposition of the complexes leading to the formation of metal oxides.

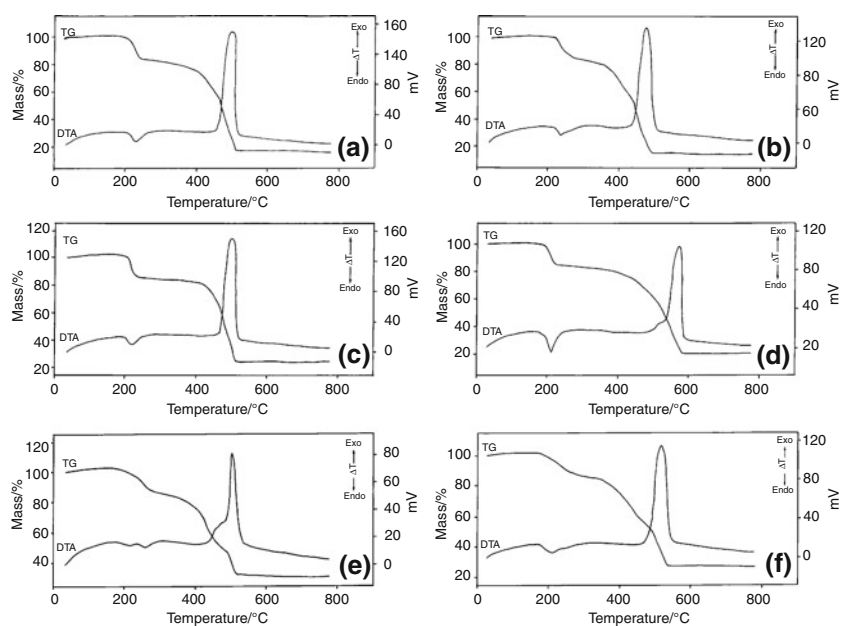


The DTA curves of these complexes exhibit an endothermic peak at  $213$ ,  $217$ , and  $220\text{ }^\circ\text{C}$ , and exothermic peak at  $573$ ,  $501$ , and  $504\text{ }^\circ\text{C}$  for Mn, Zn, and Cd complexes, respectively. Endothermic peaks are assigned to simultaneous decarboxylation of the free COOH groups and

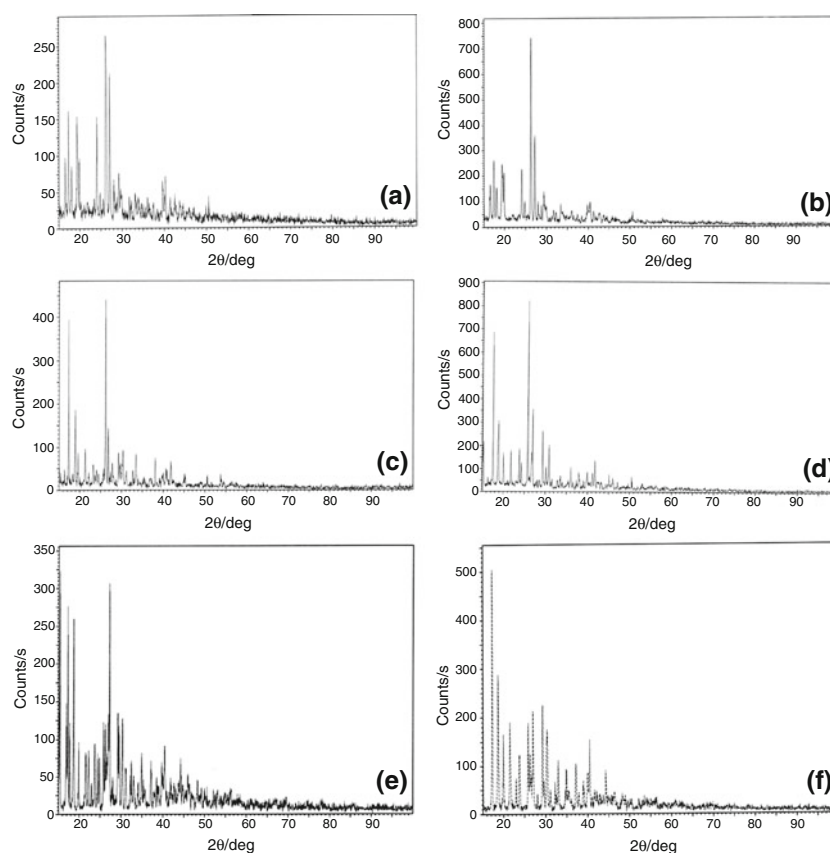
**Table 2** Thermal data of trimellitate complexes

Complex	DTA peak Temp/ $^\circ\text{C}$	Thermogravimetry		Decomposition products	
		Temp. range/ $^\circ\text{C}$	Mass loss/%		
			Obsd.		Calcd.
$(N_2H_5)_2Co(Html)_2 \cdot H_2O$	230 (+)	200–285	18.9	18.90	$(N_2H_5)_2Co(p\text{-}C_6H_4(COO)_2)_2$ $Co_3O_4$
	500 (–)	285–740	84.3	85.60	
$(N_2H_5)_2Ni(Html)_2 \cdot H_2O$	235 (+)	200–335	19.0	18.90	$(N_2H_5)_2Ni(p\text{-}C_6H_4(COO)_2)_2$ $NiO$
	480 (–)	335–715	86.0	86.60	
$(N_2H_5)_2Zn(Html)_2 \cdot 2H_2O$	210 (+)	190–325	21.0	21.26	$(N_2H_5)_2Zn(p\text{-}C_6H_4(COO)_2)_2$ $ZnCO_3$
	570 (–)	325–750	80.0	78.50	
$(N_2H_5)_2Cd(Html)_2 \cdot 2H_2O$	220 (+)	175–240	16.7	16.80	$(N_2H_5)_2Cd(p\text{-}C_6H_4(COO)_2)_2 \cdot H_2O$ $CdCO_3$
	505 (–)	240–750	70.0	72.65	
$(N_2H_5)_2Mn(Html)_2 \cdot 2H_2O$	215 (+)	200–285	18.5	18.50	$(N_2H_5)_2Mn(p\text{-}C_6H_4(COO)_2)_2 \cdot H_2O$ $MnCO_3$
	501 (–)	285–750	76.7	79.94	
$N_2H_5Cd(Html)_{1.5} \cdot 2H_2O$	249 (+)	236–305	15.50	17.00	$N_2H_5Cd(p\text{-}C_6H_4(COO)_2)_{1.5} \cdot H_2O$ $1/2(CdO + CdCO_3)$
	522 (–)	305–750	72.00	69.52	

**Fig. 1** TG-DTA curves of  
**a**  $(N_2H_5)_2Co(Html)_2 \cdot H_2O$ ,  
**b**  $(N_2H_5)_2Ni(Html)_2 \cdot H_2O$ ,  
**c**  $(N_2H_5)_2Mn(Html)_2 \cdot 2H_2O$ ,  
**d**  $(N_2H_5)_2Zn(Html)_2 \cdot 2H_2O$ ,  
**e**  $(N_2H_5)_2Cd(Html)_2 \cdot 2H_2O$ , and  
**f**  $(N_2H_5)Cd(Html)_{1.5} \cdot 2H_2O$



**Fig. 2** XRD patterns of trimellitate complexes  
**a**  $(N_2H_5)_2Co(Html)_2 \cdot H_2O$ ,  
**b**  $(N_2H_5)_2Ni(Html)_2 \cdot H_2O$ ,  
**c**  $(N_2H_5)_2Mn(Html)_2 \cdot 2H_2O$ ,  
**d**  $(N_2H_5)_2Zn(Html)_2 \cdot 2H_2O$ ,  
**e**  $(N_2H_5)_2Cd(Html)_2 \cdot 2H_2O$ , and  
**f**  $(N_2H_5)Cd(Html)_{1.5} \cdot 2H_2O$



dehydration of the complexes. In the case of Mn and Cd complexes, one water molecule is removed first and the other subsequently. Exothermic peaks depict the decomposition of the complexes leading to the formation of carbonates in the temperature range 500–573 °C.



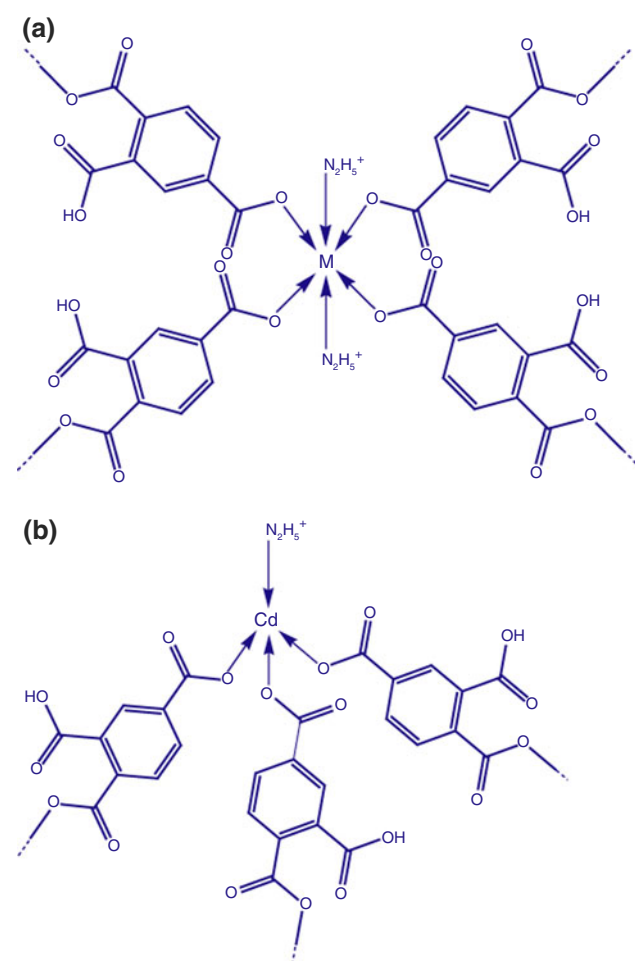
This complex also shows two peaks in its DTA curve, an endothermic at 215 °C revealing the decomposition of the complex liberating carbon dioxide and water molecules

simultaneously and an exothermic peak at 522 °C corresponding to the decomposition of the complex leading to the formation of mixture of metal oxide and carbonate.

Our attempt to separate the intermediates was failed due to their continuous decomposition as evident from the TG. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses, which are in accord with the calculated mass losses. Though the anion is the same in all the complexes, the thermal decomposition temperatures and the end product of the individual complexes vary depending upon the composition and the metal ion.

#### X-ray powder diffraction

X-ray powder diffraction pattern of the complexes are shown in Fig. 2. A comparison of the above indicates that the Ni and Co complexes are isomorphic with each other, Zn (II) and Cd (II) of the type,  $(N_2H_5)_2M(Html)_2 \cdot 2H_2O$  are



**Fig. 3** Proposed structures of **a**  $(N_2H_5)_2M(Html)_2 \cdot nH_2O$  where  $M = Mn, Co, Ni, Zn,$  and  $Cd$  and  $n = 1$  or  $2$  and **b**  $(N_2H_5)_2Cd(Html)_{1.5} \cdot 2H_2O$

also isomorphic with each other and the other two, Mn(II) and Cd (II) complexes are of different crystalline pattern.

#### Conclusions

The reaction between the transition metal nitrates with the mixture of hydrazine and trimellitic acid at pH 3.5 yielded complexes of the formulae,  $(N_2H_5)_2M(Html)_2 \cdot nH_2O$  where  $M = Mn, Co, Ni, Zn,$  and  $Cd$  and  $n = 1$  or  $2$  and  $(N_2H_5)_2Cd(Html)_{1.5} \cdot 2H_2O$ . The analytical, IR spectroscopic, and thermal data substantiate the formulation of the complexes. All the complexes undergo endothermic decomposition eliminating  $CO_2$  in the temperature region 200–250 °C, and an exothermic decomposition in the range of 500–570 °C. It is interesting to note that trimellitic acid behaves as a dianion with one free carboxylic group in all the complexes which manifest the carbonyl stretching frequency in the range of 1697–1685  $cm^{-1}$  in their IR spectra and decarboxylation during its thermal decomposition. The electronic spectroscopic data and magnetic moment value confirm their geometry and coordination number. Dihydrazinium metal trimellitate complexes have octahedral geometry and monohydrazinium cadmium trimellitate, the tetrahedral geometry. The insoluble nature in any solvent indicates their polymeric nature.

The structure of trimellitic acid is comparable with the structures of the phthalic acids (all isomers) while considering the positions of any two carboxyl groups. While extending the comparison to their complexation behavior with transition metal ions, it is observed that it resembles terephthalic acid complexes [8]. The involvement of carboxylic groups in ortho positions in complexation to metal leading to polymeric structures cannot be obviated. Even then, it is more probable and justifiable that only para carboxylic groups of trimellitic acid participate in complexation due to steric constraints. The structures of the complexes are proposed as given in Fig. 3. It is worth mentioning here that other isomers of the trimellitic acids at the same pH do not yield hydrazinium complexes, probably due to the substituent effects of carboxyl groups.

#### References

1. Choppin GR, Rizkalla EN, El-ansi TA, Dadgar A. Complexation thermodynamics of lanthanide ions by benzenepolycarboxylate ligands. *J Coord Chem*. 1994;31:297–304.
2. Wang Z-M, Van de Burgt LJ, Choppin GR. Spectroscopic study of lanthanide(III) complexes with carboxylic acids. *Inorg Chim Acta*. 1999;193:167–77.
3. Brzyska W, Kurpiel-Gorgol R, Dabkowska M. Thermal decomposition of scandium(III) benzenetricarboxylates in air and nitrogen atmospheres. *J Therm Anal Calorim*. 1983;28:333–9.

- Brzyska W, Wolodkiewicz W. Thermal decomposition of copper(II) benzenetricarboxylates in air atmosphere. *J Therm Anal Calorim.* 1986;31:961–5.
- Gajapathy D, Govindarajan S, Patil KC, Manohar H. Synthesis, characterisation and thermal properties of hydrazinium metal oxalate hydrates. Crystal and molecular structure of hydrazinium copper oxalate monohydrate. *Polyhedron.* 1983;2:865–73.
- Govindarajan S, Patil KC, Poojary MD, Manohar H. Synthesis, characterization and X-ray structure of hexahydrazinium diuranil pentaoxalate dihydrate,  $(\text{N}_2\text{H}_5)_6(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{H}_2\text{O}$ . *Inorg Chim Acta.* 1986;120:103–7.
- Sivasankar BN, Govindarajan S. Acetate and malonate complexes of cobalt(II), nickel(II) and zinc(II) with hydrazinium cation. Preparation, spectral and thermal studies. *J Therm Anal Calorim.* 1997;48:1401–13.
- Kuppusamy K, Govindarajan S. Hydrazinium cation as a ligand: preparation and spectral, thermal and XRD studies on hydrazinium metal phthalates. *Eur J Solid State Inorg Chem.* 1995;32:997–1012.
- Premkumar T, Govindarajan S. Thermoanalytical and spectroscopic studies on hydrazinium lighter lanthanide complexes of 2-pyrazinecarboxylic acid. *J Therm Anal Calorim.* 2009. doi: [10.1007/s10973-009-0117-1](https://doi.org/10.1007/s10973-009-0117-1) (online first).
- Premkumar T, Govindarajan S. Transition metal complexes of pyrazinecarboxylic acids with neutral hydrazine as a ligand. *J Therm Anal Calorim.* 2005;79:115–21.
- Premkumar T, Govindarajan S. The chemistry of hydrazine derivatives—thermal behavior and characterisation of hydrazinium salts and metal hydrazine complexes of 4, 5-imidazole-dicarboxylic acid. *Thermochim Acta.* 2002;386:35–42.
- Premkumar T, Govindarajan S. Divalent transition metal complexes of 3,5-pyrazoledicarboxylate. *J Therm Anal Calorim.* 2006;84:395–9.
- Gonsalves LR, Verenkar VMS, Mojumdar SC. Preparation and characterization of  $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 6\text{N}_2\text{H}_4$ . *J Therm Anal Calorim.* 2009;96:53–7.
- Vikram L, Sivasankar BN. Hydrazinium metal(II) and metal(III) ethylenediamine tetraacetate hydrates. *J Therm Anal Calorim.* 2008;91:963–70.
- Raju B, Sivasankar BN. Spectral, thermal and X-ray studies on some new Bis-hydrazine lanthanide(III) glyoxylates. *J Therm Anal Calorim.* 2008;94:289–96.
- Vikram L, Raju B, Ragul R, Sivasankar BN. Thermal degradation studies on some lanthanide-EDTA complexes containing hydrazinium cation. *J Therm Anal Calorim.* 2008;93:987–91.
- Vogel AI. A text book of quantitative inorganic analysis. 4th ed. London: Longman; 1986.
- Cotton FA, Wilkinson G. The elements of the first transition series. In: *Advanced inorganic chemistry*. 3rd ed. New Delhi: Wiley Eastern; 1972. p. 881.
- Figgis BN, Lewis J. The magnetic properties of transition metal complexes. In: *Progress in inorganic chemistry*. 6th ed. New York: F.A. Cotton, Interscience; 1964. p. 1430.
- Brown DB, Donner JA, Hall JW, Wilson SR, Wilson RB, Hondgson DJ, et al. Interaction of hydrazine with copper(II) chloride in acidic solutions. Formation, spectral and magnetic properties, and structures of copper(II), copper(I), and mixed-valence species. *Inorg Chem.* 1979;18:2635–41.
- Braibanti A, Dallavalle F, Pellinghelli MA, Laporati E. The nitrogen-nitrogen stretching band in hydrazine derivatives and complexes. *Inorg Chem.* 1968;7:1430–3.
- Nakamoto K. Infrared and Raman spectra of inorganic and coordination compounds. 3rd ed. New York: Wiley Interscience; 1978.
- Gonzalez-Sanchez F. Infra-red spectra of the benzene carboxylic acids. *Spectrochim Acta.* 1958;12:17–33.