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GEOMETRICAL AND OPTICAL ISOMERS OF THE NICKEL(II) COMPLEXES OF CHIRAL, TETRADENTATE UNMIXED AND MIXED SCHIFF BASES: CD AND NMR SPECTROSCOPIC STUDIES

J. P. COSTES,* J. M. DOMINGUEZ-VERA and J. P. LAURENT

Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205, route de Narbonne,
31 077 Toulouse Cedex, France

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Abstract—Electronic, circular dichroïsm (CD) and NMR spectroscopic studies (1D ^{1}H and ^{13}C, 2D ^{1}H COSY and NOESY, ^{1}H–^{13}C correlation) of several chiral unmixed Schiff base nickel complexes and chiral mixed nickel complexes have been carried out. In such Schiff base complexes, the Cotton effect associated with a given transition reflects the conformation of the chelate five-membered ring of the diamino chain. The entire set of mixed and unmixed NiN_2O_2 (S) complexes involve a chelate ring adopting, at least preferentially, a λ conformation, with the methyl substituent taking an axial orientation. This result is confirmed by the NMR study of the vicinal coupling constants $^3J_{HH}$ in the —$C(H_\alpha)(H_\beta)$—$C(H_\gamma)R$— fragments of the diamino chain. On the contrary, the unmixed NiN_4 (S) complex and the mixed NiN_3O (S) complex are clearly different. This change comes from the presence of a 5,5,5- or a 5,5,6-chelate ring arrangement around the metal atoms that leads to a larger C=N—C angle involving the imine function and, eventually, allows a shift of the methyl substituent towards a more equatorial position. Furthermore, use of 2D ^{1}H–^{13}C NMR correlations allows a straightforward attribution of the entire set of signals. In one case, these results lead to a different assignment from previously published data.

Steric and conformational effects in metal complexes of chiral tetradentate Schiff bases have been well documented. Several papers have been devoted to the analysis of their circular dichroism (CD) spectra.[1,2] However, all these studies concern unmixed Schiff bases (abbreviated as usb in the following) resulting from the reaction of one mole of a chiral diamine with two moles of a keto precursor. In the present paper we report data (CD and ^{1}H, ^{13}C NMR spectroscopies) obtained for mixed Schiff bases (abbreviated as msb in the following) complexes. As reported previously a general strategy[3–5] to prepare the msb ligands relies on the possibility of preparing tridentate "half-units" by single condensation of a keto precursor with a diamine and then reacting the "half-unit" with another keto precursor. Recently, we succeded in isolating a chiral "half-unit"[6] (structure **1** in Fig. 1). It offers the opportunity of synthesizing and studying the metal complexes of chiral mixed Schiff bases.

The complexes considered in the present work are represented in Fig. 1. For all the complexes, optical isomerism originates in the chirality (R or S) of the substituted carbon of the diamino chain and in the *gauche* conformation (δ or λ) of the five-membered ring resulting from the chelation of this diamino chain to the metal ion.[7] In addition, geometrical isomerism has to be taken into account for the msb complexes. Indeed, the methyl substituent may be located at either the C(6) (p isomer) or C(7) (r isomer) carbon atom which, due to the different natures of the keto precursors, are not equivalent.

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*Author to whom correspondence should be addressed.

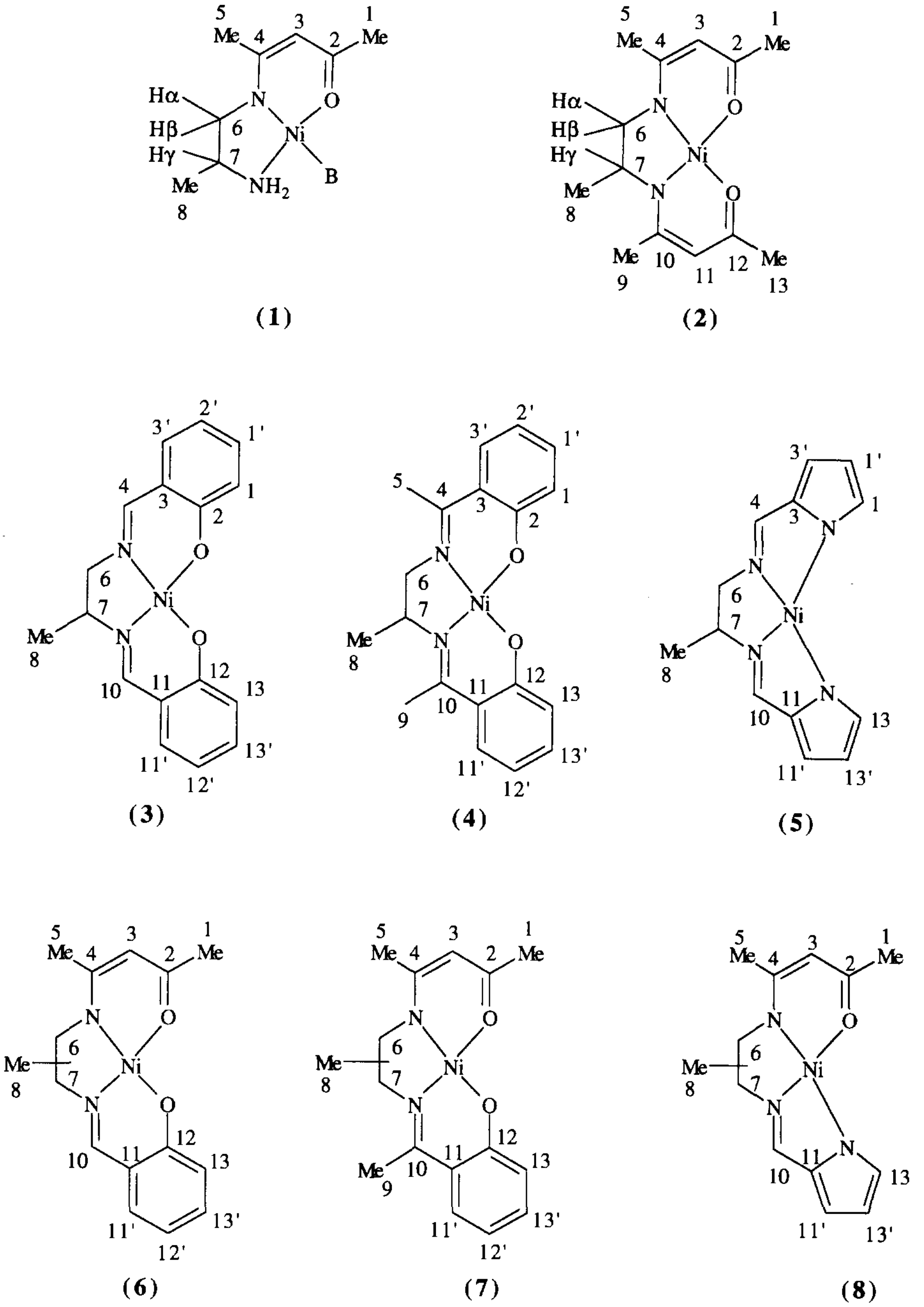

Fig. 1. Schematic representation of the complexes considered in this work.

EXPERIMENTAL

Synthesis of ligands and complexes

Reagents and solvents used were commercially available reagent quality. The "half-unit" HL^1 ligand, its complex $\mathbf{1}^6$ and the unmixed Schiff base complexes **2**–$\mathbf{5}^{8-11}$ were prepared according to published methods. The two methods used to obtain the mixed Schiff base complexes **6**–**8** are outlined here.

Complex **6***r*. To 0.5 g of **1** (1.94×10^{-3} M) in methanol (20 cm^3) was first added salicylaldehyde (0.3 g, 2.45×10^{-3} M) followed by NaOH (0.15 g, 3.9×10^{-3} M) dissolved in water (2 cm^3). The mixture was gently refluxed for 30 min. Evaporation of solvent left a solid residue that was dissolved in CH_2Cl_2, filtered and concentrated to 5 cm^3. Addition of pentane (40 cm^3) yielded a red precipitate which was filtered, washed with pentane and dried (0.44 g, 72% yield). Found: C, 56.0; H, 5.6; N, 8.5. Calc. for $C_{15}H_{18}N_2NiO_2$: C, 56.8; H, 5.7; N, 8.8%. Mass spectrum (EI and NH_3 chemical ionization): $m/z = 317$, $[C_{15}H_{19}N_2NiO_2]^+$.

Complex **7***r*. Use of hydroxyacetophenone instead of salicylaldehyde yielded **7***r* in lower yield (35%), due to its greater solubility. Found: C, 57.5; H, 6.0; N, 8.3. Calc. for $C_{16}H_{20}N_2NiO_2$: C, 58.0; H, 6.0; N, 8.5%. MS (EI and NH_3 chemical ionization): $m/z = 331$, $[C_{16}H_{21}N_2NiO_2]^+$.

Complex **8***r*. To 0.17 g of **1** (6.61×10^{-4} M) in methanol (20 cm^3) was first added pyrrole-2-carboxaldehyde (0.08 g, 8.42×10^{-4} M) followed by NaOH (0.05 g, 1.3×10^{-3} M) dissolved in water (2 cm^3). The mixture was gently refluxed for 15 min, giving an orange precipitate which was cooled, filtered, washed with diethyl oxide and dried (0.12 g, 63% yield). Found: C, 53.5; H, 6.0; N, 14.2. Calc. for $C_{13}H_{17}N_3NiO$: C, 53.8; H, 5.9; N, 14.5%. MS (EI and NH_3 chemical ionization): $m/z = 290$, $[C_{13}H_{18}N_3NiO]^+$.

Pure enantiomers of **6***r*, **7***r* and **8***r* were obtained by similar procedures and use of **1***S*.

Mixtures of r *and* p *isomers*. The same procedure was used for the three complexes. As an example, a solution of HL^1 (2.1 g, 1.35×10^{-2}M) and hydroxyacetophenone (1.83 g, 1.35×10^{-2}M) in ethanol (20 cm^3) was refluxed for 15 min. Addition of Ni $(OAc)_2 \cdot 4H_2O$ (3.37 g, 1.35×10^{-2}M), NEt_3 (1.36 g, 1.35×10^{-2} M) and heating yielded a red solution. After cooling, stirring and addition of water an orange solid precipitated. It was isolated by filtration and dried (1.9 g, 42%). Analytical results and mass spectra were identical to those of the *r* isomers for **6**–**8**.

Physical measurements

Microanalyses were performed by the Service de Microanalyse du Laboratoire LCC, Toulouse.

1D NMR spectra were obtained at 200.13 or 250.13 MHz for ^1H, at 50.32 or 62.89 MHz for ^{13}C on Bruker AC200 or WM250 spectrometers. 1D ^{13}C spectra using ^1H broadband decoupling $\{^1H\}^{13}C$ or gated ^1H broadband decoupling $\{^1H\}^{13}C$ with selective proton irradiation during acquisition were performed with the Bruker WM250 apparatus. 2D ^1H COSY and NOESY experiments using standard programs were performed on the Bruker WM250 apparatus. The data were collected with 2K complex data points in t1 dimension using a spectral width of 1400 Hz and a mixing time of 1 s for NOESY experiments; 512 experiments with spectral width of 700 Hz were recorded and zero-filled to 1K in t2 dimension. For each t1 value, 40–64 scans were signal averaged using 10 s of recycling delay. 2D pulse-field gradient HMQC ^1H–^{13}C correlations using a PFG-HMQC standard program were performed on a Bruker AMX400 spectrometer. The spectra were collected with 4K complex data points in t2 using a spectral width of 1820 Hz; 156 experiments with spectral width of 14086 Hz were recorded and zero-filled to 1K in t1 dimension. For each t1 value 32 scans were signal averaged. Squared-sinebell apodization in both dimensions was applied prior to transformation. All measurements were made at room temperature.

RESULTS AND DISCUSSION

The synthesis of the usb complexes is straightforward via the reaction of the chiral diamine (1,2-diaminopropane) with suitable keto reagents. These samples give spectral characteristics (electronic and CD spectroscopies) almost identical to those reported in the literature.[1,2] Furthermore, their identity is confirmed by their ^1H and ^{13}C NMR spectra.

As described in the Experimental section, genuine samples of **6***r*, **7***r* and **8***r* are easily obtained by reacting the complex "half-unit" (**1**) with salicylaldehyde, hydroxyacetophenone and pyrrole-2-carboxaldehyde, respectively. On the contrary, reaction of the free, uncomplexed "half-unit" with the same keto precursors and then complexation with nickel ions yields msb complexes as mixtures of *p* and *r* isomers, as the free "half-unit" exists as a mixture of *p* and *r* isomers. So, complexes **6***p*, **7***p* and **8***p* are not isolated as pure complexes but each is isolated as a mixture with its *r* homologue. We also have to note that the *r* isomer is always the most abundant. The presence of usb complexes, that could result from scrambling of keto precursors before complexation by nickel ions occurs, may be discarded. Indeed, mass spectra only display msb parent peaks without any trace of the usb parent peaks.

Electronic and circular dichroïsm spectroscopies

The relevant experimental data are reported in Tables 1 and 2. The CD spectra have been obtained with samples prepared from (*S*)-diaminopropane.

In view of its low intensity, the absorption which appears at 540–565 nm in the electronic spectra of all the complexes characterized by an N_2O_2Ni chromophore likely encompasses several possible *d*–*d* transitions.[1,12] The nature of the absorption observed at 440–450 nm is more difficult to assess since it appears as a shoulder on the low-energy side of an intense charge-transfer band peaking near 400 nm. In the case of **2** the shoulder at 445 nm has previously been attributed to a *d*–*d* transition.[1,12] No weak low-energy absorption is observed in the

Table 1. Electronic spectra of the nickel(II) complexes [λ, nm (ε_{max})] in CH_2Cl_2 solutions

1[a]	560,[b] 475 (280), 410 (6800), 350,[b] 342 (2400), 285 (5310)
2	565 (65), 445,[b] 370 (5200), 355 (5100), 300 (5800)
3	540 (180), 440,[b] 410 (6800), 390,[b] 345 (8500), 322 (8650)
4	550 (130), 440,[b] 403 (5130), 384,[b] 324 (6200)
5	480 (2375), 420,[b] 440,[b] 388 (10,210), 318 (21,380), 275 (5940)
6	540 (160), 450,[b] 410 (2680), 370 (4590), 328 (7250)
7*r*+*p*	552 (114), 440,[b] 408 (2795), 366 (5070), 326 (7140)
8*r*	380 (7930), 348 (6620), 310 (8200), 268 (6080)

[a] CH_3OH solution.
[b] Shoulder.

spectra of **5** and **8**, which contain N_4Ni and N_3ONi chromophores, respectively. This absence has been noted previously in the case of **5**.[1] It may be noted that one band originating in a *d–d* transition is observed at 500 nm in the CD spectrum of **5***S* and at 495 nm in the spectrum of **8***S*.

The CD spectra of the usb (*S*) complexes are perfectly consistent with those reported in the literature.[2] It is generally admitted that, within a series of closely related Schiff base complexes, the Cotton effect associated with a given transition reflects the conformation of the chelate five-membered ring. The spectrum obtained for **2***S* displays a mirror image relationship with that reported in the literature[11] for **2***R* [prepared from (*R*)-diaminopropane], which has been shown to have a five-membered ring with a preference for the δ conformation so that a preferential λ conformation may be assumed for **2***S*. This conformation is thus characterized by a characteristic pattern for the *d–d* bands comprising a positive band (I), a negative band (II) and a positive band (III) (cf. Table 2). Similarly signed bands are observed for **3***S*, **4***S*, **6***S* and **7***S* if we admit, as suggested previously, that due to overlapping of different signed bands and/or intrinsic low intensity, band I is lacking in the spectrum of **3***S*, and band III in the spectra of **4***S* and **6***S* (Fig. 2). Finally, we are led to the conclusion that the usb and msb complexes with an N_2O_2Ni chromophore prepared from (*S*)-diaminopropane involve a chelate ring adopting, at least preferentially, a λ conformation, with the methyl substituent taking an axial orientation. One may wonder whether this result still holds good for solid samples. Indeed, it has been reported[13] that, in solution, the copper(II) complex of the *N*,*N′*-disalicylidene-(*R*)-1,2-diaminopropane ligand has a five-membered chelate ring with a conformation opposite to that known to exist in the solid state. A comparison of the solution and solid state CD spectra of **2***S* and **7***S* (Table 2) shows that the change of phase does not affect the low energy part of the spectral pattern,

Table 2. CD spectra of the nickel(II) complexes [λ, nm ($\Delta\varepsilon$)]

1*S*[a]	577 (−0.5)I, 488 (+0.2)II, 364 (+1.5)
2*S*[b]	570 (+1.6)I, 493 (−0.2)II, 446 (+1.6)III, 415 (−ε),[c] 381 (−16.1)
2*S*[d]	571 (+), 490 (−), 450 (+), 400 (−)
3*S*[b]	568 (−0.3)II, 483 (+0.2)III, 460 (−1.5)IV, 415 (3.2)VI, 348 (3.0), 305 (4.3)
4*S*[b]	565 (+3.5)I, 499 (−ε)II, 455 (−4.1)IV, 420 (−4.0)VI, 400,[c] 375 (+2.8), 334 (−16)
5*S*[b]	500 (−0.9)I, 481 (−0.9)(II), 420 (+0.7)(III), 378 (+2.8), 312 (−2.0)
6*S*[b]	572 (+0.5)(I), 497 (−0.1)(II), 421 (−3.2), 375 (−3.3)
7*S*[b]	564 (+2.5)(I), 491 (−ε)(II), 463 (+0.5)III, 405 (−2.1), 379 (−9.7)
7*S*[d]	574 (+), 490 (−), 455 (−), 380 (−)
8*S*[b]	495 (−0.8), 408 (+0.4),[c] 380,[c] 371 (+2.20)
8*S*[d]	530 (−),[e] 410 (+), 370 (+)[e]

[a] CH_3OH solution.
[b] CH_2Cl_2 solution.
[c] Shoulder.
[d] Solid state.
[e] Broad and ill-defined band.

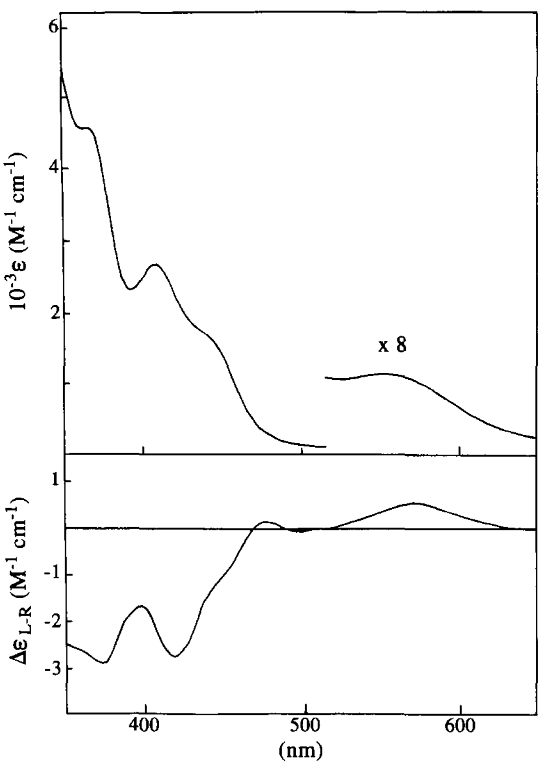

Fig. 2. Electronic (upper part) and CD (lower part) spectra of **6***S*.

suggesting that the same conformation prevails in both states. At this stage of the discussion it may be recalled that in the case of **1***S* almost identical CD spectra have been observed in solution and in the solid state.[6] However, they bear a mirror image relationship to those of **2***S* and **7***S*. The CD spectra of **5***S* and **8***rS* are markedly different from that obtained for the NiN_2O_2 (*S*) complexes. In both cases the low-energy band (500 and 495 nm) is negative, in accordance with a previous observation[1] that in complex **5***R* this band is positive. Tentatively, this behaviour was attributed to a change of conformation of the chelate ring with respect to the related N_2O_2Ni complexes. In our case this hypothesis is supported by the fact that the spectral patterns of **5***S* and **8***rS* are very similar to that of **1***S*, which has been shown to favour a δ conformation for its chelate ring,[6] with an equatorial methyl substituent. Finally, it may be noted that, in the case of **8***S*, almost identical spectra are obtained for solution and solid state samples.

^{1}H *and* ^{13}C *NMR spectroscopies*

The relevant data are quoted in Tables 3 and 4. The assignments of the ^{1}H and ^{13}C resonances result from an internal comparison of all the data obtained in the present work and from consideration of the data reported previously for similar complexes.[3,5,14] For ^{13}C NMR data, the most interesting result comes from ^{1}H–^{13}C correlation, which allows a straightforward attribution of the entire set of signals, and more particularly the methyl signals of **2**. Our assignment is not in agreement with the one reported in the literature[14] for the 8-methyl group of the diamino chain. The cross-signal between the well separated ^{1}H methyl doublet and the carbon signal at 21.4 ppm confirms our assignment unambiguously. In addition, several other 2D experiments (^{1}H COSY and NOESY) have been performed. ^{13}C NMR data for **6***p* and **8***p* are not given, due to the low proportion of these species in the **6***r*+*p* and **8***r*+*p* mixtures and the difficult assignment of several peaks.

The first aim of the NMR study is to achieve an unambiguous characterization of the various complexes and, in particular, to discriminate between the geometrical isomers. For the usb complexes, there is no possibility of geometrical isomerism. However, the presence of a substituent on the diamino bridge causes the two terminal parts of the ligand to become non-equivalent. COSY charts resulting from experiments performed on **3** and **4** show cross-signals between the H—C═N or the H_3C—C═N resonances and the resonances attributed to the protons H_α, H_β and H_γ of the diamino chain, allowing a clear distinction between the two non-equivalent moieties of these complexes. In the case of **3** for instance, we observe a connection between the H—C═N signal at 7.367 ppm and the signal at 3.440 ppm, which is obviously attributable to H_γ [C(7)H]. Conversely, the H—C═N signal at 7.409 ppm is connected to the signals at 2.940 and 3.781 ppm which arise from the H_α and H_β protons of the diamino chain. Similar data were obtained for complex **4**. As expected, the related coupling constants are small: $^4J_{HH} = 0.8$–1.4 Hz. The five CH_3 resonances in **2** are assigned via the ^{1}H–^{13}C correlation experiment.

As noted previously each of the msb complexes may exist in two isomeric forms labelled as *p* and *r* (cf. Fig. 1). The determination of the NMR parameters characterizing **6***r*, **7***r* and **8***r* is straightforward, since pure samples of these species are available. The parameters of the related *p*-isomers are extracted from the spectra of mixtures of the *p*- and *r*-forms. The resulting assignments are supported by 2D experiments. A COSY chart related to a **7***p* + **7***r* mixture shows two series of cross-signals:

(i) (Me, 1.574 ppm) $\leftrightarrow$ (H_γ, 3.690 ppm) $\leftrightarrow$ (H_β, 2.714 ppm) $\leftrightarrow$ (H_α, 3.118 ppm) and
(ii) (Me, 1.287 ppm) $\leftrightarrow$ (H_γ, 3.353 ppm) $\leftrightarrow$ (H_α, 3.477 ppm) $\leftrightarrow$ (H_β, 3.018 ppm),

Table 3. ^{1}H NMR chemical shifts [δ (ppm) vs TMS, CDCl$_3$ solutions, ambient temperature]

2[a]	CH$_3$: H(1), 1.860 or 1.852 (s), H(5), 1.811 (s), H(8), 1.282 (d), H(9), 1.864 (s), H(13), 1.860 or 1.852 (s); CH$_2$:[b] H_α, 3.065 (m), H_β, 2.590 (m); CH: H(3), 4.877 (s), H_γ, 3.226 (m), H(11), 4.834 (s).
3	CH$_3$: H(8), 1.456 (d); CH$_2$: H_α, 3.781 (m), H_β, 2.940 (m); CH: H(4), 7.409 (m), H_γ, 3.440 (m), H(10), 7.367 (s); phenyl rings: H(1), H(13), H(3′), H(11′), 6.98 (m), H(1′) and H(13′), 7.21 (m), H(2′) and H(12′), 6.50 (m).
4	CH$_3$: H(5), 2.289 (s), H(8), 1.529 (d), H(9), 2.302 (s); CH$_2$: H_α, 3.601 (m), H_β, 3.090 (m); CH: H_γ, 3.741 (m); phenyl rings: H(1) and H(13), 7.03 (m), H(1′) and H(13′), 7.12 (m), H(2′) and H(12′), 6.51 (m), H(3′) and H(11′), 7.37 (m).
5	CH$_3$: H(8), 1.350 (d); CH$_2$: H_α, 3.695 (m), H_β, 3.295 (m); CH: H(4), 7.258 (m), H_γ, 3.901 (m), H(10), 7.458 (m); pyrrole rings: H(13), 6.10 (m), H(13′), 6.57 (m), H(11′), 6.78 (m).
6*r*	CH$_3$: H(1), 1.920 (s), H(5), 1.862 (s), H(8), 1.421 (d); CH$_2$: H_α, 3.197 (m), H_β, 2.718 (m); CH: H(3), 4.948 (s), H_γ, 3.392 (m), H(10), 7.366 (s); phenyl ring: H(13), 6.93 (m), H(13′), 7.14 (m), H(12′), 6.49 (m), H(11′), 7.05 (m).
6*p*	CH$_3$: H(1), 1.845 (s), H(5), 1.802 (s), H(8), 1.301 (d); CH$_2$: H_α, 3.645 (m), H_β, 2.738 (m); CH: H(3), 4.909 (s), H_γ, not seen, H(10), 7.407 (s); phenyl ring: H(13), 6.93 (m), H(13′), 7.14 (m), H(12′), 6.49 (m), H(11′), 7.05 (m).
7*r*	CH$_3$: H(1), 1.934 (s), H(5), 1.861 (s), H(8), 1.574 (d), H(9), 2.374 (s); CH$_2$: H_α, 3.118 (m), H_β, 2.714 (m); CH: H(3), 4.959 (s), H_γ, 3.690 (m); phenyl ring: H(13), 6.95 (m), H(13′), 7.09 (m), H(12′), 6.48 (m), H(11′), 7.37 (m).
7*p*	CH$_3$: H(1), 1.926 (s), H(5), 1.917 (s), H(8), 1.287 (d), H(9), 2.343 (s); CH$_2$: H_α, 3.477 (m), H_β, 3.018 (m); CH: H(3), 4.921 (s), H_γ, 3.353 (m); phenyl ring: H(13), 6.95 (m), H(13′), 7.09 (m), H(12′), 6.48 (m), H(11′), 7.37 (m).
8*r*	CH$_3$: H(1), 1.897 (s), H(5), 1.893 (s), H(8), 1.273 (d); CH$_2$: H_α, 3.576 (m), H_β, 3.154 (m); CH: H(3), 4.970 (m), H_γ, 3.510 (m), H(10), 7.120 (m); pyrrole ring: H(13), 6.08 (m), H(13′), 6.53 (m), H(11′), 6.66 (m).

[a] Numbering scheme as described in Fig. 1.

[b] The protons of diamino chains are labelled according to the scheme N—C(H_α)(H_β)—C(H_γ)(CH$_3$)—N with $\delta H_A < \delta H_B$. Multiplicity appears in parentheses: s, singlet; d, doublet; m, multiplet.

Table 4. ^{13}C NMR data [δ (ppm) vs TMS, CDCl$_3$ solutions, ambient temperature] with numbering scheme as described in Fig. 1

2	CH$_3$: C(1), 24.3, C(5), 21.1, C(8), 21.4, C(9), 19.8, C(13), 24.3; CH$_2$: C(6), 58.9; CH: C(3), 99.5, C(7), 57.5, C(11), 99.5; CN: C(4), 164.9, C(10), 162.8; CO: C(2), 176.7, C(12), 176.7.
3	CH$_3$: C(8), 21.1; CH$_2$, C(6), 64.6; CH: C(7), 63.4; CN: C(4), 161.9, C(10), 160.4; phenyl rings: C(1) and C(13), 121.3, C(1′) and C(13′), 133.6, C(2) and C(12), 164.6, C(2′) and C(12′), 114.7, C(3) and C(11), 120.0, C(3′), 132.4 or 132.2, C(11′), 132.2 or 132.4.
4	CH$_3$: C(5), 18.0, C(8), 21.1, C(9), 16.8; CH$_2$: C(6), 60.2; CH: C(7), 58.8; CN: C(4), 168.8, C(10), 166.2; phenyl ring: C(1) and C(13), 122.8, C(1′) and C(13′), 132.1, C(2) and C(12), 164.2, C(2′) and C(12′), 116.0, C(3) and C(11), 121.2, C(3′), 128.6 or 128.4, C(11′), 128.4 or 128.6.
5	CH$_3$: C(8), 18.5; CH$_2$, C(6), 62.5; CH: C(7), 61.5; CN: C(4), 158.2, C(10), 156.4; pyrrole rings: C(1) and C(13), 136.0, C(1′) and C(13′), 111.4, C(3) and C(11), 143.1, C(3′), 116.5 or 116.3, C(11′), 116.3 or 116.5.
6*r*	CH$_3$: C(1), 24.3, C(5), 21.3, C(8), 21.9; CH$_2$: C(6), 57.9; CH: C(3), 99.7, C(7), 64.9; CN: C(4), 164.7, C(10), 160.1; CO: C(2), 177.4; phenyl ring: C(13), 121.8, C(13′), 133.4, C(12), 165.2, C(12′), 114.6, C(11), 120.1, C(11′), 131.9.
7*r*	CH$_3$: C(1), 24.3, C(5), 21.1, C(8), 21.1, C(9), 17.0; CH$_2$: C(6), 57.4; CH: C(3), 99.5, C(7), 60.0; CN: C(4), 164.8, C(10), 166.1; CO: C(2), 177.3; phenyl ring: C(13), 122.8, C(13′), 131.8, C(12), 164.4, C(12′), 114.2, C(11), 121.6, C(11′), 128.6.
7*p*	CH$_3$: C(1), 24.2, C(5), 19.7, C(8), 21.3, C(9), 18.1; CH$_2$: C(7), 61.6; CH: C(3), 99.5, C(6), 56.2; CN: C(4), 162.7, C(10), 168.7; CO: C(2), 177.2; phenyl ring: C(13), 122.7, C(13′), 131.9, C(12), 164.2, C(12′), 114.1, C(11), 121.5, C(11′), 128.5.
8*r*	CH$_3$: C(1), 24.5, C(5), 20.6, C(8), 18.2; CH$_2$: C(6), 63.0; CH: C(3), 99.8, C(7), 57.9; CN: C(4), 164.4, C(10), 154.9; CO: C(2), 176.9; pyrrole ring: C(13), 133.4, C(13′), 110.5, C(11), 141.0, C(11′), 114.7.

Table 5. Coupling constants $^nJ_{HH}$ (Hz) of diamino chains[a] ($CDCl_3$ solutions and ambient temperature)

	$^3J_{H_{C(8)}H_\gamma}$	$^3J_{H_\alpha H_\beta}$	$^3J_{H_\alpha H_\gamma}$	$^3J_{H_\beta H_\gamma}$	Others
2	6.3	12.3	5.6	$\leqslant 0.3$	
3	6.6	12.6	6.2	2.8	$^4J_{H(4)H_\alpha} = 1.4, {}^4J_{H(4)H_\beta} = 0.8$
4	6.4	13.0	5.4	$\leqslant 0.5$	
5	6.5	13.4	6.4	6.7	$^4J_{H(4)H_\alpha} = {}^4J_{H(4)H_\beta} = {}^4J_{H(10)H_\gamma} = 1.3$
6*r*	6.5	12.5	5.9	2.8	
6*p*	6.4	12.2	5.3	$\leqslant 0.5$	
7*r*	6.5	12.7	5.1	$\leqslant 0.5$	
7*p*	6.3	12.6	5.4	$\leqslant 0.5$	
8*r*	6.4	11.8	6.4	5.5	$^4J_{H(10)H_\gamma} = 1.4$

[a] The protons of diamino chains are labelled according to the scheme N—C(H_α)(H_β)—C(H_γ)(CH_3)—N with $\delta H_A < \delta H_B$.

in accordance with the presence of two different diamino chains. In addition, the presence of a cross-signal between H_3C—C═N (2.343 ppm) and H_α (3.477 ppm) allows sequence (ii) to be attributed to **7***p* and consequently sequence (i) to **7***r*. These assignments are corroborated by the NOE connectivities (H_γ, 3.690 ppm) ↔ (H_3C—C═N, 2.374 ppm) and (H_β, 3.018 ppm) ↔ (H_3C—C═N, 2.343 ppm), which are characteristic of **7***r* and **7***p*, respectively. According to its preparation, complex **8** was expected to be obtained as the *r*-isomer. The presence of a coupling constant of 1.4 Hz between H_γ (3.510 ppm) and H—C═N (7.120 ppm) and the absence of a similar coupling for H_α (3.576 ppm) and H_β (3.154 ppm) support the **8***r* identification. In the case of the related usb complex **4** small coupling constants affect H_α, H_β and H_γ (Table 5).

The data quoted in Tables 3 and 4 are related to samples prepared from (*rac*)-1,2-diaminopropane. However, for complexes **6** and **8** we note that samples from (*rac*)- and (*S*)-diamine give superimposable ^1H and ^{13}C spectra. This behaviour suggests that, in spite of the presence of two chiral elements, namely the asymmetric carbon and the five-membered chelate ring, diastereoisomeric species are absent from the mixtures prepared from (*rac*)-diamine. However, it may be consistent with the presence of enantiomers which could be identified by NMR experiments performed in a chiral medium.[15] Addition of (*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol to $CDCl_3$ solutions of **2**, **6***r* and **7***p*+*r* increases the number of signals observed in the ^1H spectra. The relevant data are quoted in Table 6. The most conspicuous effects are related to the CH_3 and CH resonances of the acetylacetone moiety. As for the diamino chain protons H_α, H_β and H_γ,

Table 6. Influence of a chiral auxiliary [(*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)-ethanol] on the chemical shifts [δ (^1H), ppm][a]

		Without auxiliary	With auxiliary
2	CH_3	1.864, 1.860, 1.852, 1.811	1.801, 1.786, 1.765, 1.746 1.717, 1.678, 1.583, 1.580
	C(7)CH_3	1.282 (d)	1.160 (d), 1.148 (d)
	C(3)H+C(11)H	4.877, 4.834	4.804, 4.784, 4.633, 4.477
6*r*	CH_3	1.920	1.802, 1.724
		1.862	1.679, 1.645
	C(7)CH_3	1.421 (d)	1.174 (d), 1.144 (d)
	C(3)H	4.948	4.684, 4.572
7*p*+*r*	CH_3	1.934, 1.926, 1.917, 1.861	1.895, 1.828, 1.805, 1.774 1.752, 1.703, 1.663, 1.572
	C(7)CH_3	1.574 (d)	1.289 (d), 1.279 (d)
	C(6)CH_3	1.287 (d)	1.047 (d), 1.030 (d)
	C(3)H	4.959, 4.921	4.839, 4.796, 4.712, 4.424

[a] All the solutions contain ~0.02 mM of complex in 0.5 cm^3 of $CDCl_3$ and, eventually, 0.1 mM of chiral reagent; d, doublet.

important overlaps of the complex multiplets occur and prevent any detailed analysis. However, the methyl resonances of the diamino chains appear as two doublets. The two sets of clearly resolved signals are conclusive evidence of the presence of two diastereoisomers (*SS* and *RS*), which result from the interaction of the two enantiomeric forms (*S* and *R*) of each complex with the reagent of chirality *S*.

With regard to stereochemical problems, particular attention has to be given to the coupling constant values characterizing the protons of the diamino chains (Table 5). It is generally accepted that the vicinal coupling constants $^3J_{HH}$ in a —$C(H_\alpha)(H_\beta)$—$C(H_\gamma)R$— fragment depend on electronic and geometric parameters. Within a series of closely related complexes such as **2**–**4**, **6** and **7** which all display an N_2O_2Ni chromophore, it is generally accepted that the vicinal coupling constants $|^3J_{\alpha\gamma}|$ and $|^3J_{\beta\gamma}|$ depend on the corresponding dihedral angles, $\theta_{\alpha\gamma}$ and $\theta_{\beta\gamma}$ respectively, via the Karplus (or Karplus-like) relation[16] and, in the present case, on the conformation of the chelate five-membered ring.

$|^3J_{\alpha\gamma}|$ varies from 5.4 to 6.3 Hz and $|^3J_{\beta\gamma}|$ from *ca* 0 to 2.8 Hz. This coupling pattern is very similar to that reported previously ($|^3J_{\alpha\gamma}| = 5.5$ Hz and $|^3J_{\beta\gamma}| = 0$ Hz) for a macrocyclic nickel(II) complex.[17] A structural determination[18] shows that the conformation of the five-membered chelate ring occurring in that complex places the methyl group in an axial position. Such a conformation is consistent with the observation of two distinct distorted *gauche* coupling constants. Interestingly, the precursor **1** has recently been shown[6] to have an equatorial methyl group and to display, in its ^1H NMR spectrum, a distorted *gauche* ($|^3J| = 4.2$ Hz) and a distorted *trans* ($|^3J| = 9.3$ Hz) coupling constant.

A more careful survey of the NMR data shows that, of the seven complexes with an N_2O_2 chromophore, five (**2**, **4**, **6***p*, **7***r*, **7***p*) are characterized by almost identical vicinal coupling constants ($|^3J_{\alpha\gamma}| \sim 5.3$ Hz and $|^3J_{\beta\gamma}| \sim 0$ Hz), while somewhat higher values (~ 6.0 Hz and ~ 2.8 Hz, respectively) are observed for **3** and **6***r*. These differences likely originate in modifications of the related dihedral angles $\theta_{\alpha\gamma}$ and $\theta_{\beta\gamma}$. For the seven complexes, the very small values of $|^3J_{\beta\gamma}|$ suggest that the $\theta_{\beta\gamma}$ angles do not differ markedly from 90° and the $\theta_{\alpha\gamma}$ angles from 30°. From the mathematical form of the Karplus relation we may conclude that the increase of $|^3J_{\alpha\gamma}|$ from *ca* 5.3 to 6.0 Hz and that of $|^3J_{\beta\gamma}|$ from *ca* 0 to 2.8 Hz would arise from a decrease of $\theta_{\alpha\gamma}$ and an increase of $\theta_{\alpha\gamma}$ around the mean values of *ca* 30° and 90°, respectively.

In fact, these modifications would correspond to a slight shift of the methyl substituent towards a less axial position in **3** and **6***r* than in the other complexes and could be attributable to a lessening of the steric constraint. Indeed, the methyl group of the diamino chain interacts with a methyl group grafted on the C(4) [or C(10)] atom in **2**, **4**, **6***p*, **7***r* and **7***p*, and with a hydrogen atom in the cases of **3** and **6***r* (cf. Fig. 1).

As reported previously, the CD spectra of **5** and **8***r* suggest that, in these complexes, the conformation corresponding to an axial (or pseudo-axial) methyl substituent is no longer favoured. As for the NMR data, we note that, although the coupling pattern observed for **5** and **8***r* is very different from those characterizing the complexes with an N_2O_2Ni chromophore, it is hardly consistent with an equatorial (or pseudo-equatorial) orientation of the methyl group. Indeed, such an orientation is expected to lead to two significantly different $|^3J|$ values corresponding to a *gauche* and a *trans* coupling constant, respectively. Actually we observe for **5** and **8***r* two nearly equal values (6.4 and 6.7 Hz for **5** and 6.4 and 5.5 Hz for **8***r*). The reasons for this discrepancy between the CD and NMR data are not clear. The structures of **5** and **8***r* have not been resolved, but the known structures of two closely related complexes, [*N*,*N*′-ethylene bis(pyrrol-2-ylmethyleneaminato)]nickel(II) (**5**′)[19] and [*N*,*N*′-ethylene (pyrrol-2-ylmethyleneaminato)(acetylacetoniminato)]nickel(II) (**8**′)[5] do not reveal any likely explanation. The two sets of structural data point to highly strained molecular structures resulting from the presence of a 5,5,5- or a 5,5,6-chelate ring arrangement around the metal atoms. Indeed, in **5**′ and **8**′ and probably in **5** and **8***r*, the central five-membered ring displays the usual *gauche* conformation. However, from the available data, we may infer that the angle C(10)—N—C(7) is larger in **5** and **8***r* than in the other complexes, leading to a decrease of the steric demand and, eventually, allowing a shift of the methyl substituent towards a more equatorial position.

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