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# Synthesis and spectroscopic characterization of five-coordinate complexes of $Ni^{2+}$ based on $N_3$-macrocycles and salicylaldiminates. Crystal structure of $[Ni(9\text{-}Me\text{-}N_3\text{-}mc)(OC_6H_4CH{=}NC_6H_5\text{-}o)](ClO_4)$ ($9\text{-}Me\text{-}N_3\text{-}mc = 2,4,4,9$-tetramethyl-1,5,9-triazacyclododec-1-ene)

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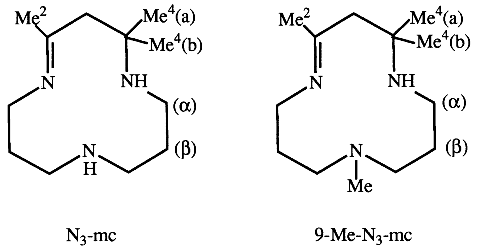
## Abstract

Five-coordinate nickel(II) complexes of the type $[Ni(N_3\text{-macrocycle})(OC_6H_4CH{=}NR\text{-}o)]^+$ ($N_3$-macrocycle = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, $N_3$-mc, or its 9-methyl derivative, 9-Me-$N_3$-mc) have been prepared by reaction between $[\{Ni(N_3\text{-macrocycle})(\mu\text{-}OH)\}_2]^+$ and the appropriate arylsalicylaldimine. An X-ray diffraction study carried out with the complex $[Ni(9\text{-}Me\text{-}N_3\text{-}mc)(OC_6H_4CH{=}NC_6H_5\text{-}o)](ClO_4)$ has established that the Ni atom presents a square pyramidal coordination and is displaced 0.30 Å out of the basal plane towards the apical N1 atom ($a = 8.552(2)$, $b = 33.398(3)$, $c = 9.630(3)$ Å, $\beta = 91.67(1)°$, monoclinic, space group $P2_1/a$, $V = 2749(1)$ Å$^3$, $Z = 4$, $D_{calc} = 1.40$ g cm$^{-3}$, $R = 0.058$, $R_w = 0.066$). These paramagnetic species have been studied by $^1$H NMR. The characteristic pattern of $N_3$-mc and 9-Me-$N_3$-mc has been established and the specific assigment of salicylaldimine resonances has been achieved by NOE measurements. The solution electronic spectra of the complexes are also suggestive of five-coordinate geometry in solution.

*Keywords:* Nickel complexes; Pentacoordinate complexes; Macrocycle complexes; Crystal structures

## 1. Introduction

The hydroxo nickel complex $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ has been used for synthetic work [1]; for example, it reacts with protic electrophiles to give complexes of the types $[\{Ni(C_6F_5)_2(\mu\text{-}X)\}_2]^{2-}$ and $[Ni(C_6F_5)_2(\mu\text{-}XY)]^-$, where X is a uninegative monodentate or exobidentate ligand and XY is a uninegative endobidentate ligand [1–6]. The nickel complex $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ is also an efficient basic catalyst in the cyclotrimerization of malononitrile [7]. Following our investigations in this field, we have now focused on the reactivity of non-organometallic hydroxo nickel complexes such as $[(N_3\text{-}mc)Ni(\mu\text{-}OH)_2Ni(N_3\text{-}mc)]^{2+}$ containing pentacoordinate nickel [8]. The properties of nickel complexes with cyclic triamines [12]-ane$N_3$ are well documented and penta- and hexacoordinate environments of the metal have been reported [8–10]. The macrocycles 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene and its 9-methyl derivative ($N_3$-mc and 9-Me-$N_3$-mc in Scheme 1) are two interesting chelating ligands from which are known hydroxo complexes formulated as $[\{M(N_3\text{-}mc)(\mu\text{-}OH)\}_2]^{2+}$ (M = Cu, Ni or Co) [8,11]. The aqueous solution equilibria of nickel(II), copper(II) and zinc(II) complexes with $N_3$-mc and other related macrocyclic ligands have also been investigated potentiometrically and spectrophotometrically and their acid dissociation constants were determined [10]. The syntheses of the 3,5-ditertbutyl-1,2-semiquinonate



Scheme 1.

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(DTBSQ) and tetrachlorocatecholate (TCCat) adducts $[M(N_3\text{-mc})(DTBSQ)]ClO_4$ and $[M(N_3\text{-mc})(TCCat)]$ $(M = Ni^{2+}, Cu^{2+})$ have been reported [12], and their magnetic properties have been correlated with the catalytic role of the metal ion in the oxidative processes of aromatic substrates. However few crystal structures of $Ni(N_3\text{-mc})$ complexes containing other bonding ligands to $Ni^{2+}$ have been determined by X-ray diffraction.

Our aim is to describe the synthesis, the spectroscopic study and the crystal structure of pentacoordinate nickel complexes $[Ni(N_3\text{-macrocycle})(N\text{-}O)]^+$ ($N_3$-macrocycle = $N_3$-mc or 9-Me-$N_3$-mc; N-O = an *N*-arylsalicylaldiminate) from the reaction between $[\{Ni(N_3\text{-macrocycle})(\mu\text{-}OH)\}_2]^{2+}$ and the corresponding *N*-arylsalicylaldimine.

## 2. Experimental

### 2.1. Materials and physical measurements

The complexes $[Ni(N_3\text{-mc})(\mu\text{-}OH)]_2(ClO_4)_2$ and $[Ni(9\text{-}Me\text{-}N_3\text{-mc})(\mu\text{-}OH)]_2(ClO_4)_2$ were synthesized by the general method of Curtis and co-workers [8], modified by Renfrew et al. [10]. The *N*-arylsalicylaldimines were prepared as described elsewhere [13] and all the solvents were dried by literature methods before use.

C, H and N analyses were carried out with a microanalyzer (Carlo Erba) and nickel was determined using an inductive coupled plasma spectrometer ICP (model Jovin-Yvon). 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 Brucker model AC 200E (standard $SiMe_4$) or a Varian Unity 300 spectrometer. Conductivities (solvent acetone; $c \approx 5 \times 10^{-4}$ mol dm$^{-3}$) were measured with a Crison 525 conductimeter. The electronic spectra (in acetone) were recorded on a Hitachi 2000V spectrophotometer.

### 2.2. Preparation of the complexes

$[Ni(N_3\text{-macrocyle})(o\text{-}RN{=}CHC_6H_4O)](ClO_4)$ ($N_3$-macrocycle = $N_3$-mc; R = $C_6H_5$ (**1**), 2,4,6-$Cl_3C_6H_2$ (**2**), 4-$ClC_6H_4$ (**3**), 4-$CH_3C_6H_4$ (**4**), 4-$OCH_3C_6H_4$ (**5**), 2-$CH_3C_6H_4$ (**6**), 2-$OCH_3C_6H_4$ (**7**); $N_3$-macrocycle = 9-Me-$N_3$-mc; R = $C_6H_5$ (**8**), 2,4,6-$Cl_3C_6H_2$ (**9**), 4-$ClC_6H_4$ (**10**), 4-$CH_3C_6H_4$ (**11**), 4-$OCH_3C_6H_4$ (**12**), 2-$CH_3C_6H_4$ (**13**), 2-$OCH_3C_6H_4$ (**14**)). In separate experiments *N*-arylsalicylaldimine ($o$-RN=$CHC_6H_4OH$) was added to a solution of $[Ni(N_3\text{-macrocycle})(\mu\text{-}OH)]_2(ClO_4)_2$ in methanol. On stirring at room temperature for 1 h a greenish solid precipitated which was filtered off and air-dried. Yields 65–90%. Green crystals of complex **8** were grown by slow vapor diffusion of hexane into a dichloromethane solution at room temperature.

Table 1
Crystallographic data for $[Ni(9\text{-}Me\text{-}N_3\text{-mc})(OC_6H_4CH{=}NC_6H_5\text{-}o)]$-$(ClO_4)$ (**8**)

| | |
|---|---|
| Formula | $C_{26}H_{37}ClN_4NiO_5$ |
| Formula weight | 579.8 |
| Temperature (K) | 294 |
| Space group | $P2_1/a$ |
| $a$ (Å) | 8.552(2) |
| $b$ (Å) | 33.398(3) |
| $c$ (Å) | 9.630(3) |
| $\beta$ (°) | 91.67(1) |
| $V$ (Å$^3$) | 2749(1) |
| $Z$ | 4 |
| $\lambda$(Mo K$\alpha$) (Å) | 0.71069 |
| $D_{calc}$ (g cm$^{-3}$) | 1.40 |
| $\mu$(Mo K$\alpha$) (cm$^{-1}$) | 8.5 |
| Absorption correction | empirical $\psi$-scan |
| Scan method | $\omega$–$2\theta$ |
| Reflections measured | 4164 ($R_{int} = 0.042$) |
| Reflections observed ($F_o > 3\sigma(F_o)$) | 2675 |
| $h, k, l$ | $\pm 9$, 0–37, 0–10 |
| $R$ [a] | 0.058 |
| $R_w$ [b] | 0.066 |
| $w$ | $1/[\sigma^2(F_o) + 0.02261 F_o^2]$ |

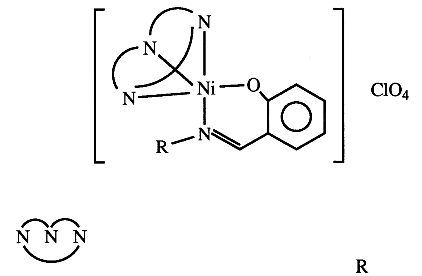
[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$.
[b] $R_w = \Sigma w|F_o - F_c|/\Sigma w F_o$.

### 2.3. X-ray data and crystal structure determination

A crystal of complex **8** (approximate dimensions 0.49 × 0.24 × 0.09 mm) was selected for the X-ray experiment and glued on the extreme of a glass capillary. Once centered in an Enraf-Nonius CAD4 diffractrometer, 25 reflections were randomly searched around $\theta = 18°$. Indexing leads to a monoclinic cell. Unscaled structural factors were obtained after Lorentz and polarization effects using the MoIEN package. The crystallographic data are shown in Table 1. See also Section 4. The structure was solved by direct methods using MULTAN 11/80 [14] and subsequent weighted Fourier syntheses both included in the MoIEN program package. Refinement was carried out using the SHELX-76 least-squares program [15]. Non-H atoms were refined anisotropically and H atoms were located by difference Fourier synthesis and refined isotropically. Final agreement factor was $R = 0.058$ ($R_w = 0.066$) for 2675 observed reflections with $F_o > 3\sigma(F_o)$. The largest shift at the last cycle was 0.61. The maximum and minimum residual Fourier peaks were 0.48(9) and −0.26(9) e Å$^{-3}$.

## 3. Results and discussion

The hydroxo complex $[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]^{2-}$ was previously used in the preparation of *N*-arylsalicylaldiminates [4]. The basic $[Ni(N_3\text{-mc})(\mu\text{-}OH)]_2(ClO_4)_2$ reacts with $o$-RN=$CHC_6H_4OH$ to yield the corresponding *N*-arylsalicylaldiminate complexes, according to Eq. (1). The resulting complexes (**1–14**) are presented in Scheme 2.



| | R |
|---|---|
| $N_3$-mc | $C_6H_5$ **1**, 2,4,6-$Cl_3C_6H_2$ **2**, 4-$ClC_6H_4$ **3**, 4-$CH_3C_6H_4$ **4**, 4-$OCH_3C_6H_4$ **5**, 2-$CH_3C_6H_4$ **6**, 2-$OCH_3C_6H_4$ **7** |
| 9-Me-$N_3$-mc | $C_6H_5$ **8**, 2,4,6-$Cl_3C_6H_2$ **9**, 4-$ClC_6H_4$ **10**, 4-$CH_3C_6H_4$ **11**, 4-$OCH_3C_6H_4$ **12**, 2-$CH_3C_6H_4$ **13**, 2-$OCH_3C_6H_4$ **14** |

Scheme 2.

$$
\begin{aligned}
&[\{\mathrm{Ni}(\mathrm{N_3\text{-}macrocycle})(\mu\text{-}\mathrm{OH})\}_2](\mathrm{ClO_4})_2 + 2o \\
&\quad -\mathrm{RN{=}CHC_6H_4OH} \\
&\quad \rightarrow 2[\mathrm{Ni}(\mathrm{N_3\text{-}macrocycle})(\mathrm{OC_6H_4CH{=}NR\text{-}}o)](\mathrm{ClO_4}) \\
&\quad + 2\mathrm{H_2O} \qquad (1)
\end{aligned}
$$

Analytical and conductance data are listed in Table 2. In acetone solution complexes **1**–**14** behave as 1:1 electrolytes [16], which is in agreement with the proposed formulae.

### 3.1. IR

The IR spectra (Table 2) of the $N_3$-mc derivatives **1**–**7** show two bands in the range 3270–3220 $cm^{-1}$ assigned to $\nu$(NH) and those of the 9-Me-$N_3$-mc derivatives **8**–**14** show only one band in the range 3280–3240 $cm^{-1}$. But all of them show a sharp band at 1635–1620 $cm^{-1}$ assigned to $\nu$(C=N) of the coordinated macrocycle. The IR spectra of the hydroxo complexes $[Ni(N_3\text{-mc})(\mu\text{-OH})]_2(ClO_4)_2$ reported by Curtis and co-workers [8] and $[Ni(9\text{-Me-}N_3\text{-mc})(\mu\text{-OH})]_2(ClO_4)_2$ prepared by Escuer et al. [11] showed the $\nu$(OH) band at ≈3600 $cm^{-1}$ which is absent in the spectra of the new *N*-arylsalicylaldiminate derivatives, but these complexes show a strong band at 1600–1610 $cm^{-1}$ due to $\nu$(C=N) of the *N*-arylsalicylaldiminate ligand. Strong bands at 1100 and 620 $cm^{-1}$ are assigned to the perchlorate anion.

### 3.2. Vis–UV

The electronic spectra (Table 2) of complexes **1**–**14** in acetone solution show an absorption in the range 16 300–17 300 $cm^{-1}$ which is in agreement with previous results for similar pentacoordinate nickel(II) complexes [11,17]. We suggest that in solution the complexes keep the five-coordinate geometry and therefore do not acquire a solvent molecule. Other intense bands at 25 300–27 700 $cm^{-1}$ are attributed to charge-transfer bands.

Table 2
Analytical and physical data for the nickel complexes

| Complex | Anal. Found (Calc.) (%) | | | | $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$) | $\nu$(N–H)$_{mc}$ ($cm^{-1}$) | $\nu$(C=N)$_{mc}$ | $\nu$(C=N)$_b$ | Vis–UV ($10^3$ $cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | Ni | C | H | N | | | | | |
| **1** | 10.3<br>(10.6) | 53.1<br>(52.8) | 6.2<br>(6.5) | 9.9<br>(9.8) | 128 | 3250<br>3230 | 1620 | 1600 | 17.1 |
| **2** | 8.3<br>(8.3) | 44.8<br>(44.9) | 4.8<br>(5.1) | 8.8<br>(8.6) | 129 | 3270<br>3250 | 1620 | 1600 | 16.6 |
| **3** | 9.8<br>(9.4) | 50.0<br>(50.3) | 5.6<br>(5.7) | 9.3<br>(9.1) | 124 | 3265<br>3250 | 1625 | 1600 | 17.3 |
| **4** | 10.1<br>(10.2) | 53.8<br>(53.5) | 6.4<br>(6.7) | 9.7<br>(9.7) | 126 | 3250<br>3230 | 1620 | 1600 | 17.1 |
| **5** | 9.8<br>(9.6) | 52.4<br>(52.8) | 6.3<br>(6.5) | 9.4<br>(9.3) | 128 | 3240<br>3220 | 1620 | 1600 | 17.2 |
| **6** | 10.1<br>(9.8) | 53.9<br>(54.1) | 6.4<br>(6.5) | 9.7<br>(9.5) | 131 | 3250<br>3230 | 1620 | 1600 | 16.9 |
| **7** | 9.8<br>(9.6) | 52.4<br>(52.0) | 6.3<br>(6.6) | 9.4<br>(9.7) | 142 | 3260<br>3240 | 1620 | 1600 | 17.2 |
| **8** | 10.1<br>(9.8) | 53.8<br>(53.7) | 6.4<br>(6.7) | 9.6<br>(9.6) | 137 | 3250 | 1620 | 1600 | 17.1 |
| **9** | 8.6<br>(8.3) | 45.7<br>(45.6) | 5.0<br>(5.1) | 8.2<br>(8.1) | 123 | 3260 | 1620 | 1610 | 17.1 |
| **10** | 9.5<br>(9.5) | 50.8<br>(51.0) | 5.9<br>(6.1) | 9.1<br>(9.4) | 125 | 3270 | 1625 | 1600 | 16.9 |
| **11** | 9.8<br>(9.9) | 54.6<br>(54.3) | 6.6<br>(6.8) | 9.4<br>(9.3) | 127 | 3260 | 1620 | 1600 | 17.2 |
| **12** | 9.6<br>(9.8) | 53.1<br>(53.4) | 6.4<br>(6.6) | 9.2<br>(9.5) | 123 | 3240 | 1620 | 1600 | 17.1 |
| **13** | 9.8<br>(9.5) | 54.6<br>(54.5) | 6.6<br>(6.6) | 9.4<br>(9.2) | 119 | 3280 | 1635 | 1610 | 16.3 |
| **14** | 9.6<br>(9.4) | 53.1<br>(52.9) | 6.4<br>(6.6) | 9.2<br>(9.0) | 134 | 3260 | 1620 | 1600 | 17.0 |

Table 3
Chemical shift data (ppm) for the macrocycles $N_3$-mc and 9-Me-$N_3$-mc

| Complex | Hα | | | | | | | | Hβ | | | | | | Me$^{4a}$ | Me$^{4b}$ | Me$^2$ | NMe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 368.0 | 347.1 | 327.2 | 311.1 | 139.6 | 50.8 | 43.8 | 41.4 | −8.1 | −9.4 | −13.0 | −17.6 | −19.9 | −24.1 | 30.5 | 29.3 | −10.6 | |
| **2** | 358.8 | 346.7 | 337.5(2H) | | 143.2 | 48.8 | 46.3 | 41.8 | −2.7 | −5.9 | −12.8 | −17.2 | −19.5 | −23.3 | 32.5 | 29.7 | −7.8 | |
| **3** | 367.2 | 353.5 | 325.1 | 317.1 | 139.6 | 49.3 | 43.9 | 38.9 | −6.3 | −8.2 | −12.9 | −17.6 | −20.1 | −24.1 | 30.5 | 29.6 | −9.5 | |
| **4** | 359.5 | 347.6 | 326.9 | 310.3 | 139.3 | 50.4 | 43.4 | 40.0 | −7.9 | −9.2 | −12.8 | −17.4 | −19.7 | −23.9 | 30.1 | 29.2 | −10.5 | |
| **5** | 363.1 | 352.0 | 328.1 | 310.4 | 139.5 | 50.0 | 43.5 | 39.1 | −8.1 | −9.4 | −12.9 | −17.4 | −19.8 | −24.0 | 29.8 | 29.3 | −10.3 | |
| **6** | 344.4(2H) | 317.2 | 311.8 | | 141.5 | 53.9 | 44.5 | 39.6 | −6.9 | −8.1 | −10.3 | −17.1 | −19.3 | −23.9 | 32.3<br>30.5 | 29.1 | −11.1 | |
| **7** | 347.0 | 339.5 | 311.6(2H) | | 143.1 | 52.9 | 46.8 | 44.4 | −7.2 | −8.7 | −12.7 | −17.4 | −19.8 | −23.4 | 30.0<br>29.3 | 28.7 | −10.3 | |
| **8** | 322.5 | 304.9 | 285.4(2H) | | 133.4 | 61.1 | 43.6 | 39.7 | −6.6 | −7.2 | −12.3 | −17.5 | −19.2 | −24.5 | 32.6 | 29.4 | −11.6 | 121.7 |
| **9** | 319.0 | 312.5 | 299.2(2H) | | 156.7 | 88.5 | 78.5 | 58.0 | −2.9 | −4.9 | −10.6 | −17.3 | −21.1 | −25.3 | 33.3 | 28.3 | −8.3 | 131.4 |
| **10** | 319.9 | 308.3 | 286.9(2H) | | 134.2 | 59.7 | 43.3 | 39.4 | −6.6 | −7.3 | −12.3 | −17.2 | −19.4 | −24.5 | 32.7 | 29.5 | −10.7 | 122.8 |
| **11** | 323.1 | 303.5 | 282.6(2H) | | 134.2 | 60.8 | 43.7 | 39.8 | −6.6 | −7.3 | −12.3 | −17.6 | −19.2 | −24.6 | 32.3 | 29.2 | −11.7 | 120.7 |
| **12** | 323.4 | 303.6 | 285.6(2H) | | 133.9 | 60.3 | 43.1 | 38.5 | −6.6 | −7.3 | −12.3 | −17.5 | −19.2 | −24.6 | 32.1 | 29.3 | −11.4 | 120.4 |
| **13** | 333.2 | 306.2 | 285.6(2H) | | 137.9 | 62.7 | 56.2 | 43.8 | −6.0 | −7.7 | −11.7 | −13.9 | −17.4 | −23.2 | 33.4<br>32.4 | 28.8 | −10.1 | 123.4 |
| **14** | 335.7 | 306.2 | 285.2(2H) | | 138.1 | 63.4 | 57.1 | 43.7 | −6.0 | −7.0 | −12.3 | −18.0 | −19.0 | −24.6 | 32.6<br>32.2 | 28.8 | −11.3 | 118.6 |

### 3.3. $^1$H NMR

The $^1$H NMR data for all of the complexes investigated are collected in Tables 3 and 4. Resonance assignments have been made on the basis of relative intensities, linewidth analysis, methyl and chloro substitution and the consideration that the $\alpha$-methylenic protons shift downfield whereas the $\beta$-methylenic protons shift upfield with respect to the diamagnetic position probably because of spin polarization mechanisms [18,19]. The most downfield and the most upfield resonances are attributed to equatorial CH since the isotropic chemical shift has been found to have angular dependence [20].

The assignment of the signal from the ring proton at position 4′ of the phenyl ring of compounds **1** and **8** was clear from its absence in the spectra of complexes in which 4′-H is substituted by chlorine (**2**, **3**, **9**, **10**), Me (**4**, **11**) or OMe (**5**, **12**). In the last ones a new methyl or methoxy resonance is present (see Table 4). Similarly the assigments of the signals from the ring protons at positions 2′ and 6′ were

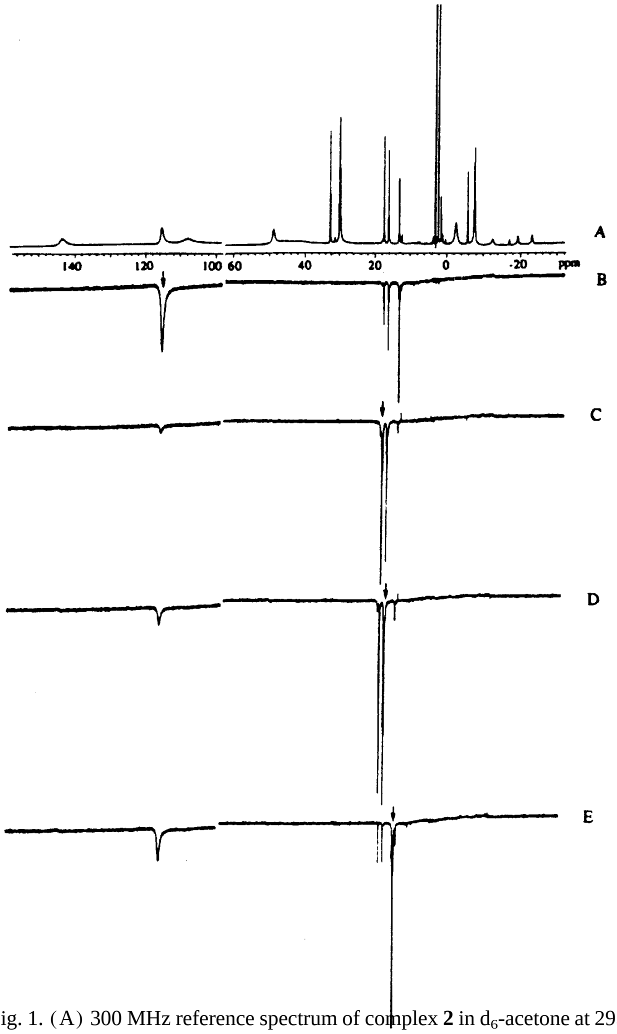


Fig. 1. (A) 300 MHz reference spectrum of complex **2** in $d_6$-acetone at 295 K. (B–E) Difference spectra generated by subtracting the reference spectrum from one in which the resonances indicated by arrows were presaturated.

readily identified by their absence in the spectra of complexes **2** and **9** in which they are substituted by chlorine. In the spectra of the 2′-Me (**6** and **13**) and 2′-OMe derivatives (**7** and **14**) the remaining 6′-H was slightly shifted and the resonances from 2′-Me and 2′-OMe were observed. The signal from the methine proton (CH=N) was not found in the spectral region studied, which is in agreement with previous observations [21].

The nuclear Overhauser effect (NOE) has been used to assign resonances in paramagnetic hemoproteins [22], a variety of metalloproteins [23] and nickel(II) thiaporphyrins [24]. The assignment of individual *N*-arylsalicylaldiminates resonances could be accomplished by NOE measurements because the narrow resonances of the complexes facilitated these experiments. The assignments for complexes **1**–**14** are presented in Table 4, and Fig. 1 shows the NOE difference spectra of complex **2** and the relevant spectrum taken with off-resonance irradiation. Irradiation of the resonance at 115.1 ppm (4-H) yields negative NOEs at 17.2 ppm (6-H), 15.9 ppm (5-H) and 12.8 ppm (3-H) (trace B). The reciprocal NOE connectivities of the 17.2, 15.9 and 12.8 ppm resonances are shown in traces C, D and E, respectively.

*Ortho*-methyl or metoxo substitution of the *N*-phenyl slows down the 'free' rotation of the $o$-Me-$C_6H_4$ substituent around the C–N bond and the resulting anisotropy produces two separate resonances for the proton 6, pseudotriplet structure of the proton 5 resonance and also two resonances for the methyl 4a bonded to N5 of the macrocycle *trans* to the C–N (N9′) bond (see Fig. 3 and Table 3). A similar behavior has been observed elsewhere [4].

### 3.4. Temperature dependence

Curie plots of 9-Me-mc-$N_3$ and $o$-PhN$=$CH$C_6H_4O^-$ proton resonances of complex **8** in acetone-$d_6$ solution are shown in Fig. 2. These plots illustrate the general tendency for the contact shifts to increase more rapidly at lower temperatures and exhibit a temperature dependence closely proportional to $T^{-1}$.

All the resonances of the salicylaldimine ring are downfield to TMS, this is in accordance with a dominant $\sigma$-delocalization pattern of spin density and is consistent with the ground state of Ni(II) which has two unpaired electrons in $\sigma$-symmetry orbitals ($d_{x^2-y^2}$, $d_{z^2}$). However the shift direction alternation of the *N*-phenyl protons is characteristic if the $\pi$-contact shift is dominant with the proton and methyl protons exhibiting shifts of opposite sign for *ortho* and *para* positions [25]. The net spin density in the $d_\pi$ orbitals could be polarized by the unpaired electrons in the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals via spin–orbit coupling. This mechanism can distribute spin density to the phenyl rings [24].

### 3.5. Crystal structure

The crystal of complex **8** consists of [Ni(9-Me-$N_3$-mc)($o$-PhN=CH$C_6H_4O$)]$^+$ cations and $ClO_4^-$ anions held together by electrostatic interactions. Fig. 3 shows an ORTEP perspective of the cation which includes the atom numbering scheme. Positional parameters are given in Table 5 and selected interatomic bond distances and angles in Table 6. The Ni atom appears in the structure as pentacoordinated and is bound to the three N atoms of the 9-Me-$N_3$-mc macrocycle and the N and O atoms of the salicylaldiminate group. The

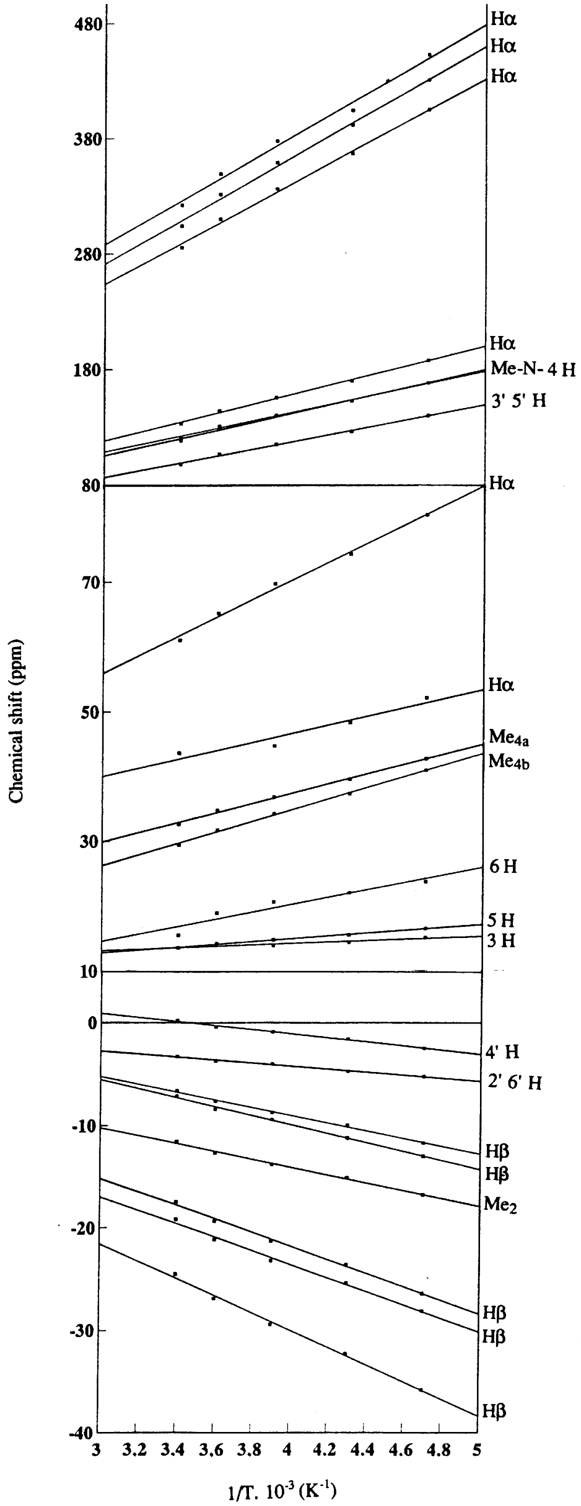
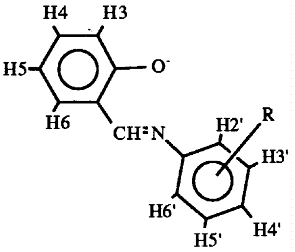


Fig. 2. Curie plot of proton resonances of complex **8**.

Table 4
Chemical shift data (ppm) for the *N*-arylsalicylaldiminate ligands



| Complex | H3 | H4 | H5 | H6 | H2′6′ | H3′5′ | H4′ |
|---|---|---|---|---|---|---|---|
| **1** | 13.0 | 109.8 | 14.1 | 16.2 | −3.2 | 102.6 | −0.1 |
| **2** | 12.8 | 115.1 | 15.9 | 17.2 | | 107.9 | |
| **3** | 14.2 | 112.3 | 16.5(2H) | | −3.2 | 103.1 | |
| **4** | 12.5 | 109.8 | 14.0 | 16.1 | −3.0 | 101.7 | 11.3($CH_3$) |
| **5** | 13.8 | 109.8 | 15.6 | 15.8 | −3.1 | 101.9 | 5.3($OCH_3$) |
| **6** | 12.8 | 104.8 | 13.6 [b] | 18.2 | −2.7(6′) | 104.6 | −0.6 |
| | | | | 17.5 | 15.5(2′-$CH_3$) | | |
| **7** | 10.9 | 107.4 | 13.5 | 18.9 | −2.7(6′) | 102.5 | −0.8 |
| | | | | 17.3 | 5.4(2′-$OCH_3$) | | |
| **8** | 13.6 | 118.6 | 13.6 | 15.5 | −3.3 | 98.1 | 0.2 |
| **9** | 12.4 | 126.8 | 15.3 | 21.1 | | 104.8 | |
| **10** | 13.6 | 120.5 | 15.5 | 15.9 | −3.5 | 98.3 | |
| **11** | 11.8 [a] | 118.4 | 13.4 | 15.3 | −3.4 | 97.2 | 11.8($CH_3$) |
| **12** | 13.3 | 118.7 | 13.3 | 14.9 | −3.4 | 97.8 | 5.6($OCH_3$) |
| **13** | 13.0 | 115.6 | 13.7 [b] | 17.5 | −3.1(6′) | 109.9 | −0.2 |
| | | | | 16.9 | 14.4(2′-$CH_3$) | | |
| **14** | 12.6 | 113.6 | 13.4 [b] | 17.6 | −3.1(6′) | 98.2 | −0.7 |
| | | | | 17.3 | 5.7(2′-$OCH_3$) | | |

[a] Overlapped by 4′-$CH_3$.
[b] Pseudotriplet.

coordination of the Ni atom is square pyramidal with the basal plane formed by O1′, N5, N9 and N9′ (Table 6). The r.m.s.d. of the plane is 0.02 Å. The Ni atom is 0.30 Å out of this plane towards the apical N1 atom. In the structure the perchlorate anion does not appear to be hydrogen bonded.

The three nitrogen donors of the macrocycle ligand occupy facial coordinative sites with the imine chelate ring in the basal plane of the square pyramid. In contrast with [Ni($N_3$-mc)]$(NCS)_2$ where the Ni–$N_3$-mc distances are not significantly different (2.04 Å, mean) [8], in complex **8** there are two Ni–N distances (Ni–N9 = 2.040(6) Å, Ni–N1 = 2.053(6) Å) shorter than the other (Ni–N5 = 2.123(6) Å). These bond lengths are similar to those found in [Ni($N_3$-mc)(TCSQ)(TCQ)] (TCSQ = tetrachlorosemiquinone, TCQ = tetrachloro-1,2-benzoquinone) [17], however the nickel–aldiminate nitrogen distance (Ni–N9′ = 2.082(6) Å) is intermediate.

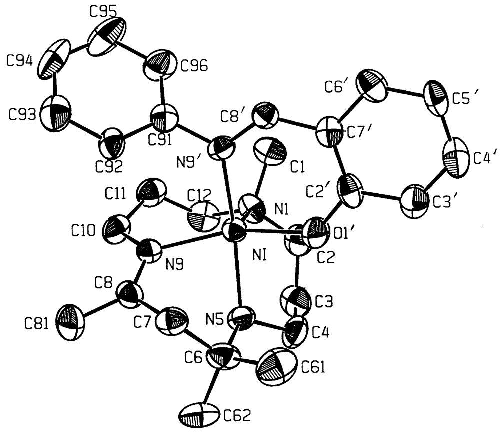


Fig. 3. An ORTEP drawing of the [Ni(9-Me-$N_3$-mc)($OC_6H_4CH{=}NC_6H_5$-*o*)$]^+$ cation.

## 4. Supplementary material

Additional material available from the Cambridge Crystallographic Data Centre comprises tables of anisotropic thermal parameters, bond distances, bond angles, and observed and calculated structure factors.

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Table 5
Atomic parameters for complex **8** with estimated standard deviations (e.s.d.s) in parentheses

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Ni | 0.0738(1) | 0.13311(3) | 0.77181(9) | 2.51(2) |
| O1′ | 0.0550(7) | 0.1860(2) | 0.6875(6) | 4.0(1) |
| C2′ | −0.0240(9) | 0.1974(2) | 0.5791(8) | 3.2(2) |
| C3′ | 0.000(1) | 0.2363(3) | 0.5250(9) | 4.1(2) |
| C4′ | −0.075(1) | 0.2500(3) | 0.4102(9) | 4.6(2) |
| C5′ | −0.183(1) | 0.2261(2) | 0.3379(8) | 3.9(2) |
| C6′ | −0.2147(9) | 0.1884(3) | 0.3869(8) | 3.7(2) |
| C7′ | −0.1379(8) | 0.1740(2) | 0.5077(8) | 2.9(2) |
| C8′ | −0.1807(8) | 0.1344(2) | 0.5539(7) | 2.8(1) |
| N9′ | −0.1231(7) | 0.1145(2) | 0.6570(6) | 2.7(1) |
| C91 | −0.1959(8) | 0.0760(2) | 0.6757(8) | 3.0(2) |
| C92 | −0.2530(8) | 0.0653(2) | 0.8041(8) | 3.2(2) |
| C93 | −0.323(1) | 0.0278(3) | 0.8192(9) | 4.4(2) |
| C94 | −0.339(1) | 0.0019(3) | 0.709(1) | 5.3(2) |
| C95 | −0.281(1) | 0.0128(3) | 0.583(1) | 5.9(3) |
| C96 | −0.209(1) | 0.0493(3) | 0.5659(9) | 4.2(2) |
| N1 | 0.2563(7) | 0.1107(2) | 0.6618(6) | 3.2(1) |
| C1 | 0.2013(9) | 0.1019(3) | 0.5186(8) | 3.9(2) |
| C2 | 0.3825(9) | 0.1409(3) | 0.6469(9) | 4.3(2) |
| C3 | 0.457(1) | 0.1593(3) | 0.7777(9) | 4.7(2) |
| C4 | 0.351(1) | 0.1841(3) | 0.8659(9) | 4.2(2) |
| N5 | 0.2294(7) | 0.1582(2) | 0.9240(6) | 2.9(1) |
| C6 | 0.135(1) | 0.1748(2) | 1.0387(8) | 3.7(2) |
| C61 | 0.074(1) | 0.2168(3) | 1.004(1) | 5.7(2) |
| C62 | 0.229(1) | 0.1748(3) | 1.1748(9) | 4.9(2) |
| C7 | −0.0092(9) | 0.1465(2) | 1.0500(7) | 3.4(2) |
| C8 | 0.0348(8) | 0.1031(2) | 1.0413(7) | 3.1(2) |
| C81 | 0.040(1) | 0.0784(9) | 1.1703(9) | 4.9(2) |
| N9 | 0.0705(7) | 0.0898(2) | 0.9210(6) | 2.8(1) |
| C10 | 0.1313(9) | 0.0493(2) | 0.9052(9) | 3.7(2) |
| C11 | 0.199(1) | 0.0435(2) | 0.7648(9) | 3.9(2) |
| C12 | 0.3234(9) | 0.0736(3) | 0.7264(9) | 4.0(2) |
| Cl1 | 0.5621(2) | 0.09443(8) | 0.1643(2) | 4.54(5) |
| O1 | 0.4252(7) | 0.0871(2) | 0.0845(7) | 6.3(2) |
| O2 | 0.5222(9) | 0.1029(3) | 0.3014(6) | 7.2(2) |
| O3 | 0.6394(9) | 0.1268(3) | 0.1054(8) | 9.3(2) |
| O4 | 0.665(1) | 0.0615(3) | 0.161(1) | 10.9(3) |

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Table 6
Selected bond distances (Å) and angles (°) for complex **8**

| | | | |
|---|---|---|---|
| Ni–N1 | 2.053(6) | Ni–N9′ | 2.082(6) |
| Ni–N5 | 2.123(6) | Ni–O1′ | 1.948(6) |
| Ni–N9 | 2.040(6) | | |
| O1′–Ni–N9′ | 89.6(2) | N9′–Ni–N5 | 164.9(2) |
| O1′–Ni–N1 | 99.8(3) | N9′–Ni–N9 | 97.7(2) |
| O1′–Ni–N5 | 88.5(2) | N1–Ni–N5 | 91.7(2) |
| O1′–Ni–N9 | 159.1(2) | N1–Ni–N9 | 97.5(3) |
| N9′–Ni–N1 | 103.5(2) | N5–Ni–N9 | 79.3(2) |