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Synthesis and characterization of new addition compounds of bis(2-hydroxyaryloximato) nickel(II) with α-diimines

Crystal and molecular structure of $[Ni(saox)_2phen]\cdot H_2O$

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Abstract

A series of new addition compounds of bis(2-hydroxyaryloximato) nickel(II), $[Ni(ox)_2]$, with an α-diimine (enR), under the general formula $[Ni(ox)_2enR]$, were synthesized and characterized. The IR and electronic excitation spectra indicate that the bidentate coordination mode of the ligands consists with the chromophore NiN_4O_2. The octahedral environment around nickel(II) was confirmed by an X-ray structure analysis of [1,10-phenanthroline-bis(2-hydroxy-benzaldoximato)nickel(II)], $[Ni(saox)_2phen]\cdot H_2O$. The equatorial plane, which encompasses the nickel atom, is formed by four nitrogen atoms, two coming from the phenanthroline molecule and two from the two molecules of the 2-hydroxybenzaldoxime (salicylaldoxime). In the apical positions lie the two deprotonated phenolic oxygen atoms of the two salicylaldoxime ligands. The thermal stability and decomposition mode were studied in nitrogen using the technique of thermogravimetry (TG/DTG). Mass spectrometry was also used, and possible fragmentation patterns are given and discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Nickel(II) complexes; 2-Hydroxyaryloximes; α-Diimines; Crystal structure; Spectroscopy; Thermal behaviour

1. Introduction

The analytical and biological importance of 2-hydroxyoximes and their chelates with some ions of 3d transition metals are well known [1–4], as well as the chelates with bidentate heterocyclic nitrogenous bases such as α-diimines [5]. Research interest for the latter compounds is enhanced in the case of the ligands 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) after the discovery of their photoredox and catalytic properties [6,7]. Because of the less-flexible nature of α-diimines, the steric effects are usually severe, resulting in different coordination numbers and unusual geometries for the metal ions. These effects usually affect the spectroscopic and other significant properties of the coordination compounds.

Spectroscopic and structural studies of nickel(II) chelates revealed the tendency of this metal ion to achieve coordination numbers exceeding four when forming bonds with nitrogen or oxygen donor atoms. While this tendency is strong in the case of the ligands bipy and phen, leading to the formation of cationic octahedral complexes [8–10], with the 2-hydroxyaryloxime (ox) ligands, nickel(II) forms neutral complexes, $[Ni(ox)_2]$, of square–planar geometry [3,11–13].

The Lewis acidity of the $[Ni(ox)_2]$ chelates renders them susceptible to nucleophilic attack and addition compounds can be obtained. While unidentate ligands, such as pyridine, may impose tetragonal distortion by occupying *trans* positions $[Ni(ox)_2(py)_2]$ [14], structural requirements of bidentate Lewis bases, such as α-diimines, dictate occupancy of *cis* positions. It has not been reported, however, in the literature any nickel(II) compound with mixed-ligands α-diimine and 2-hydroxyaryloxime, although there are mentioned complexes of nickel(II) and zinc(II) with phenanthroline and 1-(2-pyridylazo)-2-naphthol=(PAN), a compound that coordinates similarly with salicylaldoxime, under the formula [M(phen)(PAN)] [15]. Recently, mixed-ligand complexes of nickel, cobalt and copper with bipyridine or phenanthroline and the amino

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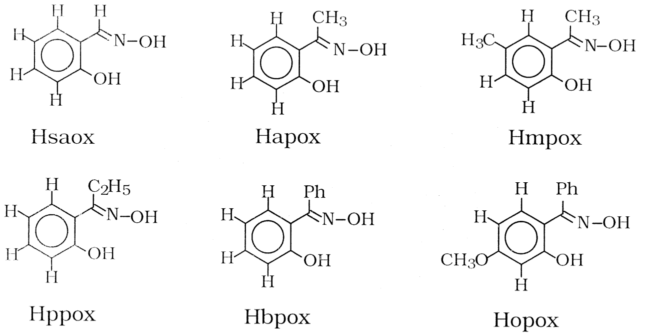
Hsaox Hapox Hmpox Hppox Hbpox Hopox

Fig. 1. Structural formulas of the 2-hydroxyaryloximes.

acid L-phenylalanine (donor atoms O, N), as well as the X-ray study of the complex [Cu(phen)(H_2O)(amino acid)]ClO_4 [16] have been reported. It is also worthwhile to mention the formation and structural characterization of a copper(II) addition compound with bipyridine and a tridentate Schiff base, derived from the condensation of 2-hydroxypropiophenone-salicylhydrazide (donor atoms N, O and O′), [Cu(bipy)(Schiff base)] [17].

For a better understanding of the bonds and structure of mixed-ligand compounds with 2-hydroxyoximes and α-diimines, we here report the synthesis of a series of new nickel(II) addition compounds with α-diimines (enR), such as bipyridine or phenanthroline and 2-hydroxyaryloximes (ox), such as 2-hydroxybenzaldoxime (salicylaldoxime, Hsaox) and its derivatives (Fig. 1). The resultant octahedral nickel(II) compounds [Ni$(ox)_2$enR], were characterized by physico–chemical methods and spectroscopic (IR, electronic, MS) studies. Their structures were verified by X-ray diffraction analysis of a representative complex, the hydrated compound [phenanthroline-bis(2-hydroxybenzaldoximato) nickel(II)], [Ni$(saox)_2$phen]·H_2O, while their thermal stability was investigated in nitrogen atmosphere by thermogravimetric studies. The compounds prepared, their elemental analyses and some physico–chemical data are listed in Table 1.

2. Experimental

2.1. Synthesis and physical methods

The synthesis of 2-hydroxyaryloximes (ox) was achieved employing literature methods [18,19]. Fig. 1 illustrates the oximes used in this work, which are: 2-hydroxybenzaldoxime or salicylaldoxime (Hsaox); 2-hydroxyphenyl, 1-ethanoneoxime or 2-hydroxyacetophenoneoxime (Hapox); 2-hydroxyphenyl, 1-propanoneoxime or 2-hydroxypropiophenoneoxime (Hppox); 2-hydroxy-5-methyl-phenyl, 1-ethanoneoxime or 2-hydroxyacetophenoneoxime (Hmpox); 2-hydroxyphenyl, 1-benzophenoneoxime or 2-hydroxybenzophenoneoxime (Hbpox); and 2-hydroxyphenyl-4-methoxy, 1-benzophenoneoxime or 2-hydroxy-4-methoxy-benzophenoneoxime (Hopox).

The α-diimines (enR), 2,2′-bipyridine (bipy) and 1,10-

Table 1
Elemental analyses and physico–chemical data of the addition compounds [Ni$(ox)_2$enR]

α/α	Compound	Colour	Yield	M.P. (°C)[a]	C%	H%	N%	μ_{eff} (μ_B)
1	[Ni$(saox)_2$bipy]·H_2O	Yellowish	62	227–229	56.58 (57.03)[b]	4.52 (4.39)	10.81 (11.13)	3.08
2	[Ni$(saox)_2$phen]·H_2O	Brownish–yellow	67	222–224	58.72 (58.98)	4.25 (4.18)	10.25 (10.62)	3.14
3	[Ni$(apox)_2$bipy]	Brownish–yellow	65	>300	58.24 (58.54)	5.03 (4.91)	10.24 (10.54)	3.06
4	[Ni$(apox)_2$phen]	Brownish–yellow	61	254–256	62.10 (62.32)	4.19 (4.48)	10.29 (10.42)	3.11
5	[Ni$(ppox)_2$bipy]·H_2O	Yellowish	75	197–199	60.26 (60.11)	4.77 (5.04)	9.68 (10.06)	3.04
6	[Ni$(ppox)_2$phen]·H_2O	Brownish–yellow	65	227–229	61.45 (61.75)	4.67 (4.84)	9.41 (9.64)	3.08
7	[Ni$(mpox)_2$bipy]	Yellowish	64	194–196	61.82 (62.07)	4.69 (4.84)	10.13 (10.38)	3.01
8	[Ni$(mpox)_2$phen]	Yellowish	61	187–189	61.53 (61.75)	4.28 (4.84)	9.34 (9.64)	3.03
9	[Ni$(bpox)_2$bipy]	Yellowish	69	231–233	67.24 (67.57)	4.19 (4.41)	8.96 (9.22)	3.19
10	[Ni$(bpox)_2$phen]	Brownish–yellow	58	214–216	68.42 (68.75)	4.11 (4.25)	8.24 (8.47)	3.07
11	[Ni$(opox)_2$bipy]·H_2O	Yellowish	63	202–204	63.38 (63.60)	4.45 (4.77)	7.53 (7.84)	3.02
12	[Ni$(opox)_2$phen]·H_2O	Brownish–yellow	60	234–236	64.41 (64.78)	4.32 (4.62)	7.21 (7.58)	3.06

[a] Decomposition.
[b] Calculated values in parentheses.

phenanthroline (phen) were purchased from Aldrich, while hexahydrated $NiCl_2$ was procured from Fluka in extra pure grade. Solvents for preparation and physical measurements of ‘extra pure’ or ‘spectro grade’, were obtained from Merck and used without further purification.

2.2. Synthesis of the addition compounds [Ni(ox)$_2$enR]

A solution of 4 mmol of 2-hydroxyaryloxime and 2 mmol of α-diimine in 25 ml of warm EtOH, which became slightly basic with 1 ml aqueous 15% NaOH, was added dropwise to a solution of 2 mmol of $NiCl_2 \cdot 6H_2O$ (0.476 g) in 15 ml of water. The solution turned darker after 5 h continuous stirring and a yellowish solid formed. The precipitate was washed with ethanol and ether and dried in vacuo. The newly prepared Ni(II) addition compounds are crystalline powders, stable in air and insoluble in almost all organic solvents.

2.3. Physical measurements

Stoichiometric analyses (C, H, N) were performed on a Perkin-Elmer 240B elemental analyzer. Molar conductivities were measured in DMF solutions employing a WTW conductivity bridge and a calibrated dip type cell. Magnetic susceptibility measurements on powdered samples were performed at 25°C employing the Faraday method on a home-built balance calibrated against $Hg[Co(SCN)_4]$. Diamagnetic corrections were estimated from Pascal’s constants. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer with a range 4000–200 cm^{-1} calibrated against polystyrene. Electronic spectra in DMSO solution were measured on a Shimatzu 160A spectrophotometer using 10-mm Teflon stoppered quartz cells. The solid-state electronic spectra were obtained from Nujol mulls. Mass spectra were run at 70 eV on an RMU-6L Hitachi Perkin-Elmer double-focusing mass spectrometer, using probe insertion for the samples.

The thermogravimetric curves TG/DTG were recorded on a Perkin-Elmer model TGA 7 thermal analyzer. Samples of ~1.5 mg were heated in platinum crucibles, in nitrogen atmosphere, within the temperature range 40–980°C. The heating rate was 10°C min^{-1}. X-ray powder diffraction analyses of the final residues were made with a Phillips PW 1130/00 X-ray diffractometer, using Cu Kα radiation.

2.4. X-ray crystallography

The X-ray data were measured on an Enraf-Nonius CAD4 automatic X-ray diffractometer employing graphite-filtered Mo Kα radiation (λ=0.71070 Å). Unit cell parameters and orientation matrix of the crystal [Ni(saox)$_2$phen]·H_2O were obtained from the setting angles of 25 reflections ($12=\theta=15°$) and refined by least-squares. Crystallographic data and other pertinent information are given in Table 2. All data were corrected for Lorentz and polarization effects.

The nickel position was detected by direct methods using the SHELXS-86 program [20], while subsequent calculations were performed employing the CRYSTALS program [21]. All non-hydrogen atoms were refined anisotropically. In the final stages of the refinement, the DIFABS method [22] was used for an absorption correction, the reflections were reweighted and an overall isotropic extinction parameter introduced. Final refinement was continued until the sum of the shift/esd (estimated standard deviation) ratio was less than 0.01. All hydrogen atoms were found but only the positions of them belonging to the methyleno and the hydroxyl groups of the oxime were refined. The rest of the atomic hydrogens were positioned geometrically, their positions recalculated after each refinement cycle. The figures of the clinographic projections were produced with the CAMERON program [23].

3. Results and discussion

The reaction of Ni^{2+} with an α-diimine (enR) and the anions of 2-hydroxyaryloxime (ox) leads, under proper conditions, to the formation of yellowish crystalline products. Their elemental analyses and the absence of electrical conductivity in DMF solutions indicate neutral compounds, with general formula [Ni(ox)$_2$enR], while their magnetic moments (μ_{eff}=~3.1 μ_B; Table 1) corroborate with octahedral coordination [24,25].

The successful isolation of these compounds depends on the concentration of the two ligands, the stereoelectronic factors of the α-diimines and the oximes, the formation of hydrogen bonds and on the pH in which the oxime can be deprotonated (usually a slightly basic environment). However, it appears that the stereochemistry of the α-diimines outweigh the importance of concentration and constitutes the determining factor for the composition of the newly prepared addition compounds, [Ni(ox)$_2$enR]. For instance, replacement of the oxime Hsaox with the bulkier Hopox does not alter the preparation process significantly. On the contrary, after the replacement of the α-diimine phen with 2,9-dimethyl-1,10-phenanthroline (neocuproin, ncup) or with 2,2′-dipyridylamine (dpamH) the isolation of the corresponding addition compounds [Ni(ox)$_2$ncup] and [Ni(ox)$_2$dpamH] is not possible.

The coordination mode of the ligands in the addition compounds was studied using spectroscopic methods. The X-ray diffraction study of [Ni(saox)$_2$phen]·H_2O provided evidence regarding the geometry around the Ni(II) ion, the configuration of the ligands and the existence of strong hydrogen bonds formed between the 2-hydroxyoxime ligands of the addition compounds.

Table 2
Crystal data and experimental details for the structural study of $[Ni(saox)_2phen]\cdot H_2O$

Formula	$[C_{26}H_{20}N_4O_4Ni]\cdot H_2O$
Molecular mass, M_r	529.19
Crystal parameters	
Crystal shape	Yellowish prisms
Crystal size (mm)	0.42×0.53×0.47
Crystal system	Monoclinic
Space group	$C2/c$
Reflections for cell measurement (°)	25 with $12 \leq \theta \leq 15$
Unit-cell dimensions	
a (Å)	7.880(1)
b (Å)	26.755(2)
c (Å)	11.172(1)
α (°)	90
β (°)	97.96(1)
γ (°)	90
V_c (Å^3)	2332.8(4)
Molecules per cell	4
D_x (Mg m^{-3})	1.829 (calculated)
Measurement of intensity data	
Instrument	CAD4-F
Radiation, wavelength	Mo Kα, $\lambda = 0.71069$ Å
Monochromator	Graphite
Scan mode	$\omega/2\theta$
Scan speed (° min^{-1})	2.5 (min.); 20.1 (max.)
ω range (°)	2.3–26.3
Reflections measured	2540
Independent reflections	2367
Reflections observed	1744 reflected $[I \geq 2\sigma(I)]$
Parameters refined	174
Indices limits	$-9 \leq h \leq 9$, $0 \leq k \leq 33$, $0 \leq l \leq 13$
$F(000)$	968
Refinement	
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.0370
$w = 1/\sigma(F_o)$	
$R_w = [\Sigma\, w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\, w(\lvert F_o\rvert^2]^{1/2}$	0.0412
Refinement method	Full-matrix least-squares on F^2

3.1. Description of the structure of $[Ni(saox)_2phen]\cdot H_2O$

The unit cell comprises four nickel atoms, each in an octahedral environment created by one phenanthroline molecule and two anions of the 2-hydroxybenzaldoxime ligand. The position parameters of $[Ni(saox)_2phen]\cdot H_2O$ reveal two separate entities: The addition compound $[Ni(saox)_2phen]$, and the water molecule that does not interact with the central metal ion.

Each molecule of $[Ni(saox)_2phen]$ is generated by symmetry from the asymmetric unit when rotated around the C_2 axis of the compound passing through the nickel atom and overlying the phenanthroline C_2 axis.

In each molecule of $[Ni(saox)_2phen]$, the nickel atom is surrounded by the six donor atoms from the ligands. The arrangement of the atoms in the ensuing NiN_4O_2 chromophore describes a distorted octahedral structure. The equatorial plane, which encompasses the nickel atom, is formed by four nitrogen atoms, two coming from the phenanthroline molecule N(2), N(2a) at a distance of 2.093(2) Å and two from the two molecules of 2-hydroxybenzaldoxime (salicylaldoxime) N(1), N(1a) at a distance of 2.045(2) Å. The four nitrogen atoms that define the equatorial plane {N(1), N(1a), N(2), N(2a)} and expressed by the equation $\{7.064x - 6.290z = -1.572\}$ present a slight deviation from it, smaller than the error for N(2) and N(2a), equal to 0.05(7) Å, while the nickel atom lies exactly on it. The two deprotonated phenolic oxygen atoms of the two salicylaldoxime ligands O(1) and O(1a) lie in the apical positions at a distance of 2.061(2) Å, while the O(1)–Ni–O(1a) angle is 171.2(1)°. The molecular structure of the compound $[Ni(saox)_2phen]\cdot H_2O$ is depicted in Fig. 2, and the interatomic distances and bond angles are given in Table 3.

The phenanthroline ligand is planar and its plane, which encompasses the nickel atom, is nearly parallel to the

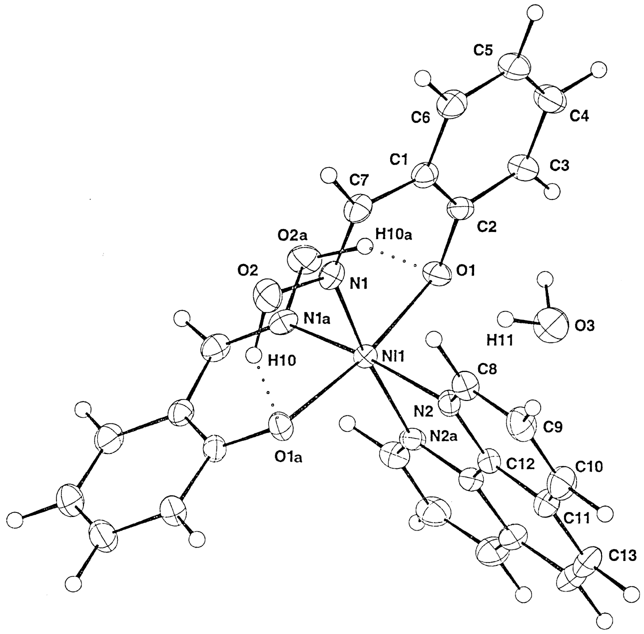

Fig. 2. CAMERON diagram and atom labelling scheme of [Ni(saox)$_2$phen]·H$_2$O.

equatorial coordination plane forming a dihedral angle of 3.4(8)°. In the rigid nickel–diimine entity, the intraligand distance N(2)–N(2a) of 2.686(4) Å and the bite angle of 79.8(1)° are similar to reported values of chelated polycyclic diimines [10]. The Ni–N(phen) bond lengths are equidistant (2.093 Å, due to symmetry reasons) and similar to the values reported for other α-diimine complexes in comparable structures [26–28].

The oximic coordination bond lengths of the octahedral compound under investigation (Ni–N(1) and Ni–O(1)= 2.045 and 2.061 Å, respectively), are appreciably longer than those reported for the corresponding square–planar complexes [Ni(ox)$_2$] [3,11–13]. Each of the two saox$^-$ ligands is bonded through the oxime nitrogen atom and the deprotonated phenolic oxygen forming a six-membered chelate ring with the metal ion. The phenyl ring of the oxime ligand and the coordinated oxygen atom are nearly coplanar with slight deviations from planarity, while the N(2) and O(2) atoms lie above and below the plane, respectively, with deviations of 0.06(8) and 0.08(8) Å. The formed mean plane {equation $-2.880x+21.041y-4.944z=6.272$} shows an almost perpendicular arrangement to both the phenanthroline plane and the coordination plane, forming with each of them dihedral angles of 86.0(7) and 96.1(7)°, respectively.

Table 3
Selected interatomic distances (Å) and bond angles (°) of [Ni(saox)$_2$phen]·H$_2$O

Ni(1)–O(1)	2.061(2)	O(1)–Ni(1)–O(1a)	171.2(1)
Ni(1)–N(1)	2.045(2)	O(1)–Ni(1)–N(1)	86.96(8)
Ni(1)–N(2)	2.093(2)	O(1a)–Ni(1)–N(1)	86.94(9)
O(1)–C(2)	1.329(3)	N(1)–Ni(1)–N(1a)	91.6(1)
O(2)–N(1)	1.397(3)	O(1)–Ni(1)–N(2)	90.85(8)
N(1)–C(7)	1.272(4)	O(1a)–Ni(1)–N(2)	95.88(8)
C(1)–C(7)	1.458(4)	N(1)–Ni(1)–N(2)	173.52(9)
		N(1a)–Ni(1)–N(2)	94.33(8)
		N(2)–Ni(1)–N(2a)	79.8(1)
		Ni(1)–O(1)–C(2)	127.7(2)
		Ni(1)–N(1)–O(2)	115.3(2)
		Ni(1)–N(1)–C(7)	130.7(2)
		O(2)–N(1)–C(7)	113.9(2)
		Ni(1)–N(2)–C(8)	129.0(2)
		Ni(1)–N(2)–C(12)	112.6(2)
		C(2)–C(1)–C(7)	124.1(3)
		C(6)–C(1)–C(7)	116.0(3)
		O(1)–C(2)–C(1)	124.1(3)
		O(1)–C(2)–C(3)	119.3(2)
		N(1)–C(7)–C(1)	123.9(2)

It is worth mentioning that rather strong intramolecular hydrogen bonds are observed between the phenolic oxygen, O(1), of one saox$^-$ ligand and the oximic hydrogen H(10a) of the second saox$^-$ ligand {O(1)–O(2a)=2.656(6) Å, O(1)–H(10a)...O(2a)=1.75(2) Å, O(1)–H(10a)–O(2a)=116(1)°}. The existence of these hydrogen bonds has a profound effect on the values observed for the oximic hydroxyl group in the vibrational spectrum, as can be seen later. Besides, the distances H(11)–O(1)=1.98(2) Å and O(1)–O(3)=3.02(3) Å, where H(11) and O(3) are atoms belonging to the water molecule, suggest a weak intermolecular hydrogen bonding interaction [29].

3.2. Infrared spectra

A plethora of discrete bands appears in the IR spectra of the new addition compounds. The bands may be classified as those originating from the 2-hydroxyoxime, those emanating from the α-diimine, those emanating from crystal water and those due to the bonds formed between nickel(II) and ligating atoms. A list of the most relevant infrared frequencies of the nickel(II) compounds is given in Table 4. The origin of the bands may be deduced by comparison with the spectra of the [Ni(ox)$_2$] and Ni(enR)X$_2$ or [Ni(enR)$_3$]$^{2+}$ compounds of known structure.

The anionic character of the 2-hydroxyoxime ligands and their bidentate coordination mode through the nitrogen atom and the phenolic oxygen are inferred from the positions and the shifts observed in the IR bands of the studied addition compounds, compared to the bands of the free ligands and the bis(2-hydroxyoxime) complexes as described elsewhere [3,30–33].

The band observed in some of the new nickel(II) compounds at ~3440 cm^{-1} is indicative of the vibration ν(OH), which is due to the non-coordinated water molecule. Bands typical of α-diimines are abound in the IR spectra of the [Ni(ox)$_2$enR] compounds. Some bands in the 1600–1400 cm^{-1} region, emanating from the pyridyl ring, a constituent omnipresent in the enR ligands, were masked

Table 4
Vibrational frequencies (ν/cm^{-1}) for selected absorption bands in the IR spectra and band maxima in the electronic excitation spectra (/μm^{-1}) of the [Ni(ox)$_2$enR] compounds[a]

α/α	Compound	ν(=N–OH)	ν(C–O)	ν(N–O)	ν(=C–H) (pyridine)	ν(Ni–N)	Band I^N ν_1	Band II^N ν_2	ν_2/ν_1	*B*
1	[Ni(saox)$_2$bipy]·H_2O	2987m	1333s	993, 907	762s, 720s	583m	1.060	1.740	1.64	1025
2	[Ni(saox)$_2$phen]·H_2O	2924m	1334s	996, 908	846s, 763s	584m	1.090	1.830	1.68	1300
3	[Ni(apox)$_2$bipy]	2770m	1330s	1010, 945	762s, 734s	588m	1.080	1.790	1.66	1137
4	[Ni(apox)$_2$phen]	2769m	1325s	1003, 937	853s, 762s	558m	1.110	1.810	1.63	1017
5	[Ni(ppox)$_2$bipy]·H_2O	2870m	1319s	985, 928	759s, 735s	556m	1.060	1.750	1.66	1007
6	[Ni(ppox)$_2$phen]·H_2O	2875m	1319s	983, 928	846s, 754s	557m	1.090	1.800	1.65	1110
7	[Ni(mpox)$_2$bipy]	2857m	1320s	1022, 956	770s, 736s	590m	1.090	1.780	1.63	1010
8	[Ni(mpox)$_2$phen]	2859m	1325s	1030, 960	849s, 727s	592m	1.090	1.750	1.60	887
9	[Ni(bpox)$_2$bipy]	2848m	1319s	1013, 939	768s, 752s	588m	1.090	1.830	1.68	1300
10	[Ni(bpox)$_2$phen]	2858m	1313s	1011, 938	841s, 754s	586m	1.090	1.790	1.65	1058
11	[Ni(opox)$_2$bipy]·H_2O	2837m	1321s	1009, 960	771s, 728s	589m	1.080	1.790	1.66	1137
12	[Ni(opox)$_2$phen]·H_2O	2834m	1340s	1013, 964	844s, 726s	590m	1.070	1.720	1.61	883

[a] s = strong, m = medium, N = Nujol.

by the more intense absorptions originating from the 2-hydroxyoxime ligands, while others were employed to reaffirm the presence of the α-diimines in the compounds under consideration. Actually, the intense band at 750±20 cm^{-1}, ascribed to the rocking vibrations of the pyridyl C–H bonds, and the band at 870±15 cm^{-1}, attributable to the deformation vibrations of the pyridyl C–H bonds disclosed the occurrence of nitrogenous bases in the prepared addition compounds.

3.3. Electronic excitation spectra

The electronic excitation spectra of the addition compounds were studied in the visible and the near-infrared region, in the solid state (nujol mulls) and in solution (DMSO). All the spectra in the solid state are of the same general form and consist of three principal bands. Band I is observed at about 1.020 μm^{-1} and band II at 1.640 μm^{-1} (Table 4), while band III at ~2.65 μm^{-1} suggests an octahedral arrangement of the ligands around Ni(II) [34]. Accordingly, these bands could be assigned to the spin-allowed excitations from $^3A_{2g}(F)$ ground state to the electronic levels $^3T_{2g}(F)$ (ν_1), $^3T_{1g}(F)$ (ν_2) and $^3T_{2g}(P)$ (ν_3). In most cases, however, the highest energy band is only poorly resolved because of overlap by the most intense charge transfer bands. Credence to this arose from the comparison of the spectra of [Ni(ox)$_2$] complexes, where two CT bands are observed at ~2.60 and ~2.70 μm^{-1} [3,12]. Besides, the weak absorption observed as a shoulder, band IV, at 1.28 μm^{-1} could be assigned to the spin-forbidden transition $^3A_{2g}(F) \rightarrow {}^1E_g(F)$.

The ligand field parameter 10 Dq was taken to be equal to the energy of the first spin-allowed transition (10 Dq = $\tilde{\nu}_1$). The Racah parameter *B* was calculated by inserting the ν_1 and ν_2 values in simplified forms of the equation for the d^8 systems. The calculated values *B* (883–1137 cm^{-1}, Table 5) were found to be quite close to the free-ion value (B_o = 1084 cm^{-1}), the exceptions being those found for the compounds [Ni(saox)$_2$phen]H_2O and [Ni(bpox)$_2$bipy] (*B* = 1300 cm^{-1}). The ν_2/ν_1 ratio for a d^8 ion in a regular octahedron is 1.8. The smaller values (1.54–1.68) observed for the compounds under consideration and the *B* values mentioned above, are indications of slight distortions of the octahedral symmetry.

In the electronic spectra of the studied compounds in solution, band II is shifted (~0.2 μm^{-1}) towards lower energy, while band I looses its intensity and becomes broader, rendering in this way uncertain its position. Based on these, we could suggest the existence of an equilibrium between octahedral and square–planar geometry in solution, resulting in some rearrangements of the ligands around Ni(II).

3.4. Mass spectra

In the mass spectra of the nickel addition compounds under investigation, the molecular ions are not detected, probably due to their high thermal instability in the ionization beam. The most prominent mass spectral peaks are given in tabular form in Table 5, while a representative spectrum for the compound [Ni(saox)$_2$phen]·H_2O is given in Fig. 3.

In the higher mass-number region, the detected ions correspond to the fragments Ni(ox)$_2^{\urcorner +}$, taking also into account the relative intensities, including the abundance ratio of nickel (^{58}Ni:^{60}Ni = 2.59:1.00). These might be regarded as direct fragments of the molecular ion, [Ni(ox)$_2$enR]$^{\urcorner +}$, resulting from the elimination of the α-diimine molecule. Evidence for this also arises from the existence of the free base, as can be deduced from the peaks at *m*/*e* 180 and 156, which correspond to the phenanthroline and dipyridyl molecule, respectively, and compose the base peak of the mass spectra.

In the low mass-number region, the intense peaks are those corresponding to the released oxime and its daughter

Table 5
The most relevant mass spectral peaks of the compounds [Ni(ox)$_2$enR]

α/α	Compound	*m/e* (R.I.)[a]
1	[Ni(saox)$_2$bipy]·H$_2$O	50(51), 51(74), 52(56), 58(11), 60(4), 64(26), 76(28), 77(25), 78(71), 91(36), 102(18), 119(19), 137(18), 155(86), 156(100), 177(10), 178(13), 282(11), 284(7), 300(6), 302(4), 312(5), 314(4), 330(37), 332(15)
2	[Ni(saox)$_2$phen]·H$_2$O	39(30), 50(15), 51(19), 58(11), 60(7), 64(24), 76(17), 77(17), 91(60), 102(13), 115(15), 119(23), 137(27), 179(40), 180(100), 282(7), 284(5), 300(7), 302(4), 312(6), 314(3), 330(20), 332(9)
3	[Ni(apox)$_2$bipy]	39(25), 40(21), 42(26), 58(19), 60(5), 63(22), 65(29), 77(37), 78(42), 91(41), 92(19), 105(65), 119(14), 120(36), 133(24), 134(37), 135(42), 149(19), 150(14), 151(58), 155(53), 156(100), 177(42), 192(74), 193(34), 194(34), 207(7), 208(6), 306(23), 312(16), 326(16), 342(42), 344(17), 358(96), 359(71), 360(28)
4	[Ni(ppox)$_2$phen]·H$_2$O	51(60), 55(13), 58(44), 60(18), 63(78), 76(94), 77(63), 90(69), 91(82), 92(54), 119(83), 120(69), 146(66), 147(35), 148(80), 149(48), 150(36), 151(46), 152(64), 153(72), 154(74), 165(82), 166(60), 179(89), 180(100), 181(87), 193(48), 201(43), 204(53), 205(54), 206(70), 220(12), 221(16), 238(32), 370(47), 372(18), 386(73), 387(48), 388(63)
5	[Ni(mpox)$_2$phen]	39(42), 41(39), 42(44), 51(46), 55(60), 56(30), 77(85), 78(59), 91(43), 105(78), 121(80), 147(37), 149(48), 150(11), 152(16), 161(27), 165(29), 179(40), 180(100), 191(24), 204(20), 206(27), 220(7), 222(12), 386(22), 388(16)
6	[Ni(bpox)$_2$bipy]	40(28), 44(30), 50(28), 51(58), 52(30), 64(12), 77(17), 78(63), 92(4), 101(6), 102(9), 103(11), 152(46), 155(83), 156(100), 157(39), 182(12), 195(6), 196(4), 197(3), 213(30), 252(7), 254(6), 482(12), 484(5)
7	[Ni(bpox)$_2$phen]	50(61), 51(71), 52(48), 57(10), 62(49), 63(70), 64(63), 76(61), 77(100), 78(52), 92(54), 93(43), 103(54), 120(40), 121(60), 139(39), 151(37), 152(56), 153(56), 167(66), 179(61), 180(72), 195(71), 196(64), 210(31), 213(50), 252(7), 254(8), 268(4), 270(3), 482(15), 484(7)
8	[Ni(opox)$_2$bipy]·H$_2$O	51(92), 52(68), 63(24), 64(28), 76(41), 77(40), 78(92), 79(46), 101(20), 102(26), 103(29), 104(24), 155(98), 156(100), 157(71), 227(7), 228(6), 243(30), 446(8), 448(3), 542(8), 544(3)

[a] R.I. = Relative intensity.

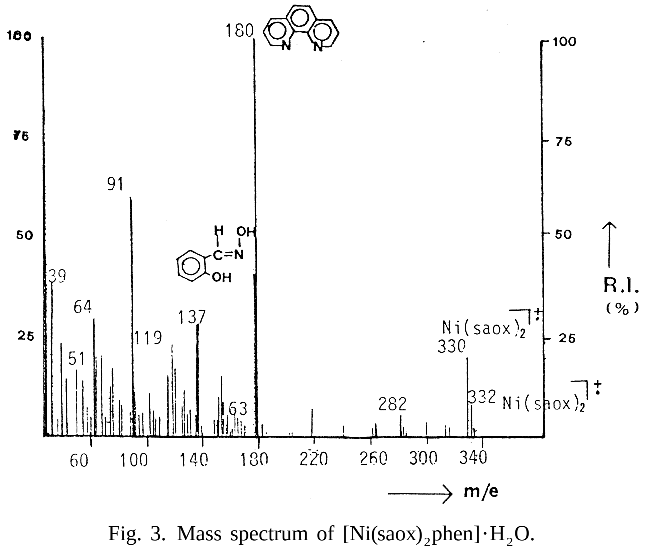

Fig. 3. Mass spectrum of [Ni(saox)$_2$phen]·H$_2$O.

fragments following well-known pathways [35–38]. The decomposition modes of the Ni(ox)$_2^{\urcorner +}$ ions are in agreement with those reported previously for the [Ni(ox)$_2$] complexes with the same 2-hydroxyaryloxime ligands [35,39]. A simplified picture of the main fragmentation pathway for the studied addition compounds is presented in Fig. 4.

3.5. Thermal behaviour

The thermal behaviour of the six nickel addition compounds under investigation was studied using the simultaneous thermogravimetry/derivative thermogravimetry (TG/DTG) technique, in nitrogen atmosphere over the temperature range 40–980°C. Representative thermal curves for [Ni(saox)$_2$bipy]·H$_2$O are given in Fig. 5 and thermoanalytical data derived from the thermal curves are presented in Table 6.

The anhydrous studied compounds, after the elimination of the crystal water molecule in the range 60–110°C, decompose in three or four stages. Their thermal decompo-

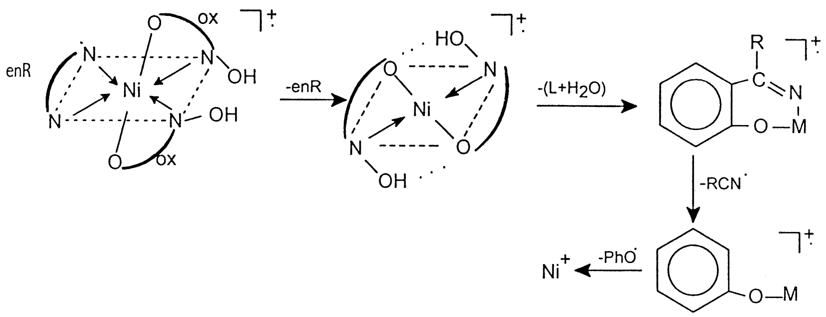

Fig. 4. Possible fragmentation pattern of the [Ni(ox)$_2$enR] compounds.

sition mode does not follow a definite mode, depending on the oxime ligand. It was quite surprising that the decomposition does not begin with the elimination of the α-diimine molecule as expected and deduced from the mass spectral data. It proceeds mostly with rupture of the bonds inside the first 2-hydroxyoxime ligand, resulting in the elimination of a nitrile and a phenanthroline molecule, in agreement with the thermal decomposition mode of the [Ni(ox)$_2$] complexes [39]. The second molecule of the oxime ligand is subsequently eliminated, with rupture of the coordination bonds and finally, the α-diimine molecule is gradually eliminated over the temperature 500°C. In some cases, the last procedure can be merged, resulting in the simultaneous elimination of the oxime and the α-diimine ligands.

In all cases, the intermediates formed are unstable and undergo further decomposition at higher temperatures, until the stable NiO is formed at about 940°C, as verified from the X-ray powder diffraction data.

Supplementary data

Supplementary data (Tables 1s–7s with crystallographic data of the compound [Ni(saox$_2$)phen]·H_2O and Figs. 1s–2s concerning the unit cell and the excitation spectrum of it, respectively) are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 114439.

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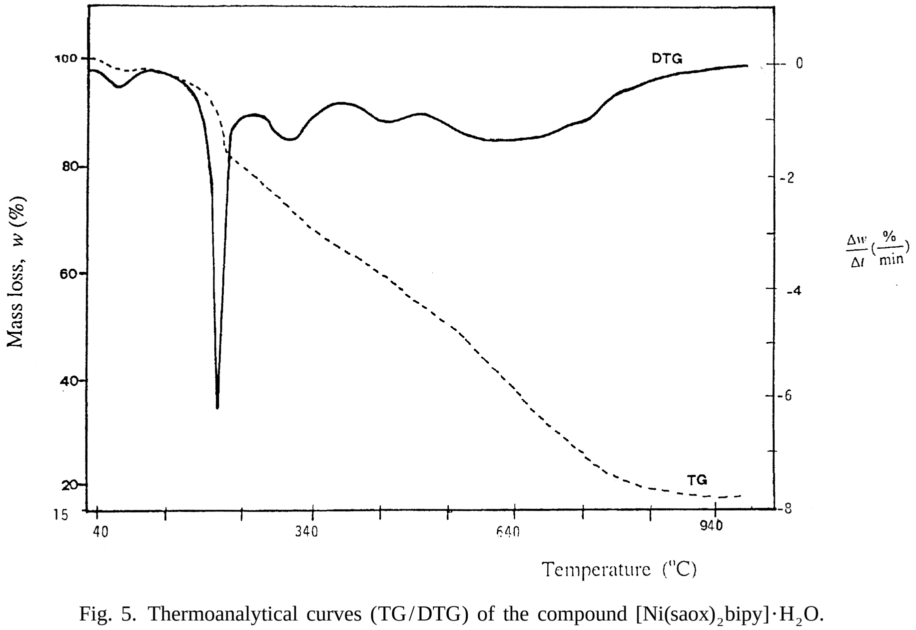

Fig. 5. Thermoanalytical curves (TG/DTG) of the compound [Ni(saox)$_2$bipy]·H_2O.

Table 6
Thermoanalytical data (TG/DTG) for the [Ni(ox)$_2$enR] compounds in nitrogen

Compound	Stage	Temperature range (°C)	DTG max. (°C)	Mass loss (%)	Evolved moiety formula	Mass calc. (%)
[Ni(saox)$_2$bipy]·H_2O		60–110	76	3.4	H_2O	3.56
	1	110–270	225	17.8	C_6H_4OH	18.41
	2	270–420	326, 473	32.0	saox + HCN	32.28
		420–550				
	3	550–960	770	31.3	bipy	30.89
	Residue	>960		15.5	NiO	14.85
[Ni(saox)$_2$phen]·H_2O		60–110	80	3.6	H_2O	3.4
		110–205	Plateau			
	1	205–270	240	8.4	HCNO	8.13
	2	270–440	330, 360	14.0	C_6H_5	15.55
	3	440–960	500, 745	60.0	saox + phen	59.7
	Residue	>960		14.0	NiO	14.18
[Ni(apox)$_2$bipy]	1	150–230	219	21.7	C_6H_4CNO	22.9
	2	230–345	286	19.8	C_6H_4CN	19.8
	3	345–425	376	13.1	$2(CH_3OH)$	12.4
	4	425–800	550, 665	30.8	bipy	30.29
	Residue	>800		14.6	NiO	14.56
[Ni(ppox)$_2$phen]·H_2O		60–110	80	3.0	H_2O	3.1
	1	200–290	265	16.2	C_6H_4OH	15.9
	2	290–530	360	9.2	C_2H_5CN	9.4
	3	530–900	670(br)	58.6	ppox + phen	58.8
	Residue	>900		13.0	NiO	12.8
[Ni(mpox)$_2$phen]	1	100–420	318	29.4	Hmpox	29.1
	2	420–980	647, 757br	57.0	L + ox + phen	57.8
	Residue	>980		13.6	NiO	13.2
[Ni(opox)$_2$bipy]·H_2O		60–110	80	2.8	H_2O	2.5
	1	110–210	198	18.2	$CH_3OC_6H_3CN$	18.4
	2	210–300	272	12.6	PhOH	13.1
	3	300–650	360, 470	33.6	Hopox	33.9
	4	650–960	670	22.4	bipy	21.7
	Residue	>960		10.4	NiO	10.5

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