Metallic complexes with furan oximes. Part 5-Synthesis and characterization of 5-nitro-2-furfuraldoxime complexes with 3d element dihalides.

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Summary

Following our investigations into the complexing properties of 5-substituted 2-furfuraldoximes, we describe here the first complexes obtained from 5-nitro-2-furfuraldoxime (5-NO$_2$-FDH or L) and 3d element dihalides, formulated as [ML$_2$X$_2$], [ML$_3$X$_2$] and [ML$_4$X$_2$] (M = Co, Ni or Cu; X = Cl or Br). The structures are discussed on the basis of analytical, i.r. spectral data and thermal analysis.

Introduction

In our continuing investigations of furanic oximes as ligands[1,2] we describe here some complexes derived from 5-nitro-2-furfuraldoxime and copper(II), nickel(II) and cobalt(II) chlorides or bromides. The therapeutic properties of 5-nitrofurans are well known: they show a bactericidal activity[3-7] but, as far as we know, their complexing properties towards transition metal salts have yet to be studied. In a preceding paper[1], we demonstrated that no change occurs in the coordination mode when a methyl or an ethyl group is located at the 5-position of the furan ring. The aim of this work is to describe the effect of the nitro group in the same position.

Experimental

The ligand 5-nitro-2-furfuraldoxime or nifuroxime (*E* isomer) from Janssen was used as supplied.

Preparation of the complexes

Unless otherwise indicated, the complexes were prepared in anhydrous EtOH from 1.56 g (0.01 mol) of 5-nitro-2-furfuraldoxime (used vol. in brackets). After verifying the purity by t.l.c., the products are finally dried under reduced pressure at room temperature. They are slightly hygroscopic and must be kept in a dry atmosphere.

Dichlorobis(5-nitro-2-furfuraldoxime)copper(II)

To copper (II) chloride (CuCl$_2$·2H$_2$O) (0.86 g, 0.05 mol, 13 cm^3), a solution of the oxime (100 cm^3) was added slowly at room temperature. After 10 min, the brown solid which appeared was removed by filtration, washed twice with EtOH and then with small quantities of *n*-pentane.

Dibromobis(5-nitro-2-furfuraldoxime)copper(II)

An EtOH solution (15 cm^3) of CuBr$_2$ (1.12 g, 5 mmol) was cooled in an ice-bath and the oxime (62.5 cm^3) was added slowly. After 1 h stirring at *ca.* 4 °C, a brown solid appeared. It was isolated by filtration and washed with *n*-pentane.

Dichlorobis(5-nitro-2-furfuraldoxime)nickel(II)

NiCl$_2$·6H$_2$O (1.25 g, 5.25 mmol) was dissolved in EtOH (16 cm^3). The solution was held at the reflux temperature, then, a solution of the ligand (75 cm^3) was added dropwise. After refluxing for 1.5 h, a yellow solid precipitated which was removed and washed in *n*-pentane.

Dichlorotris(5-nitro-2-furfuraldoxime)nickel(II)

NiCl$_2$·6H$_2$O (2.33 g, 7.2 mmol) was dissolved in EtOH (20 cm^3) and heated to the reflux temperature. The solution of the ligand (97.5 cm^3) was added slowly. The reflux temperature was maintained for 30 min after the addition. On cooling, the complex partly precipitated. After removing the solvent at room temperature under reduced pressure, the residue was washed with cyclohexane.

Dibromobis(5-nitro-2-furfuraldoxime)cobalt(II)

Under EtOH reflux, the ligand (87.5 cm^3) was added dropwise to a solution (20 cm^3) of CoBr$_2$·6H$_2$O (1.75 g, 4.5 mmol). After 1 h refluxing, and slow cooling, the solvent was removed under reduced pressure at room temperature. The residue was then washed with *n*-pentane.

Dibromotetrakis(5-nitro-2-furfuraldoxime)cobalt(II)

The EtOH solution containing a slight excess of CoBr$_2$·6H$_2$O (0.84 g, 0.026 mol, 50 cm^3) was added to the EtOH solution of the ligand (100 cm^3) and cooled in an ice-bath. After stirring for 1 h 30 min at *ca.* 4 °C, the solvent was removed at room temperature under reduced pressure. The dark pink residue was then washed with a little EtOH and finally with *n*-pentane.

Physical measurements

The analytical and spectral techniques were described previously[2]. The d.s.c. curves were recorded using a Mettler TC11 T.A. processor with a d.s.c. 30 furnace (J. P. Benoit and M. C. Vénier, Laboratoire de Pharmacotechnie, Faculté de Pharmacie, Angers) from ambient temperature up to 300 °C at a rate of 10 °min^{-1}, in

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Table 1. Analytical data for the complexes

Compound	Colour	Yield (%)	M.p. (°C)	Found (Calcd.) (%)				Λ^a (S cm² mol⁻¹)	mol. wt[b]	μ^c (B.M.)
				C	H	X	M			
[CuCl₂L₂]	yellow green	48	224	26.6 (26.9)	1.8 (1.9)	15.5 (15.9)	11.1 (11.2)	16.7	insol. (446)	1.86
[CuBr₂L₂]	brown	70	213	23.1 (22.4)	1.5 (1.5)	29.9 (29.9)	11.0 (11.8)	14.3	460 (535)	1.76
[NiCl₂L₂]	green	51	257	27.1 (27.2)	1.9 (1.8)	16.5 (16.0)	13.2 (13.3)	30.1	550 (442)	3.33
[NiL₃]Cl₂	green	75	210	30.1 (30.1)	2.1 (2.0)	11.3 (11.8)	9.0 (9.8)	31.2	insol. (598)	3.16
[CoBr₂L₂]	dark pink	74	201	20.5 (22.6)	1.7 (1.5)	31.2 (30.1)	10.6 (11.1)	24.6	insol. (531)	1.95
[CoBr₂L₄]	dark pink	59	128	28.3 (28.5)	1.8 (1.9)	18.9 (18.9)	6.2 (6.9)	35.6	600 (843)	2.95

[a] NaI in EtOH (10^{-3} mol dm⁻³), 33.9 S cm⁻² mol⁻¹; [b] insol., not sufficiently soluble in PhNO₂, [c] diamagnetism corrected.

Al crucibles (40 μl). The crucibles were closed or pierced with two holes. The reference was an identical empty crucible.

Results and discussion

The analytical data of these new complexes are reported in Table 1. They show that three series of complexes could be obtained: [ML₂X₂], [ML₃]X₂ and [ML₄X₂]. The [ML₃]X₂ series was not isolated with, for example, 5-methyl- or 5-ethyl-2-furfuraldoxime[1], but Shukla et al.[8] prepared the [CoCl₂(FDH)₃] complex, where FDH is 2-furfuraldoxime.

The molar conductances in EtOH correlate with those previously obtained from our previous work[1,2,11]. They show that these new compounds are non-ionic species and that the two halides lie in the inner coordination sphere of the cation. The [NiL₃]Cl₂ complex exhibits a higher molar conductance than the other species or NaI (reference solution) but comparable with that of [CoCl₂(FDH)₃][8] and, in this case, the chloride ions are not in the coordination sphere of the metal and the correct formula is thus [NiL₃]Cl₂. Finally, the molar mol. wt indicate the process of monomeric compounds.

The magnetic moments of the copper and nickel complexes are typical for high-spin species. On the other hand, the cobalt(II) compounds exhibit low values corresponding to low-spin species.

Ligand geometry

5-Nitro-2-furfuraldoxime is shown in Figure 1. Although it is possible to separate the *E* and *Z* isomers of the ligand[9], the coordination modes described below (see Table 2) show that this is not necessary. In addition, we noticed that the O—H vibration regions (i.r. spectrum) for commercial 5-nitro-2-furfuraldoxime are typical of the *E*-predominant isomer, according to Hadzi and Premru[10].
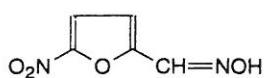
Figure 1. 5-nitro-2-furfuraldoxime (5-NO₂-FDH).

I.r. spectra

The main i.r. spectral data for the ligand and its complexes are reported in Table 2. As expected, the vibration bands related to the nitro group, *e.g.* ν(N—O) and ν(C—N), are not shifted when passing from the ligand to the complex, and this group is not involved in the coordination.

We observed that the main series of i.r. vibration bands (Table 3), *e.g.* ν(C=N), ν(N—O (oxime)], δ(C—O—C) and ring breathing bands, exhibit a slight shift to higher wave numbers for the N—O oxime stretching band. Comparison of these variations with those obtained with FDH[11], M5FDH or ET5FDH[1] revealed no significant changes for [ML₂X₂] and [ML₄X₂](L = 5-NO₂ furfuraldoxime) complexes. Consequently, 5-NO₂-FDH acts as a bidentate ligand O-cycle and O-oxime atoms, whereas it is through a monodentate ligand (N-oxime) in the [ML₄X₂] series. This fact is confirmed by the presence of two bands due to the M—O (cycle) stretching vibration in the 670–620 cm⁻¹ region, the M—O(oxime) at *ca.* 500 cm⁻¹ in [ML₂X₂] complexes, and at *ca.* 220 cm⁻¹ for ν[M—N(oxime)] in the [ML₄X₂] series[12].

In addition, all the complexes exhibit a single band for the metal–halide vibration (Table 2), typical of *trans* octahedral complexes as reported by Nakamoto[13]. This band is missing [NiL₃]Cl₂ since the chloride ions are not in the inner sphere of the cation as described above.

The spectra of [NiL₃]Cl₂ shows the same metal–oxygen vibration bands, *e.g.* ν[N—O(ring)] at 530 and ν[N—O(oxime)] at 669 and 641 cm⁻¹, at a lower wave number than in the [ML₂X₂] spectra. So, in this complex, the ligand is bidentate and the coordinating atoms are O-ring and O-oxime ones. On the other hand, the ν(O—H) vibration band at 3265 cm⁻¹ is assigned to intramolecular hydrogen bonding, as observed in [CoCl₂(FDH)₃][8]. However, if the octahedral geometry is maintained, it is not possible to determine the actual isomer because of the lack of ν(Ni—Cl).

Electronic spectra

The electronic spectra were recorded in ethanol solutions. The [CuBr₂L₂] and [CuCl₂L₂] species exhibit a broad band at 11050 and 11550 cm⁻¹, respectively, representative of a *z*-axis distorted *trans* octahedral complex, but it

Table 2. I.r. spectra (cm⁻¹) for 5-NO₂-FDH and its complexes

Compound	v(O-H)	δ(O-H)	v(C=N)	v[N-O (oxime)]	Ring breathing	Ring	v[N-O (nitro)]	v[C-N (nitro)]	v(M-X)	v(M-O)ᵃ
5-NO₂-FDH	3270 3170	1418 1325	1635	970	1025	1578 1478 1187 937 900	1530 1350	821 809		
[CuCl₂L₂]	3435 3170	1430 1312	1632	975	1038	1574 1482 1195 960 905	1528	849	270	500(r) 670(o) 645(o)
[CuBr₂L₂]	3430 3170	1422 1315	1630	978	1035	1578 1479 1195 1179 909 901	1530 1355	848 829	200	510(r) 675(o) 653(o)
[NiCl₂L₂]	3450 3180	1437 1320	1629	972	1032	1571 1480 1192 958 907	1523 1360	832 819	245	490(r) 675(o) 650(o)
[NiCl₂L₃]	3265	1413 1320	1635	972	1028	1577 1485 1188 950 910	1535 1351	837 811		530(r) 669(o) 641(o)
[CoBr₂L₂]	3380 3270	1412 1325	1635	972	1032	1571 1478 1192 952 904	1530 1352	825 810	315	455(r) 672(o) 639(o)
[CoBr₂L₄]	3435 3270	1410 1308	1635	970	1034	1571 1473 1195 955 935	1530 1352	822 810	322	–

ᵃ r. M—O (ring); o. M—O (oxime).

Table 3. Shifts of the main i.r. vibration bands (cm⁻¹) in the complexes

Compound	v(C=N)	v(N-Ox)	δ(C—O—C)	Ring breathing
[CuCl₂L₂]	−3	+5	+7	+13
[CuBr₂L₂]	−5	+8	+9	+10
[NiCl₂L₂]	−6	+2	+7	+7
[NiL₃]Cl₂	0	−8	+4	+3
[CoBr₂L₂]	0	+2	+4	+7
[CoBr₂L₄]	0	0	+3	+9
[CoBr₂(M5FDH)₂][1]	+16	+7	+16	
[CoCl₂(FDH)₃][8]	+18			

is not possible to observe the three bands (or the three shoulders) which would help to calculate 10 Dq according to Billing and Underhill[14], as reported for M5FDH or E5FDH complexes[1].

The nickel compounds were not soluble enough in EtOH to assign the first v_1 band in the near-i.r. region and, consequently, 10 Dq. The v_2 bands appear at *ca.* 16000 cm⁻¹ and the v_3 bands at *ca.* 13200 cm⁻¹.

Finally, [CoBr₂L₂] showed a v_2 band at 15270 cm⁻¹ (calcd.: 15970 cm⁻¹), a v_3 band at 17500 cm⁻¹ (16950 cm⁻¹), leading to 10 Dq = 8135 cm⁻¹ and B = 760 cm⁻¹. The [CoBr₂L₄] compound has a v_2 band at 15300 cm⁻¹ (15315 cm⁻¹) and a v_3 band at 17700 cm⁻¹ (17720 cm⁻¹), with 10 Dq = 8150 cm⁻¹ and B = 770 cm⁻¹. These values

were obtained through König's relationships[15]. It is noteworthy that, in electronic transitions, the energies of the corresponding levels are the same irrespective of whether they are calculated on a weak or a strong ligand field basis[16]. The 10 Dq values are comparable with those previously published for methyl or ethyl 5- substituted furfuraldoxime[1] but B values, on the other hand, are lower. A similar value was observed in the complex ion [Co(4-methylpyridine)₆]²⁺[16]. This shows that the bond between Co²⁺ and 5-NO₂-FDH is more covalent than the bond between the same ion and 5-methyl-FDH or 5-ethyl-FDH[1]. The nitro group induces a greater electronic delocalization along the molecule. In the whole series, the *trans* octahedral geometry is confirmed.

Table 4. Thermal analysis data (d.s.c.) for ligand, mixtures and complexes

Compound of mixture	Crucible[a]	Main peaks (°C). $[\Delta H (\text{kJ mol}^{-1})]$				
$5\text{-}NO_2\text{-}FDH$ (L)	c			157 [+37]		202 [−180]
	o			157 [+25]		205 [−195]
$[CuL_2Cl_2]$	c	126 [+23]	143 [−28]	157 [−65]		275 [−200]
	o	115 [+67]	151 [+13]	163 [−78]		
$[CuL_2Br_2]$	c	131 [−7]	160 [−185]	208 [−20]		262 [−39]
	o		172 [−244]	190 [−8]		275 [−9]
$[NiL_2Cl_2]$	c					247 [−407]
	o					248 [−317]
$[NiL_3]Cl_2$	c		186 [−44]			222 [−119]
	o	85 [−7]	166 [−72]		195 [−160]	
$[CoL_2Br_2]$	c			210 [−53]		
	o			208 [−280]		265 [−206]
$[CoL_4Br_2]$	c	103 [−21]	141 [−454]			269 [−934]
	o		144 [−239]			269 [−546]
$[NiCl_2(M5FDH)_4]$[b]	c					234 [−516]
	o				244 [+21]	250 [+2]
$[Ni(H_2O)_6]Cl_2$[c]	c	103 [+123]			193 [+22]	244 [+20]
	o	86 [−216][e]			174 [+36]	252 [+9]
$2L + 1NiCl_2$[d]	c	163 [+]	175 [−]		222 [−]	
$3L + 1NiCl_2$[d]	c	147 [−]	167 [−]		213 [−]	
$4L + 1NiCl_2$[d]	c	137 [+]	162 [−]		207 [−]	
	o	101 [+]	158 [−]		201 [−]	

[a] c. Closed, o. open. [b] M5FDH, 5-methyl-2-furfuraldoxime; [c] Prolabo p.a.; [d] the molar enthalpies cannot be calculated, the sign is given; [e] fused peaks with several shoulders.

Thermal analysis

We recorded two series of d.s.c. diagrams: the first with closed and the second with open crucibles. For the sake of comparison, we recorded the d.s.c. curves of the similar compound $[NiCl_2(M5FDH)_4]$[1], where M5FDH is a 5-methyl-2-furfuraldoxime, and of the present ligand, as well as those of mixtures in the proportions of one $NiCl_2$ 2, 3 or 4 molecules of 5-nitro-2-furfuraldoxime. In all three cases, the molar enthalpies could not be calculated as the molar mol. wt is unknown. These results are reported in Table 4 and the diagrams are shown in Figure 2.

The ligand melts at 157 °C ($\Delta H \approx 30 \text{ kJ mol}^{-1}$), typical of E 5-$NO_2$-FDH[17–19], and decomposes at ca. 200 °C ($\Delta H \approx -185 \text{ kJ mol}^{-1}$), as indicated by an exothermic peak. There is no significant difference between closed and open crucibles in this context, which demonstrates the absence of an intramolecular exothermic reaction in the temperature range studied.

The nickel(II) chloride hexahydrate shows an endotherm at 103 °C in the closed crucible ($\Delta H \approx 123 \text{ kJ mol}^{-1}$) due to the elimination of coordinated water. This peak is absent in d.s.c. diagrams recorded with an open crucible but there is a series of exothermic peaks and shoulders at ca. 86 °C (see Figure 2). We believe that this is a result of the displacement of chloride ions from the outer coordination sphere of Ni^{2+} into its inner sphere giving $[NiCl(H_2O)_5]^+$ and $[NiCl_2(H_2O)_4]$, respectively. We note that many complicated temperature- and concentration-dependent equilibria occur in nickel(II) octahedral complexes, and that they involve various structural types[20]. This fact explains the differences appearing in the d.s.c. diagrams 1 and 2 (see Figure 2) obtained with an open and a closed crucible, respectively.

The d.s.c. curves of the complexes show interesting features. First, there is no endotherm at 157 °C (ligand m.p.) in the d.s.c. diagrams of either complexes or mix-

tures. Second, very few endothermic peaks are observed (see Table 4): for $[CuCl_2(5\text{-}NO_2\text{-}FDH)_2]$ at 126 °C ($\Delta H = +23 \text{ kJ mol}^{-1}$) in a closed crucible and at 115 °C (67 kJ mol^{-1}) and 151 °C (13 kJ mol^{-1}) in open crucibles; for $[CuBr_2(5\text{-}NO_2\text{-}FDH)_2]$ at 192 °C ($\Delta H = +7 \text{ kJ mol}^{-1}$) in the open crucible only; for $[NiCl_2(M5FDH)_4]$ at 244 °C (21 kJ mol^{-1}) in the closed crucible and at 250 °C (2 kJ mol^{-1}) in the open one. In this last compound, it is interesting to note that these values fit with those observed in the $[Ni(H_2O)_6]Cl_2$ diagrams under the same experimental conditions.

On the other hand, it has been demonstrated by t.g.a. that in similar complexes of FDH with divalent copper, nickel and cobalt, metallic oxide formation occurs in the 380–500 °C range[21]. This phenomenon, however, was not observed in our study.

The diagrams for the nickel(II) complex with M5FDH, e.g. $[NiCl_2(M5FDH)_4]$, show an exotherm at 234 °C (-516 kJ mol^{-1}) in the closed crucible and two endothermic peaks (244 and 250 °C) in the open crucible, attributed to nickel chloride as indicated above. The $[NiL_2Cl_2]$ species is more thermally stable as no phenomenon appears up to 247 °C. For the complex $[NiL_3]Cl_2$, two exotherms are observed in the closed crucible and three in the open one; in this case, the very weak endothermic peak at 85 °C (-7 kJ mol^{-1}) can be attributed to vaporization associated with traces of ethanol.

The diagrams of the three mixtures show three endotherms: in the mixture of two L and one $NiCl_2$ it corresponds to the melting of L, slightly shifted to higher temperatures; in the mixture of four L with one $NiCl_2$, in an open crucible at 101 °C and in a closed one at 137 °C, in the 200–225 °C range, several exothermic peaks are observed in the $[CuCl_2L_2]$ and $[NiL_3]Cl_2$ diagrams.

It is noteworthy that $[CuCl_2L_2]$ exhibits an endothermic peak at 126 °C (closed) or 115 °C (open), which corresponds to the m.p. of Z-5-NO_2-FDH[17–19]. In addition,
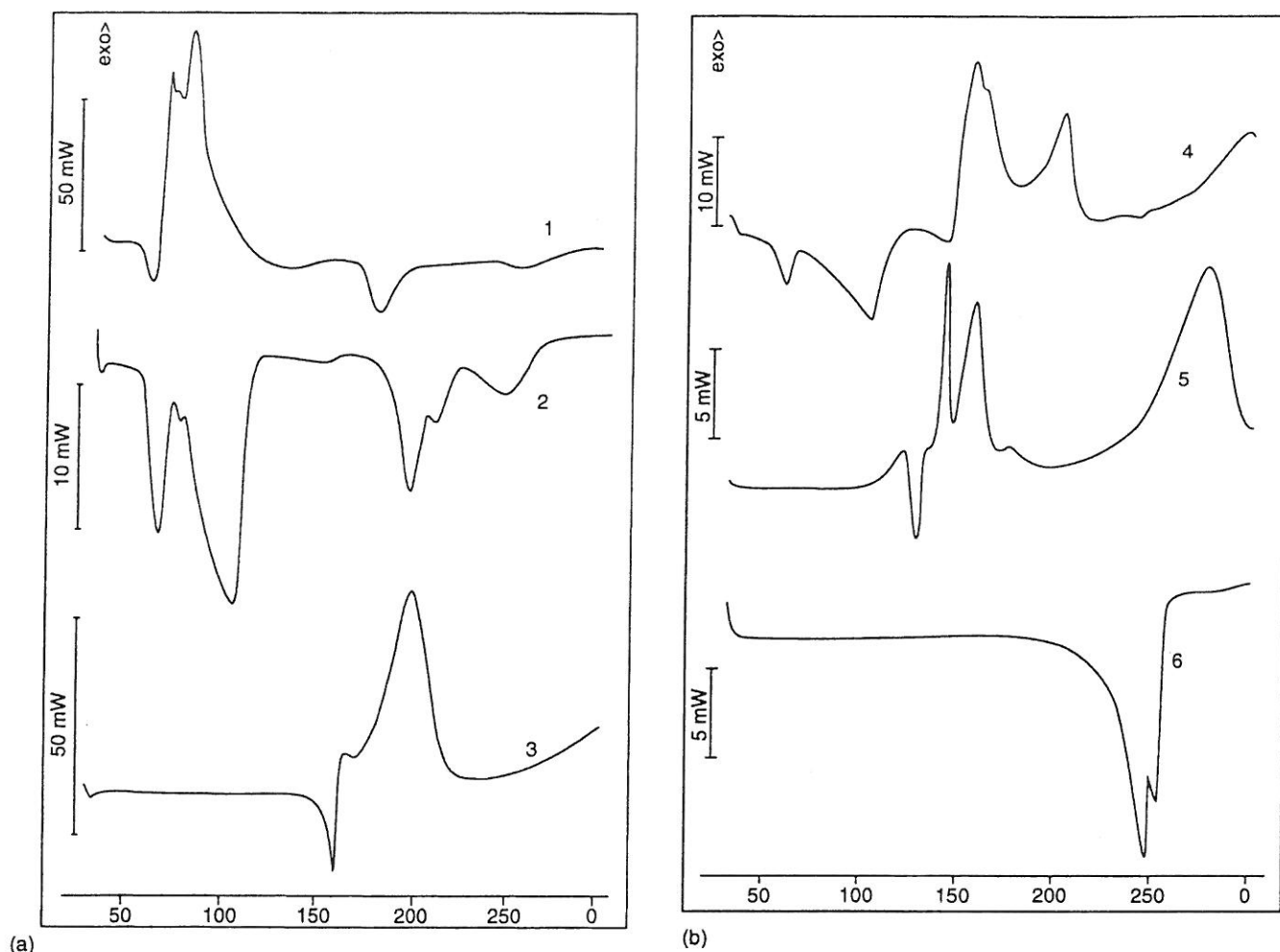
Figure 2. D.s.c. curves (c, closed crucible, o, open crucible). (a) 1, NiCl$_2$ o; 2, NiCl$_2$ c; 3, 5-NO$_2$-FDH c; (b) 4, 1NiCl$_2$ + 4 5-NO$_2$-FDH o; 5, [CuCl$_2$L$_2$] c; 6, [NiCl$_2$(M5FDH)$_4$] o.

there is an exotherm at 157 °C (closed) and 163 °C (open) instead of the expected endotherm, and ΔH remains of the same magnitude (*ca.* −70 kJ mol^{-1}). The [CuBr$_2$L$_2$] complex exhibits only exothermic peaks even at the temperature of the m.p.s. of the two isomers of the ligand.

The numerous exothermic peaks with various molar enthalpies (from −10 to −900 kJ mol^{-1}) derive from reactions between the ligand and the metallic halide and/or the decomposition of the oxime moiety as indicated by the invariable exothermic peak at 200–205 °C in the 5-NO$_2$-FDH diagram. Moreover, we believe that no reaction occurs between the nitro group or the nitrogen oxides formed and the remaining functional groups of the ligands; this is because of the absence of modification of ligand diagrams when passing from closed to open crucibles. The results obtained with the physical mixtures of Ni^{2+} with various proportions of the ligand suggest that no reaction occurs between the ligand and the Cu^{2+}, Ni^{2+} or Co^{2+} ions, or chloride and bromide. However, we cannot exclude oxidative decomposition of the complexes as described in Bucci *et al.*[25] in the case of pyridine–aldoxime copper(II) complexes. In these species, decomposition proceeds in two steps: the first is the loss of the organic ligands (exothermic) and the second, with various exotherms in a dioxygen atmosphere and some

small endotherms under dynamic dinitrogen, attributed to the oxidative decomposition of the stable intermediates obtained in the first step. Finally, the [NiCl$_2$(M5FDH)$_4$] complex shows completely different behaviour: it is very stable up to 240 °C. In the open crucible, the first endotherm (36 kJ mol^{-1}) could be attributed to the melting of the species, whereas in a closed crucible an exothermic reaction is observed.

The cobalt(II) complexes are slightly different. The [CoBr$_2$L$_2$] compound is very stable up to 210 °C irrespective to the recording conditions (Table 4). On the other hand, [CoBr$_2$L$_4$] is less stable and behaves identically in both closed and open crucibles, except that a small exotherm at 103 °C of low enthalpy (−21 kJ mol^{-1}) is formed in a closed capsule. In this compound, the first exotherm can be attributed to the loss of two ligands before oxidizing decomposition of the ligand at *ca.* 265 °C. Similar reaction enthalpy values have been observed for cobalt(II) complexes with toluidines[22]. In addition, the [CoCl$_2$(FDH)$_2$] complex in an open crucible leads to an endotherm at 181 °C (+91 kJ mol^{-1}) and an exotherm at 205 °C (−330 kJ mol^{-1})[23], without any peak corresponding to the m.p.s. of the two isomers of the ligand[24]. This behaviour is not comparable with those of the cobalt[II] 5-NO$_2$-FDH complexes.

The d.s.c. diagrams show that there is a wide variety of behaviour for all the species when the temperature rises from ambient to 300 C. It is therefore possible to make two general observations: (1) the diagrams of the complexes differ from those of the mixtures in the same ratio because of the formation of the coordination bonds; (2) the 5-NO₂-FDH ligand does not react like other 5-substituted 2-furfuraldoximes, *i.e.* M5FDH or 5-ethyl-2-furfuraldoxime (E5FDH).

Conclusions

We have prepared and structurally characterized six new complexes with 5-nitro-2-furfuraldoxime (L) and copper(II), nickel(II) and cobalt(II) chlorides and bromides. The analytical data and the i.r. and electronic spectra show clearly that the nitro group is not affected by chelation. The i.r. and electronic spectra show that: (1) the complexes belonging to $[ML_2X_2]$ and $[ML_4X_2]$ series are *trans* octahedral; (2) in this two series, 5-NO₂-FDH reacts like FDH, M5FDH and E5FDH, and coordinates through the same atoms.

In addition, it is possible to obtain the $[ML_3]X_2$ complex with nickel(II) chloride only. In this case, the ligand is bidentate through the O-ring and O-oxime atoms and the chloride ions are not in the inner coordination sphere of the Ni^{2+} ion.

Further study of the d.s.c. diagrams from ambient to 300 C shows the absence of reactivity by the nitro group, but the decomposition, probably through oxidizing pathways, is different according to the nature of the central ion. The d.s.c. diagrams of the previously studied ligands, *e.g.* FDH, M5FDH or E5FDH, are different, indicating that the nitro group introduced in position 5 into the heterocycle induces different thermic behaviour.

Although methyl or ethyl groups introduced in position 5 in the furan ring do not modify the mode of coordination[1], the presence of a nitro group in the same position leads to some additional conclusions: it is possible to obtain the $[ML_3]X_2$ complex when L = 5-nitro-2-furfuraldoxime, and not 5-methyl- or 5-ethyl-2-furfuraldoxime, and the decomposition does not follow the same pathway. However, attemps to prepare $[NiCl_2L_2]$, $[CoCl_2L_2]$ or $[CoCl_2L_4]$ were unsuccessful.

On the other hand, the $[CuCl_2L_2]$ complex exhibits cytotoxic properties towards human cancer cell cultures and further experiments are now in progress[26].

Acknowledgements

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