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#### SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 33, No. 7, pp. 1171–1186, 2003

## Binary and Mixed Ligand Complexes of Nifuroxime, Spectral, and Thermal Studies

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#### ABSTRACT

Complexes of nifuroxime (*anti*-5-nitro-2-furfuraldoxime, 5N-FDH) with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), La(III) and UO<sub>2</sub>(VI) have been prepared and characterized by elemental analyses, conductivity measurements, spectral and thermal studies. Also, some mixed nifuroximato-phenylalaninato, -tyrosinato or -methioninatonickel(II) complexes have been prepared and characterized by the previous methods. The complexes have the general formulae:  $[M(5N-FD)_2 \cdot mH_2O]_n$ ;  $[La(5N-FD)(OOCCH_3)_2(H_2O)_2]_2$ ;  $[UO_2(5N-FD)_2] \cdot 2H_2O$  and  $[Ni(5N-FD)(L)] \cdot H_2O$  where M = Mn(II) Co(II), Ni(II), Cu(II), Zn(II) or Cd(II); m = 0 for M = Mn(II), m = 1 for M = Co(II), Ni(II) or

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Cd(II) and m = 2 for M = Cu(II) or Zn(II); L = phenylalaninate, tyrosinate or methioninate. All complexes were isolated at pH 6 using NH<sub>4</sub>OH solution. Nifuroxime acts as a uninegative ligand in all complexes with various modes of coordination. Thermogravimetric studies show a rapid decomposition stage for all the complexes accompanied by other slow stages; the final product of all complexes is the metal oxide.

Key Words: Nifuroxime; Metal oximate; Amino acids.

#### **INTRODUCTION**

Oximes are well known for their complexing properties.<sup>[1,2]</sup> They are often used for analytical and biological purposes.<sup>[3,4]</sup> 2-Furfuraldoxime and its complexes have been widely studied.<sup>[5–7]</sup> Furfuraldoxime acts as a potential ligand towards many transition metal cations. Bouet et al.<sup>[6]</sup> studied the influence of side chain substituents in position five of furfuraldoxime on its coordinating behaviour. What has not been reported, in the literature are any solid metal complexes containing the radiosensitizer and bioreductive *anti*-5-nitro-2-furfuraldoxime [nifuroxime, Figure 1(a)]. Therefore, we have embarked on the synthesis and characterization of new Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), La(III) and UO<sub>2</sub>(VI) binary complexes of nifuroxime. Also, in view of the importance of metal-amino acid complexes in the fields of biological studies and chemotherapy,<sup>[8–10]</sup> we have synthesized and studied some mixed Ni(II) complexes containing



Figure 1. Structures of the ligands.

nifuroxime and amino acids (L-phenylalanine, L-tyrosine and L-methionine) (Figure 1b).

#### EXPERIMENTAL

#### General

Micro analyses (C, H, N, S) were performed using an Analytischer Funktionstest Vario E1 elemental analyzer. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer in the 200–4000 cm<sup>-1</sup> range using KBr discs. Electronic spectra in DMF solution and in the solid state were obtained using a Shimadzu UV-2101 PC spectrophotometer. Conductivity measurements (in DMF) were made using a LF Digi-550 conductance bridge. Mass spectra were run at 70 eV on a Jeol JMS<sub>600</sub> apparatus, applying the ionization method (EI+). The thermogravimetric analyses were determined using a Sartorius 200 MP electrobalance converted to a thermobalance by the addition of a small furnace and sample holder. The temperature was measured using a chromal-alumal thermocouple attached to a Soar ME-550 digital multimeter, the heating rate was adjusted to be 8 °C min<sup>-1</sup>.

#### **Starting Materials**

Nifuroxime was BDH grade.  $MnCl_2 \cdot 4H_2O$ ,  $CoCl_2 \cdot 6H_2O$ ,  $NiCl_2 \cdot 6H_2O$ ,  $CuCl_2 \cdot 2H_2O$ ,  $ZnCl_2 \cdot H_2O$ ,  $CdCl_2 \cdot 2.5H_2O$ ,  $La(OOCCH_3)_3 \cdot 2H_2O$  and  $UO_2 \cdot (NO_3)_2 \cdot 6H_2O$  were of analytical grade.

#### **Preparation of Complexes**

#### **Binary Complexes**

Since the preparation of the complexes followed essentially similar procedures, a general method will be described. A solution of nifuroxime (0.3 g, 1.9 mmol) in methanol (15 mL) was added to the metal salt solution (3.8 mmol) in 10 mL aqueous methanolic solution (50:50 V/V). The reaction mixture was stirred for 2 hours. Addition of  $NH_4OH$  (0.2 M) to adjust the pH at 6 gave the corresponding products: a light yellow Mn(II) complex, yield 0.24 g; a dark brown Co(II) complex, yield 0.30 g; a yellowish brown Ni(II) complex, yield 0.32 g; a dark green Cu(II) complex,

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yield 0.31 g; a light yellow Zn(II) complex, yield 0.26 g; a yellow Cd(II) complex, yield 0.25 g; a bright yellow La(III) complex, yield 0.95 g and a yellow UO<sub>2</sub>(VI) complex, yield 0.37 g. The products were filtered, washed with methanol (5 mL) and dried over  $P_4O_{10}$ .

Mixed-Ligand Complexes

Preparation of the Ni(II) mixed-ligand complexes followed the same procedure. The preparation of (nifuroximato)(phenylalaninato)nickel(II) is typical. A solution of nifuroxime (0.3 g, 1.9 mmol) in methanol (15 mL) was added to 0.45 g (1.9 mmol) of nickel chloride hexahydrate in aqueous methanolic (50:50 V/V) solution (10 mL). The solution mixture was treated with 0.31 g (1.9 mmol) phenylalanine in 20 mL methanol. The resulting solution was stirred for 3 hours. A yellowish-brown product was obtained by treating the above reaction mixture with NH<sub>4</sub>OH (0.2 M) to adjust the pH at 6.5. The deposited solid was filtered, washed with methanol and dried over P<sub>4</sub>O<sub>10</sub>; yield 0.65 g.

#### **RESULTS AND DISCUSSION**

The reaction between MCl<sub>2</sub>·xH<sub>2</sub>O, La(OOCCH<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O or UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>· 6H<sub>2</sub>O with nifuroxime (5N-FDH) in the molar ratio 1:2 or 1:1 and at pH 6 affords the corresponding complexes. The synthesis of the various complexes may be represented as follows:

$$nMCl_{2} \cdot xH_{2}O + 2n(5N-FDH)$$

$$\xrightarrow{\text{methanol/H}_{2}O} [M(5N-FD)_{2} \cdot mH_{2}O]_{n} + 2nHCl$$
(1)

M = Mn (1), Co (2), Ni (3), Cu (4), Zn (5) or Cd (6); x = 1-6 and m = 0 for Mn(II), m = 1 for Co(II), Ni(II), Cd(II) and m = 2 for Cu(II) and Zn(II).

$$2\text{La}(\text{OOCCH}_3)_3 \cdot 2\text{H}_2\text{O} + 2(5\text{N-FDH}) \xrightarrow[\text{MH}_4\text{OH}]{\text{MH}_4\text{OH}} \xrightarrow[\text{MH}_4\text{OH}]{\text{MH}_4\text{OH}} \xrightarrow[\text{MH}_4\text{OH}]{\text{MH}_4\text{OH}} (2)$$

$$\frac{\text{UO}_{2}(\text{NO}_{3})_{2} \cdot 6\text{H}_{2}\text{O} + 2(5\text{N-FDH})}{\frac{\text{methanol/H}_{2}\text{O}}{\text{NH}_{4}\text{OH}}} [\text{UO}_{2}(5\text{N-FD})_{2}] \cdot 2\text{H}_{2}\text{O} (\textbf{8}) + 2\text{HNO}_{3}$$
(3)

Also, the reaction between  $NiCl_2 \cdot 6H_2O$ , nifuroxime and various amino acids in the molar ratio 1:1:1 yields the corresponding mixed-ligand complex according to the following general equation:

$$\begin{array}{c} \text{NiCl}_{2} \cdot 6\text{H}_{2}\text{O} + 5\text{N} \cdot \text{FDH} + \text{HL} \\ \xrightarrow{\text{methanol/H}_{2}\text{O}} & [\text{Ni}(5\text{N} \cdot \text{FD})\text{L}] \cdot \text{H}_{2}\text{O} + 2\text{HCl} \end{array}$$
(4)

where L = phenylalaninate (phala) (9), tyrosinate (tyr) (10) or methioninate (met) (11).

The present compounds are sufficiently stable under normal atmospheric conditions. They are insoluble in many common polar or non-polar solvents but soluble in DMF and DMSO giving rise to non-conducting solutions. Physical characterisation, microanalytical, and molar conductance data of the complexes are given in Table 1. The complexes were identified by elemental analyses, spectral data (IR, UV-Vis, MS) and thermal studies.

#### **IR** Spectra

The infrared spectra in the region 4000-400 cm<sup>-1</sup> provide some information regarding the mode of coordination in the complexes in comparison with that of the free ligand. Generally, furfuraldoxime has three potential coordinating sites<sup>[5]</sup> which are the furanic O-ring, O-oxime and Noxime. In the case of our ligand (nifuroxime) there is the NO<sub>2</sub> group besides the above mentioned three coordinating sites. Thus, on complexation of 5N-FDH it has been expected that the main perturbed vibrations in its spectrum are O-H stretching, N-O stretching, C=N stretching, NO<sub>2</sub> stretching and ring breathing. In addition, new bands arise from the following new bonds: metal-N and metal-O (ring or oxime).<sup>[11]</sup> The most relevant bands and proposed assignments for the free ligand and the complexes are listed in Table 2. The spectra of the binary complexes are very similar to one another except for [La(5N-FD)(OOCCH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> and [UO<sub>2</sub>(5N-FD)<sub>2</sub>]·2H<sub>2</sub>O. However, all are different from the spectrum of the free ligand. The anionic character of the nifuroxime ligand and its coordination mode through the nitrogen and oxygen atoms or the ringoxygen and oxime-oxygen are inferred from the positions and the shifts in the IR bands of the studied compounds, compared to the bands of the free ligand. Bands at 3010 and 3160 cm<sup>-1</sup> of the free ligand are attributable to the v(OH) vibration of the N-OH group.<sup>[5]</sup> On the other hand, all complexes show no IR bands in this region (3010-3160 cm<sup>-1</sup>), indicating that the oxime proton is fully removed.<sup>[12]</sup>

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Table 1. Elemental and physical properties of the complexes.

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	Comnlex (emnirical formula)		Analysi	s found (c	alcd) %	WV	u M	Yield
	(formula weight)	Color	С	Н	Ν	$(\Omega^{-1} \text{ cm}^{-2} \text{mol}^{-1})$	(C)	(%)
(1)	$[Mn(5N-FD)_2]_n$	Light-yellow	32.73	1.65	15.51	11.2	200	68
	$(C_{10}H_6MnN_4O_8)$ (365.12)		(32.89)	(1.66)	(15.35)			
5	$[Co(5N-FD)_2 \cdot H_2O]_n$	Dark-brown	31.11	2.06	14.37	9.3	235	82
	$(C_{10}H_8CoN_4O_9)$ (387.13)		(31.02)	(2.08)	(14.48)			
3	$[Ni(5N-FD)_2 \cdot H_2O]_n$	Yellowish-brown	30.97	2.04	14.36	12.2	130	86
	$(C_{10}H_8N_4NiO_9)$ (386.91)		(31.04)	(2.08)	(14.48)			
(4)	$[Cu(5N-FD)_2 2H_2O]_n$	Dark green	29.40	2.49	13.67	8.7	135	78
	$(C_{10}H_{10}CuN_4O_{10})$ (409.75)		(29.31)	(2.46)	(13.68)			
<b>(2</b> )	$[Zn(5N-FD)_2 \cdot 2H_2O]_n$	Light yellow	29.15	2.47	13.64	8.9	195	65
	$(C_{10}H_{10}N_4O_{10}Zn)$ (411.58)		(29.18)	(2.45)	(13.62)			
9	$[Cd(5N-FD)_2 \cdot H_2O]_n$	Yellow	27.30	1.81	12.75	10.9	270	58
	$(C_{10}H_8CdN_4O_9)$ (440.60)		(27.26)	(1.83)	(12.75)			
6	[La(5N-FD)-(OOCCH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub>	Bright yellow	24.16	2.94	6.28	9.4	175	55
	$(C_9H_{13}LaN_2O_{10})$ (448.12)		(24.12)	(2.92)	(6.25)			
8	$[UO_2(5N-FD)_2]\cdot 2H_2O$	Yellow	19.52	1.61	9.12	10.6	285	62
	$(C_{10}H_{10}N_4O_{12}U)$ (616.24)		(19.49)	(1.64)	(6.09)			
6	[Ni(5N-FD)(phala)]·H <sub>2</sub> O	Yellowish-brown	42.38	3.80	10.63	8.6	290	85
	$(C_{14}H_5N_3NiO_7)$ (395.99)		(42.46)	(3.82)	(10.61)			
(10)	$[Ni(5N-FD)(tyr)] \cdot H_2O$	Brown	40.87	3.64	10.25	11.3	270	73
	$(C_{14}H_{15}N_3NiO_8)$ (411.99)		(40.81)	(3.67)	(10.20)			
(11)	$[Ni(5N-FD)(met)] \cdot H_2O$	Light orange	31.66	3.96	11.07	12.1	270	79
	$(C_{10}H_{15}N_3NiSO_7)$ (380.01)		(31.60)	(3.98)	(11.06)			

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	Ι	able 2. IF	R spectral bands (c	$m^{-1}$ ) for (5N-FD)	H) and its l	binary and n	nixed-ligand	complexes. <sup>a</sup>	
Species	v(C=N)	v(N-O)	Ring breathing	(C-0-C) def.	$v(NH_2)$	V <sub>s</sub> (COO)	v <sub>as</sub> (COO)	v(M-O)	v(M-N)
5N-FDH	1620 s	960 s	1020 s	1250 m	I	I	I	I	
(1)	1665 m	990 m	1010 m	1250 m	I	I	Ι	610 w	425 m
(2)	1665 m	970 m	1010 s	1250 s	I	I	I	660 m	420 w
(3)	1670 m	980 w	1010 s	1250 s	Ι	Ι	Ι	640 w	410 m
(4)	1660 m	985 m	1000 s	1250 s	I	I	I	670 w	410 m
(5)	1680 w	985 w	1005 s	1245 s	I	I	Ι	640 m	425 m
(9)	1665 m	990 m	1015 m	1250 s	I	I	I	620 w	415 m
<b>(</b> -)	1670 w	980 w	1010 m	1250 m	I	1420 m	1560 m	650 m	405 m
(8)	1620 m	970 m	1000 s	1230 s	I	I	I	660 m	I
(6)	1655 w	990 m	1005 s	1250 s	3340 w	1445 s	1560 s	640 w, 680 w	420 m, 460 w
(10)	1650 m	985 w	1005 m	1250 s	3345 w	1440  s	1565 m	665 w, 670 w	425 m, 520 w
(11)	1650 m	975 w	1005 m	1250 s	3350 w	1440 s	1560 m	645 w, 660 w	420 m, 450 w

<sup>a</sup>s (strong), m (medium), w (weak).



For the complexes (1)-(7) and (9)-(11) bands in the region 1650-1680 cm<sup>-1</sup> are assigned to v(C=N) which is observed in the free ligand at 1620 cm<sup>-1</sup>. This blue-shift may indicate that the bond order of the carbonnitrogen link is increased upon coordination to the various metal ions.<sup>[13]</sup> However, this band appears at the same position as in the free ligand (1620  $cm^{-1}$ ) for the complex [UO<sub>2</sub>(5N-FD)<sub>2</sub>]·2H<sub>2</sub>O, indicating that the C=N group is not taking part in coordination. From the shift in the N-O vibration to higher frequency  $(970-990 \text{ cm}^{-1})$  for all complexes (1)-(11)one can conclude that the ligand does not exist in the oxime form. Taking the C-O-C stretching frequency of furan as a criterion for the denticity of this ligand, there is no shift of this band in all complexes (Table 2), except for complex (8) in which there is a red-shift by  $20 \text{ cm}^{-1}$  compared to that of the free ligand. This may mean that the furan oxygen does not participate in coordination for all complexes but is taking part in coordination in the uranyl complex.<sup>[13]</sup> The strong withdrawing effect of the NO<sub>2</sub> group may alter the furan oxygen to participate in coordination. In the spectra of the complexes additional bands appear in the regions 1420-1445 cm<sup>-1</sup> and 1560-1565 cm<sup>-1</sup>. For complexes (7) and (9)-(11), these are assigned to  $v_s(COO)$  and  $v_{as}(COO)$ , respectively. This defines bidentate chelating acetato groups ( $\Delta v = v_{as} - v_s = 1560 - 1420 = 140 \text{ cm}^{-1}$ )<sup>[14]</sup> for complex (7) and suggests the presence of an ionized and coordinated carboxylate group of the amino acid in complexes (9)-(11).

For the latter three complexes (9)–(11), the v(N–H) band appears in the  $3340-3350 \text{ cm}^{-1}$  region.<sup>[15]</sup> The presence of water of crystallisation in the complexes (2)–(6) and (8)–(11) is shown by a broad band in the 3450–3580 cm<sup>-1</sup> region, while the intense band at 3350 cm<sup>-1</sup> is assigned to v(OH), the frequency of coordinated water for complex (7). The new band in the 610–680 cm<sup>-1</sup> range is attributable to the M–O bond. For the UO<sub>2</sub> complex (8), the band appearing at 880 cm<sup>-1</sup> corresponds to v(O=U=O). For all complexes, except (8), the M–N bond is observed in the 405–460 cm<sup>-1</sup> region. The band which appears at 1350–1355 cm<sup>-1</sup> for all complexes is assigned to v<sub>s</sub>(NO<sub>2</sub>), which demonstrates that no important spectral changes are found for this band compared with that in the free ligand (1350 cm<sup>-1</sup>), indicating that the NO<sub>2</sub> group in 5N-FDH does not participate in coordination.

#### **Electronic Absorption Spectra**

The electronic spectra of the complexes were recorded in solution (DMF) and in the solid state (Nujol mull) (Table 3). The Ni(II) binary complex (3) shows two broad bands at 613 and 544 nm; these bands could

*Table 3.* Electronic spectral data (nm) ( $\varepsilon_{max}$ ,  $M^{-1}cm^{-1}$ ) of the complexes in DMF solution and in the solid state.

Complex	d-d	Charge transfer	Intraligand transition
(1)	_	405 <sup>a</sup>	377 <sup>a</sup> , 261 <sup>a</sup>
(2)	880 (98), 530 (324)	426 (2301)	391 (31220), 277 (10262)
(3)	613 (106), 544 (266)	427 (1017)	340 (27550), 264 (12371)
(4)	625 (178), 477 (822)	444 (2033)	352 (32662), 268 (11135)
(5)	_	406 <sup>a</sup>	355 <sup>a</sup> , 257 <sup>a</sup>
(6)	_	417 <sup>a</sup>	338 <sup>a</sup> , 254 <sup>a</sup>
(7)	_	433 <sup>a</sup>	358 <sup>a</sup> , 250 <sup>a</sup>
(8)	-	547 <sup>a</sup> , 433 (1015)	356 (15232), 249 (11452)
(9)	633 (117), 888 (92)	424 (1813)	335 (21613), 277 (18658)
(10)	642 (123), 875 (85)	421 (2050)	358 (21613), 279 (18340)
(11)	630 (136), 890 (77)	454 (2076)	332 (22615), 275 (19918)

<sup>a</sup>Nujol mull.

be assigned to the transitions  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$  (v<sub>1</sub>),  ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$  (v<sub>2</sub>), respectively, as seen in other Ni(II) square-planar complexes.<sup>[16]</sup> The broad shoulder at 427 nm in solution and shoulders at 416 and 377 nm in the solid state can be assigned to the  $d-\pi^*$  transition. The UV-Vis spectra of the cobalt(II) complex (2) in DMF and/or Nujol are identical and show a shoulder at 530 nm. The existence of this shoulder suggests either octahedral or square-planar structure around the cobalt(II) ion.<sup>[17]</sup> The observation of a narrow band at 880 nm supports the existence of a square-planar structure around cobalt(II) ion.<sup>[17]</sup> The intense band at 426 nm, could be assigned to a charge transfer transition  $(M \rightarrow L)$ . The electronic spectrum of the Cu(II) complex (4) in solution displayed two weak and broad bands around 625 and 477 nm which may be assigned to  $^2B_{1g}\!\rightarrow{}^2E_g$  and  $^2B_{1g}\!\rightarrow{}^2A_{1g}$  transitions, respectively, in an idealized square-planar symmetry. This complex in the Nujol mull spectrum displays a band at 557 nm which could be taken as evidence for distortion from the planar configuration in the solid state. A charge transfer band appears at 444 nm. Bands appearing in the 340-391 and 264-277 nm regions for the above complexes (2), (3) and (4) may be assigned to the  $\pi - \pi^*$  and  $n - \pi^*$  intraligand transitions, respectively.

The Nujol mull spectra of the Mn(II), Zn(II) and Cd(II) complexes (1), (5) and (6) (Table 3) show three bands at 405, 377, 261 nm; 406, 355, 257 nm and 417, 338, 254 nm, respectively. The first intense band of all is assigned to charge transfer (L  $\rightarrow$  M), while the latter two bands are less intense and are attributed to  $\pi - \pi^*$  and  $n - \pi^*$  intraligand transitions, respectively.



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For the La(III) complex (7), the solid state spectrum shows peaks at 433, 358 and 250 nm. The first band was assigned to charge transfer and the latter two bands to intraligand transitions  $(\pi - \pi^* \text{ and } n - \pi^*)$ . The f-f transition of the lanthanum ions in the visible region may be obscured due to the broad charge-transfer band. The UO<sub>2</sub>(VI) complex (8) exhibits bands in DMF due to the  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions at 356 and 249 nm, respectively. The broad band at 433 nm can be assigned to charge-transfer from the uranyl oxygen to the uranium f orbitals.<sup>[18]</sup> The ligand-to-uranium charge transfer transition band appears in the Nujol mull spectrum at 547 nm.

The electronic spectra of the mixed-ligand Ni(II) complexes (9)–(11) in DMF show a broad band in the 630–642 nm region which is assigned to the  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$  transition in square-planar Ni(II) complexes.<sup>[16]</sup> Bands at 421–454 nm can be assigned to charge transfer transitions. The strong absorption band appearing in the 332–335 nm region could be assigned to the  $\pi-\pi^*$  transition of the nifuroximate moiety, while the intense broad band located in the 275–279 nm region could be ascribed to the intraligand transition of the amino acid moiety. The  $n-\pi^*$  transition of the nifuroximate moiety is probably obscured by the relatively strong absorption band of the amino acid moiety.

#### **Mass Spectra**

The mass spectra of some of the complexes were recorded to help determine their stoichiometric composition. For the Cu(II) binary complex (**4**), the molecular ion peak ( $C_{10}H_{14}CuN_4O_{12}$ ) appears at m/z = 409.5 (calc. 409.8). Other low-intensity peaks appear at m/z = 415.5 and 432.3; and may support a bridged structure of the complex to form a polynuclear compound (Figure 3) through the deprotonated oximate oxygen.<sup>[19]</sup> However, the Ni(II) binary complex (**3**) shows the highest mass number at m/z = 386 (calc. 386.9) which corresponds to the molecular ion  $C_{10}H_8N_4NiO_9$ . This confirms the stoichiometry of these complexes as being of the ML<sub>2</sub> type.

On the other hand, for the  $UO_2(VI)$  complex (8) and  $[Ni(5N-FD)-(phala)] \cdot H_2O$  (9) the molecular ion peaks were not detected, probably due to the high thermal instability of these complexes in the ionization beam.

From the foregoing results we may suggest that nifuroxime coordinates through the N (oxime) atom and is bridged by the deprotonated oximate to another metal ion in complexes (1)-(7) and (9)-(11). In view of the effective bridging function of the oximate group, many workers have studied oximates or dioximates as bridging<sup>[12,19-23]</sup> ligands. The X-ray crystal structure of a binulcear Cu(II)Cu(II) complex doubly bridged by oximate oxygens has been reported.<sup>[22]</sup> However, nifuroxime acts as a monoanionic

bidentate ligand through the furan-oxygen and oxime-oxygen atoms in complex (8), which may be attributable to the stronger U–O bond than U–N bond.<sup>[7]</sup>

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#### **Thermal Analysis**

All the prepared complexes decompose with explosive force. This difficulty of obtaining the thermograms of these complexes has been

		Temperature	DTG	Mass l	oss, %	Evolved mojety
Complex	Stage	range (°C)	max (°C)	Found	Calcd.	(residue)
(1)	1	50-155	100	32.7	32.6	$2NO_2 + HCN$
	2	160-175	165	43.1	43.6	rest of ligand
	Residue	>175		24.1	23.8	(MnO <sub>2</sub> )
(3)	1	50-90	85	5.0	4.7	H <sub>2</sub> O
	2	110-130	125	58.2	58.9	5N-FD +
						$NO_2 + HCN$
	3	130-295	240	17.4	17.1	rest of ligand
	Residue	>295		19.4	19.3	(NiO)
(4)	1	50-90	75	8.5	8.8	$2H_2O$
	2	90-175	140	13.5	13.2	2HCN
	3	175-185	180	58.9	58.6	rest of ligand
	Residue	>185		19.1	19.4	(CuO)
(6)	1	45-80	75	14.9	14.5	$H_2O + N_2O$
	2	80-125	115	16.5	16.6	$NO_2 + HCN$
	3	25-255	205	39.5	39.8	rest of ligand
	Residue	>255		29.0	29.1	(CdO)
(7)	1	75-175	140	8.0	8.0	$4H_2O$
	2	175-185	180	30.5	30.8	$2(C_5H_2N_2O_3)$
		185-275	plateau			
	3	275-450	375	10.0	10.1	rest of ligand
	Residue	>450		51.4	51.1	$(La_2(CO_3)_3)$
						$>800 ^{\circ}C (La_2O_3)$
(8)	1	70-165	100, 145	30.6	31.0	$2H_2O + 5N-FD$
(0)	2	165-205	175	23.8	23.5	rest of ligand
	Residue	>205		45.5	45.5	$(U_3O_8)$
(9)	1	65-105	95	4.9	4.5	H <sub>2</sub> O
	2	150-230	190	41.3	41.5	phala
	3	230-245	235	35.4	35.1	5N-FD
	Residue	>245		18.5	18.9	(NiO)

Table 4. Characterized thermoanalytical data (TG/DTG) for the complexes.



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El-Said



*Figure 2.* TG-DTG curves of (a)  $[Ni(5N-FD)_2 \cdot H_2O]_n$  (3), (b)  $[Cu(5N-FD)_2 \cdot 2H_2O]_n$  (4), and (c)  $[La(5N-FD)(OOCCH_3)_2(H_2O)_2]_2$  (7).

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overcome by using a sample of Al<sub>2</sub>O<sub>3</sub> pre-calcined at 1000 °C as a diluent. Each complex was admixed with 20% by weight Al<sub>2</sub>O<sub>3</sub>. The thermal behaviour of some the complexes were studied using TG/DTG technique in air over the temperature range from ambient to 600 °C. Thermogravimetric data are shown in Table 4 and thermograms in Figure 2. All of the studied complexes decompose in two or three stages, the second or third stage of each is a very rapid one. Complexes (3), (4) and (9) lose water at 85, 75 and 95 °C corresponding to 5% (calc. 4.7%), 8.5% (calc. 8.8%) and 4.9% (calc. 4.5%) weight loss, respectively. This suggests that these complexes contain water of crystallization (one molecule for complexes (3) and (9) and two for complex (4)). For complex (6) the water molecule is evolved with NO<sub>2</sub> at 75 °C (Table 4). However, for complex (7) two water molecules are evolved at 140 °C indicating the presence of coordinated water. The first decomposition step for complex (8) is a composite one including loss of two water molecules and the oxime moiety. Depending on the percentage weight loss, it was obvious that the decomposition in these complexes proceeds mostly with rupture of the bonds inside the oxime



Figure 3. Proposed structures of the complexes.

ligand, resulting in the elimination of NO<sub>2</sub> and HCN molecules<sup>[24]</sup> (Figure 2 and Table 4). Depending upon the percentage weight loss and the IR spectra, the end product of the complexes (**3**), (**4**), (**6**) and (**9**) is NiO, CuO, CdO and NiO, respectively. For complex (**8**) it is U<sub>3</sub>O<sub>8</sub> and for complex (**7**) it is La(CO<sub>3</sub>)<sub>3</sub>, which upon heating in an external oven at 800 °C changes to La<sub>2</sub>O<sub>3</sub>. The proposed residue for complex (**1**) is MnO<sub>2</sub>. If the final stage in the decomposition of the complexes is the most rapid one, the residue was obtained at lower temperatures. This is examplified for complexes (**1**), (**4**), and (**8**) (Table 4, Figure 2b). This may be due to burning-off of the decomposition products to form the metal oxide residue rapidly.<sup>[25]</sup> In all cases, the intermediates formed are unstable and undergo further decomposition at higher temperatures.

Based on the above studies, tentative structures for the complexes (Figure 3) have been proposed.

### REFERENCES

- Masoud, S.M.; Ali, G.Y.; Youssef, A.R. Coordinating behaviour of some oximes. Pol. J. Chem. 1986, 60, 731–740.
- Masoud, S.M.; Ali, G.Y.; Youssef, A.R. Coordinating behaviour of some oximes. Chem. Abstr. 1987, 107, 189488g.
- Reddy, V.K.; Reddy, S.M.; Reddy, P.R.; Reddy, T.S. Spectrophotometric determination of cobalt(II) and gold(III) in the presence of potassium persulfate using resacetophenone oxime. Indian J. Chem. Sec., A. Inorg. Bioinorg. Chem. 2000, 39, 557–559.
- Alexandrova, L.; D'yachenko, O.G.; Kazankov, G.M.; Polyakov, V.A.; Samuleev, P.V.; Sansores, E.; Ryabov, A.D. Mechanism of biologically relevant deoxygenation of dimethyl sulfoxide coupled with Pt(II) to Pt(IV) oxidation of orthoplatinated oximes. Synthetic, kinetic, electtochemical, x-ray structural and density functional study. J. Am. Chem. Soc. 2000, 21, 5189–5200.
- Bouet, G.M.; Dugué, J. Metal complexes with 2-furfuraldoxime. Transition Met. Chem. 1990, 15, 257–263.
- Bouet, G.M.; Dugué, J.; Keller-Besrest, F. Metal complexes with furan oximes, part IV. Synthesis and characterization of 5-substituted 2furfuraldoxime complexes with 3d element dihalides. Transition Met. Chem. 1990, 15, 5–8.
- Singh, S.; Chakravorty, V.; Dash, K.C. Mono-, bi and trinuclear dioxouranium(VI) complexes with oximes and polydentate Schiff bases. Indian J. Chem. **1989**, 28A, 255–257.

- 8. Howe-Grant, M.E.; Lippard, S.L.; Sigel, H. *Metal Ions in Biological Systems*; Marcel Dekker: New York, 1980.
- Feng, M.; Yang, Y.; He, P.; Fang, Y. Spectroscopic studies of copper(II) and iron(II) complexes of adriamycin. Spectrochim. Acta, Part A 2000, 56 (3), 581–588.
- Blais, M.J.; Kayali, A.; Berthan, G. Histamine as a ligand in blood plasma. Part 4. potentiometric investigation of complex formation in the Cu(II)-cystinate, Cu(II)-lysinate, Cu(II)-histamine-cystinate and Cu(II)histamine-lysinate system. Inorg. Chim. Acta 1981, 56, 5–9.
- 11. Ferraro, J.R. Low-Frequency Vibrations of Inorganic and Coordination Compounds; Plenum: New York, 1971.
- Zhang, S.W.; Liao, D.Z.; Jiang, Z.H.; Wang, G.L. Synthesis and magnetic properties of cobalt(II)-palladium(II)-cobalt(II) trinuclear complexes bridged by an extended α-benzyldioximato group. Synth. React. Inorg. Met.-Org. Chem. **1996**, *26* (7), 1101–1111.
- 13. Nour, E.M.; Taha, A.A.; Alnaimi, I.S. Infrared and raman studies of  $[UO_2(Salen)(L)]$  ( $L = H_2O$  and  $CH_3OH$ ). Inorg. Chim. Acta **1988**, 141, 139–144.
- 14. Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Ed.; Wiley: New York, 1986.
- Gupta, M.; Strivastava, M.N. Synthesis and characterization of mixed ligand complexes of copper(II), nickel(II), cobalt(II) and zinc(II) with glycine and uracil or 2-thiouracil. Polyhedron 1985, 4 (3), 475–479.
- 16. Bailor, J.C.; Emeléus, H.J. *Comprehensive Inorganic Chemistry*; Pergamon Press Ltd: Oxford, 1973.
- Lever, A.B.P. Inorganic Electronic Spectroscopy; Elsevier: Amsterdam, 1968.
- Chattopadhyay, P.; Sinha, C. Synthesis and characterization of uranyl complexes and their peroxo derivartives with some thio-Schiff bases. Indian J. Chem., Sect. A **1996**, *35* (6), 523–526.
- 19. Zhang, S.W.; Yan, S.P.; Liao, D.Z.; Jiang, Z.H.; Liu, Y.J.; Wang, G.L. Synthesis and magnetism of homo-trinuclear Ni<sup>II</sup>-Ni<sup>II</sup>-Ni<sup>II</sup> complexes bridged by  $\alpha$ -furyldioximato groups. Pol. J. Chem. **1997**, *71* (3), 314–319.
- Zhang, S.W.; Yan, S.P.; Liao, D.Z.; Jiang, Z.H.; Liu, Y.J.; Wang, G.L. Synthesis and magnetism of homo-trinuclear Ni<sup>II</sup>-Ni<sup>II</sup>-Ni<sup>II</sup> complexes bridged by α-furyldioximato groups. Chem. Abstr. **1997**, *127*, 43926 q.
- Costes, J.P.; Dahan, F.; Dupuis, A.; Laurent, J.P. Briding ability of a novel polydentate ligand (H<sub>2</sub>L) comprising an oxime function. Structures of a mononuclear precursor (NiL) and a dinuclear Cu<sub>2</sub><sup>II</sup> complex. Magnetic properties of mononuclear (Ni<sup>II</sup> and Cu<sup>II</sup>), dinulcar



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 $(Cu_2^{II}, Ni_2^{II}, Ni^{II}Cu^{II}$  and  $Cu^{II}Cr^{III}$ ). J. Chem. Soc. Dalton Trans. **1998**, 8, 1307–1314.

- Luneau, D.; Oshio, H.; Okawa, H.; Koikawa, M. Kida, Sigeo. Synthesis, structure and magnetism of binuclear Cu(II) Cu(II), Cu(II) Ni(II), and Ni(II) Ni(II) complexes doubly bridged by oximate groups. Bull. Chem. Soc. Jpn. **1990**, *63*, 2212–2217.
- 23. Zhang, S.W.; Liao, D.Z.; Jiang, Z.H.; Wana, G.L. Synthesis and magnetic properties of chromium(III)-nickel(II)-chromium(III) trinuclear complexes with extended dioximato groups. Polyhedron **1996**, *15* (23), 4289–4293.
- Kantauri, M.L.; Hatzidimitriou, A.; Uddin, M. Synthesis and characterization of new addition compounds of bis(2-hydroxyaryloximato)nickel(II) with α-diimines. Crystal and molecular structure of [Ni (SaOx)<sub>2</sub>Phen]·H<sub>2</sub>O. Polyhedron **1999**, *18*, 3441–3450.
- 25. Bell, C.F.; Morcom, R.E. Coordination compounds of manganese(II) with 1,10-phenanthroline. J. Therm. Anal. **1979**, *17*, 7–18.

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