JOM 23782

Bis(pentafluorophenyl) derivatives of nickel(II) with anionic bidentate Schiff base ligands

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(Received February 10, 1993)

Abstract

The hydroxo-complex $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ reacts with salicylaldehyde in a 1:2 molar ratio to give the mononuclear anionic derivative $[Ni(C_6F_5)_2(o\text{-}OC_6H_4CHO)]^-$. The coordinated salicylaldehydate does not react with amines but proton abstraction from the preformed salicylaldimines by the hydroxo-complex leads to the formation of the corresponding complexes $[Ni(C_6F_5)_2(o\text{-}R\text{-}N=CHC_6H_4O)]^-$ [R = CH_3, C_2H_5, $CH(CH_3)_2$, $CH_2C_6H_5$, C_6H_5, $p\text{-}ClC_6H_4$, $p\text{-}BrC_6H_4$, $o\text{-}CH_3C_6H_4$, $p\text{-}CH_3C_6H_4$, $o\text{-}CH_3OC_6H_4$, $p\text{-}CH_3OC_6H_4$, or [α-naphthyl]. All the complexes have been isolated as the $[N^nBu_4]^+$ salts and have been characterized by partial elemental analyses, conductance measurements, thermal analysis, and spectroscopic (IR, V-UV, and ^1H and ^{19}F NMR) methods.

1. Introduction

The syntheses of binuclear anionic complexes of general formula $[\{Ni(C_6F_5)_2\}(\mu\text{-}OH)\}_2]^{2-}$ [R = C_6F_5 (M = Ni [1,2], Pd [1,3], Pt [1,4]), 2,4,6-$C_6F_3H_2$ (M = Pd [5]), or C_6Cl_5 (M = Pd [6], Pt [4])] have been reported recently. Their use as precursors in synthetic work is based on the considerable nucleophility of the bridging OH groups. Thus these hydroxo-complexes react with protic acids H(L–L) to give mono- or bi-nuclear anionic species [2–6] depending on the exo- or endo-bidentate nature of the deprotonated acid, $(L\text{–}L)^-$. Mononuclear neutral complexes have been obtained by reaction of the hydroxo-complex with a neutral donor in the presence of acid [4,5], and deprotonation of amines or alcohols by the hydroxo-complex in the presence of carbon disulfide leads to the corresponding dithiocarbamato- or xanthato-complexes respectively [7].

Salicylaldiminatonickel(II) complexes have been extensively studied and thoroughly reviewed [8–10]. Following our systematic study of the reactivity of hydroxo-complexes of the nickel group elements, we have now investigated the reactions of $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ with salicylaldehyde ($o\text{-}HOC_6H_4CHO$) and a number of salicylaldimines ($RNCHC_6H_4OH$).

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2. Experimental

2.1. Instrumentation and starting materials

C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyser. IR spectra were recorded on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. NMR data were recorded on a Bruker AC 200E (^1H) or a Varian Unity 300 (^{19}F) spectrometer. Conductance measurements were performed with a Crison 525 conductimeter (solvent acetone; $c \approx 10^{-3}$ mol l^{-1}). The electronic spectra were recorded on a Hitachi 2000U spectrometer. Thermal-analysis studies were carried out on a Mettler TA-3000 system provided with a Mettler TG-50 thermobalance and DSC-20 differential scanning calorimeter. The TG and DSC curves were obtained at a heating rate of 5°C min^{-1} in a current of air (100 ml min^{-1}) over the temperature range 20–700°C.

The *N*-arylsalicylaldimines were prepared as described in ref. 13 and ethanol solutions of *N*-alkylsalicylaldimines were prepared through addition of the amine to a solution of salicylaldehyde in ethanol. The complex $[N^nBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$ was prepared as described elsewhere [7] and all the solvents were dried by literature methods before use.

2.2. Preparation of the complexes

$[N^nBu_4][Ni(C_6F_5)_2(o\text{-}OC_6H_4CHO)]$ (I). 24.2 μl (0.231 mmol) of salicylaldehyde (C_6H_4OHCHO) were

0022-328X/93/$6.00

added to a solution of $[N^nBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.15 g, 0.115 mmol) in dichloromethane (5 ml). After stirring at room temperature for 30 min, the solution was concentrated under reduced pressure to half the original volume, and hexane was slowly added to precipitate an orange solid, which was filtered off, washed with hexane and air-dried.

$[N^nBu_4][Ni(C_6F_5)_2(o\text{-}RN{=}CHC_6H_4O)]$ [R = CH_3 (**II**), C_2H_5 (**III**), $CH(CH_3)_2$ (**IV**), or $C_6H_5CH_2$ (**V**)]

In separate experiments, ethanolic solutions containing the stoichiometric amount (0.23 mmol) of the corresponding *N*-alkylsalicylaldimine (o-R–N=CH-C_6H_4OH) was added to a solution of $[N^nBu_4]_2$ $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.15 g, 0.115 mmol) in dichloromethane (5 ml). The solution was boiled under reflux for 15 min, then concentrated under reduced pressure until *ca.* one-fifth of the initial volume. Slow addition of hexane caused the precipitation of the title complexes, which were filtered off, washed with hexane and air-dried.

$(N^nBu_4)[Ni(C_6F_5)_2(o\text{-}ArN{=}CHC_6H_4O)]$ [Ar = C_6H_5 (**VI**), p-ClC_6H_4 (**VII**), p-BrC_6H_4 (**VIII**), o-MeC_6H_4 (**IX**), p-MeC_6H_4 (**X**), o-$MeOC_6H_4$ (**XI**), p-$MeOC_6H_4$ (**XII**), α-naphthyl (**XIII**). In separate experiments, *N*-arylsalicylaldimine (o-Ar–N=CH–C_6H_4OH) (0.23 mmol) was added to a solution of $[N^nBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$ (0.15 g, 0.115 mmol) in dichloromethane (5 ml). The solution was boiled under reflux for 1 h. Slow addition of hexane caused the precipitation of the complexes, which were filtered off and air-dried.

TABLE 1. Analytical data, yields and molar conductivities for the nickel complexes

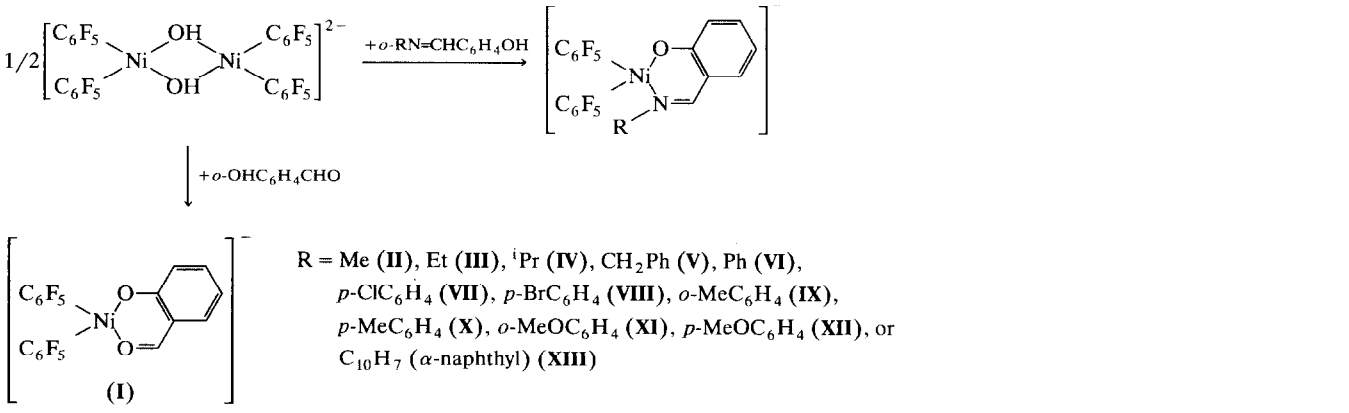
Compound	Yield (%)	Colour	Analysis [found(calc) %]			Λ_M[a]
			C	H	N	
I	71	Orange	55.3 (55.6)	5.9 (5.5)	2.1 (1.9)	99
II	64	Yellow	56.7 (56.2)	6.1 (5.7)	3.2 (3.6)	104
III	92	Yellow	55.9 (56.7)	6.0 (5.9)	3.2 (3.5)	105
IV	91	Yellow	57.1 (57.2)	6.4 (6.4)	3.4 (3.5)	101
V	65	Yellow	59.3 (59.6)	5.7 (5.7)	3.2 (3.3)	97
VI	89	Orange	59.4 (59.2)	6.0 (5.6)	3.2 (3.3)	107
VII	81	Yellow	56.9 (56.8)	5.6 (5.2)	2.4 (3.2)	98
VIII	90	Orange	54.0 (54.1)	5.1 (4.9)	2.9 (3.1)	97
IX	91	Yellow	59.4 (59.6)	6.1 (5.7)	3.4 (3.3)	105
X	85	Orange	59.3 (59.6)	6.0 (5.7)	2.9 (3.3)	108
XI	89	Orange	58.9 (58.5)	5.9 (5.6)	3.4 (3.2)	104
XII	86	Orange	58.2 (58.5)	6.0 (5.6)	2.9 (3.2)	108
XIII	80	Orange	60.5 (61.0)	5.7 (5.4)	2.9 (3.1)	97

[a] $Ohm^{-1}\ cm^2\ mol^{-1}$ (in acetone solution, $c \approx 10^{-3}$ M).

3. Results and discussion

The proton resonance at δ −5.7 for the OH bridges in $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ is consistent with its chemical reactivity towards protic acids [7]. In this way, when the hydroxo-nickel complex reacts with salicylaldehyde the corresponding bis(pentafluorophenyl)salicylaldehydatonickelate(II) (**I**) is obtained as the tetrabutylammonium salt (Scheme 1).

However, complex **I** does not react with amines to give the corresponding salicylaldiminate derivatives. These complexes are readily prepared by reaction of $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ with the preformed salicylaldimine. In every case the reaction was carried out in dichloromethane and the isolated complexes (**II–XIII**) are presented in Scheme 1. The acidic proton of the



Scheme 1. Preparation of the nickel complexes (isolated as NBu_4^+ salts).

TABLE 2. IR and V-UV data for the nickel complexes

Compound	Selected IR bands (cm^{-1})			V-UV spectra [a] ($\times 10^{-3}$ cm^{-1})
	ν(C=N)	ν(M–N)	ν(M–O)	
I	–	–	620	21.7
II	1600	465	580	22.5
		410		
III	1600	460	580	22.6
		400		
IV	1610	465	580	22.4
		400		
V	1610	495	565	22.2
		465		
VI	1600	545	520	21.4
	1575	460		
VII	1605	525	430	21.6
	1580	440		
VIII	1605	530	460	21.6
	1575	460		
IX	1605	495	540	21.8
	1585	460		
X	1600	500	530	21.7
	1580	460		
XI	1605	470	525	21.9
	1585	415		
XII	1600	500	525	21.5
	1580	455		
XIII	1595	505	540	21.6
	1580	470		

[a] In acetone solution.

salicylaldimine is abstracted by the hydroxo-complex, initiating the formation of the $(o\text{-R–N=CHC}_6\text{H}_4\text{O})^-$ ligand and providing the metal substrate [the $\text{Ni}(\text{C}_6\text{F}_5)_2$ moiety] which is trapped by the anionic ligand with the concomitant release of water to form the new nickel complexes. The individual yields and colours of the complexes are collected in Table 1.

The new bis(pentafluorophenyl)nickel(II) derivatives are air-stable solids and their acetone solutions exhibit conductance values (Table 1) corresponding to 1:1 electrolytes [13].

The IR spectra of the complexes show absorptions attributed to the C_6F_5 group [14] at *ca.* 1630m, 1490vs, 1050s and 950vs cm^{-1}, as well as a broad or split band at *ca.* 780 cm^{-1} for the so-called X-sensitive mode of C_6F_5, which is characteristic of the *cis*-$M(C_6F_5)_2$ fragment [15–17]. The spectra of *N*-alkylsalicylaldiminate complexes exhibit fewer bands than the spectra of the *N*-arylsalicylaldiminate complexes. This has been attributed [18] to less vibrational coupling in the *N*-alkylsalicylaldimines (conjugation of the heterocyclic ring with the phenyl ring of the *N*-aryl group will facilitate vibrational coupling in the *N*-aryl series). The C=N, Ni–O and Ni–N stretching modes have been tentatively assigned and they are shown in Table 2. All the

TABLE 3. ^{1}H and ^{19}F NMR data for the nickel complexes [a,b,c]

Compound	^{1}H δ/ppm ($SiMe_4$)	^{19}F δ/ppm ($CFCl_3$)
I	6.41 ($2H^{3,5}$)	−116.6 (d, br, $4F_o$)
	7.17 ($1H^4$)	−165.6 (t, $1F_p$, J_{mp} = 19 Hz)
	7.26 ($1H^6$)	−166.0 (t, $1F_p$, J_{mp} = 20 Hz)
	8.84 ($1H^\alpha$)	−167.9 (m, $4F_m$)
II	2.71 (3H, Me)	−115.1 (m, $2F_o$)
	6.29 ($1H^5$)	−116.4 (m, $2F_o$)
	6.35 ($1H^3$)	−166.6 (t, $1F_p$, J_{mp} = 18 Hz)
	6.96 ($1H^4$)	−167.2 (m, $1F_p + 4F_m$)
	7.04 ($1H^6$)	
	7.87 ($1H^\alpha$)	
III	1.05 (3H, Et)	−113.8 (m, $2F_o$)
	2.79 (2H, Et)	−116.4 (m, $2F_o$)
	6.28 ($1H^5$)	−166.7 (t, $1F_p$, J_{mp} = 18 Hz)
	6.33 ($1H^3$)	−167.4 (m, $1F_p + 4F_m$)
	6.95 ($1H^4$)	
	7.05 ($1H^6$)	
	7.87 ($1H^\alpha$)	
IV	1.08 (6H, ^{i}Pr)	−114.0 (m, $2F_o$)
	1.25 (1H, ^{i}Pr)	−116.9 (m, $2F_o$)
	6.28 ($1H^5$)	−165.8 (t, $1F_p$, J_{mp} = 18 Hz)
	6.32 ($1H^3$)	−167.1 ($2F_m$)
	6.94 ($1H^4$)	−167.3 (t, $1F_p$, J_{mp} = 19 Hz)
	7.11 ($1H^6$)	−167.9 ($2F_m$)
	7.96 ($1H^\alpha$)	
V	4.15 (2H, CH_2)	−114.1 (m, $2F_o$)
	6.30 ($1H^5$)	−116.4 (m, $2F_o$)
	6.37 ($1H^3$)	−166.0 (t, $1F_p$, J_{mp} = 18 Hz)
	6.99 ($1H^4$)	−167.4 ($1F_p + 4F_m$)
	7.10 (6H, Ph and H^6)	
	7.97 ($1H^\alpha$)	
VI	6.34 ($1H^5$)	−114.8 (m, $2F_o$)
	6.43 ($1H^3$)	−116.1 (m, $2F_o$)
	6.95 (5H, Ph)	−166.5 (t, $1F_p$, J_{mp} = 18 Hz)
	7.05 ($1H^4$)	−166.8 (t, $1F_p$, J_{mp} = 19 Hz)
	7.17 ($1H^6$)	−167.9 (m, $4F_m$)
	7.91 ($1H^\alpha$)	
VII	6.35 ($1H^5$)	−114.8 (m, $2F_o$)
	6.43 ($1H^3$)	−116.3 (m, $2F_o$)
	7.00 (4H, C_6H_4)	−166.4 (t, $1F_p$, J_{mp} = 18 Hz)
	7.06 ($1H^4$)	−166.8 (t, $1F_p$, J_{mp} = 18 Hz)
	7.17 ($1H^6$)	−167.7 (m, $4F_m$)
	7.93 ($1H^\alpha$)	
VIII	6.35 ($1H^5$)	−114.7 (m, $2F_o$)
	6.48 ($1H^3$)	−116.4 (m, $2F_o$)
	6.88 (2H, C_6H_4)	−166.1 (t, $1F_p$, J = 19 Hz)
	7.14 (4H, C_6H_4 and $H^{4,6}$)	−167.3 (m, $1F_p + 4F_m$)
	7.93 ($1H^\alpha$)	
IX	2.64 (3H, CH_3)	−113.2 (m, $1F_o$)
	6.34 ($1H^5$)	−114.8 (m, $1F_o$)
	6.51 ($1H^3$)	−116.0 (m, $1F_o$)
	6.78 (4H, C_6H_4)	−117.3 (m, $1F_o$)
	7.05 ($1H^4$)	−166.8 (t, $1F_p$, J_{mp} = 19 Hz)
	7.16 ($1H^6$)	−167.0 (t, $1F_p$, J_{mp} = 19 Hz)
	7.79 ($1H^\alpha$)	−167.9 (m, $4F_m$)

TABLE 3 (continued)

Compound	^1H δ/ppm ($SiMe_4$)	^{19}F δ/ppm ($CFCl_3$)
X	2.11 (3H, CH_3)	−115.0 (m, $2F_o$)
	6.34 ($1H^5$)	−116.5 (m, $2F_o$)
	6.42 ($1H^3$)	−167.0 (t, $1F_p$, J_{mp} = 20 Hz)
	6.80 (4H, C_6H_4)	−167.2 (t, $1F_p$, J_{mp} = 21 Hz)
	7.04 ($1H^4$)	−168.1 (m, $4F_m$)
	7.15 ($1H^6$)	
	8.89 ($1H^\alpha$)	
XI	3.75 (3H, OCH_3)	−113.5 (br, $1F_o$)
	6.32 ($1H^5$)	−115.2 (br, $1F_o$)
	6.42 ($1H^3$)	−116.1 (br, $2F_o$)
	6.57 (2H, C_6H_4)	−167.0 (t, $1F_p$, J = 20 Hz)
	6.87 (2H, C_6H_4)	−167.2 (t, $1F_p$, J = 20 Hz)
	7.04 ($1H^4$)	−168.2 (br, $2F_m$)
	7.11 ($1H^6$)	−168.7 (br, $2F_m$)
	7.78 ($1H^\alpha$)	
XII	3.62 (3H, OCH_3)	−114.7 (m, $2F_o$)
	6.33 ($1H^5$)	−116.1 (m, $2F_o$)
	6.42 ($1H^3$)	−167.2 (t, $1F_p$, J = 21 Hz)
	6.54 (2H, C_6H_4)	−168.0 (m, $1F_p + 4F_m$)
	6.84 (2H, C_6H_4)	
	7.04 ($1H^4$)	
	7.15 ($1H^6$)	
	7.90 ($1H^\alpha$)	
XIII	6.36 ($1H^5$)	−112.6 (m, $1F_o$)
	6.50 ($1H^3$)	−114.3 (m, $1F_o$)
	7.14 (4H, $C_{10}H_7$)	−115.7 (m, $1F_o$)
	7.41 (2H, $C_{10}H_7$)	−117.1 (m, $1F_o$)
	7.56 ($1H^4$)	−167.05 (pseudo q, $2F_p$) [d]
	7.64 ($1H^6$)	−167.8 (m, $1F_m$)
	7.98 ($1H^\alpha$)	−168.2 (m, $3F_m$)
	8.75 (1H, $C_{10}H_7$)	

[a] Solvent $(CD_3)_2CO$. [b] Additional peaks from $[N^nBu_4]^+$ are found at δ 3.6 (NCH_2), 1.9 (NCH_2CH_2), 1.5 (CH_2CH_3) and 0.9 (CH_3), with intensity ratio 2:2:2:3, respectively. [c] Abbreviations: br = broad, d = doublet, t = triplet, q = quartet, m = multiplet. [d] This signal consists of two overlapping triplets at δ −167.0 (t, $1F_p$, J = 22 Hz) and −167.1 (t, $1F_p$, J = 21 Hz).

complexes give an absorption band in their electronic spectra (Table 2), overlapping a charge-transfer band, which may be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in a square-planar ligand field [19].

The ^1H and ^{19}F NMR data of complexes **I–XIII** are collected in Table 3. The ^{19}F spectra of all the complexes are consistent with the presence of two nonequivalent C_6F_5 groups. Since each C_6F_5 ring should give three resonances with intensity ratio 2:1:2 ($2F_o$:$1F_p$:$2F_m$), the spectra would be expected to show six resonances arising from two freely rotating C_6F_5 groups. The spectrum of complex **IV** shows the expected six resonances but only four or five resonances are found in the spectra of complexes **I–III**, **V–VIII** and **X** because of the coincidence of some signals. Nevertheless complex **I** gives two signals in the *p*-fluorine region and two resonances are also observed in the *o*-fluorine region of the spectra of complexes **II**, **III**, **V–VIII**, **X** and **XII**, indicating the nonequivalence of the C_6F_5 rings.

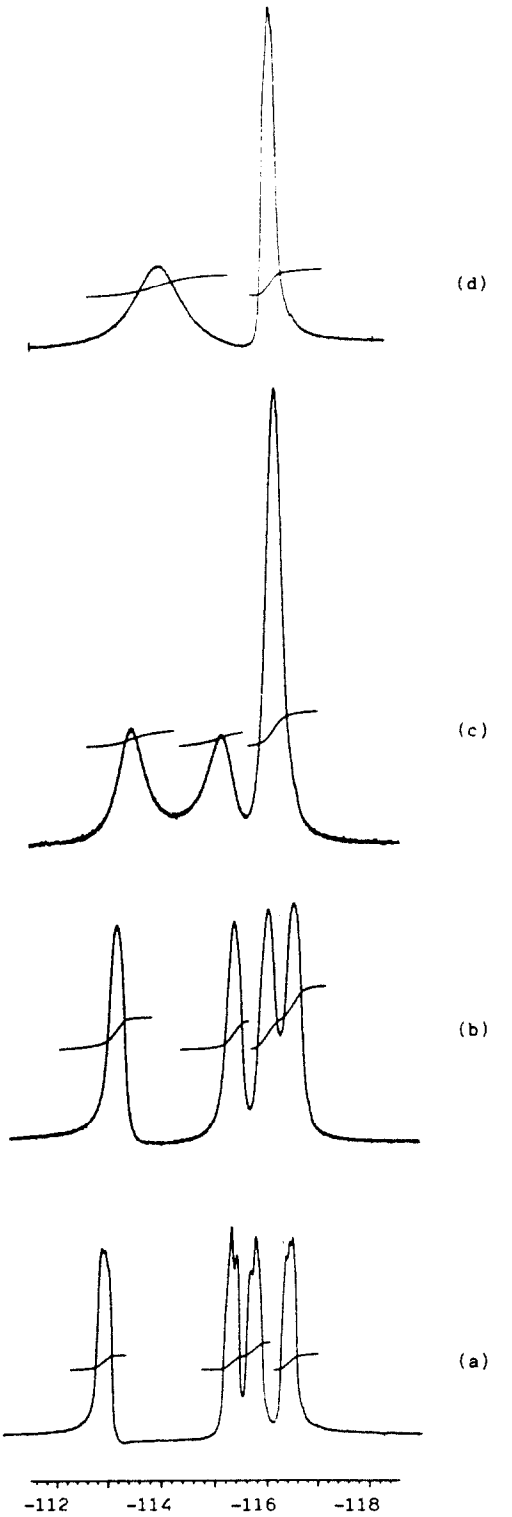


Fig. 1. ^{19}F NMR spectrum (*o*-fluorine region only) of complex **XI**: (a) at −20°C; (b) at 0°C; (c) 20°C; (d) 40°C (see text).

Because of inter-ring coupling, the *o*-fluorine resonances of these salicylaldiminate complexes do not show the characteristic low-field multiplet (or doublet if $J_{AX} \neq 0$, all the other coupling constants being zero) corresponding to an AA'MXX' ($F_oF'_oF_pF_mF'_m$) spin system; instead, an asymmetric, poorly resolved multiplet is found. The ^{19}F NMR spectra of complexes **IX** and **XIII** show the effect of frozen rotation of the *o*-tolyl and *α*-naphthyl substituents around the C–N bond and the resulting anisotropy produces four separate resonances (in the ratio 1:1:1:1) for the *o*-fluorines. Each *o*-fluorine gives a multiplet which is similar to those found in the spectra of all the other salicylaldiminate complexes.

TABLE 4. TG and DTG data for the nickel complexes in a flow of air

Compound	Step	Temperature range (°C)	DTG_{max} (°C)	Weight loss (%)
I	1	131–289	166	49.8
	2	289–462	409	35.0
	Residue	> 600	–	13.9
II	1	152–310	189	63.6
	2	310–493	403	25.4
	Residue	> 600	–	11.0
III	1	155–298	193	65.9
	2	303–466	406	24.1
	Residue	> 600	–	10.0
IV	1	142–306	178	59.1
	2	306–526	415	30.9
	Residue	> 600	–	10.0
V	1	155–311	195	58.3
	2	311–488	416	32.0
	Residue	> 600	–	9.7
VI	1	146–250	192	56.6
	2	250–478	409	34.7
	Residue	> 600	–	8.7
VII	1	149–310	195	55.0
	2	310–530	407	34.7
	Residue	> 600	–	10.3
VIII	1	149–307	191	54.0
	2	309–497	417	36.4
	Residue	> 600	–	9.6
IX	1	141–301	222	67.3
	2	302–443	396	24.4
	Residue	> 600	–	8.3
X	1	138–308	196	57.9
	2	308–494	401	31.2
	Residue	> 600	–	10.9
XI	1	153–315	187	62.3
	2	315–468	403	29.8
	Residue	> 600	–	7.9
XII	1	145–322	199	59.5
	2	322–460	389	32.5
	Residue	> 600	–	8.0
XIII	1	173–304	224	50.3
	2	304–470	415	37.9
	Residue	> 600	–	11.8

TABLE 5. DSC data for the nickel complexes in flowing air

Compound	Temperature range (°C)	DSC peak (°C)	Enthalpy change	Enthalpy change (kJ mol^{-1})
I	85–130	122	endo	27.1
	139–225	163	exo	
	297–513	474	exo	
II	97–115	108	endo	29.7
	157–217	183	exo	
	270–552	406	exo	
III	122–158	152	endo	32.4
	158–198	183	exo	
	309–530	475	exo	
IV	105–134	126	endo	28.2
	144–215	176	exo	
	239–537	464	exo	
V	106–120	114	endo	24.6
	158–216	189	exo	
	251–522	447	exo	
VI	107–129	123	endo	32.9
	173–217	188	exo	
	270–508	461	exo	
VII	89–108	101	endo	28.8
	166–253	187	exo	
	299–582	501	exo	
VIII	162–217	186	exo	
	257–579	509	exo	
IX	156–171	164	endo	38.8
	193–533	459	exo	
X	81–129	112	endo	31.9
	161–218	186	exo	
	284–529	446	exo	
XI	134–150	143	endo	30.2
	154–222	179	exo	
	300–524	459	exo	
XII	80–106	99	endo	28.4
	159–219	186	exo	
	280–546	449	exo	
XIII	216–267	230	exo	
	270–542	497	exo	

The ^{19}F NMR spectrum of complex **XI** at room temperature shows three broad 1:1:2 resonances in the *o*-fluorine region, suggesting that the methoxo-group slows down the "free" rotation of the *o*-$MeOC_6H_4$ substituent. Figure 1 shows the ^{19}F NMR spectra of complex **XI** as a function of temperature. At low temperature, the rotation is sufficiently sluggish to make the *o*-fluorine atoms distinguishable by their different chemical shifts and four 1:1:1:1 resonances are observed. As the temperature is raised, the signals broaden (as required by the Uncertainty Principle) and coalescence of the two closest resonances (which may be assigned to the C_6F_5 *trans* to N) is observed at 20°C. The two more separated resonances coalesce at 40°C, and a time-averaged signal only is seen for the two *o*-fluorine atoms of each C_6F_5 ring. Sharp signals were not obtained because the acetone solution could not be heated above 40°C. So, for conditions of slow

exchange (−20°C) the behaviour of complex **XI** is similar to that of **IX** and **XIII** and for fast exchange (40°C) the spectrum appears to be essentially similar to those of all the other salicylaldiminate complexes. At 20°C an intermediate behaviour is observed.

The thermogravimetric (TG and DTG) and differential scanning calorimetry (DSC) data for the nickel complexes are presented in Tables 4 and 5, respectively. The TG curves in an air flow exhibit a two-stage decomposition pattern, but the thermal decomposition is not simple and stable intermediate products were not found. In all the complexes, the final pyrolysis product corresponds to nickel(II) oxide. The DSC curves (also in a current of air) show one endothermic peak due to melting of the sample and two exothermic peaks due to simultaneous decomposition and combustion of the evolved gas. The values of the melting enthalpies, calculated by integration of DSC endothermic peaks, are listed in Table 5.

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