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Nickel(II) chelates with N-phenethyl-iminodiacetate(2-)-like ligands: Synthesis, crystal structure and spectroscopic studies

Dheerendra Kumar Patel[a,*], Duane Choquesillo-Lazarte[c], Alicia Domínguez-Martín[b], Josefa María González-Pérez[b] & Juan Niclós-Gutiérrez[b]

[a]Department of Chemistry, Govt Sanjay Gandhi Smriti Post Graduate College Ganjbasoda, University of Barkatullah, Bhopal (MP) India

[b]Department of Inorganic Chemistry, Faculty of Pharmacy, University of Granada, E-18071 Granada, Spain

[c]Laboratorio de Estudios Cristalográficos, IACT-CSIC, P.T. Ciencias de la Salud, Granada, Spain

*E-mail: dkprewa@yahoo.co.in

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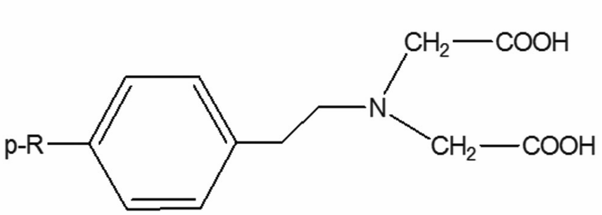
The stoichiometric reactions between Ni(II) hydroxy-carbonates and N-*p*-(R)-H_2pheida derivatives (R = MeO or F for MOpheida or Fpheida, respectively) yield two binary compounds [Ni(MOpheida)(H_2O)$_3$] (**1**) and [Ni(Fpheida)(H_2O)$_3$] (**2**). The crystal of compounds **1** and **2** are iso-type; space group $P2_1/c$. Our crystallographic results revealed that both studied metal-chelates have molecular structure and the used p-R substituents on the pheida skeleton yield the same structural features. The IDA moiety of pheida-like ligands exhibit the *fac*-NO_2 conformation (**1** & **2**). Crystal structure of H_2Fpheida free acid have also been reported herein.

Keywords: Nickel(II), Iminodiacetate derivatives, Metal-chelate, Crystal structure

Iminodiacetate(2-) and N-R substituted-iminodiacetate(2-) (IDA and IDA-like) are important tri-dentate chelating agents which are able to bind the metal from the three coordination sites. The coordination polyhedron of metal centers are fullfilled by aqua ligands and/or a large variety of monodentate or bidentate auxiliary ligands[1-5]. Some recent studies have revealed that the type of non coordinating N-R-IDA substituent strongly influences the molecular recognition pattern between copper(II)-IDA-like chelates and the N-rich base adenine[6-8]. Interestingly, the Cu(II)-(pheida) chelate (where, pheida is N-phenethyliminodiacetate(2-) ion, Ph-CH_2CH_2N $(CH_2CO_2^-)_2$ ion) binds the adenine (Hade) in the bridging mode μ_2-N3,N7-H(N9)ade to give a tetranuclear molecule, as proved by its crystallographic results[1]. The crystal structure of the free ligand H_2pheida is also known as well as a salt with the bis-chelate anion $[Cu(pheida)_2]^{2-}$ and $[Cu(phen)_3]^{2+}$ as counter ion[9]. Moreover, a ternary complex with hypoxanthine nucleo-base as auxiliary ligands also reported recently [Cu(pheida)(Hhyp)(H_2O)]·$2H_2O$ [4]. No other structural data concerning (N-pheida-like)-metal ion complexes are found in the CSD database. The *mer*-NO_2 or *fac*-NO_2 which is a conformation of IDA moiety, have been observed for most of the octahedral metal complexes irrespective of metal center. In contrast, the conformational behavior is versatile for copper(II) complexes where IDA arm adopted *mer*-NO_2 and/or *fac*-NO+O (apical/distal), *fac*-O_2+N(apical/distal)[1]. The molecular structure of the chelating ligand is depicted in Scheme 1.

The aim of this work is to investigate the presence of IDA moiety and the crystal building in Ni(II) chelates with two p-R-substituted pheida-like ligands having methoxy or fluoro as R-group in order to see the effect of p-R- substitutive group on molecular and



Ligand (H$_2$L)	R =	Space group of the complex
H_2Mopheida	CH_3O-	$P2_1/c$
H_2Fpheida	F-	$P2_1/c$

Scheme 1 — Molecular structure of chelating ligand, N-(*p*-R-phenethyl)-iminodiacetic acid crystal pattern. In this context, we are reporting here two molecular binary complexes [Ni(MOpheida)(H_2O)$_3$] (**1**) and [Ni(Fpheida)(H_2O)$_3$] (**2**).

Materials and Methods

The acid form of tridentate chelating ligands (H_2MOpheida and H_2Fpheida), were obtained as previously reported for N-phenethyl-iminodiacetic acid (H_2pheida)[6], but using 4-Methoxy-phenethylamine and 4-Fluoro-phenethylamine instead of N-phenethylamine. These amines were purchased from Aldrich and used without further purification. Nickel(II) basic carbonate [($NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$), Merck, Ni 47%] used as received. In order to accurate the amount required Ni(II) source for each synthesis, elemental micro-analysis and thermogravimetric (TG) analysis of these reagents is encouraged.

Elemental micro-analysis was carried out with a Fisons–Carlo Erba EA 1108 elemental micro-analyzer. Infrared spectra were recorded in the range 4000-400 cm^{-1} with a Jasco FT-IR 410 spectrometer using KBr pellets. Electronic (diffuse reflectance) spectra were recorded in a Varian Cary-5E spectrophotometer. TG analysis (pyrolysis) of the studied compounds (295~800 ºC) were carried out in CO_2-free dry-air flow (100 mL/min.) by a Shimadzu Thermobalance TGA–DTG–50H instrument, until a series of FT-IR spectra of gasses were recorded (to identify the evolved gases) using a coupled FT-IR Nicolet Magma 550 spectrometer.

Synthesis of the chelators

H_2MOpheida and H_2Fpheida free acids were isolated by reaction of potassium chloroacetate (2 mmol) with the appropriate amine (1 mmol) in alkaline aqueous solution (pH ~ 11) at 80-90 ºC, in 2 h. Then reaction mixture was cooled to room temperature (~ 25 ºC) and acidified with HCl, 6N (pH ~ 3-2.5) until desired white product precipitated. New addition of 6N HCl, gave successive fractions of the ligand, was collected by filtration, washed with water and re-crystallized in water by reaction with $NaHCO_3$ (until complete solution appeared) followed by addition of the equivalent amount of 6N HCl, desired acid again obtained. Crystals of H_2MOpheida and H_2Fpheida were grown by re-crystallization in water-ethanol (30:70) mixture. Anal.: Calc. (%) for (H_2MOpheida) $C_{13}H_{17}NO_5$: C, 58.14; H, 6.58; N, 5.57. Found: C, 57.90; H, 5.89; N, 6.02%. FT-IR (frequency, cm^{-1}): 3035, 2990 and 2965 ν(C-H) modes; 2700-2300, 2520 for ν(N^+-H); 3495m (broad), 1710, 1194 and 726, ν(O-H), ν(C=O), δ(O-H) and π(O-H) of free acid –COOH group; 1600 and 1384 for ν_{as} and ν_s of –COO^-; 1181(intense) for ν_{as}(C-O-C). Anal. Calc.(%) for (H_2Fpheida) $C_{12}H_{14}FNO_4$: C, 56.14; H, 5.60; N, 5.57. Found: C, 56.04; H, 5.02; N, 5.09. FT-IR (frequency, cm^{-1}): various peaks (3000-2900) for ν(C-H) modes; peaks at 2670-2350, including one at 2524 for ν(N^+-H); 3500m (broad), 1725, 1200 and 730 for ν(O-H), ν(C=O), δ(O-H) and π(O-H) of –COOH; 1602 and 1382 for ν_{as} and ν_s of –COO^-, respectively.

Synthesis of molecular compounds (1 and 2)

A general procedure to obtain the studied binary molecular Ni(II) compounds can be described as follows: $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (0.34 mmol, 0.13 g) and appropriate N-substituted iminodiacetic acid (H_2L, 1 mmol) stirred well in 120 mL water in a Kitasato flask, by heating (25 min, t ~ 60 ºC) and stirring under reduced pressure in order to remove CO_2, a by-product of reaction. The resulting clear greenish solution was filtered without vacuum (to remove small amount of un-reacted metal carbonates) directly on a crystallisation device. By slow evaporation of clear solution at room temperature, abundance of crystals was found. The product were washed with cool water and air-dried. Yields were variable, but usually over 50%. Anal.: Calc.(%) for compound [Ni(MOpheida)(H_2O)$_3$] (**1**), ($C_{13}H_{21}NNiO_8$) (MW, 378.00): C, 41.31; H, 5.60; N, 3.71; Ni, 15.53. Found (%): C, 41.02; H, 5.40; N, 3.62; Ni, 15.21. Anal.: Calc.(%) for complex [Ni(Fpheida)(H_2O)$_3$] (**2**), ($C_{12}H_{18}FNNiO_7$) (MW, 365.97): C, 39.38; H, 4.96; N, 3.83; Ni, 16.04. Found (%): C, 39.28; H, 4.83; N, 3.53; Ni, 15.93.

X-ray diffraction data collection and refinement

Suitable light green crystals (**1**, **2**) were used for data collection. Data were collected with Bruker X8 Kappa APEXII Bruker SMART CCD 1000 (**2**, 100 K) or Bruker X8 Proteum (**1**, 293 K) diffractometers. The data were processed with SAINT (**2**)[10] or APEXII (**1**)[11] and corrected for absorption using SADABS[12]. The structures were solved by direct methods[13], which revealed the position of all non-hydrogen atoms. These atoms were refined on F^2 by a full- matrix least-squares procedure using anisotropic displacement parameters[14]. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 times than those of the respective atom. Geometric calculations were carried out with PLATON[15] and drawings were produced with PLATON and MERCURY[16]. The calculated parameters are given in Table 1.

Results and Discussion

Structure of H_2Fpheida acid

Crystal structures of H_2Fpheida have been carried out. Tables about amino-diacid may be obtained from corresponding deposited files. The crystal structure of free acid shown in Fig. 1, gives the numbering scheme adopted for the atoms. The compound exists as zwitterions intra-stabilized by one N^+-H···O (carboxylate) H-bonding N(2)-H(2)···O(2) (2.784 Å, 144.7°) interaction. There are no π,π-stacking interactions between adjacent aryl rings observed. In the crystal of H_2Fpheida, two similar but different zwitterions exist in the asymmetric unit. The hydrophilic and hydrophobic arms of Fpheida acid oriented towards internal and external faces. Each of these zwitterions builds H-bonded chains. Additional H-bonds and very weak π,π-stacking interactions between different $H_2Fpheida^{\pm}$ zwitterions build a 3D crystal.

Structure of Ni(II) compounds

Selected bond lengths (Å) and *trans*-angles (°) between L-M-L are given in Table 2. Both compounds have a general formula [M(II)(pheida-like)$(H_2O)_3$]. The compounds crystallize in the monoclinic system, space group $P2_1/c$ thus, they are iso-type crystals. Consequently, structure of both compounds could be discussed at the same time. Structure of compound **1** and **2** are shown in Fig. 2 and 3, respectively. In these complexes, the coordination bond length and angles as well as the internal geometry of the ligands have normal values. The unit cell contains four asymmetric non-hydrated complex molecules. The hydrophobic non-coordinating arm of the p-R-pheida ligands in both complexes (**1** & **2**) oriented towards internal

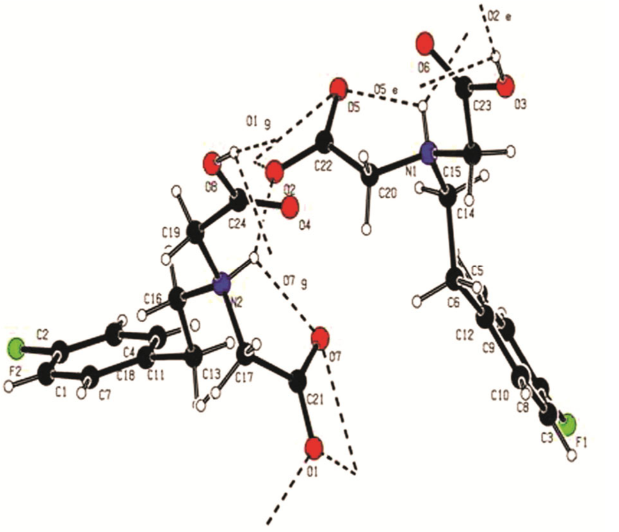


Fig. 1 — Asymmetric unit of H_2Fpheida consist two similar but not equivalent molecules, recognizes to each other by an intermolecular hydrogen bonding interaction type N-H···O (2.805 Å, 153.60°)

Table 1 — Details of crystallographic data and refinement for compounds **1** & **2** and ligand (Fpheida)

Compound	1	2	Ligand
Empirical formula	$C_{13}H_{21}NNiO_8$	$C_{12}H_{18}FNNiO_7$	$C_{12}H_{14}FNO_4$
Formula weight	378.02	365.98	255.24
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	P2(1)2(1)2(1)
Unit cell dimensions (Å/°)			
a (Å)	18.9968(18)	16.869(5)	8.6859(7)
b (Å)	7.6962(7)	7.704(2)	12.1529(9)
c (Å)	11.2889(11)	11.407(3)	22.8553(18)
β (°)	98.010(4)	90.283(5)	90
V (Å^3)	1634.4(3)	1482.4(7)	2412.6(3)
Z	4	4	8
Calculated density (Mg $^{m-3}$)	1.536	1.640	1.405
Absorption coefficient (mm^{-1})	2.092	1.354	0.115
F (000)	792	760	1072
Crystal size (mm)	0.22 x 0.14 x 0.02	0.29 x 0.14 x 0.05	0.10 x 0.39 x 0.41
Θ Range data collected (°)	2.35 to 66.37	1.21 to 25.68	1.78 to 27.99
Reflections collected/unique	2633 [R(int) = 0.0473]	12446/2816 [R(int) = 0.0529]	14601/5563 [R(int) = 0.0379]
Max/min transmission	0.9594 and 0.6561	0.9354 and 0.6949	1.0000 and 0.8035
Data/restraints/parameters	2633 / 0 / 209	2816 / 0 / 199	5563 / 0 / 336
Goodness-of-fit on F^2	1.142	1.116	0.863
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0449, wR2 = 0.1352	R1 = 0.0578, wR2 = 0.1608	R1 = 0.0429, wR2 = 0.0665
R indices (all data)	R1 = 0.0542, wR2 = 0.1505	R1 = 0.0729, wR2 = 0.1769	R1 = 0.0883, wR2 = 0.0755

Table 2 — Coordination bond distance (Å) and *trans*-angles (º) for compounds **1** & **2**

Compound	**1**	**2**
M-N	Ni(1)-N(1) 2.130(2)	Ni(1)-N(1) 2.106(4)
M-O	Ni(1)-O(20) 2.089(2)	Ni(1)-O(1) 2.073(3)
M-O	Ni(1)-O(21) 2.045(2)	Ni(1)-O(2) 2.035(3)
M-O	Ni(1)-O(22) 2.037(2)	Ni(1)-O(3) 2.028(3)
M-O	Ni(1)-O(4) 2.050(2)	Ni(1)-O(11) 2.026(3)
M-O	Ni(1)-O(8) 2.025(2)	Ni(1)-O(21) 2.041(3)
O-M-N	O(20)-Ni(1)-N(1) 170.84(9)	O(1)-Ni(1)-N(1) 171.20(13)
O-M-O	O(21)-Ni(1)-O(4) 175.82(8)	O(11)-Ni(1)-O(3) 176.54(12)
O-M-O	O(8)-Ni(1)-O(22) 176.08(9)	O(2)-Ni(1)-O(21) 172.87(12)

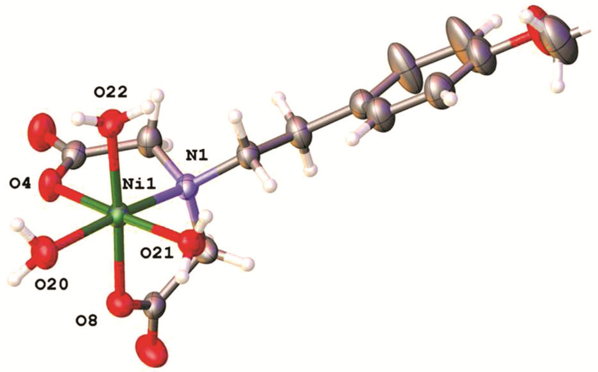


Fig. 2 — Structure of non-hydrated compound [Ni(Mopheida)(H_2O)$_3$] (**1**), with the numbering of coordination atoms

faces of the packing unit. Noteworthy, the Ni-N(1), 2.130(2) and 2.106(4) coordination bond is longest one for compounds **1** & **2**, respectively. It is interesting to note that the *trans*-angles involving (aqua)O-M-N(IDA-like) bond are found lower (ranging from 170.8º to 171.2º) than others (carboxylate)O-M-O(aqua) coordination bond (ranging from 172.9º to 176.5º) in both compounds. In the crystal of **1** and **2** inter-molecular hydrogen bonding interaction of the type (aqua)O-H···O(COO) of chelates (□2.9 Å, 270º) have been observed. The Ni(II)-N and/or Ni(II)-O coordination bond lengths and *trans*-angles are similar to other reported Nickel(II) chelates with IDA-like ligands[1,17]. The pheida-like ligands exhibit a *fac*-NO_2 conformation for the IDA moiety, with both chelate rings sharing the metal-N bond nearly perpendicular. The FTIR, electronic spectra and thermogravimetric plots are given in Supplementary Data, Fig. S1-S5.

Properties of Ni(II) compounds

The studied compounds have been characterized by elemental analysis, FT-IR and UV-visible as well as thermal stability. A summary of some physical properties of the studied Ni(II) compounds is shown in Table 3. The iso-type crystals (**1** & **2**) exhibit very similar FT-IR spectra. Noticeably, the spectrum of compound **1** shows the ν_{as}(C-O-C) band at 1184±1 cm^{-1} which is not observed for compound **2**. It may also interesting to see that in the spectrum of compound **2,** a sharp peak is observed at 1222 cm^{-1}, which correspond to fluoro group[18]. The electronic spectra of Ni(II) complexes are typical octahedral and the Ni(II)-chelate spectra show the transition $^3A_{2g} \rightarrow {}^3T_{2g}$ occurs at Δ_o ~9240 or ~9490 cm^{-1}, that is at higher Δ_o values than that of hexaaqua cation (~8500 cm^{-1}) as should be expected for their $NiNO_5$

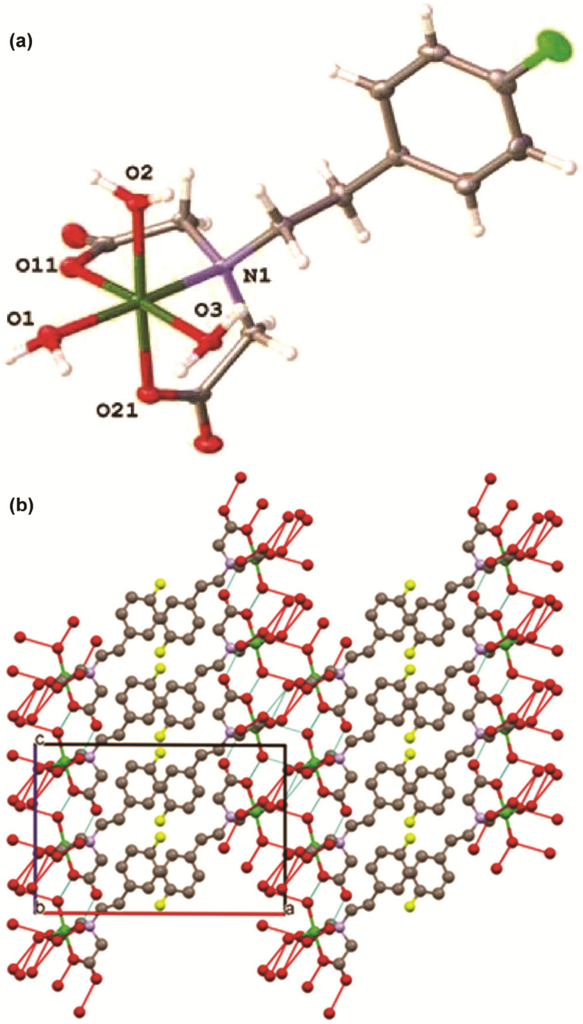


Fig. 3 — (a) Structure of non-hydrated compound [Ni (Fpheida)(H_2O)$_3$] (**2**), with the numbering of coordination atoms and (b) H-bonded layer parallel to *ac* plane, with the F-phenethyl arms of the F-pheida ligand towards its internal faces (**2**). A detail of intermolecular H-bonding (greenish colour) of the type O(COO)···H (H_2O) and other weak interactions (radish colour)

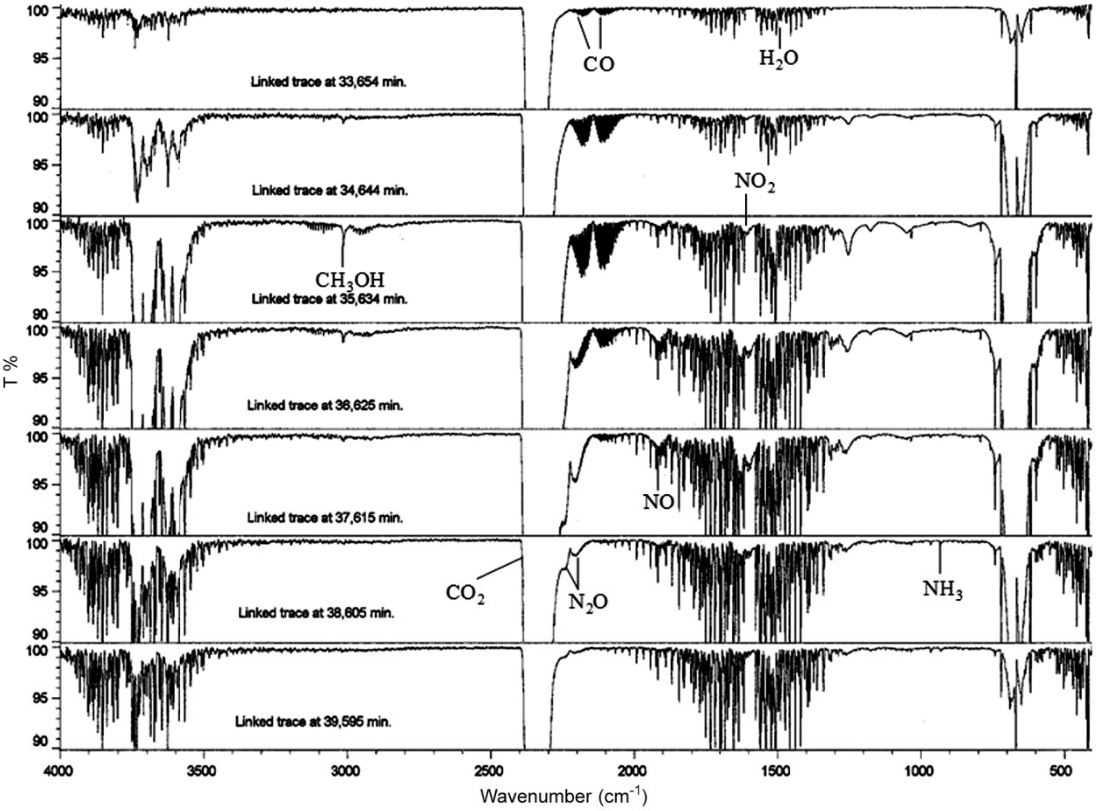


Fig. 4 — Selected FT-IR spectra for identification of evolved gasses in the different steps of decomposition and pyrolysis of compound [Ni(MOpheida)(H_2O)$_3$] (**1**)

Table 3 — Summary of the IR spectra, TG and electronic spectra results for the complexes **1** & **2**

Compound	**1**	**2**
IR peaks (cm^{-1})		
H_2O		
ν_{as}	3385	3399
νs	3224	3190
δ	1611	1616
COO		
ν_{as}	1582	1579
νs	1411	1410
π (C-H)	739	741
C-O-C	1184	-
F	-	1222
Thermal stability		
Steps	3	4
Δt (°C)	90-460	90-530
1st step loss	H_2O	H_2O,CO_2(t)
2nd step loss	H_2O,CO_2(t)	H_2O,CO_2
3rd step	* + CH_4, CH_3OH, CH_3CHO	* + CH_4, NH_3
Residue	NiO	NiO
Electronic spectra		
ν_{max} (cm^{-1})	9240	9490

* = H_2O, CO_2, CO, N_2O, NO, NO_2

chromophores. Indeed the crystal field splitting value in octahedral environment yield the increasing order of Δ_o [Ni(H_2O)$_6$]$^{2+}$ (8500 cm^{-1}) < [Ni(IDA-Like)(H_2O)$_6$] (9240 cm^{-1}) < [Ni(NH_3)$_6$]$^{2+}$ (10750 cm^{-1}). Therefore, the ligands reported herein should be placed in between H_2O and NH_3 in the nephelauxetic series[19]. The thermobalance were coupled to FT-IR spectrophotometer in order to identify a series of 20-25 FT-IR spectra of the evolved gases. Compounds **1** & **2**, show one or two overlapped steps for aqua ligand loss (at 90-220 ºC). These aqua ligands are lost alone or with trace amount of CO_2. The pyrolytic steps of the organic ligands produce a variety of gasses. In addition of CO_2, CO, H_2O and sometimes CH_4, N_2O or very trace amount of NO and NO_2 also evolved correspond to oxidative degradation of coordinating arms of the pheida ligand. Noteworthy, the production of methanol is only observed for complex **1** which can be attributed to the CH_3O- a *para*-substitutive group on MOpheida ligand (Fig. 4). Interestingly, in the spectrum of compound **1** the production of trace amount of CH_3CHO is also observed[1]. At the end Ni(II) compounds give residue of NiO at 390-530 ºC with calculated and experimental values in agreement within approximately 1%.

Conclusions

In conclusion, both studied compounds have molecular structure with octahedral metal(II) ion coordination geometry and the IDA moiety of pheida-like ligands exhibit the *fac*-NO_2 conformation. In the iso-type compounds (**1** & **2**) the R group (MeO or F) of p-R-pheida ligands are not involved in relevant inter-ligand interactions. It is worth noting that two *cis*-aqua ligands *trans* two the carboxylate arm of IDA-Like ligands in the Ni(II) complexes give the possibility for further studies of mixed-ligand metal complexes with a variety of mono- and bi-dentate ligands.

Supplementary Data

Crystallographic data for the crystal structures reported in this paper have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication Number CCDC-750077 (**1**), 750078 (**2**). Copies of the data can be obtained free of charge on application to CCDC. Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(06)806-811_SupplData.pdf.

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