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# Thermal stability and crystallographic characterization of mononuclear Ni(II) and heterodinuclear Ni(II)-Co(II) complexes of the reduced ONNO type Schiff base

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## Abstract

In this study, the ONNO type Schiff base ligand N, N'-bis(2-hydroxyphenylidene)-1,3-propanediamine ($LH_2$) was reduced and converted into a tetradentate phenolic amine ligand, N, N′-bis(2-hydroxybenzyl)-1,3-diaminopropane ($L^HH_2$). First, a mononuclear $[NiL^HCl(DMF)]_2(DMF)$ complex **(I)** was obtained with the reduced ligand in dimethylformamide (DMF). $CoCl_2$ was then added to the complex **I** to give the heterodinuclear $[NiL^HCoCl_2(DMF)_2]$ complex **(II)**. The complexes were characterized by elemental analysis, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and single-crystal X-ray diffraction (XRD). The XRD analysis of complex **I** revealed that one phenolic oxygen persisted in its coordinated phenol form, while the charge of Ni(II) was observed to be neutralized by a chloride ion and a phenolate ion. The Ni(II) center ion in the complex exhibited octahedral coordination, being surrounded by two phenolic oxygens, two aminic nitrogens, an oxygen from a DMF molecule, and a chloride ion. In complex **II**, the Ni(II) ion was coordinated by two phenolic oxygens, two aminic nitrogen, and two DMF oxygens. The Co(II) ion was found to have a tetrahedral coordination sphere with two phenolate oxygens and two chloride ions. Thermogravimetric analysis demonstrated distinct thermal behaviors for mononuclear and heterodinuclear complexes. The mononuclear complex exhibited stability up to 210 °C and an exothermic reaction at 510 °C in an oxygen atmosphere, resembling energetic materials. The heterodinuclear complex

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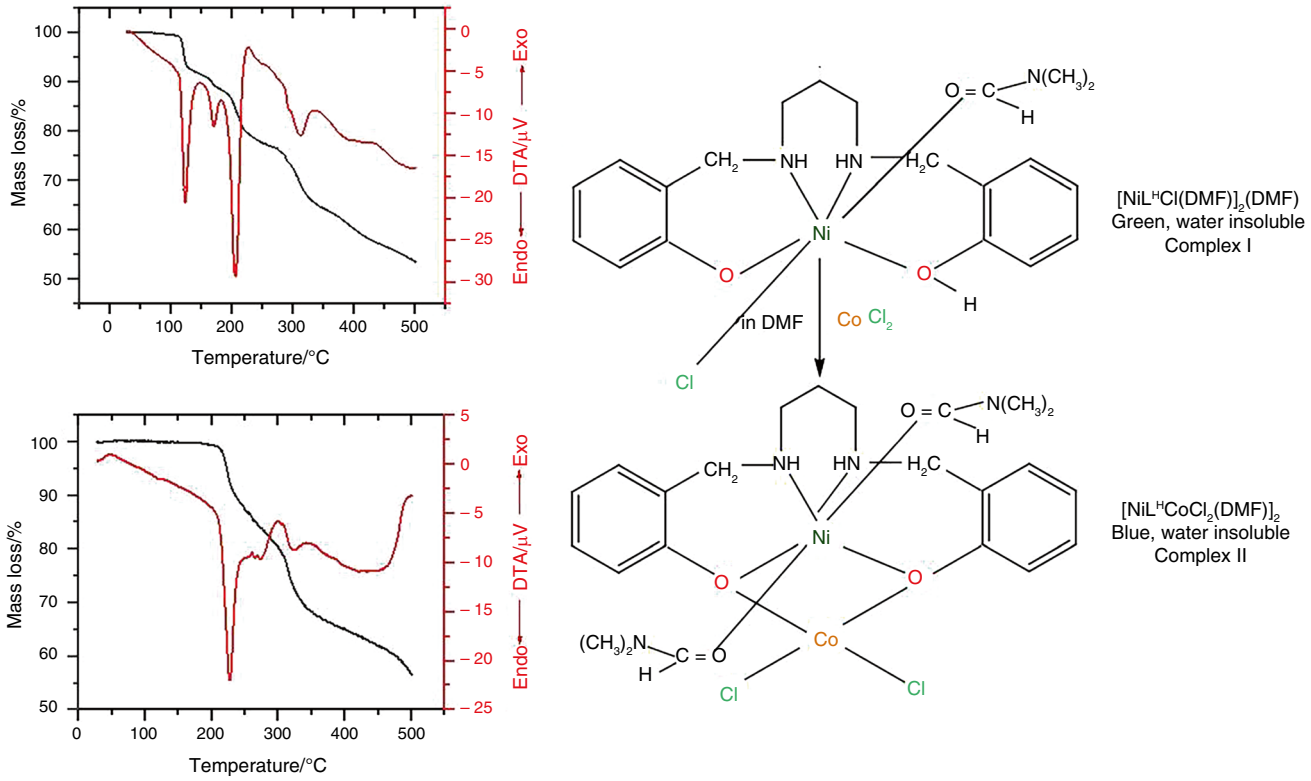
showed higher thermal stability and a distinct decomposition pathway, influenced by Co(II) coordination. These findings highlight the significance of heterometallic coordination in thermal properties and controlled decomposition applications.

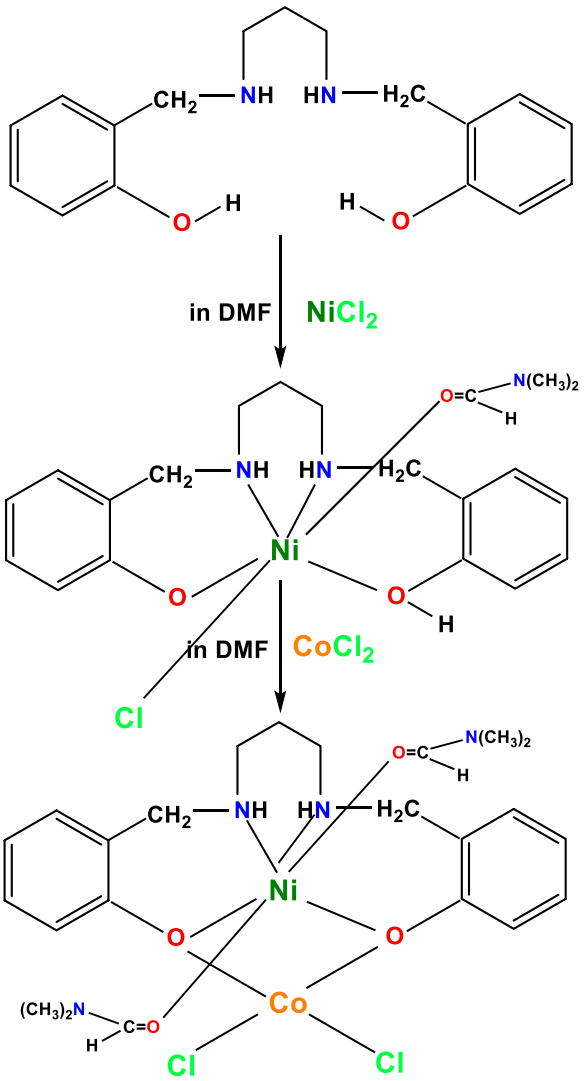



**Keywords** Ni-Co Heterodinuclear complex · Reduced Schiff bases · ONNO type Schiff base · Thermogravimetry

## Introduction

TheONNO-type Schiff base, N, N′-bis(salicylidene)-1,3-diaminopropane ($LH_2$), is a ligand synthesized through the reaction of 1,3-diaminopropane with salicylaldehyde, a process recognized since 1946 [1, 2]. On the other hand, the reduced form of Schiff base, N, N′-bis(2-hydroxybenzyl)-1,3-diaminopropane ($L^HH_2$), has attracted the attention of researchers for over twenty years [3–5] and is also recognized for its mono-, oligo-, and multinuclear complexes. In addition, these ligands have been reported to form mono- and polynuclear coordination compounds. Among the multinuclear species, di-[6–8], tri-[9–12], and polycentric [6–18] examples have been reported. The mononuclear, four-coordinated Cu(II) and Ni(II) complexes of $LH_2$, namely, CuL and NiL, have been known to exist and be stable since 1985 [19]. However, Cu(II) and Ni(II) complexes of these two metal ions with the reduced ligand $L^HH_2$ are very few in the literature. It was reported by Taylor et al. that mononuclear, tetradentated [$CuL^H$] was synthesized but did not crystallize to the correct dimensions for a suitable X-ray diffraction analysis [20]. No data were discovered in the published literature pertaining to the Ni(II) complex.

The first aim of this study was to synthesize and isolate the $NiL^H$ complex. For this purpose, various polar organic solvents were employed, resulting in a mononuclear [$NiL^HCl$(DMF)] complex **(I)** in dimethylformamide (DMF). It has been known for a long time that the NiL mononuclear complex coordinates with the metal ion via phenolic oxygens together with other metal ions in the medium and turns into dinuclear complexes [18]. According to the information, the prepared complex **I** was dissolved in DMF, $CoCl_2$ was added to the medium, and a new heterodinuclear [$NiL^HCoCl_2(DMF)_2$] complex **(II)** was obtained, Fig. 1. The analysis of both complexes was conducted through single-crystal X-ray diffraction techniques in the context of molecular modeling. In addition, thermogravimetric analysis revealed that the complexes exhibit peculiar (out of the ordinary) thermal characteristics.




N, N'-bis(2-hydroxybenzyl)-1,3-diaminopropane ($L^HH_2$)

$[NiL^HCl(DMF)]_2(DMF)$
Green,water insoluble
Complex **I**

$[NiL^HCoCl_2(DMF)_2]$
Blue, water soluble
Complex **II**

**Fig. 1** Formation of the complexes

## Experimental

### Materials and apparatus

The reagents were supplied by Merck and Fluka companies and used without further purification. A Fourier Transform Infrared spectrometer (FTIR, Shimadzu IRAffinity-1) equipped with three reflection ATR units, with an accuracy of 4 cm-1, was used. The C, H, and N analyses were performed on an Eurovector 3018 CHNS analyzer. Metal analyses were performed using a GBC Avanta PM Model atomic absorption spectrometer in FAAS mode. For this purpose, the complex (2–3 mg) was dissolved in 1.0 mL $HNO_3$ (63%) with heating, diluted to 100.0 mL, and fed to the nebulizer of the atomic absorption spectrometer for metal analysis. Chloride analysis was carried out titrimetrically using the Volhard method. As a pretreatment, approximately 0.5 g of the complex was dissolved in 10.0 mL $HNO_3$ (63%) with heating, and this solution was diluted to twice the volume with pure water and back-titrated with 0.05 M $AgNO_3$ and KSCN. The mass spectra of the ligand and complexes were obtained by a Shimadzu QP2010 Plus GC/MS spectrometer equipped with a direct inlet (DI) unit with an electron impact (EI) ionizer. The DI temperature was varied between 40–140 °C, and ionization was carried out using electrons with an energy of 70 eV. The NMR spectrum of the ligand is recorded on the Bruker Ultrashield 300 MHz NMR spectrometer using $d_6$-DMSO as a solvent. The thermogravimetric analyses were performed using a Shimadzu DTG-60H. In thermogravimetric analyses, the temperature was varied between 30–600 °C under an $N_2$ atmosphere in platinum pans with a heating rate of 10 °C $min^{-1}$. Calibration of the instrument was done with metallic In and Zn.

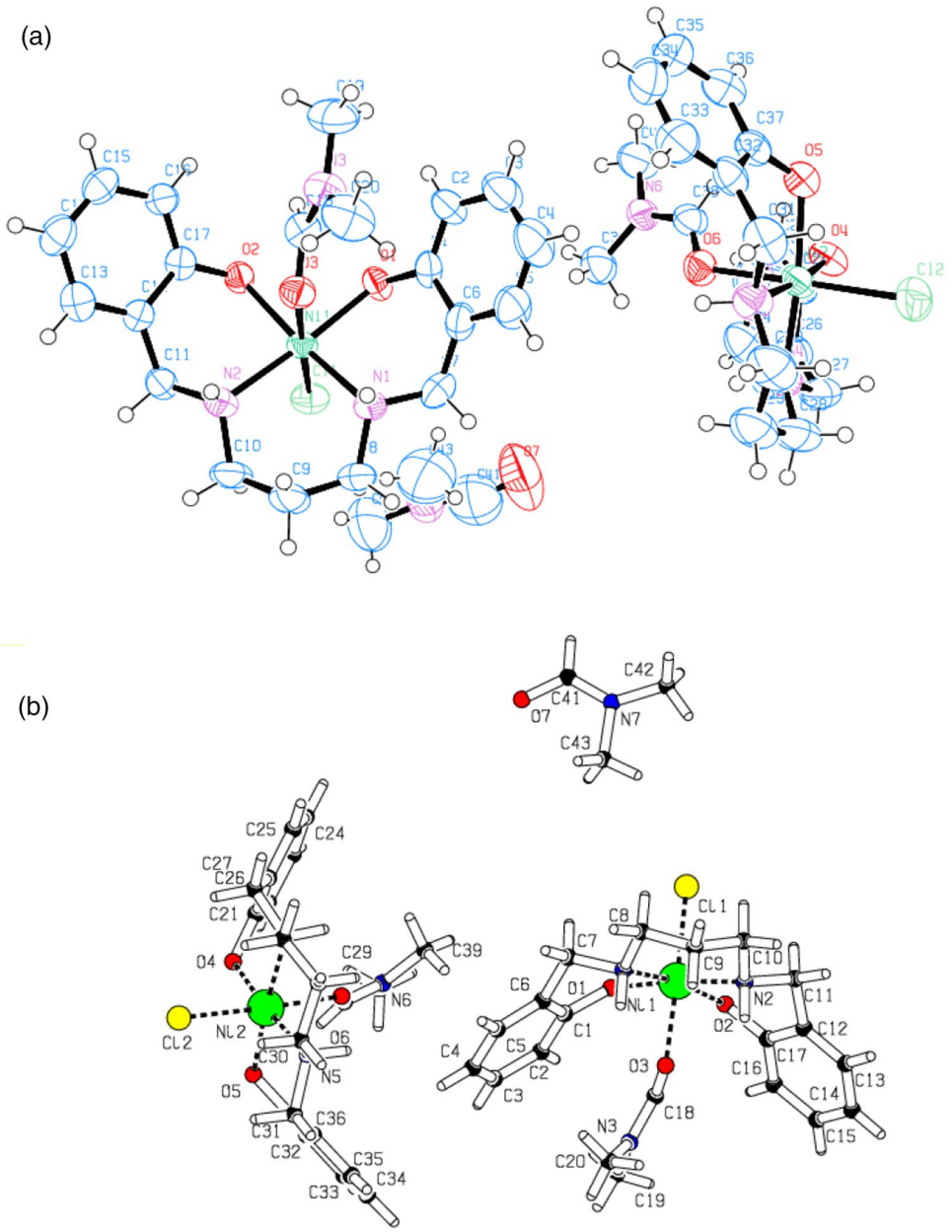



**Fig. 2** **a** Ortep drawing of complex I; **b** Pluton drawing of complex I

## X-ray crystallography

### Crystal structure determination

The crystal structures of complex **I** and complex **II** were determined by single-crystal X-ray diffraction. Reflection data were collected at room temperature on a Bruker APEX II CCD diffractometer [21]. Absorption correction was done by using SADABS [19]. The structures were solved by direct methods using *SHELXT 2018/2* [20] and refined by full-matrix least squares on $F^2$ using *SHELXTL-2019* [21]. Material preparation for publication is carried out by using PLATON [22], ORTEP software within WinGX [23], and Mercury 4.0 [24] programs.

In complex **I**, all non-hydrogen atoms in the structure were located from difference Fourier maps and refined anisotropically. The hydrogen atoms of the CH groups in the DMF molecules, which were coordinated to the Ni atom, were located from difference Fourier maps and refined isotropically. All other hydrogen atoms were placed geometrically and refined as riding atoms with related groups (CH3) C–H = 0.96 Å, (CH2) C–H = 0.97 Å, and (CH) C–H = 0.93 Å.

In complex **II**, all non-hydrogen atoms were located using difference Fourier syntheses and refined with anisotropic displacement factors. All hydrogen atoms, except those of the methyl group, were located from difference Fourier syntheses and refined isotropically. Hydrogen atoms of methyl

**Table 1** Crystal and Structure Refinement Data of complexes I and II

| Complex | Complex I | Complex II |
|---|---|---|
| Empirical formula | $2(NiClC_{20}H_{27}N_3O_3).C_3H_7NO$ | $NiCoCl_2C_{23}H_{34}N_4O_4$ |
| Formula weight | 976.30 | 619.08 |
| Temperature /K | 293(2) | 293(2) |
| Wavelength /Å MoKα | 0.71073 | 0.71073 |
| Crystal system | monoclinic | orthorhombic |
| Space group | $P2_1/c$ | Pbca |
| *a* (Å) | 17.383(6) | 13.648(6) |
| *b* (Å) | 14.796(4) | 19.669(10) |
| *c* (Å) | 19.291(6) | 21.054(11) |
| *α* (°) | 90 | 90 |
| *β* (°) | 103.123(7) | 90 |
| *γ* (°) | 90 | 90 |
| V (Å$^3$) | 4832(3) | 5651(5) |
| Z | 4 | 8 |
| Dc /g cm$^{-3}$ | 1.342 | 1.455 |
| μ/mm$^{-1}$ | 0.943 | 1.476 |
| F(000) | 2056 | 2568 |
| Crystal description / color | block / green | block / blue |
| Crystal size /mm | 0.10×0.10×0.15 | 0.10×0.11×0.14 |
| Θ range for data collection /° | 3.038—25.496 | 2.443—25.499 |
| Measured ref. / $R_{int}$ | 64,049 / 0.1855 | 75,365 / 0.0972 |
| Independent / [I > 2σ(I)] ref | 8451 / 4044 | 5254 / 3318 |
| No. of parameters | 557 | 409 |
| Final $R_1$ / $wR_2$ indices [$I > 2\sigma(I)$] | 0.1589 / 0.1753 | 0.0420 / 0.1106 |
| $R_1$, $wR_2$ indices (all data) | 0.0568 / 0.1243 | 0.0921 / 0.1517 |
| Goodness-of-fit on $F^2$ | 0.874 | 0.788 |
| $\Delta\rho_{max}$ / $\Delta\rho_{min}$ /e / Å$^3$ | 0.845 / −0.303 | 0.360 / −0.288 |
| CCDC number | 2386686 | 2388104 |

groups were calculated to their idealized positions and refined as riding atoms with a C–H distance of 0.96 Å. The molecular structure and crystal packing of the title complex are illustrated in Figs. 1 and 2. The crystallographic data collection and refinement details are given in Table 1. The selected bond distances, bond angles, and hydrogen bond geometry are detailed in Tables 2–4.

Crystallographic data (fractional atomic coordinates, anisotropic displacement parameters, and molecular dimensions) for complexes **I** and **II** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2386686 and 2388104, respectively.

## Preparation of the ligands

***LH₂***: The Schiff base, $LH_2$, was prepared via the condensation reaction of 2-hydroxybenzaldehyde and 1,3-diaminopropane in ethanol (EtOH). 12.2 g of 2-hydroxybenzaldehyde was dissolved in 100.0 mL of EtOH under heating up to the boiling point. Then, 3.70 g of 1,3-diaminopropane was dissolved in another beaker in 30.0 mL of EtOH and added to a 2-hydroxybenzaldehyde solution. The mixture was kept for 10–12 h, and the crystals obtained were filtered and dried at room temperature.

Yield: 90%, mp: 58–59 °C.

***L$^H$H₂***: The reduced ligand ($L^HH_2$) was obtained by the reduction of N, N'-bis(2-hydroxyphenylidene)-1,3-propanediamine ($LH_2$) with $NaBH_4$ in methanol (MeOH). In compliance with the literature [6]. 3.0 g of $LH_2$ was dissolved in 70.0 mL of MeOH. The resulting mixture was heated to 50 °C, and solid $NaBH_4$ was slowly added until the mixture became colorless. After 10 min of stirring, 300.0 mL of ice-water mixture was added. The final mixture was kept aside for 24 h. The resulting white precipitate was filtered and dried in the air. The product bis-N, N′(2-hydroxybenzyl)-1,3-propanediamine ($L^HH_2$) was recrystallized from hot EtOH:$H_2O$ (2:1, v/v).

Yield: 55–60%, mp: 107 °C (determined by TG).

Elemental Analysis, $C_{17}H_{22}N_2O_2$: Expected % C: 71.30, H: 7.74, N: 9.78; Found % C: 70.86, H: 6.69, N: 9.41.

**Table 2** Selected bond lengths and angles within of coordination sphere

| Complex I | | Complex II | |
|---|---|---|---|
| Bond lengths/Å | Bond angles/° | Bond lengths/Å | Bond angles/Å |
| Ni1—Cl1 2.3983(17) | N1—Ni1—Cl1 95.96(14) | Ni—N1 2.083(4) | Co—O1—Ni 97.29(13) |
| Ni2—Cl2 2.3992(19) | N2—Ni1—Cl1 93.62(14) | Ni—N2 2.100(4) | Co—O2—Ni 97.28(12) |
| Ni1—O1 2.069(3) | O1—Ni1—Cl1 91.34(11) | Ni—O1 2.100(3) | N1—Ni—N2 95.44(15) |
| Ni1—O2 2.054(3) | O2—Ni1—Cl1 92.64(11) | Ni—O2 2.089(3) | N1—Ni—O1 93.17(14) |
| Ni1—O3 2.149(4) | O3—Ni1—Cl1 178.35(11) | Ni—O3 2.083(3) | N1—Ni—O2 172.53(14) |
| Ni2—O4 2.070(4) | N1—Ni1—N2 92.20(17) | Ni—O4 2.129(3) | N1—Ni—O4 88.85(15) |
| Ni2—O5 2.059(4) | N1—Ni1—O3 83.53(17) | Co—O1 1.990(3) | N2—Ni—O1 171.39(13) |
| Ni2—O6 2.124(4) | N2—Ni1—O3 87.98(16) | Co—O2 2.001(3) | N2—Ni—O4 91.43(14) |
| Ni1—N1 2.097(4) | O1—Ni1—N1 89.27(15) | Co—Cl1 2.2646(19) | O1—Ni—O4 88.72(13) |
| Ni1—N2 2.105(4) | O1—Ni1—N2 174.65(16) | Co—Cl2 2.2739(16) | O2—Ni—N2 91.71(13) |
| Ni2—N4 2.098(5) | O1—Ni1—O3 87.08(14) | | O2—Ni—O1 79.69(12) |
| Ni2—N5 2.081(5) | O2—Ni1—N1 171.04(17) | | O2—Ni—O4 93.16(12) |
| | O2—Ni1—N2 89.78(15) | | O3—Ni—N1 86.00(15) |
| | O2—Ni1—O1 87.99(14) | | O3—Ni—N2 94.26(14) |
| | O2—Ni1—O3 87.81(14) | | O3—Ni—O1 86.35(13) |
| | N4—Ni2—Cl2 94.41(16) | | O3—Ni—O2 91.31(12) |
| | N5—Ni2—Cl2 95.13(15) | | O3—Ni—O4 172.66(13) |
| | O4—Ni2—Cl2 92.08(13) | | Cl1—Co—Cl2 113.28(6) |
| | O5—Ni2—Cl2 92.60(12) | | O2—Co—Cl1 117.31(10) |
| | O6—Ni2—Cl2 177.84(12) | | O2—Co—Cl2 108.66(9) |
| | N4—Ni2—O6 84.35(18) | | O1—Co—Cl1 118.76(10) |
| | N5—Ni2—N4 90.9(2) | | O1—Co—Cl2 110.97(10) |
| | N5—Ni2—O6 86.66(18) | | O1—Co—O2 84.50(12) |
| | O4—Ni2—N4 89.95(18) | | C1—O1—Co 127.1(3) |
| | O4—Ni2—N5 172.65(18) | | C17—O2—Co 128.9(3) |
| | O4—Ni2—O6 86.16(15) | | |
| | O5—Ni2—N4 172.56(18) | | |
| | O5—Ni2—N5 90.95(17) | | |
| | O5—Ni2—O4 87.30(15) | | |
| | O5—Ni2—O6 88.57(15) | | |

**Table 3** Hydrogen geometry of complex I

| D | H | A | D-H | H…A | D…A | D-H…A |
|---|---|---|---|---|---|---|
| C8 | H8B | Cl1 | 0.97 | 2.94 | 3.518(7) | 119.3 |
| C10 | H10A | Cl1 | 0.97 | 2.89 | 3.473(7) | 119.6 |
| C30 | H30B | Cl2 | 0.97 | 2.92 | 3.503(8) | 119.4 |
| N1 | H1N | $O7^{i}$ | 0.98 | 2.47 | 3.171(11) | 127.9 |
| C18 | H18 | O2 | 0.92(4) | 2.62(4) | 3.037(7) | 108(3) |
| C38 | H38 | O5 | 0.87(6) | 2.47(6) | 3.035(8) | 123(5) |
| C8 | H8B | Cl1 | 0.97 | 2.94 | 3.518(7) | 119.3 |
| C10 | H10A | Cl1 | 0.97 | 2.89 | 3.473(7) | 119.6 |
| C28 | H28A | Cl2 | 0.97 | 2.99 | 3.536(7) | 117.2 |
| C30 | H30B | Cl2 | 0.97 | 2.92 | 3.503(8) | 119.4 |
| N1 | H1N | $O7^{i}$ | 0.98 | 2.47 | 3.171(11) | 127.9 |
| C38 | H38 | O5 | 0.87(6) | 2.47(6) | 3.035(8) | 123(5) |

Symmetry code: (i) 1-x, -1/2 + y, 1/2-z

**Table 4** Hydrogen geometry of complex II

| D | H | A | D-H | H…A | D…A | D-H…A |
|---|---|---|---|---|---|---|
| N2 | H2N | $Cl2^{i}$ | 0.87(5) | 2.78(5) | 3.617(4) | 162(4) |
| C2 | H2 | Cl1 | 0.93(4) | 2.93(5) | 3.653(6) | 136(3) |
| C18 | H18 | $Cl2^{i}$ | 1.06(5) | 2.74(5) | 3.392(5) | 119(3) |
| C21 | H21 | Cl2 | 1.01(4) | 2.82(5) | 3.706(6) | 148(3) |
| C23 | H23B | $Cl2^{ii}$ | 0.96 | 2.82 | 3.760(7) | 167.4 |

Symmetry code: (i) −1/2 + x, y, 3/2-z; (ii) 1-x, 1-y, 1-z

IR ($cm^{-1}$), $\nu_{N-H}$: 3307, $\nu_{C-H(Ar)}$: 3055–3023, $\nu_{C-H(Aliph)}$: 2967–2823, $\nu_{C=C(ring)}$: 1606–1595, $\nu_{C-O(Phenol)}$: 1253–1099, $\delta_{C-H(Ar)}$: 752. (Fig. S1).

$^{1}$H NMR data in $d_6$-$CH_3SOCH_3$ (δ, ppm): 7.03 (multiplet, $H_{Ar}$), 6.90 (broad, N–H and OH), 6.67 (multiplet, $H_{Ar}$), 3.80 (singlet, -**$CH_2$**-NH-), 2.56 (triplet, -NH-**$CH_2$**-), 1.64 (pentet, -$CH_2$-**$CH_2$**-$CH_2$-) (Fig. S2).

$^{13}$C NMR data in $d_6$-DMSO (δ, ppm): 157.64, 128.43, 127.78, 124.02, 118.34, 115.40 (Aromatic ring), 50.80 (–**$CH_2$**-NH-), 46.29 (-NH-**$CH_2$**-), 28.94 (-$CH_2$-**$CH_2$**-$CH_2$-) (Fig. S3).

m/z: 286 (molecular peak), 179 [HO-$C_6H_4$-$CH_2$-NH-$CH_2$-$CH_2$-$CH_2$-NH]$^+$, 163 [HO-$C_6H_4$-$CH_2$-NH-$CH_2$-$CH_2$-$CH_2$]$^+$, 150 [HO-$C_6H_4$-$CH_2$-NH-$CH_2$-$CH_2$]$^+$, 134 [HO-$C_6H_4$-$CH_2$-NH-$CH_2$]$^+$, 122 [HO-$C_6H_4$-$CH_2$- NH]$^+$, 107 [HO-$C_6H_4$-$CH_2$]$^+$ (base peak), 90 [$C_6H_4$-$CH_2$]$^+$, 77 [$C_6H_5$]$^+$ (Figs. S4-S5).

## Preparation of the complexes

*Complex I*, [Ni$L^{H}$Cl(DMF)]$_2$(DMF); 0.02 mol (5.72 g) $L^{H}H_2$ was dissolved in 60 mL MeOH: DMF mixture (2:1, v/v) with stirring and heated to 70 °C. At this temperature, a solution of 0.02 mol (0.475 g) $NiCl_2.6H_2O$ in 30 mL MeOH: DMF (1:1, v/v) was added. The resulting mixture was left aside for 2–3 days. The precipitate was filtered with a Buchner funnel. The green crystals were dried in the air.

Yield: 55–60%, mp: not observed; decomposition starts from 250 °C (the decomposition was discussed in the section concerning the thermal analysis).

Elemental Analysis, $C_{43}H_{61}N_7O_7Cl_2Ni_2$: Expected % C: 52.90, H: 6.29, N: 10.04, Cl: 7.26 Ni: 12.03; Found % C: 52.45, H: 5.97, N: 9.79, Cl: 7.05, Ni: 12.03.

IR ($cm^{-1}$): $\nu_{N-H}$: 3271, $\nu_{C-H(Ar)}$: 3034, $\nu_{C-H(Aliph)}$: 2951–2856, $\nu_{C=O(DMF)}$: 1670, $\nu_{C=N(DMF)}$: 1643, $\nu_{C=C(ring)}$: 1597, $\delta_{CH2}$: 1462, $\nu_{C-O(Phenol)}$: 1276–1087, $\delta_{C-H(Ar)}$: 738 (Fig. S6).

*Complex II*, [Ni$L^{H}$ $CoCl_2(DMF)_2$]; approximately 0.32 g of complex I was dissolved in a hot 30 mL DMF-MeOH mixture, and a solution of $CoCl_2.6H_2O$ in 30 mL DMF-MeOH (1:1) was added to this solution. The mixture was set aside for one day. After this period, the dark blue crystals of the target complex were dried in the air. Yield: 70–75%, mp: not observed; decomposition starts from 260 °C (the

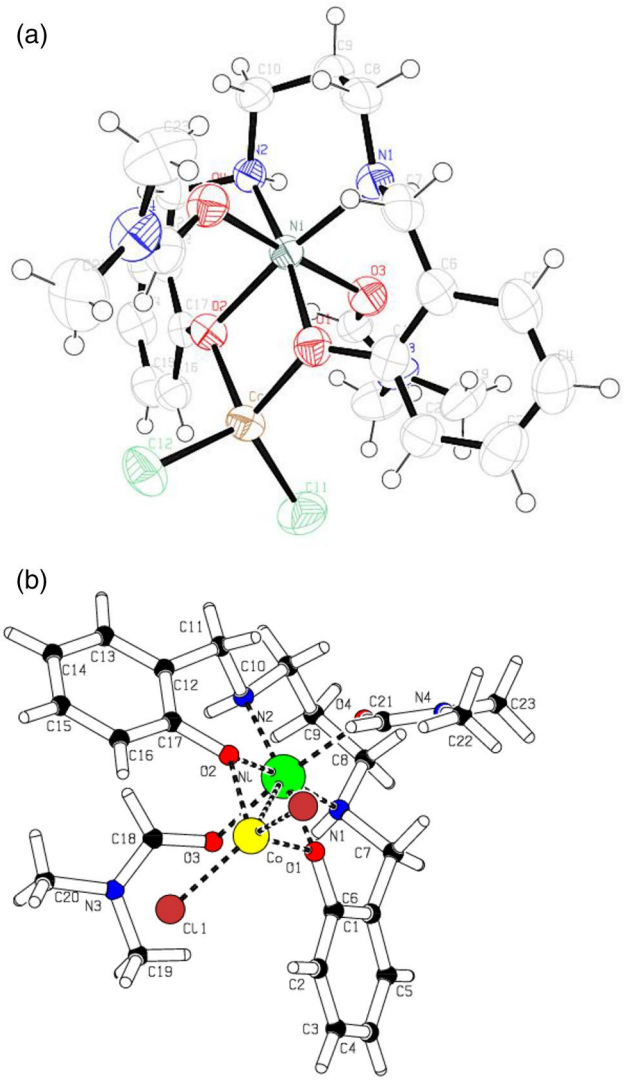



**Fig. 3** **a** Ortep drawing of complex II, the coordination sphere is seen as octahedral; **b** Pluton drawing of complex II, the coordination sphere is seen as octahedral

**Table 5** Comparison of bond lengths and angles of similar complexes

| Complex | M–M /Å | M–O /Å | O–M–O /° | φ /° | Reference |
|---|---|---|---|---|---|
| (1) | 3.0695 (11) | 1.986(4)–2.019 (5) | 78.80(18)–80.19 (18) | 8.95 (16) | [25] |
| (2) | 3.0757 (6) | 1.938(3)–2.010 (3) | 75.0(1)–78.1 (1) | 14.0 (4) | [26] |
| (3) | 3.0917 (15) | 1.995(6)–2.031 (6) | 78.2(2)–79.8 (2) | 11.1 (3) | [27] |
| (4) | 3.161 (1) | 1.991(3)–2.058 (3) | 75.90(10)–78.56 (10) | 3.07 (1) | [28] |

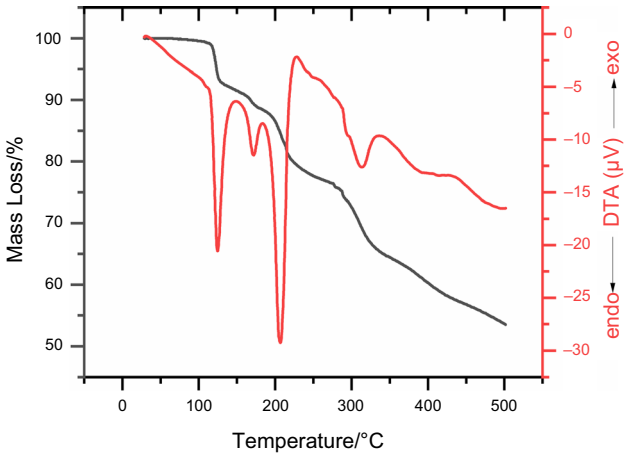



**Fig. 4** TG curve of the complex I

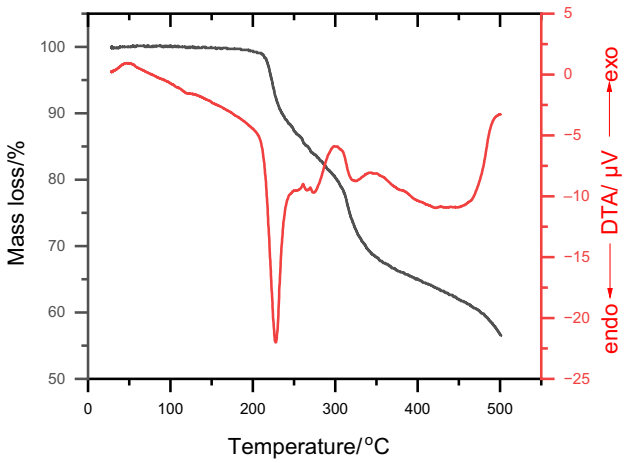



**Fig. 5** TG curve of the complex II

decomposition was discussed in the section concerning the thermal analysis).

Elemental Analysis, $C_{23}H_{34}N_4O_4Cl_2NiCo$: Expected % C: 44.62, H: 554, N: 9.04, Cl: 11.45, Ni: 9.48, Co: 9.53; Found % C: 44.47, H: 5.88, N: 8.799, Cl: 10.85, Ni: 9.28.

IR ($cm^{-1}$): $\nu_{N-H}$: 3251–3217, $\nu_{C-H(Ar)}$: 3023–3031, $\nu_{C-H(Aliph)}$: 2929–2860, $\nu_{C=O(DMF)}$: 1651, $\nu_{C=N(DMF)}$: 1643, $\nu_{C=C(ring)}$: 1597, $\delta_{CH2}$: 1483, $\nu_{C-O(Phenol)}$: 1263, $\delta_{C-H(Ar)}$: 756 (Fig. S7).

## Results

### Crystal structures

The Ortep and Pluton drawings of complex **I** and the atom-numbering scheme are shown in Fig. 2a, b, whereas that of heterodinuclear complex **II** is depicted in Fig. 3a, b. The Pluton drawing was added because it shows the coordination better.

Figure 2a, b illustrates that during the crystallization process of the complex designated as [$NiL^HCl(DMF)$], which was isolated in a DMF medium, two complex units are accompanied by a DMF molecule acting as a solvate. Therefore, it is more appropriate to depict the stoichiometry of complex **II** in the solid state as complex **I**. The Ni(II) ion is located in the complex in an octahedral coordination sphere by two phenolic oxygen atoms of the organic ligand, two aminic nitrogen atoms, a chloride ion, and the oxygen of a DMF molecule. The Ni(II) ion's charge was neutralized by a phenolate and a chloride, while the second phenol group participated in coordination as a phenol. The bond angles in Table 2 show that the octahedron is slightly distorted. The angles on the axial axes for Cl2Ni2O6 and Cl1Ni1O3 were measured at 178.35(11) ° and O6 Ni2 Cl2 at 177.84(12) °. Additionally, the angles

**Table 6** Thermoanalytical data of the complexes were prepared

| Complex | 1th Thermal Reaction | | | 2nd Thermal Reaction | | |
|---|---|---|---|---|---|---|
| | Temperature range /°C | Mass Loss/% | | Temperature range /°C | Mass Loss /% | |
| | | Expected | Found | | Expected | Found |
| **I** | 124–135 | 7.46 | 7.55 ± 0.04 | 205–260 | 22.64 | 23.86 ± 1.45* |
| **II** | 220–260 | 23.75 | 24.54 ± 1.09 | 260–400 | * | – |

*After 260 °C, it cannot be measured clearly

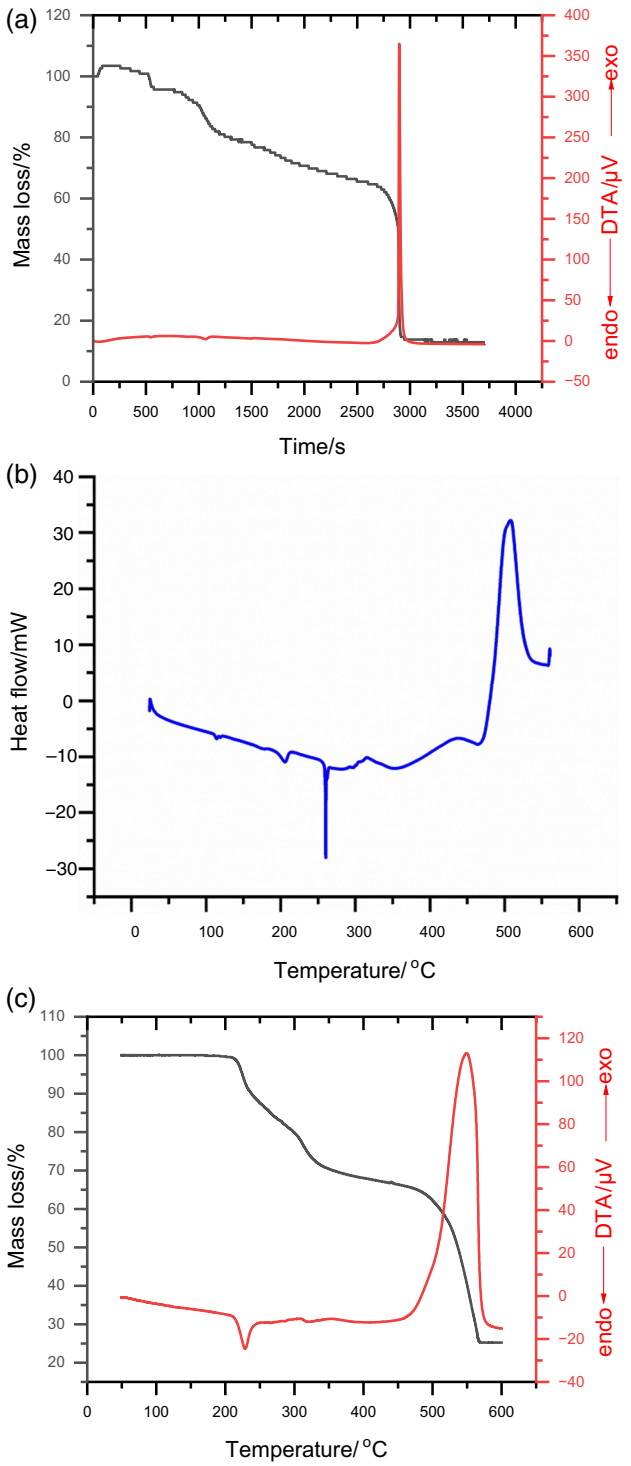



**Fig. 6** **a** Curve of time-mass loss-DTA of complex I in $O_2$ atmosphere. **b** DSC curve of complex I in $O_2$ atmosphere, (1.394 mg sample give 6.52 kJ $g^{-1}$ combustion energy at 504–510°), **c** TG curve of complex II in $O_2$ atmosphere

O1 Ni1 N2, O5 Ni2 N4, and O4 Ni2 N5 were recorded as 174.65(16)°, 172.65(18)°, and 172.56(18)°, respectively. The values obtained are in proximity to 180°, suggesting that the distortion present is minimal. In complex **I,** the monoclinic unit cell contains four asymmetric units with two [NiL$^{H}$Cl(DMF)] molecules and one DMF molecule in each asymmetric unit. The coordination around Ni is a distorted octahedron involving one Cl atom, two O atoms, and two N atoms from salpd$^{2-}$ ligand, and an O atom of the DMF group occupies the apical position. In the coordination sphere, the average Ni – O and Co – N bond lengths in the basal plane are 2.063(4) and 2.095(5) Å, while the average Ni – Cl and Ni – O distances in the apical position are 2.3988(19) and 2.137(4) Å, respectively. The Ni1 and Ni2 atoms in each asymmetric unit are located 0.122 and 0.130 Å from the mean coordination planes consisting of atoms O1/O2/N1/N2 and O4/O5/N4/N5, respectively. The dihedral angle between the mean coordination planes consisting of atoms O1/O2/N1/N2 and O4/O5/N4/N5 of two molecules in the asymmetric unit is 74.00°.

The coordination of the Ni(II) ion in the heterodinuclear complex **II** exhibits similarities. Figure 3a, b illustrates the coordination of the Ni(II) ion within an octahedral geometry characterized by an $O_4N_2$ configuration. This configuration involves two phenolic oxygen atoms from the organic ligand, two aminic nitrogen atoms, and two oxygen atoms from the DMF molecule. Within the complex structure, the oxygen atoms of the organic ligand formed a μ-bridge while simultaneously coordinating with the Co(II) ion. The Co(II) ion is in a tetrahedral coordination sphere between two chloride ions and two oxygen atoms. The angle values around the Co(II) ion presented in Table 2 range from 84.50 to 118.76°, suggesting that the tetrahedral geometry associated with the Co(II) ion maintains a relatively stable conformation without significant distortion. Furthermore, the angles along the axial axes of the octahedron containing the Ni (II) ion in this complex were determined to be N2NiO1 at 171.39(13) ° and O3NiO4 at 172.66(13) °. Similarly, it was concluded that the deformation of the octahedron was minimal. The distinction between this complex and the mononuclear complex **I** is caused by the change that occurs in the phenolic oxygen atoms. In the mononuclear complex, the charges of the Ni(II) ion are neutralized by a chloride and a phenolate, whereas in complex **II**, both phenol groups are converted to phenolates and neutralize Ni(II). The structure includes one octahedron and one tetrahedron, which share one edge. The coordination polyhedron around the $Ni^{2+}$ ion is a distorted octahedron (Fig. 3). Two iminic N and two phenolic O atoms of the salpd$^{2-}$ ligand constitute the basal plane of the octahedron, while the O atoms of the two DMF groups occupy apical positions and complete the sixfold coordination. The average Ni–O and Ni–N distances in the basal plane are 2.095 (3) and 2.092 (4) Å, while the Ni–O3 and Ni –O4 distances in the apical position are 2.083 (3) and 2.129 (3) Å, respectively. The $Ni^{2+}$ ion is located 0.019 Å from the mean coordination plane consisting of atoms O1, O2, N1

and N2. The dihedral angle between the Ni/O1/C1/C6/C7/N2 and Ni/O2/C17/C12/C11/N1 chelate rings is 5.96°, All the chelate rings around Ni, except for one, are planar. The **Ni**/N2/C8/**C9**/C10/N1 ring is in a half-chair conformation, the atom Ni and C9 being located 0.701 Å and 0.726 Å from the mean plane defined by the other four atoms.

The $Co^{2+}$ ion has a distorted tetrahedral coordination. The average Co–Cl and Co–O distances in the basal plane are 2.2693(19) and 1.996(3), respectively. The Cl1–Co–Cl2 and O1–Co – O2 angles are 113,28(6) and 84,50(12), respectively. The Cl1/Co/Cl2 plane and the least-squares plane defined by the Ni coordination atoms O1/O3/N1/N2 of $salpd^{2-}$ ligand are almost perpendicular; the dihedral angle is 88.81°. The bridging plane is not completely planar; the dihedral angle between the planes through atoms O1/Co/O2 and O1/Ni/O2 is 11.15°. The Ni·· ·Co distance [3.070(3) Å] is long for a direct interaction.

A comparison of the dihedral angle (°) between the O–M1–O and O–M2–O bridging planes, where M indicates a metal ion ($Zn^{2+}$, $Ni^{2+}$ or $Cu^{2+}$), along with the related M–O distance ranges, O–M–O angle ranges and M·· ·M distances, are given in Table 5 for the four oxygen-bridged dinuclear complexes reported previously by our laboratory. From this table, the remarkable similarity of the four structures is obvious.

## Thermal analysis

The presence of coordinated and solvate molecules within the complex structure makes TG analysis an effective method for explaining the structural details. The TG curves of the complexes are illustrated in Figs. 4, 5, while the thermoanalytical data derived from these curves are summarized in Table 6.

In Fig. 4, the first group expected to thermally dissociate from complex **I** is the solvate DMF group. At temperatures exceeding 120 °C, DMF exhibited a tendency to separate from the structure, and the expected mass loss (7.55%) was determined with remarkable accuracy. The decomposition of the coordinated DMF molecules in Complex I was observed through two endothermic signals at approximately 160 and 180 °C. The observed total mass loss of 23.86% at approximately 220 °C suggests that three DMF molecules were step-by-step disassociated from the structure of Complex I (Table 6). The endothermic mass loss noted after 260 °C is attributed to the decomposition of the organic groups within the complex. The observed decomposition continues even at temperatures reaching 400 °C (Fig. 4). The results obtained from the TG curves confirm the stoichiometry of the $[NiL^{H}Cl(DMF)]_2(DMF)]$ complex and support the single-crystal XRD findings.

The thermal property of complex **II** exhibits slight variations (Fig. 5). Interestingly, the two DMF molecules did not separate from the structure until 220 °C. However, following this temperature, DMF molecules were noted to have dissociated from the structure through an endothermic reaction, and the expected mass loss (23.75%) and calculated mass loss (24.54%) were found to be remarkably similar. Similar to the mononuclear complex, the decomposition process is initiated after 260 °C in this complex. The thermal reactions possible in TG analysis are formulated below:

$$\left\{\left[NiL^{H}Cl(DMF)\right]_2(DMF)\right\}_{(s)} \xrightarrow[-DMF_{(g)}]{} 2[NiLHCl(DMF)]_{(s)} \quad 1^{th} \text{ thermal reaction}$$

$$\left[NiL^{H}Cl(DMF)\right]_{(s)} \xrightarrow{260-400\,^{\circ}C} \text{Decomposed} \quad 2^{nd} \text{ thermal reaction}$$

$$\left[NiL^{H}CoCl_2(DMF)_2\right]_{(s)} \xrightarrow[-DMF_{(g)}]{} \left[NiL^{H}CoCl_2(DMF)\right]_{(s)} \quad 1^{th} \text{ thermal reaction}$$

$$\left[NiL^{H}CoCl(DMF)\right]_{(s)} \xrightarrow{260-400\ ^{\circ}C} \text{Decomposed} \quad 2^{nd} \text{ thermal reaction}$$

TG analyses were performed in an oxygen atmosphere to determine the residual amounts of the complexes following complete decomposition (Fig. 6). Due to that, complex **I** exhibited a strong exothermic reaction similar to that of energetic materials at 510 °C in an $O_2$ environment. Thermogravimetric analysis (Fig. 6a) was conducted utilizing a minimal quantity (1.6 mg). The energy released in this exothermic reaction was measured using Differential Scanning Calorimetry (DSC) and determined to be 6.52 kJ $g^{-1}$ (Fig. 6b).

Due to the rapid nature of the explosion, it was not possible to acquire any observable temperature mass loss or temperature DTA curves. Consequently, the curves for this material in the $O_2$ atmosphere were represented as time-dependent (Fig. 6a). As illustrated in Fig. 6a, the decomposition of complex **I** started after reaching 260 °C, without any notable mass loss detected until 460 °C. Furthermore, the decomposition of the residue in an atmosphere of $O_2$ occurred within a remarkably limited temperature range at 510 °C, characterized by a highly strong exothermic reaction. This presents rather unconventional circumstances (Fig. 6b). Similarly, the decomposition of complex II began at 260 °C, with no observable mass loss until it reached 450 °C. Following this temperature, the organic component undergoes complete transformation into gaseous products through a strong exothermic reaction, resulting in a residue of approximately 25% after a mass loss of 74.68%.

The calculated residue amount (25%) suggests that the residue may be NiO and CoO (24.26%). These findings confirm the accuracy of the stoichiometric calculations pertaining to the heterodinuclear complex.

## Conclusions

In this study, mononuclear Ni(II) $[NiL^{H}Cl(DMF)]_2(DMF)$ (**I**) and heterodinuclear Ni(II)-Co(II) $[[NiL^{H}CoCl_2(DMF)_2]$ (**II**) complexes were synthesized using a reduced ONNO-type Schiff base ligand ($L^{H}H_2$). In complex **I**, DMF molecules behave as coligands, thereby making the d orbitals of Ni(II) appropriate for octahedral coordination. Thus, in addition to the oxygen and nitrogen donors present in the $L^{H}H_2$ ligand, a DMF molecule and a chloride ion complete the coordination as coligands. Since the chloride ion is negatively charged, one of the phenolic groups participates in the coordination as phenolate. When $CoCl_2$ is added to the medium, the Co(II) ion coordinates with the oxygen atoms of the $L^{H}H_2$ ligand that also coordinates with Ni(II). The reduction of electron density on the phenolic oxygen atoms results in the Ni(II) ion exhibiting a greater affinity for electrons compared to the phenolic O atoms. In this case, the phenol group is converted to a phenolate, and the weak chloride coligand is separated and replaced by a DMF molecule. Thermogravimetric analyses have elucidated both the thermal stability and coordination characteristics of these complexes. Coordinatively bound molecules and solvate molecules move away from the complex at non-high temperatures. In complex **I**, the solvate DMF leaves the structure at 124 °C, while the other DMF molecules leave the structure above 200 °C and give a non-uniform mass loss. Moreover, complex **I** exhibited stability up to 210 °C, while complex **II** showed a higher thermal stability. Complex **I** exhibited a strong exothermic reaction at 510 °C in an $O_2$ atmosphere, similar to that observed in energetic substances. These findings suggest that such complexes have potential for applications in materials science that require controlled energy release.

ONNO-type Schiff base ligands and their reduced derivatives have been among the most interesting research topics in coordination chemistry and materials science for many years. Such ligands have been synthesized to form mono-, oligo-, and multinuclear complexes. Studies on their structural, magnetic, catalytic, and thermal properties have been widely reported in the literature. Future studies should aim to create new multinuclear coordination structures with extended investigations with other transition metals.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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