Energetic trinuclear Ni^{II}–Ni^{II}–Ni^{II} complexes at high temperature

Alternative explosives

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Abstract Two ONNO type naphtaldehyde derivative Schiff base compounds were reduced and two symmetric phenol-amine ligands containing naphthalene groups were obtained; bis-N,N′[(2-hydroxy-1-naphtyl) methyl]-1,3-propanediamine (NAFL^H) and bis-N,N′[(2-hydroxy-1-naphtyl) methyl]-2,2′-dimetyhyl-1,3-propanediamine (NAFLDM^H). Homotrinuclear Ni(II) complexes of these ligands were prepared. The solid-state molecular structures of representative nickel complex of NAFLDM^H were determined using single crystal X-ray diffraction analysis. The terminal Ni(II) ions were found to be situated in between the donor atoms of the organic ligand. The central Ni(II) ion was observed to be bonded via two different μ-bridges. The phenolic oxygens and carboxylate ion were seen to form two different μ-bridges. TG analysis proved that the compounds have different thermal characteristics than those cited in literature. The complexes showed extreme exothermic degradation reactions in inert atmosphere. The complexes are ruptured with a two stepped exothermic reaction which appears huge heat over 300 °C. The heat appeared in O$_2$ atmosphere is observed to be higher than the heat appeared in inert atmosphere. Revealed heat is observed to be higher than the conventional explosive materials.

Keywords DTA · Energetic complexes · Explosives · TG · Trinuclear complexes

Introduction

Azomethine compounds are known to form secondary amines in amfiprotic media using NaBH$_4$. Bis-N,N′(salicylidene)-1,3-propanediamine and derivatives are known to form polynuclear complexes [1–7]. These Schiff bases tend to form homo and heterotrinuclear complexes with acetate, benzoate, nitrate ions, etc. Literature reports bis-N,N′(2-oxybenzyl)-1,3-propanediamine compounds to form phenol-amine structured ONNO type ligands, which tend to form homotrinuclear complexes [8–10]. This structure resembles the ligand studied in this manuscript with the exception that the phenyl rings are substituted with naphtelene rings. The mononuclear Ni(II) complexes of this compound has previously been reported [11], but we were not able to find any studies dealing with multi nuclear complexes.

In this study, bis-N,N′(2-hydroxy-1-naphtylidene)-1,3-propanediamine (NAFL) and bis-N,N′(2-hydroxy-1-naphtylidene)-2,2′-dimethyl-1,3-propanediamine (NAFLDM) were synthesized and further reduced to (NAFL^H) and NAFLDM^H using NaBH$_4$.
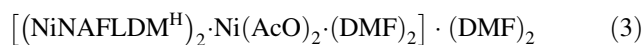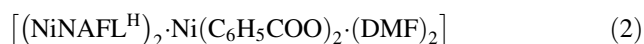
Trinuclear Ni(II) complexes of these compounds were prepared. Two different μ-bridges were formed with acetate and benzoate ions and four different trinuclear complexes were prepared.

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$$\left[(NiNAFL^{H})_{2} \cdot Ni(AcO)_{2} \cdot (DMF)_{2}\right] \cdot 2DMF \qquad (1)$$

$$\left[(NiNAFL^{H})_{2} \cdot Ni(C_6H_5COO)_{2} \cdot (DMF)_{2}\right] \qquad (2)$$

$$\left[(NiNAFLDM^{H})_{2} \cdot Ni(AcO)_{2} \cdot (DMF)_{2}\right] \cdot (DMF)_{2} \qquad (3)$$

$$\left[(NiNAFLDM^{H})_{2} \cdot Ni(C_6H_5COO)_{2} \cdot (DMF)_{2}\right] \qquad (4)$$

Appropriate crystals of compound (**3**) were obtained and the crystal structures of complex [(NiNAFLDM^{H})$_2$· Ni(AcO)$_2$·(DMF)$_2$]·(DMF)$_2$ were further confirmed by single crystal X-ray diffraction (DMF: dimethylformamide).

Experimental

NAFL and NAFLDM were obtained in EtOH media using 2-hydroxy-1-naphtaldehyde, 1,3-propanediamine and 2,2′-dimetyhyl-1,3-propanediamine.

0.01 mole of the Schiff base was heated in 50 mL 2-PrOH to 80 °C. To this solution was added solid NaBH$_4$ while continously stirring. To this mixture 10 mL MeOH was added. NaBH$_4$ was continued to be added to the solution until a colorless solution was obtained, which was then poured into a 300 mL ice-water mixture and left to stand for a day. The white precipitate was the reduced Schiff base compounds NAFL^{H} and NAFLDM^{H}.

Preparation of compounds

Four different complexes were prepared from two Schiff base ligands and two different μ-bridges. The general procedure is as follows.

0.002 mole of the reduced Schiff base was dissolved in 50 mL DMF and heated to 100 °C. To this mixture was added the hot solution of 0.712 g (0.003 mole) NiCl$_2$.6H$_2$O in 20 mL MeOH and 0.006 mole of NaCH$_3$COO or NaC$_6$H$_5$COO in 10 mL of hot water. The mixture was left to stand for a day and the light blue crystal precipitates were filtered and dried in open air. The masses used for the complexes are listed below.

Preparation of complexes

(1) 0.770 g (0.002 mole) NAFL^{H}, 0.492 g (0.006 mole) NaCH$_3$COO
(2) 0.770 g (0.002 mole) NAFL^{H}, 0.725 g (0.006 mole) NaC$_6$H$_5$COO
(3) 0.822 g (0.002 mole) NAFLDM^{H}, 0.492 g (0.006 mole) NaCH$_3$COO
(4) 0.822 g (0.002 mole) NAFLDM^{H}, 0.725 g (0.006 mole) NaC$_6$H$_5$COO

Ni analyses of these complexes were performed with a GBC Avanta PM model AAS and nitrogen analysis was done using the classic Kjeldahl method. IR spectrums were obtained with a Mattson FTIR 1000 with KBr disks. NMR spectrums of the ligand and complexes were obtained on a Perkin Elmer Spectrum 100. Thermogravimetric studies were performed on a Shimadzu DTG-60H instrument under N$_2$ and O$_2$ atmosphere, with a heat rate of 10 °C min^{-1}. TG analysis were repeated at least three times for each complexes under both N$_2$ and O$_2$ atmosphere and the standard deviation values for the mass loss data were calculated.

X-ray diffraction structure analysis

In order to determine the crystal and molecular structures of the compound (**3**), [(NiNAFLDM^{H})$_2$·Ni(AcO)$_2$·(DMF)$_2$]· (DMF)$_2$, x-ray diffraction data were collected at room temperature on an *Enraf–Nonius CAD4* diffractometer [12]. The $\omega/2\theta$ scan technique was used to record the intensities for all reflections with graphite-monochromated CuK$_\alpha$ ($\lambda = 1.54184$ Å) radiation. The Enraf-Nonious program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and also preliminary cell parameters. Refined cell parameters and their estimated standard deviations were obtained from least-square refinement of 25 accurately centered reflections in the range of 22.41°–42.32°. During data collection, three standard reflections were periodically measured every 120 min, the compounds showed 8% intensity variation. Data reduction was carried out using *XCAD4* [13]. The structures were solved by Patterson methods and refined using the program *SHELX* [14]. A full-matrix least-squares refinement on F^2 was done.

A chemical diagram of the title compound is given in Fig. 1. For all non-hydrogen atoms anisotropic displacement parameters were refined. Hydrogen atoms of the NH groups taken from a difference Fourier map were refined with isotropic thermal parameters. All other hydrogen atoms of the compound were placed geometrically and a riding model was used with U_{iso}(H) = 1.5 U_{eq}(C) for methyl hydrogen's and U_{iso}(H) = 1.2 U_{eq}(C) for others. Absorption correction (ψ-scan) [15] was applied to intensity values ($T_{max} = 0.741$, $T_{min} = 0.674$). Crystal and experimental data are given in Table 1. Selected bond lengths and angles are given in Table 2. The graphical representations of the structures were made with *ORTEP* [16] and *MERCURY* [17]. Perspective view of the molecules is given in Fig. 2. Hydrogen bond and molecular packing geometry of the title molecule was calculated with *PLATON* [18].
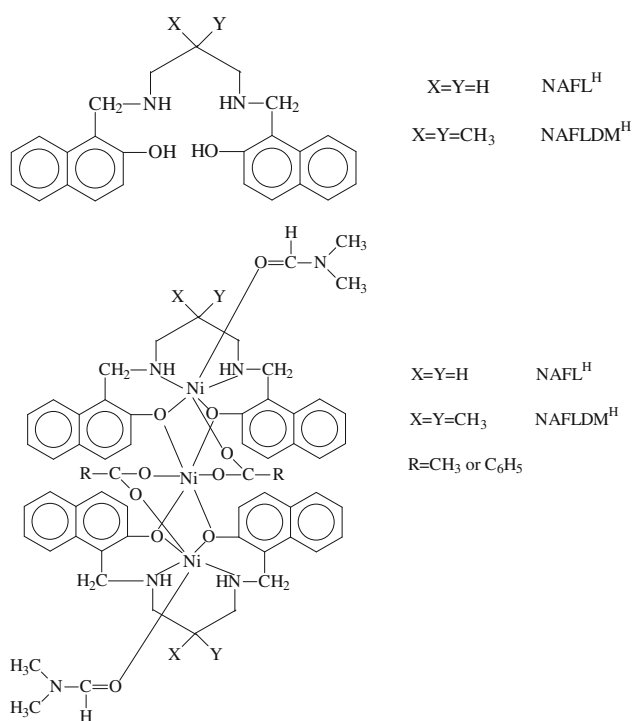
Fig. 1 Chemical formulas of the ligands and the complexes

Table 1 Crystal data and results of structure refinement for compound **3**

Chemical formula	Ni[Ni(C$_{27}$H$_{28}$N$_2$O$_2$)(C$_2$H$_3$O$_2$)(C$_3$H$_7$NO)]$_2$ (C$_3$H$_7$NO)$_2$
Formula weight/g mol^{-1}	1411.57
Crystal system	Monoclinic
Space group	P2$_1$/n
a/Å	15.747(2)
b/Å	11.782(2)
c/Å	19.516(6)
β/°	92.75(2)
Cell volume/Å^3	3616.7(14)
Z	2
D_{calc}/g cm^{-3}	1.293
Crystal size/mm^3	0.3 × 0.3 × 0.2
μ/mm^{-1}	1.419
F(000)	1,492
θ-range for data collection/°	3.52–74.23
Reflections collected/unique	6,929/6,739
Unique reflections [I > 2σ(I)]	4,717
No. of parameters	407
(GOF) Goodness-of-fit-ref	1.038
R [I > 2σ(I)]	R$_1$ = 0.0674, wR$_2$ = 0.1813
ρ_{max} and ρ_{min}/e Å^{-3}	0.884 and −0.469

Inspection of bond lengths and bond angles given in Table 2 for the Ni[Ni(C$_{27}$H$_{28}$N$_2$O$_2$)(C$_2$H$_3$O$_2$)(C$_3$H$_7$NO)]$_2$ (C$_3$H$_7$NO)$_2$ reveals that the Ni–O, N–C, O–C and C–C

Table 2 Selected average bond lengths and angles for compound **3** (Å, °)

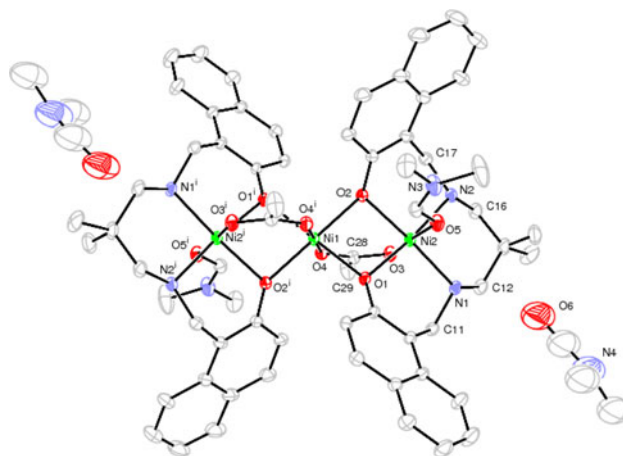| Ni1⋯Ni2	3.0551(11)	Ni2–N1	2.083(4)
Ni1–O1	2.040(3)	Ni2–N2	2.088(4)
Ni1–O2	2.064(3)	Ni2–O5	2.118(3)
Ni1–O4	2.115(3)	O3–C28	1.262(5)
Ni2–O1	2.023(3)	O4–C28	1.252(5)
Ni2–O2	2.068(3)	C28–C29	1.506(7)
Ni2–O3	2.037(3)	N2–C17	1.491(6)
N1–C11	1.492(6)	N2–C16	1.463(6)
N1–C12	1.469(5)	O6⋯N1^{ii}	3.204(15)
Ni1–O1–Ni2	97.54(12)	N2–Ni2–O1	173.80(13)
Ni1–O2–Ni2	95.36(12)	N2–Ni2–O2	91.85(13)
O1–Ni1–O2	81.69(11)	N2–Ni2–O3	89.95((14)
O1–Ni1–O4	86.58(12)	N2–Ni2–O5	85.73(14)
O2–Ni1–O4	85.96(12)	O1–Ni2–O2	82.00(11)
N1–Ni2–N2	93.22(15)	O1–Ni2–O3	90.93(12)
N1–Ni2–O1	92.90(13)	O1–Ni2–O5	93.63(13)
N1–Ni2–O2	174.52(13)	O2–Ni2–O3	90.83(13)
N1–Ni2–O3	91.25(14)	O2–Ni2–O5	91.77(12)
N1–Ni2–O5	86.53(14)	O3–Ni2–O5	175.02(12)

Symmetry code ii: −x, 1 − y, 1 − z

Fig. 2 ORTEP drawing of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level. H atoms are not shown for clarity (Symmetry code i: −x, −y, −z)

bonds are of usual length and angle as compared to the similar compounds [3, 6–10].

Results and discussion

Previous studies dealing with homotrinuclear Ni^{2+} complexes of ONNO type Schiff base compounds have been reported in literature [3, 6–10]. In this study, salicylaldehyde ring has been replaced by a naphthalene ring. The

crystal structure of this complex has similar properties to those seen in literature. The crystal structure of the title compound **3** contains a linear $Ni^{2+}–Ni^{2+}–Ni^{2+}$ trinuclear complex in which a central Ni1 atom is located on an inversion centre and terminal Ni2 atoms are related by an inversion centre (Fig. 2). The coordination sphere of the complex is similar to those reported in literature. The central Ni^{2+} ion is in a distorted octahedral coordination environment within the O_6 coordination sphere. The bond distance and angle ranges around Ni1 are 2.040(3)–2.115(3) Å and 81.69(11)–86.58(12)°. The terminal Ni^{2+} ions have distorted octahedral coordination environments and these are situated in the N_2O_4 coordination sphere. The two phenolic oxygens and two aminic nitrogens form a plane and the terminal Ni2 atoms are situated in the middle of this plane; which forms the basal plane of the distorted octahedron with the average Ni2–O and Ni2–N coordination distances are 2.0455(3)–2.0855(3) Å. The oxygen atom of a DMF molecule coordinates the terminal Ni^{2+} ions [Ni2–O5 2.118(3) Å]. On the other side of the plane the Ni2 atom is coordinated by the oxygen atom of the acetate or benzoate ions [Ni2–O3 2.037(3) Å] which results in the Ni2 atom being situated inside the octahedron. The other oxygen atom of the benzoate ion form a μ-bridge and bonds both the terminal and central Ni2 atoms. Similarly, the phenolic oxygens of the organic

Table 3 Structural parameters of hydrogen bonds between donor (D), acceptor (A) and hydrogen (H)

D–H···A	D–H/Å	A···H/Å	D···A/Å	D–H···H/°
C16–H16B···O3	0.97	2.57	3.104(6)	115
C32–H32A···O5	0.96	2.35	2.717(9)	102
N1–H1···O6[ii]	0.91(2)	2.41(4)	3.204(15)	147(5)
C2–H2···O4[iii]	0.93	2.56	3.241(5)	131
C22–H22···O4[iii]	0.93	2.52	3.190(6)	129
C30–H30···O4[iii]	0.93	2.44	3.358(6)	168

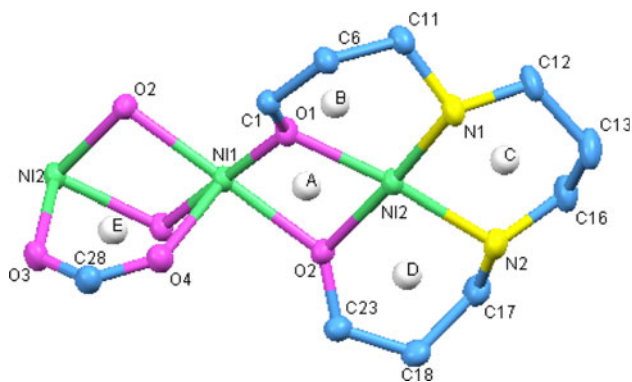Symmetry codes ii: $-x, 1-y, 1-z$ and iii: $-x, 2-y, -z$

Fig. 3 View of the center of rings

Table 4 Elemental analysis, important IR and ^{1}H-NMR data

Ligand or complex	Elemental analysis						Important IR data/cm^{-1}								^{1}H-NMR data/ppm δ			
	N/%		Ni/%				ν_{N-H}	$\nu_{C-H (Ar)}$	$\nu_{C-H (Aliph)}$	$\nu_{C=C}$	δ_{CH_2}	$\delta_{C-H(Ar)}$	$\nu_{C=O (DMF)}$		H_{Ar}	N–H	N–CH$_2$	CH$_2$
	Expected	Found	Expected	Found														
NAFL^H	7.28	7.36					3,286	3,055 3,018	2,870 2,929	1,599	1,475	762	–		6.95 7.80	4.72	2.55	1.65
NAFLDM^H	6.79	7.12					3,289	3,062 3,021	2,865 2,940	1,598	1,481	767	–		7.05 8.10	4.25	2.45	0.95
[(NiNAFL^H)$_2$·Ni(CH$_3$COO)$_2$·(DMF)$_2$] (**1**)	8.29	8.49	13.03	12.96			3,271	3,052 3,030	2,840 2,951	1,600	1,479	770	1,654					
[(NiNAFL^H)$_2$·Ni(C$_6$H$_5$COO)$_2$·(DMF)$_2$] (**2**)	6.32	6.11	13.25	12.94			3,266	3,071 3,028	2,826 2,948	1,602	1,476	763	1,651					
[(NiNAFLDM^H)$_2$·Ni(CH$_3$COO)$_2$·(DMF)$_2$] (**3**)	7.32	7.08	13.16	12.88			3,280	3,055 3,021	2,864 2,935	1,601	1,485	759	1,654					
[(NiNAFLDM^H)$_2$·Ni(C$_6$H$_5$COO)$_2$·(DMF)$_2$] (**4**)	6.17	5.96	12.94	12.91			3,277	3,057 3,019	2,866 2,942	1,600	1,473	761	1,652					

ligand coordinate both the terminal and central Ni^{2+} ions and form a μ-bridge (Fig. 2). The overall result is three edge-shared octahedrons in which the closest Ni···Ni distance is 3.0551(11) Å. The coordination characteristics of the compound are very similar to those seen in literature whereas the thermal characteristics show significant differences.

The hydrogen bonding geometry and conformation of the rings in the title molecule were analyzed using *PLATON*. The crystal is held together with inter and intra molecular hydrogen-bonding, details of which are given in Table 3. The data given in Table 3 were obtained with the help of the software. Only one of these data, N1–H1···O6^{ii} is a real hydrogen bond while others are not. These geometrical formations are called agostic interaction [19].

Ring puckering analysis shows that the chelate rings formed by the organic ligand that coordinates the terminal Ni^{2+} ions are not planar, whereas naphthalene groups are in planar conformation (Fig. 3) [20, 21].

Dihedral angle between the planes I & II and II & III are 17.55° and 36.03°, respectively. The Ni2 and C13 atoms are diagonally positioned from chelate ring C and these atoms are at distance of 0.731(6) and −0.865(1) Å, respectively, from the plane III.

Tables 4 and 5 give some elemental analysis results, important IR data and thermoanalytical data. As some of the complexes did not totally dissolve in DMSO only some of the NMR results were given. TG-DTA curves of compounds 1 and 3 are given in Fig. 4a, b. Three thermal reactions for the degradation of these compounds can be observed (Fig. 4a, b; Table 5). The first reaction observed between 140 and 180 °C is endothermic. The mass loss in the reaction corresponds to the loss of DMF molecules from the structure. This mass loss has been very useful in determination of the complex stochiometry and solvated DMF molecules. It is not possible to estimate the changes in the organic group of the molecule during the second and the third thermal reactions since they are so extremely exothermic. As a result of the exothermic reactions, the remaining organic part leaves the structure with exothermic degradation and NiO residue is left. This is a situation observed for explosive materials [22, 23].

Table 5 Thermoanalytical data of the complexes

Complex	1st thermal reaction			Temp. range of 2nd and 3rd thermal reaction/°C		NiO residue	
	Loss of DMF			2nd thermal reaction	3rd thermal reaction	Expected/%	Found/%
	Temperature range/°C	Expected/%	Found/%				
[(NiNAFL^H)$_2$·Ni(CH$_3$COO)$_2$·(DMF)$_2$]·2DMF (1)	91–210 DTA peak: 158	21.56	21.70 ± 0.86	220–290 DTA peak: 268 exothermic	298–410 DTA peak: 399 exothermic	16.54	15.74 ± 0.25
[(NiNAFL^H)$_2$·Ni(C$_6$H$_5$COO)$_2$·(DMF)$_2$] (2)	145–182 DTA peak: 159	10.96	10.67 ± 0.45	235–281 DTA peak: 266 exothermic	320–425 DTA peak: 408 exothermic	16.82	14.91 ± 0.34
[(NiNAFLDM^H)$_2$·Ni(CH$_3$COO)$_2$·(DMF)$_2$]·2DMF (3)	139–180 DTA peak: 159	16.38	16.32 ± 0.26	238–290 DTA peak: 268 exothermic	295–420 DTA peak: 412 exothermic	13.63	12.91 ± 0.28
[(NiNAFLDM^H)$_2$·Ni(C$_6$H$_5$COO)$_2$·(DMF)$_2$] (4)	143–184 DTA peak: 159	10.52	10.79 ± 0.34	242–304 DTA peak: 266 exothermic	328–426 DTA peak: 420 Exothermic	12.69	12.91 ± 0.96
[(NiNAFL^H)$_2$·Ni(CH$_3$COO)$_2$·(DMF)$_2$]·2DMF (1) (O$_2$ atmosphere)	131–183 DTA peak: 157	21.56	21.48 ± 0.28	243–254	361–366	16.54	8.41 ± 2.10
[(NiNAFL^H)$_2$·Ni(C$_6$H$_5$COO)$_2$·(DMF)$_2$] (2) (O$_2$ atmosphere)	142–183 DTA peak: 156	10.96	10.62 ± 0.38	245–256	367–373	16.82	5.87 ± 1.42
[(NiNAFLDM^H)$_2$·Ni(CH$_3$COO)$_2$·(DMF)$_2$]·2DMF (3) (O$_2$ atmosphere)	136–173 DTA peak: 152	16.38	15.31	248–255	361–368	13.63	7.61 ± 2.11
[(NiNAFLDM^H)$_2$·Ni(C$_6$H$_5$COO)$_2$·(DMF)$_2$] (4) (O$_2$ atmosphere)	133–179 DTA peak: 155	10.52	10.09	245–254	365–373	12.69	7.42 ± 1.86

Fig. 4 a The TG-DTA curves of the complex (**1**). **b** The TG-DTA curves of the complex (**3**)

Fig. 5 a The TG-DTA curves of the complex (**1**) in O_2 atmosphere. **b** The TG-DTA curves of the complex (**3**) in O_2 atmosphere

The thermal reactions in explosive materials are so called "inner" reactions, exchange of oxygen does not occur. There are many studies about energetic materials in literature. These energetic materials are generally nitrogen-rich or they contain oxidizing ions such as nitrate, perchlorate along with organic groups [24–30]. The TG-DTA curves seen in Fig. 4a, b were obtained in a N_2 atmosphere. Although the number of oxygen and nitrogen atoms in the complex structure are insufficient to transform all C atoms to gaseous compounds all the organic part is seen to have been lost at 420 °C leaving only NiO as residue.

TG-DTA curves under O_2 atmosphere were also obtained as given in Fig. 5a, b. The products of the exothermic reaction are more volatile and the degradation is observed to continue in a smaller temperature range; under O_2 atmosphere the exothermic reaction proceeds in 10 °C range. The sample amount that the instrument could tolerate was 1–2 mg. The shift of the thermal reaction temperature to lower values is expected under O_2 atmosphere. The complexes show explosive behavior under O_2 atmosphere. We can deduce that these complexes will behave as explosive material when coupled with oxidizing agents like KNO_3, $NaNO_3$, $Ba(NO_3)_2$, etc.
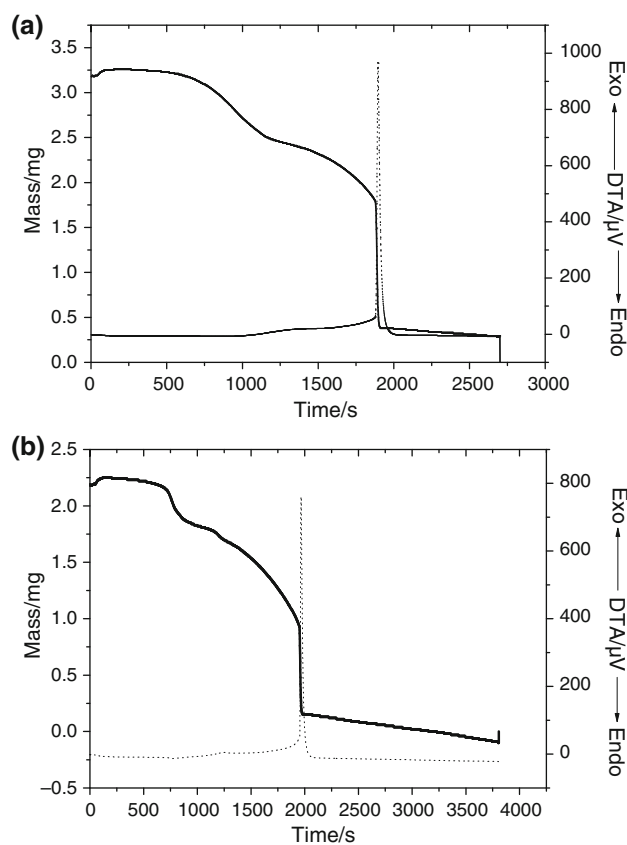
It is not possible to write the thermal degradation reaction under N_2 atmosphere. The inner reaction equation can be written according to the oxygen balance parameter [31]. Even if the oxygen balance was calculated the reaction equation could only be hypothetic. Within a 80–90 °C temperature range, an exothermic reaction of a 10 kJ g^{-1} is observed leaving only NiO as residue. Under O_2 atmosphere, the reaction is extremely fast within a range of 6–7 °C. The NiO residue is less than the expected resulting in a high standard deviation value. The resulting exothermic reaction was observed to resemble those of explosive material resulting in a "shrapnel" effect which explains why the residual NiO is less than expected.

In previous studies, the thermal degradation of homotrinuclear Ni(II) complexes were studied [9, 32] the only difference being the presence of phenyl rings. These reactions were observed to be endothermic. These are similar to the results obtained up to the 140–180 °C range corresponding to loss of DMF molecules. But in the presence of the naphthalene ring at higher temperatures exothermic reactions are observed. The present data, without using TGA technique, is insufficient in writing the thermal degradation mechanism.

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