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THERMAL DECOMPOSITION OF SOME LINEAR TRINUCLEAR SCHIFF BASE COMPLEXES WITH ACETATE BRIDGES

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Ni(II)–M(II)–Ni(II) nuclear structured complexes were prepared from N,N'-bis(salicylidene)-1,3-propanediamine (LH_2) and its derivatives N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-propanediamine ($LDMH_2$) and N,N'-bis(salicylidene)-2-hydroxy-1,3-propanediamine (LOH_3), where *M* represents one of the following metal ions; Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II). Two different μ-bridges are found between the metal nucleus of the complexes. The phenolic oxygens and acetate ions tend to form μ-bridges between the terminal Ni(II) ions and central metal(II) ion. The coordinatively bonded DMF molecules, in the complexes, were observed to abandon the structure between 160–180°C. Further heating resulted primarily in the thermal decomposition of the complexes above 310°C, whereas metal oxide residue mixtures were observed above 650°C.

Keywords: *DSC, TG-DTA, trinuclear Schiff base complex*

Introduction

N,N'-bis(salicylidene)-1,3-propanediamine is an ONNO type tetranuclear ligand known to give polynuclear complexes since 1990 [1–4]. The derivatives of this ligand also carry the same characteristics [5–9] and are known to form mononuclear complexes [10, 11] which tend to form dinuclear complexes via the phenolic oxygens [12, 13]. In addition they can form trinuclear complexes with the help of anions like acetate, formate and nitrate [2, 3, 9]. The general formula of these trinuclear complexes is shown in Fig. 1. The spectrum of the trinuclear complexes support the X-ray studies in literature [1–3, 9, 14–16].

In this study, firstly mononuclear Ni(II) complexes were prepared using the ligands LH_2, $LDMH_2$ and LDH_3 (NiL, NiLDM and NiLOH). Subsequently these mononuclear complexes were reacted in DMF media with various metal(II) acetate compounds resulting in the formation of the 18 trinuclear complexes referred in this study. The thermal behaviour of these complexes was investigated using thermogravimetric (TG) and differential scanning calorimetry (DSC) methods. The heat of absorption, at temperatures where the DMF molecules leave the solid structure have been measured. The coordinative bond energies of DMF were calculated by subtracting the evaporation enthalpies and amounts of heat uptaken from the heat of adsorption.

In recent years, manuscripts dealing with thermal analysis of polynuclear metal ion Schiff base complexes are insufficient and we have come across only one paper related to a study with a dinuclear nickel(II) complex [17]. However, there are many studies dealing with the thermal degradation of some complexes, synthesized from ONO, ONNO and ONS type Schiff bases with Co(II), Cu(II), Zn(II), Cd(II) and Fe(II) ions, between room temperature and 750°C [18–24].

In this study, TG curves were obtained between room temperature–450°C and in addition between room temperature–750°C at three or four different heating rates.

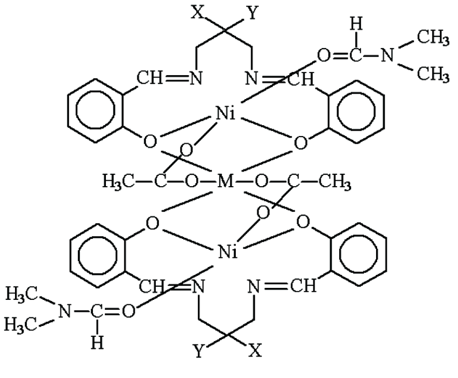

Fig. 1 Schematic structure of trinuclear complexes; *M*: Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; *X*: H, *Y*: H ligand L^{2-}; *X*: CH_3, *Y*: CH_3 ligand LMD^{2-}; *X*: H, *Y*: OH ligand LOH

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Experimental

Preparation of complexes

N,N'-bis(salicylidene)-1,3-propanediamine (LH_2) and its derivatives N,N'-bis(salicylidene)-2,2'-dimethyl-1,3-propanediamine ($LDMH_2$) and N,N'-bis(salicylidene)-2-hydroxy-1,3-propanediamine (LOH_3) were prepared from the condensation reaction of salicylaldehyde and the appropriate diamine with a 2:1 mol ratio in ethanol media. The diamines used here are 1,3-propanediamine, 2,2'-dimethyl-propanediamine and 2-hydroxy-1,3-propanediamine.

Each complex in question was prepared in two stages.

(*i*) Stage 1: Preparation of the mononuclear Ni(II) complexes (NiL, NiLDM, NiLOH) – 0.005 mol of the Schiff base (LH_2, $LDMH_2$ and LOH_3) was desolved in 50 mL hot ethanol. To this solution was added 10 mL concentrated ammoniac and the solution of 1.200 g (0.005 mol) $NiCl_2{\cdot}6H_2O$ in 30 mL hot water. The resulting mixture was left to stand for 2–3 h. The green precipitate was filtered and dried at 413 K. The green coloured complex contains ammoniac in its structure. At 413 K the ammoniac evaporates from the structure leaving a brown coloured mononuclear complex.

The elemental analysis results and important IR data of the complexes, NiL ($C_{17}H_{16}N_2O_2Ni$), NiLDM ($C_{19}H_{20}N_2O_2Ni$) and NiLOH ($C_{17}H_{16}N_2O_3Ni$), are given in Tables 1 and 2.

(*ii*) Stage 2: Preparation of the trinuclear complexes – 0.001 mol of the mononuclear complexes prepared in stage 1 were dissolved in 60 mL of hot DMF and heated to 110°C. To this was added the solution of 0.0005 mol $M(AcO)_2{\cdot}xH_2O$ in 20 mL hot methanol (M=Cu^{2+}, x=1; M=Co^{2+}, x=4; M=Mn^{2+}, x=4; Ni^{2+}, x=4; M=Zn^{2+}, x=2; M=Cd^{2+}, x=4). The mixtures were left to stand for 2–4 days. The resulting crystals were filtered, washed in ethanol and left to dry in atmospheric conditions:

$$\mathrm{DMF{\cdot}NiL{\cdot}M(AcO)_2{\cdot}NiL{\cdot}DMF}$$
$$\mathrm{DMF{\cdot}NiLDM{\cdot}M(AcO)_2{\cdot}NiLDM{\cdot}DMF}$$
$$\mathrm{DMF{\cdot}NiLOH{\cdot}M(AcO)_2{\cdot}NiLOH{\cdot}DMF}$$

where M=Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}. The elemental analysis results and important IR data of the complexes are given in Tables 1 and 2.

Measurement techniques

Elemental analysis was performed on a Eurovector 3018 C,H,N,S analyzer instrument. Nickel analysis was done gravimetrically using dimethylglyoxime, whereas other metal analysis was performed on a Hitachi 8200 model atomic adsorption spectrometer. IR spectrums were obtained on a Mattson FTIR 1000 instrument using the KBr disk technique.

TG-DTA curves were obtained using a Shimadzu TG-60H instrument. Aluminium pans were used for curves obtained between room temperature and 450°C, whereas platinum pans were used for curves obtained between room temperature and 750°C. The curves were obtained under nitrogen atmosphere with a flow rate of 100 mL min^{-1}. The heating rate was 10°C min^{-1} for the curves obtained between room temperature and 750°C, and 5, 10, 20, 30°C min^{-1} for those obtained between room temperature and 450°C.

DSC curves were obtained on a Shimadzu DSC-60 instrument between room temperature and 450°C with a heating rate of 10°C min^{-1} under nitrogen atmosphere with a flow rate of 30 mL min^{-1}. Shimadzu Al pressure proof pans (34 μL) were used in determination of the specific heat capacity values (C_p) of DMF. These values were calculated using the TA 60 WS Specific Heat Capacity software version 1.02. Six examples of these curves are given in Fig. 2.

Results and discussion

Previous X-ray studies have proven the complexes synthesized to be trinuclear in structure [2, 3, 9, 11, 14–16]. Elemental analysis results and important IR bands of the 18 complex structures studied are given Tables 1 and 2, respectively. Although the difference between some elemental analysis data, especially for C, are higher than 0.5%, most results are in the expected range. The C analysis results are a little over the acceptable deviation range but analysis of each specimen was repeated only once, as reliable X-ray results were obtained leaving no need for repetition. IR values are as expected and more importantly agreeable with previous literature data. The $\gamma_{C=N}$ band seen at higher values than 1634 cm^{-1}, for the ligand alone, shifts by 10–15 cm^{-1} to more lower energy values with the formation a complex. In addition coordinative bonding of DMF is understood from the band observed at approxiamately 1650 cm^{-1}.

Thermal analysis of the complexes display three thermal reactions as seen from Figs 2–4. The first thermal reactions is due to the separation of the DMF groups, coordinatively bonded to the terminal Ni(II) ions. The temperature range of this reaction, for the NiL (Figs 2a–f) and NiLDM (Figs 3a and b) trinuclear complexes, is 140–190 and 150–255°C for the NiLOH (Figs 4a and b) trinuclear complexes. The reason for this difference lies in the formation of hydrogen bonds between the –OH groups, found in the NiLOH terminal groups, and DMF groups. The presence of these bonds

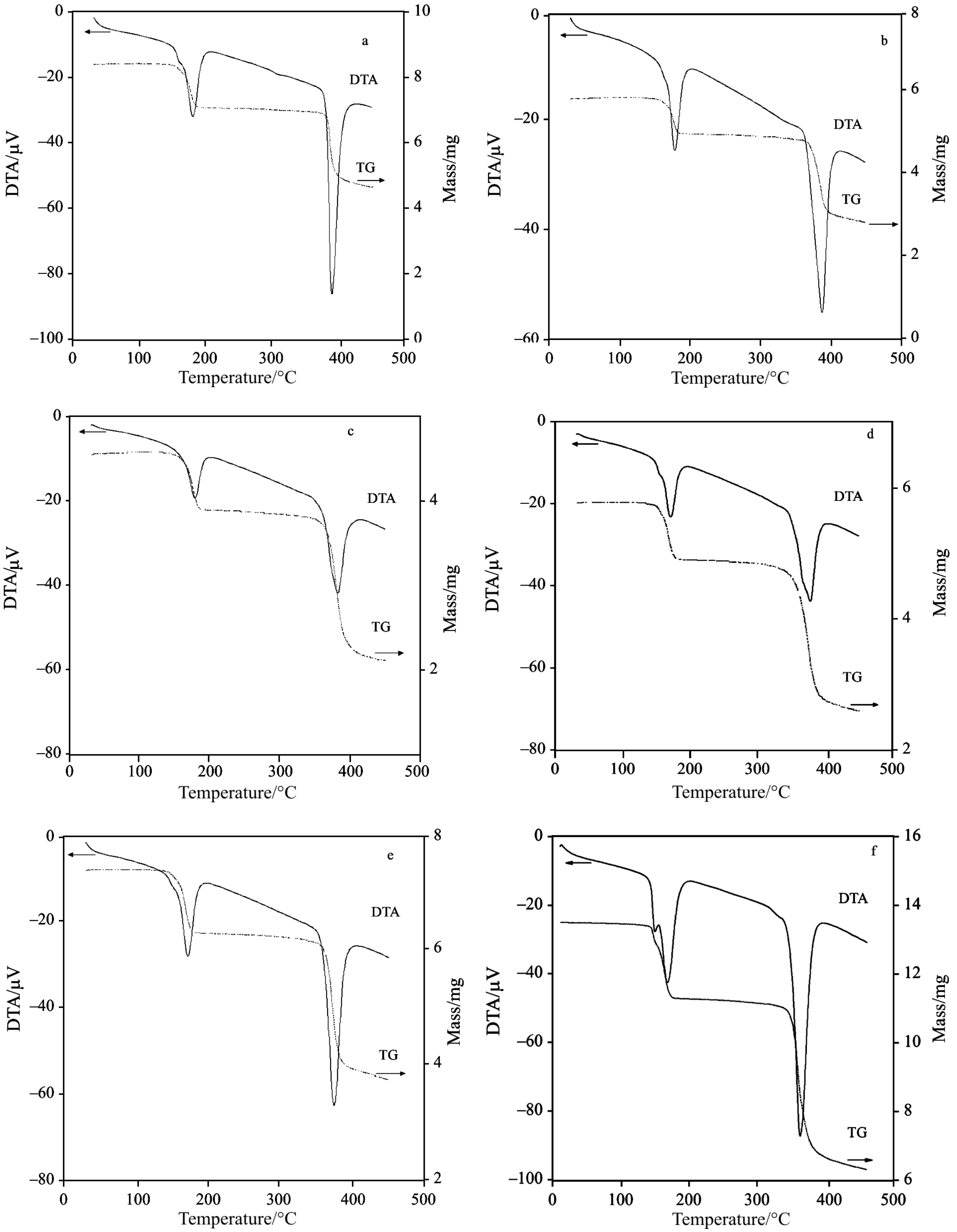

Fig. 2 TG-DTA curve of a – $(NiL)_2Mn(AcO)_2{\cdot}DMF_2$, b – $(NiL)_2Co(AcO)_2{\cdot}DMF_2$, c – $(NiL)_2Ni(AcO)_2{\cdot}DMF_2$, d – $(NiL)_2Cu(AcO)_2{\cdot}DMF_2$, e – $(NiL)_2Zn(AcO)_2{\cdot}DMF_2$, f – $(NiL)_2Cd(AcO)_2{\cdot}DMF_2$

Table 1 Elemental analysis results of complexes and ligands

Complex	Closed formula	Expected/%					Found/%				
		C	H	N	Ni	M	C	H	N	Ni	M
LH_2	$C_{17}H_{18}N_2O_2$	72.32	6.42	9.92	–	–	72.40	6.61	9.56	–	–
$LDMH_2$	$C_{19}H_{22}N_2O_2$	73.52	7.14	9.02	–	–	73.46	6.97	8.80	–	–
LOH_3	$C_{17}H_{18}N_2O_3$	68.44	6.08	9.38	–	–	67.98	6.36	9.14	–	–
NiL	$C_{17}H_{16}N_2O_2Ni$	60.22	4.76	7.89	17.31	–	59.81	4.50	7.80	17.76	–
NiLDM	$C_{19}H_{20}N_2O_2Ni$	62.32	5.50	7.64	16.03	–	61.52	5.13	7.93	17.01	–
NiLOH	$C_{17}H_{16}N_2O_3Ni$	57.51	4.54	7.88	16.53	–	57.50	4.41	7.66	17.09	–
$(NiL)_2Mn(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{10}Ni_2Mn$	52.99	5.25	8.42	11.77	5.50	53.41	5.36	8.63	12.01	5.71
$(NiL)_2Co(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{10}Ni_2Co$	52.78	5.23	8.39	11.73	5.89	52.86	5.02	8.47	12.24	5.69
$(NiL)_2Ni(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{10}Ni_3$	52.79	5.23	8.39	17.60	–	52.17	4.91	8.41	17.89	–
$(NiL)_2Cu(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{10}Ni_2Cu$	52.53	5.21	8.35	11.67	6.31	52.31	5.40	8.64	10.97	6.38
$(NiL)_2Zn(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{10}Ni_2Zn$	52.44	5.20	8.33	11.64	6.48	52.27	5.23	8.55	11.66	6.01
$(NiL)_2Cd(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{10}Ni_2Cd$	50.10	4.96	7.96	11.13	10.65	49.81	4.63	8.21	10.57	11.01
$(NiLDM)_2Mn(AcO)_2{\cdot}DMF_2$	$C_{48}H_{60}N_6O_{10}Ni_2Mn$	54.73	5.74	7.97	11.14	5.21	54.51	5.88	8.22	11.07	4.86
$(NiLDM)_2Co(AcO)_2{\cdot}DMF_2$	$C_{48}H_{60}N_6O_{10}Ni_2Co$	54.52	5.72	7.94	11.10	5.58	53.56	5.74	8.16	10.20	4.94
$(NiLDM)_2Ni(AcO)_2{\cdot}DMF_2$	$C_{48}H_{60}N_6O_{10}Ni_3$	54.54	5.72	7.95	16.65	–	54.88	5.81	7.99	17.24	–
$(NiLDM)_2Cu(AcO)_2{\cdot}DMF_2$	$C_{48}H_{60}N_6O_{10}Ni_2Cu$	54.28	5.69	7.91	11.06	5.98	53.78	5.47	8.34	11.01	5.83
$(NiLDM)_2Zn(AcO)_2{\cdot}DMF_2$	$C_{48}H_{60}N_6O_{10}Ni_2Zn$	54.19	5.68	7.89	11.03	6.14	53.42	5.43	8.11	10.91	5.77
$(NiLDM)_2Cd(AcO)_2{\cdot}DMF_2$	$C_{48}H_{60}N_6O_{10}Ni_2Cd$	51.90	5.44	7.56	10.56	10.11	52.32	5.76	6.89	10.92	9.38
$(NiLOH)_2Mn(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{12}Ni_2Mn$	51.32	5.09	8.16	11.40	5.33	52.04	4.82	8.12	10.56	4.84
$(NiLOH)_2Co(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{12}Ni_2Co$	51.14	5.07	8.13	11.36	5.70	50.83	4.86	8.37	10.91	5.62
$(NiLOH)_2Ni(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{12}Ni_3$	51.16	5.07	8.13	17.04	–	51.32	5.23	8.26	17.12	–
$(NiLOH)_2Cu(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{12}Ni_2Cu$	50.91	5.05	8.09	11.31	6.12	51.27	5.36	7.94	10.86	6.04
$(NiLOH)_2Zn(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{12}Ni_2Zn$	50.83	5.04	8.08	11.29	6.29	52.37	4.98	7.78	10.46	5.73
$(NiLOH)_2Cd(AcO)_2{\cdot}DMF_2$	$C_{44}H_{52}N_6O_{12}Ni_2Cd$	48.63	4.82	7.73	10.80	10.34	48.57	4.54	7.52	10.94	9.41

Table 2 Important IR data of the complexes

Complex	IR/cm^{-1}						
	$\gamma_{\mathrm{OH\ (Aliph)}}$	$\gamma_{\mathrm{C{-}H\ (Ar)}}$	$\gamma_{\mathrm{C{-}H\ (Aliph)}}$	$\gamma_{\mathrm{C{=}O\ (DMF)}}$	$\gamma_{\mathrm{C{=}N}}$	$\delta_{\mathrm{CH_2}}$	$\delta_{\mathrm{C{-}H\ (Ar)}}$
$\mathrm{LH_2}$	2736	3015 3054	2841 2937	–	1634	1468	758
$\mathrm{LDMH_2}$	2713 2848	3009 3053	2848 2961	–	1635	1464	760
$\mathrm{LOH_3}$	3396 2712–2658	3034 3073	2860 2918	–	1638	1490	752
NiL	–	3023 3054	2863 2924	–	1623	1475	756
NiLDM	–	3013 3049	2851 2937	–	1626	1480	757
NiLOH	3271	3034 3057	2857 2932	–	1627	1458	760
$\mathrm{(NiL)_2Mn(AcO)_2{\cdot}DMF_2}$	–	3031 3049	2941 2867	1651	1626	1473	754
$\mathrm{(NiL)_2Co(AcO)_2{\cdot}DMF_2}$	–	3029 3051	2927 2854	1652	1625	1480	756
$\mathrm{(NiL)_2Ni(AcO)_2{\cdot}DMF_2}$	–	3055 3031	2943 2861	1651	1627	1474	757
$\mathrm{(NiL)_2Cu(AcO)_2{\cdot}DMF_2}$	–	3051 3028	2926 2851	1650	1626	1479	757
$\mathrm{(NiL)_2Zn(AcO)_2{\cdot}DMF_2}$	–	3029 3054	2928 2853	1651	1625	1487	762
$\mathrm{(NiL)_2Cd(AcO)_2{\cdot}DMF_2}$	–	3023 3052	2936 2848	1649	1625	1470	757
$\mathrm{(NiLDM)_2Mn(AcO)_2{\cdot}DMF_2}$	–	3007 3039	2843 2934	1649	1624	1483	758
$\mathrm{(NiLDM)_2Co(AcO)_2{\cdot}DMF_2}$	–	3027 3051	2845 2955	1649	1626	1481	760
$\mathrm{(NiLDM)_2Ni(AcO)_2{\cdot}DMF_2}$	–	3023 3052	2829 2937	1650	1626	1479	758
$\mathrm{(NiLDM)_2Cu(AcO)_2{\cdot}DMF_2}$	–	3019 3051	2828 2924	1646	1624	1481	759
$\mathrm{(NiLDM)_2Zn(AcO)_2{\cdot}DMF_2}$	–	3007 3049	2831 2945	1651	1625	1473	757
$\mathrm{(NiLDM)_2Cd(AcO)_2{\cdot}DMF_2}$	–	3024 3061	2856 2947	1650	1625	1471	757
$\mathrm{(NiLOH)_2Mn(AcO)_2{\cdot}DMF_2}$	3287	3029 3054	2867 2919	1651	1623	1448	759
$\mathrm{(NiLOH)_2Co(AcO)_2{\cdot}DMF_2}$	3271	3029 3047	2847 2926	1649	1621	1457	757
$\mathrm{(NiLOH)_2Ni(AcO)_2{\cdot}DMF_2}$	3391	3027 3051	2851 2936	1652	1622	1461	758
$\mathrm{(NiLOH)_2Cu(AcO)_2{\cdot}DMF_2}$	3254	3028 3055	2860 2927	1651	1625	1453	760
$\mathrm{(NiLOH)_2Zn(AcO)_2{\cdot}DMF_2}$	3291	3028 3053	2854 2936	1652	1622	1451	757
$\mathrm{(NiLOH)_2Cd(AcO)_2{\cdot}DMF_2}$	3288	3019 3041	2843 2924	1650	1620	1457	761

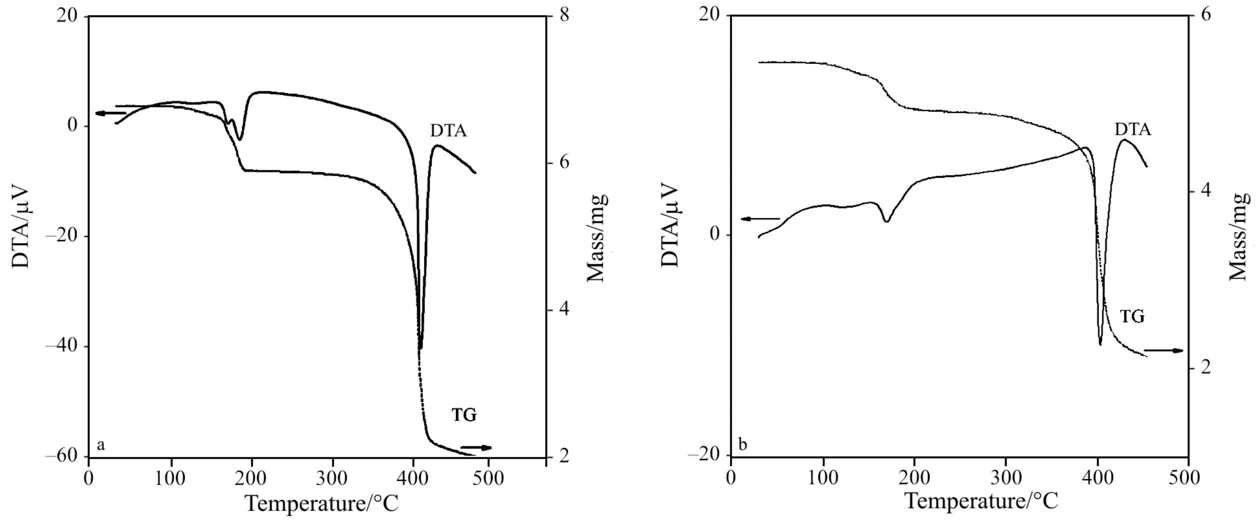

Fig. 3 TG-DTA curve of a – $(NiLDM)_2Co(AcO)_2{\cdot}DMF_2$, b – $(NiLDM)_2Cu(AcO)_2{\cdot}DMF_2$

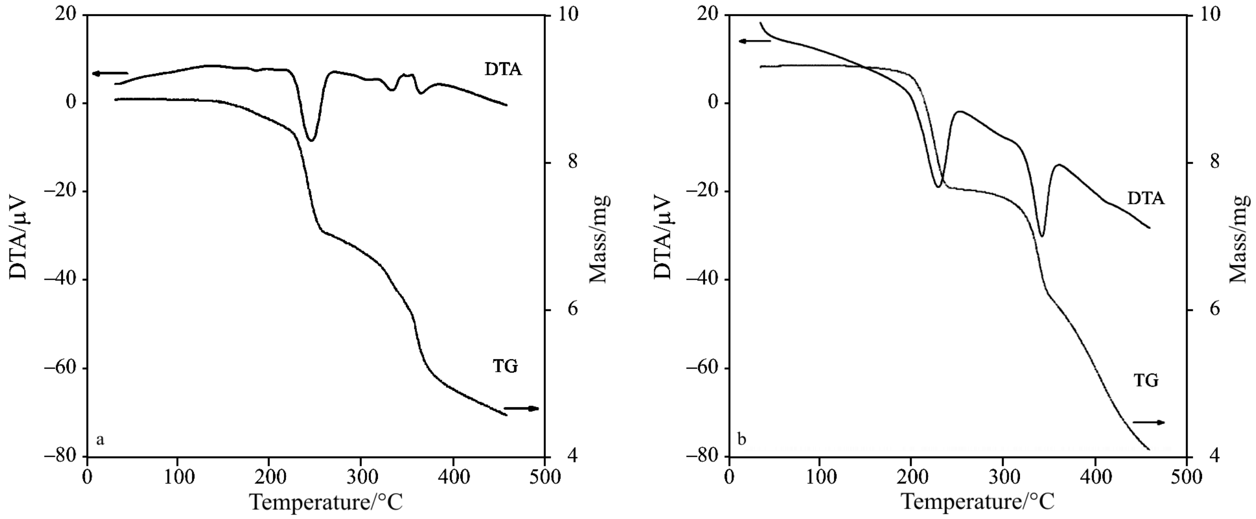

Fig. 4 TG-DTA curve of a – $(NiLOH)_2Ni(AcO)_2{\cdot}DMF_2$, b – $(NiLOH)_2Cd(AcO)_2{\cdot}DMF_2$

elevates the temperature at which the terminal DMF groups leave the structure in trinuclear complexes of NiLOH, resulting in wider temperature ranges (Figs 4a and b). However the mass loss is in the expected range. Previous X-ray studies have proven the presence of these hydrogen bonds [25].

The second thermal reaction, which begins at approximately 300°C, is due to thermal degradation. The degradation reaction is seen to spread out within a temperature range of approximately 50°C for the NiL, 100°C for the NiLDM and 110°C for the NiLOH complexes. The mass loss for the NiL complexes is due to degradation of the aliphatic groups of the terminal NiL groups and to conversion of the central Ni(II) acetate groups to acetone and carbondioxide.

The NiLDM complexes, on the other hand, show higher degrees of mass loss than expected during the thermal reaction, the thermal reaction temperature reaching almost 450°C. At this temperature the conversion of the central and terminal groups to Ni(II) oxide is a possibility, leading to higher values of mass loss as observed.

In contrast to the other complex structures, complexes of NiLOH show the mass loss during the second thermal reaction to be lower than expected, probably due to an interaction between the –OH groups of the aliphatic chain and the terminal Ni(II) ions. The mass loss in these complexes corresponds to the separation of acetone and carbondioxide from the aliphatic groups, with the exception of the HO–C–group situated at the center of the trimethylene bridge, and the central Ni(II) ion.

There are detailed studies dealing with the degradation of metal acetate compounds in literature

[26]. The degradation reaction starts around 300°C the first product being acetone. Similarly, recent reports, dealing with degradation of mononuclear Cu(II), Ni(II), Zn(II), Cd(II), Fe(II) Schiff base complexes, have shown the thermal degradation reaction to start in the range 280–300°C. Another study has suggested the degradation reaction to proceed via the neighbouring aliphatic groups to the coordinatively bonded nitrogen donor atoms [22].

The second thermal degradation observed, in this study, is the total of the two reactions; degradation of aliphatic groups of the ONNO type ligand surrounding the terminal Ni(II) ions and degradation of the acetate groups, surrounding the central Ni(II) ion, to acetone and carbondioxide. As specified before, the mass loss of the NiL trinuclear complexes are as expected whereas the mass loss of the NiLDM and NiLOH trinuclear complexes are higher and lower than expected, respectively.

The NiLDM complexes contain two methyl groups attached to the trimethylene bridge. These are open ended groups which and atoms situated at open ends of the aliphatic groups show a high degree of vibration whereas methyl groups situated on aromatic ring structures show limited vibration. The thermal ellipsoids of open ended groups are always larger than those on ring structures, a fact frequently observed during X-ray studies. In addition there is not any interaction between the terminal Ni(II) ions and the methyl groups. As the vibration amplitude increases with temperature, the two methyl groups puts more strain on the six membered chelate ring of NiLDM compared to NiLOH. The thermal strain created by the methyl groups leads to earlier degradation of the aromatic groups. As a result mass loss due to degradation is higher in the NiLDM complexes and the reaction temperature is seen to be spread to a wider range. On the other hand, trinuclear complexes which include terminal NiLOH molecules possess an –OH group attached to the methylene bridge. This –OH group can interact with the terminal Ni(II) ion. Many studies in literature, dealing with dinuclear complexes, show the –OH group to interact with metal ions as a donor [27]. For this reason, in contrast to NiLDM containing complexes, in NiLOH containing complexes the –OH group makes degradation of the chelate ring difficult and delays the degradation of the ring. The same situation is observed with the mononuclear complexes.

The second thermal degradation reaction temperature range for NiL, NiLDM and NiLOH are 323–410, 337–421 and 275–413°C, respectively. Although the widest range is for NiLOH, a lower degree of mass loss from the chelate ring is observed, meaning complete degradation of the structure does not occur. On the other hand, degradation of the aromatic groups are also included within the temperature range of NiLDM. Similar results have also been observed for the trinuclear complexes.

The benefit of the DSC curves for these complexes, lies in the fact that the bond energies of the DMF molecules, coordinated to the terminal Ni(II) ions in the complex, can be approximately calculated. The DMF molecules abandon the complex structures between 140–190°C (150–255°C for the NiLOH trinuclear complexes) without degradation of the complex. Experiments have shown the DMF molecules to be coordinated to the remnants with recrystallization in DMF. The heat absorbed during the first thermal endothermic reaction was measured and the coordinative bond energy of the DMF molecules for each trinuclear complex was calculated according to the following equation.

$$\begin{gathered}\text{(coordinative bond energy per DMF molecule)=}\\ \text{(heat measured from DSC curve for first thermal reaction)/2–}\\ –(\Delta H_{\text{evaporation}}\ \text{at boiling point of DMF})/2+(\Delta T C_{\text{p}})/2\end{gathered}$$

where ΔT is the difference between the final temperature of the thermal reaction and the boiling point of DMF. The calculated values have been tabulated in Table 4.

The boiling point of DMF at 1 atm is 149.1°C. If the heat of evaporation is calculated according to the Trouton law it is found to be 37.2 kJ mol^{-1}. The heat of absorption of DMF from DSC studies, after total evaporation at 106°C, was found to be 37.16±2.12 kJ mol^{-1}. The C_{p} values were calculated, using the software as 144.27±8.89 J mol^{-1} between 170–210°C and used in calculation of the coordinative bond energy of DMF molecules. For example, the final temperature for the first reaction, from Table 3, for the $(\text{NiL})_2\text{Ni(AcO)}_2\cdot\text{DMF}_2$ complex is 193°C and the measured heat of absorption 97.96 kJ mol^{-1}. Taking into consideration the boiling point of DMF as 149.1°C the coordinative bond energy per DMF molecule is calculated to be 5.49 kJ mol^{-1}.

$$\begin{gathered}\text{(coordinative bond energy per DMF molecule)=}\\ \{97960–2[37.16+(193–149.1)\cdot 144.27]\}/2\end{gathered}$$

The results in Table 4 are reasonable and most of the coordinative bond energies are seen to be at this level. The effect of the hydrogen bond between the terminal DMF molecules and OH group in NiLOH containing complexes and the two methyl groups in NiLDM containing complexes can clearly be seen. The hydrogen bond makes separation of the DMF molecules from the complex resulting in higher heats of absorption.

Table 3 Thermoanalytical data of the complexes

Complex	Peak 1 DMF loss				Peak 2 degradation				Oxide formation 650°C	
	T_{range}/°C	Mass loss/%		Heat measured with DSC	T_{range}/°C	Mass loss/%		Heat measured with DSC	Mass loss/%	
		expected	found			expected	found		expected	found
NiL	–	–	–	–	323–410	28.31	28.02	19.64	22.03	23.17
NiLDM	–	–	–	–	337–421	33.78	67.07	83.34	20.35	21.34
NiLOH	–	–	–	–	275–413	31.57	28.25	31.85	21.06	23.14
$(NiL)_2Mn(AcO)_2\cdot DMF_2$	149–186	14.64	14.94	105.46	371–421	29.48	28.98	270.35	22.09	23.17
$(NiL)_2Co(AcO)_2\cdot DMF_2$	152–205	14.58	14.08	107.96	360–411	29.36	30.95	285.40	22.41	23.36
$(NiL)_2Ni(AcO)_2\cdot DMF_2$	147–193	14.58	14.38	97.96	351–405	29.37	30.56	277.85	22.38	22.66
$(NiL)_2Cu(AcO)_2\cdot DMF_2$	140–189	14.51	14.31	96.14	343–395	29.23	31.37	240.90	22.76	22.88
$(NiL)_2Zn(AcO)_2\cdot DMF_2$	149–184	14.49	14.34	112.22	351–391	29.17	28.62	286.76	22.90	22.69
$(NiL)_2Cd(AcO)_2\cdot DMF_2$	154–197	13.84	14.58	109.99	354–398	27.87	27.75	190.07	26.34	27.53
$(NiLDM)_2Mn(AcO)_2\cdot DMF_2$	137–196	13.86	13.85	78.16	353–461	30.58	47.23	283.45	20.92	20.17
$(NiLDM)_2Co(AcO)_2\cdot DMF_2$	141–189	13.81	13.27	84.26	356–457	30.46	56.12	298.28	21.28	20.98
$(NiLDM)_2Ni(AcO)_2\cdot DMF_2$	163–212	13.82	14.00	94.67	352–446	30.47	58.37	347.52	21.20	21.10
$(NiLDM)_2Cu(AcO)_2\cdot DMF_2$	148–201	13.75	13.86	83.17	348–437	30.33	54.67	265.17	21.56	20.93
$(NiLDM)_2Zn(AcO)_2\cdot DMF_2$	158–209	13.73	13.22	95.27	354–452	30.28	55.18	342.28	21.70	20.38
$(NiLDM)_2Cd(AcO)_2\cdot DMF_2$	134–191	13.15	12.94	102.94	373–441	28.99	50.54	356.20	25.02	24.52
$(NiLOH)_2Mn(AcO)_2\cdot DMF_2$	147–239	14.18	15.86	168.12	318–447	31.68	23.48	121.27	21.42	21.23
$(NiLOH)_2Co(AcO)_2\cdot DMF_2$	155–247	14.13	16.20	172.27	322–455	31.55	24.15	82.18	21.72	20.93
$(NiLOH)_2Ni(AcO)_2\cdot DMF_2$	163–255	14.13	15.44	176.24	295–397	31.56	23.89	88.75	21.69	21.53
$(NiLOH)_2Cu(AcO)_2\cdot DMF_2$	141–237	14.07	15.68	165.16	283–392	31.56	22.17	76.18	22.16	21.75
$(NiLOH)_2Zn(AcO)_2\cdot DMF_2$	165–244	14.04	15.38	194.36	298-399	31.36	26.24	134.23	22.20	21.39
$(NiLOH)_2Cd(AcO)_2\cdot DMF_2$	190–244	13.43	15.22	199.20	310-439	30.00	30.43	181.36	25.57	24.08

All data have been given for a heating rate of 10°C min^{-1}

Table 4 Coordinative bond energies calculated for DMF during the first thermal reaction

Complex	Heat measured from DSC curve/kJ mol^{-1}	Calculated coordinative bond energy/kJ mol^{-1}
$(NiL)_2Mn(AcO)_2 \cdot DMF_2$	105.46	10.25
$(NiL)_2Co(AcO)_2 \cdot DMF_2$	107.96	8.76
$(NiL)_2Ni(AcO)_2 \cdot DMF_2$	97.96	5.49
$(NiL)_2Cu(AcO)_2 \cdot DMF_2$	96.14	5.15
$(NiL)_2Zn(AcO)_2 \cdot DMF_2$	112.22	13.90
$(NiL)_2Cd(AcO)_2 \cdot DMF_2$	109.96	10.91
$(NiLDM)_2Mn(AcO)_2 \cdot DMF_2$	78.16	*
$(NiLDM)_2Co(AcO)_2 \cdot DMF_2$	84.26	*
$(NiLDM)_2Ni(AcO)_2 \cdot DMF_2$	94.67	2.49
$(NiLDM)_2Cu(AcO)_2 \cdot DMF_2$	83.17	*
$(NiLDM)_2Zn(AcO)_2 \cdot DMF_2$	95.27	1.84
$(NiLDM)_2Cd(AcO)_2 \cdot DMF_2$	102.94	8.26
$(NiLOH)_2Mn(AcO)_2 \cdot DMF_2$	168.12	33.93
$(NiLOH)_2Co(AcO)_2 \cdot DMF_2$	172.27	34.85
$(NiLOH)_2Ni(AcO)_2 \cdot DMF_2$	176.24	35.68
$(NiLOH)_2Cu(AcO)_2 \cdot DMF_2$	165.16	32.74
$(NiLOH)_2Zn(AcO)_2. \cdot DMF_2$	194.36	41.33
$(NiLOH)_2Cd(AcO)_2 \cdot DMF_2$	199.20	48.75

Conclusions

Ni(II)–M(II)–Ni(II) nuclear structured complexes were prepared from three ONNO type Schiff base compounds and thermally analysed. *M* in these complex structures stands for either of the following metal ions; Mn(II), Co(II), Cu(II), Zn(II) and Cd(II). Each complex contains μ-bridges of acetate groups between the Ni(II) and M(II) ions in the frame of the structure. Experiments showed the coordinative bonds between the DMF molecules and terminal Ni(II) ions to break in the temperature range 160–190°C. Degradation of the aliphatic groups of the Schiff base and acetate bridges was observed near 300°C. Thermogravimetric analysis was very successful in determination of complex stoichiometry. Results showed the coordinative bond energies, of solvents like DMF, to be comparable to the hydrogen bond levels.

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