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Five-coordinate β-ketoiminate derivatives of the (N_3-macrocycle)nickel(II) fragment (N_3-macrocycle = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene and its 9-methyl derivative)

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Abstract—The hydroxo complexes $[\{Ni(N_3\text{-macrocycle})(\mu\text{-OH})\}_2](ClO_4)_2$ (N_3-macrocycle = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (N_3-mc) and 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene (9-Me-N_3-mc)) react with the appropriate β-ketoimine to give five-coordinate nickel(II) complexes of the type $[Ni(N_3\text{-macrocycle})(C_6H_5COCHC(NR)CH_3)](ClO_4)$. The complexes have been studied by spectroscopic (IR, UV–vis, ^1H NMR and NOE) and thermal methods. An X-ray diffraction study carried out with the complex $[Ni(9\text{-Me-}N_3\text{-mc})\{C_6H_5COCHC(NC_6H_5)CH_3\}](ClO_4)$ has established that the Ni atom presents a square pyramidal coordination and is displaced 0.325(1) Å out of the basal plane towards the apical N1 atom. © 1997 Elsevier Science Ltd

Since the first reports on the syntheses of binuclear anionic hydroxo complexes of general formula $[\{MR_2(\mu\text{-OH})\}_2]^{2-}$ (M = Ni, Pd, Pt; R = C_6F_5, $C_6F_3H_2$, C_6Cl_5) [1–6], these compounds have been widely used as precursors for the preparation of mono- or binuclear anionic species depending on the exo-or endo- bidentated nature of the reacting deprotonated acid used [2–11]. Mononuclear neutral complexes have been prepared by reaction of the hydroxo complex with neutral ligands in the presence of acid [4], and dithiocarbamate or xanthate derivatives have been prepared by deprotonation of amines or alcohols in the presence of carbon disulfide by the hydroxocomplex [8]. Following our systematic study of the reactivity of hydroxo complexes of the nickel group elements towards protic ligands, we have now investigated the reactivity of non-organometallic hydroxo nickel complexes such as $[(N_3\text{-mc})Ni(\mu\text{-OH})_2Ni(N_3\text{-mc})]^{2+}$ (N_3-mc = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene) containing pentacoordinate nickel [12] towards protic O-N ligands. The N_3-cyclic triamine is known to form very stable octahedral complexes with the three nitrogen atoms occupying exclusively facial positions [13,14]. Nickel complexes with the above N_3-cyclic triamine have been reported and the properties of penta- and hexacoordinate derivatives have been documented [12,15,16].

In a previous paper, the reactivity of the binuclear hydroxocomplexes $[\{Ni(N_3\text{-macrocycle})(\mu\text{-OH})\}_2](ClO_4)_2$ towards aryl salicylaldimines o-RN = CHC_6H_4OH were discussed and new five-coordinate complexes of Ni^{II} were characterized [17]. In this paper we present the synthesis and characterization of five-coordinate β-ketoiminate complexes containing the (N_3-macrocycle)Ni(II) fragment.

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EXPERIMENTAL

C, H and N analyses were carried out with a microanalyzer Carlo Erba. IR spectra were recorded on a Perkin–Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. The NMR spectra of acetone-d_6 solutions were recorded on a Bruker model AC 200E (standard $SiMe_4$) or a Varian Unity 300 spectrometer. Conductivities (solvent acetone; $c \approx 5 \times 10^{-4}$ mol l^{-1}) were measured with a Crison 525 conductimeter. The electronic spectra (in acetone) were recorded on a Hitachi 2000 V spectrophotometer. Thermal-analysis studies were carried out on a Mettler TA-3000 system provided with a Mettler TG-50 thermobalance. The TG 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 30–600°C.

The complexes $[Ni(N_3\text{-mc})(\mu\text{-OH})]_2(ClO_4)_2$ (N_3-mc = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene) and $[Ni(9\text{-Me-}N_3\text{-mc})(\mu\text{-OH})]_2(ClO_4)_2$ (9-Me-N_3-mc = 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene) were synthesized by the general method of Curtis [12,16,18]. The β-ketoimines were prepared by condensation of the corresponding primary amine with benzoylacetone [19]. The solvents were all dried before use.

Preparation of the complexes

$[Ni(N_3\text{-macrocycle})(C_6H_5COCHC(NR)CH_3)](ClO_4)$ (N_3-macrocycle = N_3-mc; R = C_6H_5, **1**, 4′-$CH_3C_6H_4$, **2**, 4′-$OCH_3C_6H_4$, **3**, 2′-$CH_3C_6H_4$, **4**, 2′-$OCH_3C_6H_4$, **5**; N_3-macrocycle = 9-Me-N_3-mc; R = C_6H_5, **6**, 4′-$CH_3C_6H_4$, **7**, 4′-$OCH_3C_6H_4$, **8**, 2′-$CH_3C_6H_4$, **9**, 2′-$OCH_3C_6H_4$, **10**). In separate experiments, the corresponding β-ketoimine [$C_6H_5COHCHC(NR)CH_3$; 0.300 mmol] was added to a solution of $[Ni(N_3\text{-macrocycle})(\mu\text{-OH})]_2(ClO_4)_2$ (0.150 mmol) in methanol (20 ml). On stirring at room temperature for 1 h, a green solid precipitated which was filtered off and air-dried. The individual yields are listed in Table 1.

Green crystals of complex **6** suitable for X-ray diffraction were grown by slow vapor diffusion of hexane into a dichloromethane solution at room temperature.

Crystal structure determination

A crystal of complex **6** (approximate dimensions 0.53 × 0.26 × 0.17 mm) was selected for the X-ray experiment and glued on the extreme of a glass capillary. Once centered in an Enraf Nonius CAD4 diffractometer, 25 reflections were randomly searched around $\theta = 18°$. Indexing led to a monoclinic cell. Unscaled structural factors were obtained after Lorentz, polarization and absorption corrections (max and min absorption correction factors were 0.9999 and 0.9588), which were applied using MolEN package [20]. The crystallographic data are shown in Table 2. The structure was solved by Patterson methods using SHELX-86 [21]. Refinement was carried out using SHELX-93 least-squares program [22]. Non H-atoms were refined anisotropically and H-atoms were located by difference Fourier synthesis and refined isotropically. The perchlorate anion was refined as two rotationally disordered groups with partial occupation factors of 0.57(2) and 0.43(2). Final agreement factor was $R = 0.045$ ($Rw = 0.0977$ for 8957 observed reflections with $F_o > 3\sigma(F_o)$. The largest shift at the last cycle was 0.78. The maximum and minimum residual Fourier peaks were 0.34 and −0.27 e/Å^3. Additional material deposited with the Cambridge Crystallographic Data Centre comprises tables of atomic fractional coordinates, anisotropic thermal parameters, bond distances and bond angles.

RESULTS AND DISCUSSIONS

In a similar way to that previously reported for the salicylaldiminate derivatives [9,17], the acid-base reaction between $[\{Ni(N_3\text{-macrocycle})(\mu\text{-OH})\}_2]^{2+}$ and the corresponding ketoimine leads to the formation of the new ketoiminate complexes. The isolated nickel(II) compounds (**1–10**) are presented in Scheme 1. Their individual yields and analytical data are collected in Table 1. The new ketoiminate derivatives are air-stable solids and their acetone solutions exhibit conductance values (Table 1) corresponding to 1 : 1 electrolytes [23].

The Ni(II) derivatives show in their IR spectra (Table 3) the absorptions attributed to the β-ketoiminate ligand: ν(C=N) 1585–1575 cm^{-1}, ν(C=O) 1555–1550 cm^{-1} and ν(C=C) 1510–1490 cm^{-1}. These assignments are in agreement with previous results [24]. It should be noted however that in the pseudo aromatic chelate ring, both the C=O and the C=N bonds would be expected to have partial double bond character and factors such a delocalization may have an effect upon the stretching frequency and so the conjugated bonded carbonyl, the C=C and C=N vibrations might all be expected at wavenumbers lower than 1600 cm^{-1}. The spectra also exhibit two bands in the ranges 3265–3245 cm^{-1} and 1630–1625 cm^{-1} respectively assigned to ν(N—H) and ν(C=N) of the coordinated macrocycle. The characteristic absorptions of the perchlorate anion appear at 1090 and 620 cm^{-1}.

The electronic spectra (Table 3) of complexes **1–10** in acetone solution show an absorption in the range of 16,560–17,560 cm^{-1} which is in agreement with previous results for similar pentacoordinate nickel(II) complexes [17]. The expected band at *ca* 26,000 cm^{-1} for pentacoordinate nickel(II) complexes could not be observed in the spectra because of the presence of a very intense charge-transfer absorption in this spectral region. These results suggest that the complexes do

Table 1. Yields, analytical data and conductivity values for the nickel complexes

Complex		Yield (%)	Analysis (%)[a] C	H	N	Λ_M[b]
$[Ni(C_{12}H_{25}N_3)\{C_6H_5COCHC(NC_6H_5)CH_3\}]ClO_4$	**1**	75	55.9 (55.5)	6.8 (6.5)	9.4 (9.2)	136
$[Ni(C_{12}H_{25}N_3)\{C_6H_5COCHC(NC_6H_4CH_3\text{-}4')CH_3\}]ClO_4$	**2**	80	55.7 (56.0)	7.3 (7.0)	9.1 (9.0)	135
$[Ni(C_{12}H_{25}N_3)\{C_6H_5COCHC(NC_6H_4OCH_3\text{-}4')CH_3\}]ClO_4$	**3**	75	54.2 (54.7)	6.7 (6.5)	9.0 (8.8)	129
$[Ni(C_{12}H_{25}N_3)\{C_6H_5COCHC(NC_6H_4CH_3\text{-}2')CH_3\}]ClO_4$	**4**	85	56.1 (56.0)	6.8 (7.0)	8.9 (9.0)	117
$[Ni(C_{12}H_{25}N_3)\{C_6H_5COCHC(NC_6H_4OCH_3\text{-}2')CH_3\}]ClO_4$	**5**	70	54.3 (54.7)	7.0 (6.5)	9.0 (8.8)	138
$[Ni(C_{13}H_{27}N_3)\{C_6H_5COCHC(NC_6H_5)CH_3\}]ClO_4$	**6**	70	56.2 (56.2)	6.4 (6.6)	8.8 (9.0)	144
$[Ni(C_{13}H_{27}N_3)\{C_6H_5COCHC(NC_6H_5CH_3\text{-}4')CH_3\}]ClO_4$	**7**	70	56.0 (56.6)	7.5 (7.1)	8.7 (8.8)	134
$[Ni(C_{13}H_{27}N_3)\{C_6H_5COCHC(NC_6H_5OCH_3\text{-}4')CH_3\}]ClO_4$	**8**	80	55.0 (55.4)	7.2 (6.6)	8.5 (8.6)	128
$[Ni(C_{13}H_{27}N_3)\{C_6H_5COCHC(NC_6H_4CH_3\text{-}2')CH_3\}]ClO_4$	**9**	80	56.2 (56.6)	7.9 (7.1)	8.9 (8.8)	115
$[Ni(C_{13}H_{27}N_3)\{C_6H_5COCHC(NC_6H_4OCH_3\text{-}2')CH_3\}]ClO_4$	**10**	75	55.2 (55.4)	6.7 (6.6)	8.6 (8.6)	142

[a] Calculated values in parentheses.
[b] $\Omega^{-1}\ cm^2\ mol^{-1}$

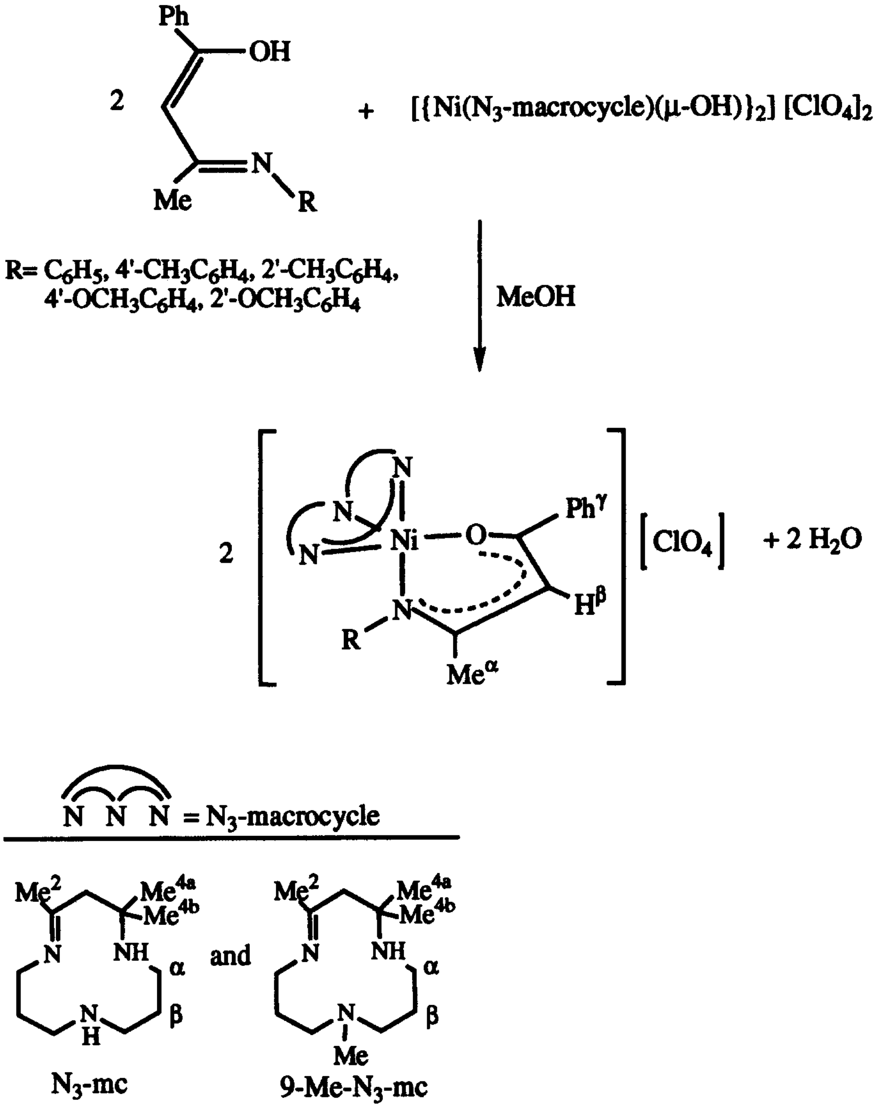
Table 2. Crystallographic data for $[Ni(9\text{-}Me\text{-}N_3\text{-}mc)(C_6H_5COCH(NC_6H_5)CH_3)](ClO_4)$ (**6**)

Formula	$C_{29}H_{41}ClN_4NiO_5$
Formula weight	619.82
Temperature (K)	293
Space group	$P2_1/c$
a (Å)	9.687(3)
b (Å)	20.054(3)
c (Å)	15.042(3)
β (°)	91.56(2)
V (Å^3)	2921.0(12)
Z	4
λ (Mo-Kα) (Å)	0.71069
D_{cal} (g cm^{-3})	1.41
μ (Mo-Kα) (cm^{-1})	8.01
Absorption correction	empirical ψ-scan
Scan method	ω–2θ
Independent reflections	8501 (R_{int} = 0.0282)
Reflections collected	8957
h, k, l	0–13, 0–28, ±21
R^a (I > 2σ(I))	0.0450
$wR2^b$	0.0977
W	$1/[\sigma^2(F_o)+(0.056F_o^2)^2]$

[a] $R = \Sigma|F_o\text{-}F_c|/\Sigma F_o$.
[b] $wR2 = \Sigma w\,(F_o^2\text{-}F_c^2)/\Sigma wF_o^2$.

not acquire a solvent molecule in solution and keep the five-coordinate geometry.

The ^{1}H NMR data for complexes **1**–**10** are collected in Tables 4 and 5. The resonance line pattern observed for the macrocycle ligands can be reasonably assigned on the basis of the considerations used in previous studies of nickel(II) macrocyclic complexes [17]. The α-methylen and β-methylen protons shift downfield and upfield respectively from the diamagnetic position. Equatorial protons are expected to experience larger contact shifts than axial protons and therefore the most downfield resonances are due to α-CH_{eq} and the most upfield ones to β-CH_{eq}. The assignment of the signals from the methyl groups of the macrocycles (Me^2) and the β-ketoimines (α-Me) could be accomplished by NOE (nuclear Overhauser effect) measurements. Figure 1 shows the NOE difference spectra of complex **1** and the relevant spectrum taken with off-resonance irradiation. The irradiation of the 3′ and 5′ protons resonance at 93.9 ppm yields negative NOEs at −10.5 ppm, the signal assigned to the α-Me of the β-ketoamine ligand. The β-H of these ligands shifts more upfield (< −40 ppm) than the β-CH_2 of the macrocycles (≈ −23 ppm). The resonances of N-phenyl ring protons could be assigned on the



Scheme 1. Reaction scheme and proton labelling.

Table 3. IR and UV–vis data for nickel complexes

Complexes	Relevant IR bands (cm^{-1})					UV–vis spectra[a] ($\times 10^{-3}$ cm^{-1})
	ν(N—H)[b]	ν(C═N)[b]	ν(C═N)	ν(C═O)[c]	ν(C═C)[c]	
1	3265[d]	1625	1580	1550	1500	17.39
2	3265[d]	1630	1580	1550	1495	16.86
3	3245[d]	1625	1575	1550	1490	17.01
4	3265[d]	1630	1580	1555	1500	17.04
5	3245[d]	1625	1585	1555	1570	17.44
6	3265	1625	1585	1550	1495	17.17
7	3265	1630	1580	1550	1495	17.10
8	3245	1625	1575	1550	1490	17.17
9	3265	1625	1585	1555	1500	16.56
10	3265	1625	1580	1555	1500	17.56

[a] In acetone solution.
[b] Macrocycle.
[c] Ketoiminate.
[d] With a shoulder.

Table 4. Chemical Shift Data (ppm) for the macrocycles mc-N_3 and 9-Me-mc-N_3

Complex	Hα								Hβ						Me [4a]	Me [4b]	Me [2]	NMe
1	364.0	336.5	306.2	144.1	97.0	61.9	42.8	37.7	−8.3	−11.9	−15.2	−17.1	−20.3	−23.3	27.2	10.8	−13.9	
2	358.0	335.2	304.5	144.3	96.3	61.9	48.5	37.3	−8.3	−12.3	−15.0	−16.7	−20.1	−23.2	27.2	10.8	−14.0	
3	341.2	333.7	301.1	143.7	96.0	61.2	43.8	38.1	−8.2	−11.9	−14.9	−16.7	−19.9	−23.0	27.1	10.8	−13.7	
4	340.0	332.2	304.2	147.0	98.0	65.0	55.3	37.3	−9.5	−15.6	−16.1	−16.7	−20.1	−22.8	26.9	10.5	−12.1	
															27.5		−14.2	
5	350.1	330.2	303.5	148.8	96.3	57.4	52.7	40.8	−11.2	−12.7	−13.8	−17.1	−19.6	−22.4	26.8	10.9	−13.2	
																	−15.5	
6	298.2	285.3	276.2	137.1	103.3	71.1	43.1	37.1	−4.1	−9.5	−10.4	−17.8	−20.1	−23.7	27.2	11.2	−14.7	124.9
7	302.0	284.5	276.5	137.3	103.4	70.9	45.1	36.2	−4.5	−9.5	−11.0	−17.8	−20.0	−23.6	27.2	11.1	−14.7	124.5
8	294.1	283.3	275.6	136.9	103.0	70.0	43.5	37.2	−4.1	−9.2	−10.5	−17.2	−19.9	−23.6	27.0	11.0	−14.5	122.9
9	299.5	283.5	275.8	135.5	99.3	72.3	66.2	36.7	−4.6	−8.2	−10.9	−17.1	−19.5	−22.6	27.1	11.0	−13.2	127.3
															26.3	10.8	−14.2	
10	297.7	284.5	141.6	120.1	103.2	70.1	65.4	37.6	−3.5	−10.2	−17.9	−19.8	−23.0	−23.8	27.0	11.1	−13.7	127.4
																10.7	−14.4	

Table 5. Chemical Shift Data (ppm) for the N-benzoylacetoiminate ligands

Complex	α-CH_3	β-H	γC_6H_5				2′6′-H	3′5′-H	4′-H
1	−10.5	−44.0	17.1	15.3	14.7	10.0	−2.0	93.9	−2.7
2	−10.5	−44.1	16.8	16.0	15.2	9.9	−2.0	93.6	14.6 (4′-CH_3)
3	−10.7	−43.9	16.0	14.9	14.7	9.9	−1.9	92.9	5.8 (4′-OCH_3)
4	−11.3	−43.5	16.1	15.9	15.3	11.2	−1.9 (6′H)	94.7 87.8	−2.9
	−10.9	−40.3					12.6 (2′-CH_3)		
5	−10.6	−44.5	16.0	15.6	14.5	9.2	−1.8 (6′H)	91.6 86.7	−2.4
	−10.4	−40.3					6.8 (2′-OCH_3)		
6	−12.1	−44.7	16.9	15.3	10.6		−2.3	92.3	−2.3 (overlap.)
7	−12.1	−44.5	16.6	15.4	15.2	10.6	−2.3	91.9	14.6 (4′-CH_3)
8	−12.4	−44.3	15.7	15.3	14.8	10.6	−2.4	91.6	5.8 (4′-OCH_3)
9	−12.7	−46.5	17.2	16.6	15.0	12.4	−2.2 (6′H)	92.5 88.9	−2.5
	−12.1	−40.6					15.6 (2′-CH_3)		
10	−12.6	−45.5	18.2	16.0	15.5	15.1	−2.1 (6′H)	99.3 92.7	−2.3
	−11.7	−40.8					6.1 (2′-OCH_3)		

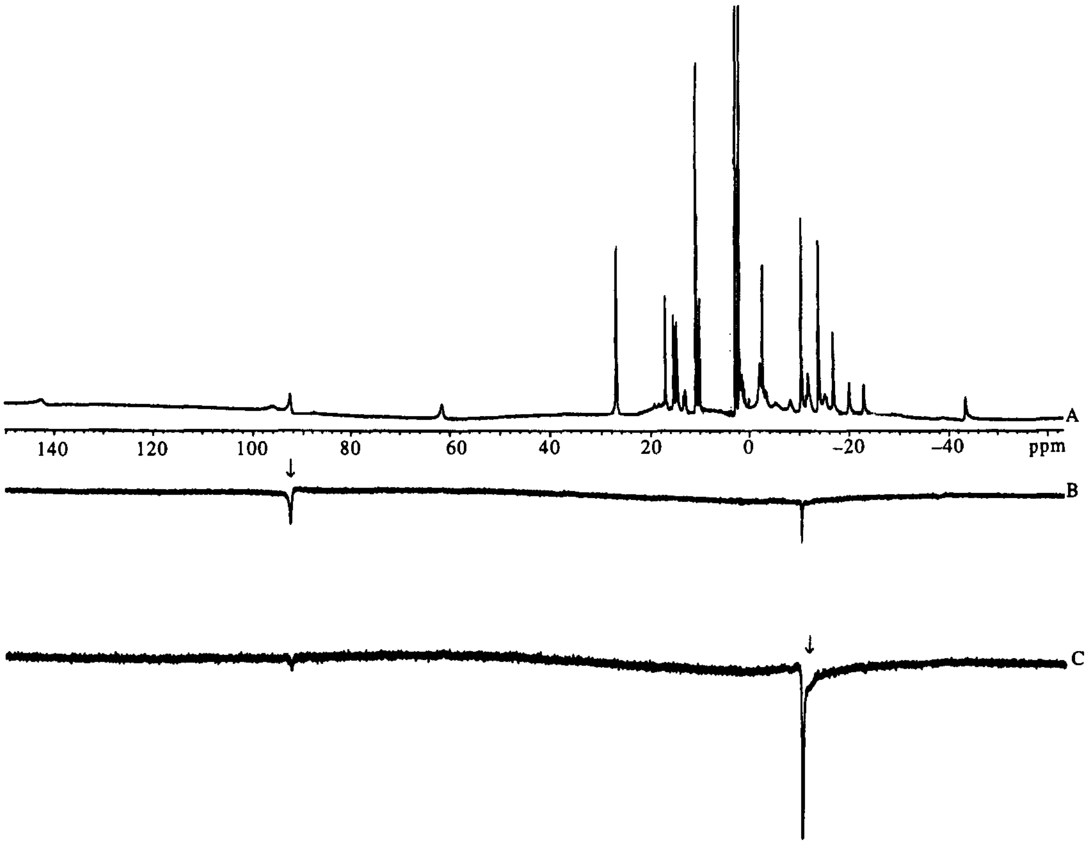


Fig. 1. (A) 300 MHz reference spectrum of complex **1** in d_6-acetone at 295 K. (B,C) Difference spectra generated by subtracting the reference spectrum from one in which the resonances indicated by arrows were presaturated.

Table 6. Selected bond distances (Å) and angles (°) for complex **6**

Ni—O(1′)	1.958(2)		
Ni—N(9)	2.052(2)		
Ni—N(1)	2.064(2)		
Ni—N(5)	2.129(2)		
Ni—N(5′)	2.065(2)		
O(1′)—Ni—N(9)	160.78(8)	N(1)—Ni—N(5′)	108.54(8)
O(1′)—Ni—N(1)	98.75(8)	O(1′)—Ni—N(5)	89.62(8)
N(9)—Ni—N(1)	97.04(8)	N(9)—Ni—N(5)	79.32(8)
O(1′)—Ni—N(5′)	89.63(7)	N(1)—Ni—N(5)	90.56(8)
N(9)—Ni—N(5′)	95.68(8)	N(5′)—Ni—N(5)	160.77(8)

Table 7. Thermal analysis data for the nickel complexes in a flow of air

Complex	Step	$T_i - T_f$ (°C)	DTG_{max} (°C)	Δm (%)	$\Delta m_{calc.}$ (%)
1	1	179–378	195	51.00	51.31
	2	389–478	448	38.60	39.00
	residue	>600		8.00	
2	1	177–353	195	50.47	50.15
	2	397–489	409	40.10	40.38
	residue	>600		4.54	
3	1	175–361	191	48.15	48.88
	2	393–478	458	42.12	41.88
	residue	>600		4.82	
4	1	177–367	193	49.43	50.15
	2	371–485	437	40.47	40.38
	residue	>600		9.45	
5	1	175–407	207	48.59	48.88
	2	427–499	468	40.76	41.88
	residue	>600		9.89	
6	1	212–388	228	52.19	52.41
	2	412–459	429	37.76	38.12
	residue	>600		4.48	
7	1	201–399	221	50.21	51.25
	2	399–492	455	40.28	39.49
	residue	>600		7.95	
8	1	206–389	219	50.21	49.98
	2	389–477	448	39.29	40.98
	residue	>600		8.47	
9	1	201–390	211	51.25	51.25
	2	413–488	459	39.59	39.49
	residue	>600		7.45	
10	1	206–399	223	50.31	49.98
	2	403–498	462	39.49	40.98
	residue	>600		8.59	

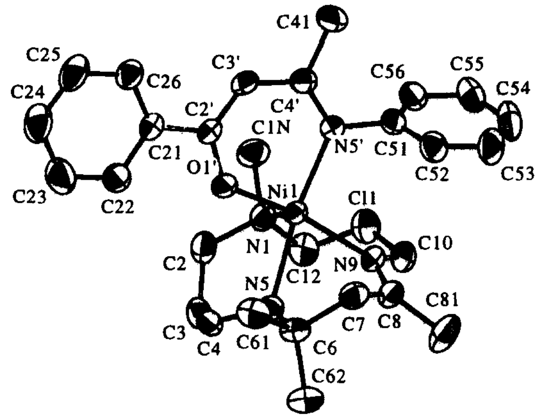


Fig. 2. An ORTEP drawing of the [Ni(9-Me-N_3-mc)(C_6H_5COCHC(NC_6H_5)CH_3)]$^+$ cation.

basis of methyl or methoxy substitution at position 4′ or 2′. In these cases a new methyl or methoxy resonance is present (see Table 5). It is also clear the absence in the spectra of complexes **2, 3, 7, 8** and **4, 5, 9, 10,** of the signal from these ring protons which have been substituted. The shift direction alternation of the N-phenyl protons is characteristic when the π-contact shift is dominant. However the resonances of γ-phenyl ring farther to the nickel atom have the smaller shift. All the resonances of the γ-phenyl ring are downfield to TMS in accordance with a dominant σ-delocalization pattern of spin density consistent with the ground state of Ni^{II}; therefore the unpaired electrons could polarize the net spin density in the d_π orbitals. In the spectra of the 2′-Me (**4, 9**) and 2′-OMe derivatives (**5, 10**) two resonances for α-Me and β-H from the β-ketoimine ligand and for Me [4b] and Me^2 from the macrocycle can be observed (see Tables 4 and 5). This could be due to slowdown of the 'free' rotation around the C—N bond which should cause two distinguishable isomers at the NMR time scale. A similar behaviour has been reported elsewhere [9].

Figure 2 shows an ORTEP drawing of the [Ni(9-Me-N_3-mc)(C_6H_5COCHC(NC_6H_5)CH_3)]$^+$ cation. The nickel atom is pentacoordinated with a square pyramid arrangement of the chelating atoms. The three nitrogen atoms of the N_3- macrocycle occupy the apical position and two adjacent equatorial ones, whereas the other two positions correspond to the β-ketoiminate group. Some selected bond distances and angles referring to the coordination polyhedron are included in Table 6. The nickel atom is 0.325(1) Å out of the basal plane (N5-N9-N5′-O1′, rmsd = 0.023) towards atom N(1). This plane is nearly coplanar [2.4(1)° to the O(1′)-C(2′)-C(3′)-C(4′)-N(5′) mean plane (rmsd 0.020)]. Phenyl rings form, with this last plane, dihedral angles of 6.7(2)° (C(21) → C(26), rmsd 0.005) and 69.6(8)° (C(51) → C(56), rmsd 0.008). The shortest contact between the cation complex and the perchlorate anion is C(12)—H(12)···OA(3) (2.486 Å).

The thermogravimetric data for the compounds **1**–**10** are presented in Table 7. The TG curves exhibit an interesting two-stage decomposition pattern. The first stage is in the range 175–378°C for **1**–**5** and 201–399°C for **6**–**10**. In this stage one mol of the macrocycle and one mol of perchlorate are evolved. The next stage ranges from 370–489°C for **1-5** and from 389–492°C for **6**–**10** and is attributed to evolution of one mol of the β-ketoimine ligand.

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