Stereoisomerism in the Nickel(II) Complexes of a Chiral Tridentate Ligand: Solid-State and Solution Study

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A novel chiral and terdentate ligand, 7-amino-4,6(7)-dimethyl-5-aza-3-hepten-2-one (abbreviated ApnH₃) has been synthesized. In keeping with the occurrence of two possible locations for the methyl substituent grafted on the diamino chain, the chirality of the substituted carbon atom, the conformation of the five-membered chelate ring and, possibly, the chirality of the second ligand, the related nickel(II) complexes, (ApnH₂)NiN₃ and [(ApnH₂)-NiPy]ClO₄ may exist as a variety of geometrical and optical isomers. Solid-state (X-ray diffraction) and solution (NMR in achiral and chiral media, electronic and circular dichroism spectroscopies) studies show that no more than two isomers do exist. In both cases the methyl substituent is remote from the imino nitrogen and it adopts an equatorial orientation while an axial position is observed in the complexes of the related quadridentate Schiff base. In fact the two diasteroisomers display an enantiomeric relationship. The complex (ApnH₂)NiN₃ prepared from (*rac*)-diaminopropane crystallizes in the monoclinic space group $P2_1/c$ with four formula weights in a cell having the dimensions $a = 9.117(1)$ Å, $b = 8.738(1)$ Å, $c = 14.160(2)$ Å, and $\beta = 99.73(2)°$.
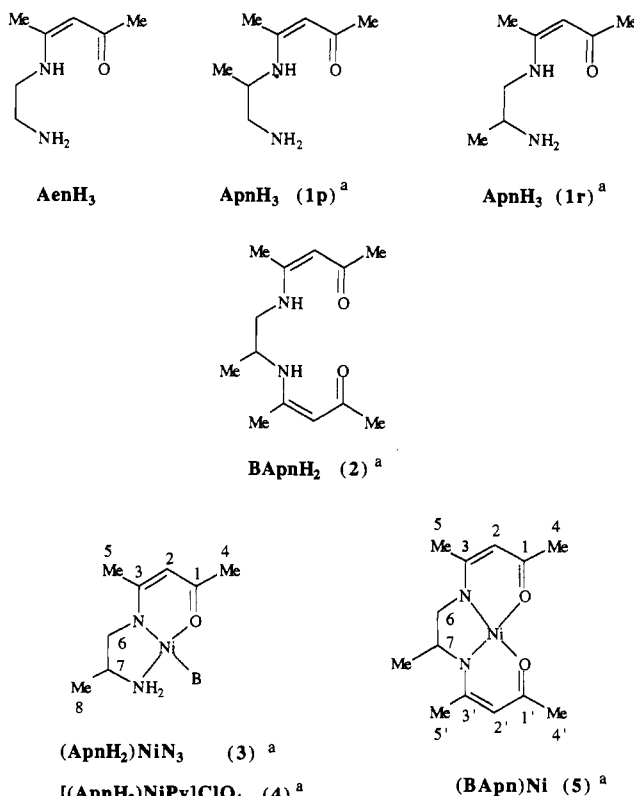
Introduction

In previous papers,[1–3] we have emphasized the synthetic possibilities of a terdentate Schiff base, the "half-unit" 7-amino-4-methyl-5-aza-3-hepten-2-one, AenH₃ (Chart 1). Indeed this molecule offers convenient routes to different types of homo- and heteropolynuclear complexes useful as magnetic models and/or as precursors of electric materials.

A way to increase further the interest of the ligand would be to create, in its structure, supplementary complexing sites to allow an extension of the number and nature of the coordinated metal ions. This could be easily performed by substituting a complexing group for a proton on the diamino backbone.[4] However this strategy would yield a number of isomeric species.

The present paper is devoted to a study (solid state and solution) of these stereochemical problems in the case of a simplified model, 7-amino-4,6(7)-dimethyl-5-aza-3-hepten-2-one, involving a methyl group as substituent and its nickel(II) complexes (ApnH₂)-NiN₃ (**3**) and [(AnpH₂)NiPy]ClO₄ (**4**). The complex (BApn)Ni (**5**) formed by the related quadridentate ligand **2** is included in this study for comparison. This complex has been previously described.[5,6]

A single Schiff-base condensation of acetylacetone onto 1,2-diaminopropane (pnH₄) will lead to two geometrical isomers with the methyl group located either in the vicinity of (**1p**), or remote from (**1r**), the imino nitrogen. Obviously, this type of isomerism is meaningless in the case of the quadridentate Schiff base **2** and its complexes. Optical isomerism originates in the chirality (*R*

Chart 1. Ligands and Nickel Complexes Considered in This Study with the Subscript r Omitted in Formulating Complexes 3 and 4[a]

AenH₃   **ApnH₃ (1p)**[a]   **ApnH₃ (1r)**[a]

BApnH₂ (2)[a]

(ApnH₂)NiN₃   (3)[a]

[(ApnH₂)NiPy]ClO₄ (4)[a]   **(BApn)Ni (5)**[a]

[a] The protons of the diamino chain are labeled according to the scheme N–C(Hₐ)(Hᵦ)–C(Hᵧ)(CH₃)–N.

or *S*) of the substituted carbon atom and in the *gauche* conformation (λ or δ)[7] of the five-membered ring resulting from

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the chelation of the diamino chain to the metal ion.[2,6,8-12] Due to the planarity of the six-membered ring formed by the acetylacetone moiety chelating the metal ion and that of the N_3-ONi chromophore, other sources of optical isomerism have not to be considered, provided the auxiliary ligand B (B = N_3^-, Py, ...), which completes the coordination sphere, be achiral.

Seemingly, there are to date very few reports[13,14] of metal complexes deriving from chiral terdentate Schiff bases in spite of the fact that, due to their chemical versatility, these complexes would be suitable starting materials for studying chirality effects.[12,13,15] Steric and conformational effects in metal complexes are best documented for quadridentate chiral Schiff bases deriving from salicylaldehyde and to a certain extent for bases deriving from acetylacetone.[6,11,12,14,16]

Experimental Section

Preparation of Ligands and Complexes. The preparation of ApnH$_3$ (**1**) is identical to that previously reported[17] for AenH$_3$. A solution of 2,4-pentanedione (11.8 g, 118 mmol) in CHCl$_3$ (50 mL) was slowly added, with stirring, to (*rac*)- or (*S*)-1,2-diaminopropane (10 mL, 118 mmol) in CHCl$_3$ (80 mL) over 1 h. The aqueous phase then was discarded and the solvent removed by rotary evaporation to leave a yellow oil which, according to spectroscopic data (*vide infra*), contained the two geometrical isomers **1p** and **1r**. No attempt was made to separate these isomers since, under the experimental conditions described below, only the r-isomer was found capable of reacting with the nickel(II) ions. In the following, the subscript **r** will be omitted in formulating the complexes.

Complex 3, (ApnH$_2$)NiN$_3$, (7-amino-4,7-dimethyl-5-aza-3-hepten-2-onato(1–))nickel(II) azide, was obtained by adding to a solution of the crude ligand, *i.e.* a mixture of **1p** and **1r** (1 g, 6.4 mmol) in ethanol (50 mL), first triethylamine (0.65 g, 6.4 mmol) and then nickel(II) acetate tetrahydrate (1.58 g, 6.4 mmol). The resulting solution was heated and stirred to achieve complete dissolution of the nickel salt. Sodium azide (0.4 g, 6.4 mmol) then was added at once, as a solid. Ten minutes later, heating was stopped. The red precipitate which appeared was filtered out 1 h later, washed with ethanol and diethyl oxide, and dried by suction. Anal. Calc for C$_8$H$_{15}$N$_5$NiO: C, 37.5; H, 5.9; N, 27.3; Ni, 22.7. Found: C, 37.6; H, 5.9; N, 27.2; Ni, 21.9.

Structural and NMR spectroscopic data (*vide infra*) show that this sample does not contain any amount of the related p-isomer.

Complex 4 [(ApnH$_2$)NiPy]ClO$_4$, (7-amino-4,7-dimethyl-5-aza-3-hepten-2-onato(1–))(pyridine)nickel(II) perchlorate, was prepared in a similar way to that used for [(AenH$_2$)NiPy]ClO$_4$.[18] To a stirred ethanolic (50 mL) solution of crude ligand, **1p + 1r** (2 g, 12.8 mmol), triethylamine (1.9 mL, 12.8 mmol), and pyridine (1 g, 12.8 mmol) was added nickel perchlorate hexahydrate (4.8 g, 12.8 mmol) as a solid. One hour later butanol (50 mL) was added. The mixture was set aside for 24 h. The microcrystalline product which appeared was filtered out and dried by suction. Anal. Calc for C$_{13}$H$_{20}$ClN$_3$NiO$_5$: C, 39.7; H, 5.1; Cl, 9.0; N, 10.7; Ni, 15.0. Found: C, 39.7; H, 5.7; Cl, 8.8; N, 10.6; Ni, 15.1.

Electrical conductivity measurements (Λ = 110 Ω^{-1} m^2 equiv^{-1} in acetone) confirmed that complex **4** is a 1/1 electrolyte. From NMR data it might be concluded that the sample only contained the r-isomer.

Complex 5, (BApn)Ni, was prepared as described in the literature.[5] Anal. Calc for C$_{13}$H$_{20}$N$_2$NiO$_2$: C, 52.8; H, 6.8; N, 9.5; Ni, 20.0. Found: C, 52.4; H, 6.7; N, 9.4; Ni, 19.7.

Caution! Although we experienced no difficulties with the compounds isolated as their perchlorate salts and with the compounds containing

Table 1. Crystallographic Data for (ApnH$_2$)NiN$_3$[a]

chem formula	C$_8$H$_{15}$N$_5$ONi
fw: 255.95	λ = 0.710 73 Å
T = 20 ± 1 °C	Z = 4
space group: $P2_1/c$ (No. 14)	$F(000)$ = 536
a = 9.117(1) Å	ρ_{calc} = 1.529 g cm^{-3}
b = 8.738(1) Å	μ = 17.3 cm^{-1}
c = 14.160(2) Å	transm coeff = 0.811–0.995
β = 99.73(2)°	$R(F_o)$ = 0.027
V = 1111.8(6) Å^3	R_w = 0.031

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] (Å^2 × 100) with Esd's in Parentheses

atom	x	y	z	U_{eq}
Ni	0.48506(5)	0.28295(6)	0.94265(3)	3.43(7)
O	0.3656(3)	0.3587(3)	0.8359(2)	3.9(4)
C(1)	0.4095(4)	0.4585(4)	0.7780(2)	4.0(6)
C(2)	0.5452(4)	0.5212(4)	0.7861(3)	4.5(7)
C(3)	0.6678(4)	0.4884(4)	0.8615(3)	3.9(6)
C(4)	0.2877(4)	0.4978(5)	0.6943(3)	5.3(8)
C(5)	0.8111(5)	0.5730(5)	0.8586(3)	5.1(7)
N(1)	0.6516(3)	0.3940(3)	0.9281(2)	3.7(5)
C(6)	0.7750(4)	0.3727(5)	1.0075(3)	4.2(7)
C(7)	0.7590(5)	0.2206(6)	1.0527(3)	5.9(8)
C(8)	0.8595(4)	0.1928(5)	1.1482(3)	5.4(8)
N(2)	0.6034(3)	0.2012(4)	1.0539(2)	4.3(5)
N(3)	0.3267(4)	0.1539(4)	0.9665(2)	4.4(6)
N(4)	0.1967(4)	0.1878(4)	0.9295(2)	4.7(6)
N(5)	0.0756(4)	0.2117(5)	0.8987(3)	6.8(8)

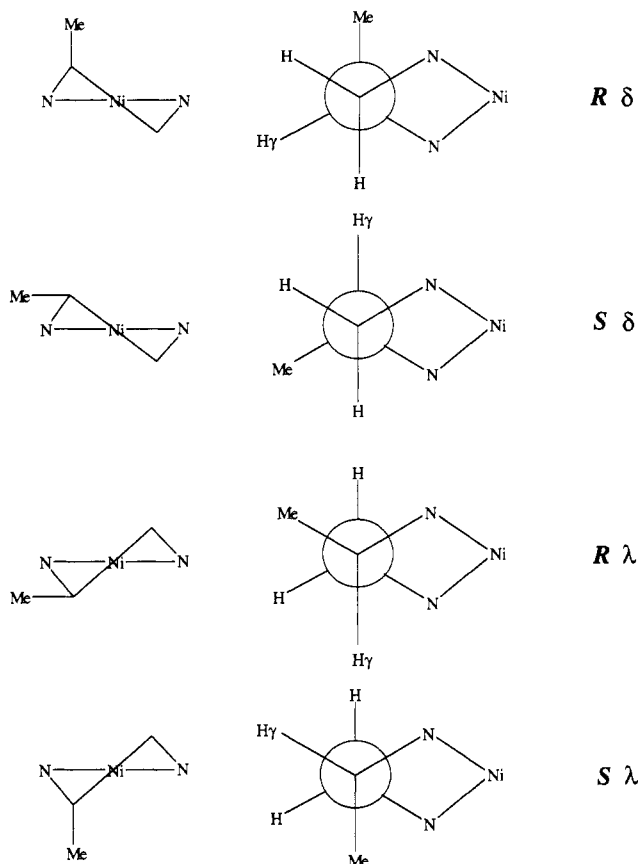[a] $U_{eq} = \frac{1}{3}[U_{11} + U_{22} + U_{33}]$.

azide entities, the unpredictable behavior of these complexes necessitates extreme caution in their handling.[19]

X-ray Crystallography for Complex 3. Crystals were obtained by slow evaporation of an acetone–ethanol solution of the product prepared from (*rac*)-1,2-diaminopropane. An orange plate crystal of dimensions 0.35 × 0.30 × 0.20 mm was used for the data collection on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters were obtained by a least-squares fit of 25 reflections with θ = 10–13°. Crystal data for (ApnH$_2$)NiN$_3$ (**3**) are summarized in Table 1. A total of 2552 intensity data were collected using the ω–2θ technique to a maximum 2θ of 54° (h, k,±l). The scan width for each reflection was 1.10 ± 0.35 tan θ with a variable speed of 0.97–5.09°/min. Three standard reflections were monitored every 2 h. No systematic variations in intensities were found. Data were reduced in the usual way with the MolEN package.[20] An empirical absorption correction[21] was applied on the basis of ψ scans. After the merging of equivalent reflections (R_{av} = 0.018), there were 2411 independent reflections and 1453 with $I > 3\sigma(I)$. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis.[22] After a few cycles of refinement with the SHELX-76 program[23] using full-matrix least-squares techniques, the hydrogen atoms were located in a difference Fourier map and their positions were fixed in the subsequent cycles of refinement. All non-H atoms were refined anisotropically. Atomic scattering factors (f', f'') were taken from the literature.[24] On the final refinement cycle, the maximum shift/esd was equal to 0.008 with 1453 observations and 136 variable parameters and the fit with unit weights was S = 0.92. A final difference Fourier map showed a maximum residual peak of 0.4 e/Å^3. Table 2 lists the atomic positions for the non-hydrogen atoms.

Materials and Methods. All starting materials were commercially available and of reagent grade. (*S*)-1,2-diaminopropane was purchased

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(24) *International Tables for X-Ray Crystallography*. The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, pp 99–101, Table 2.3.1, p 149.

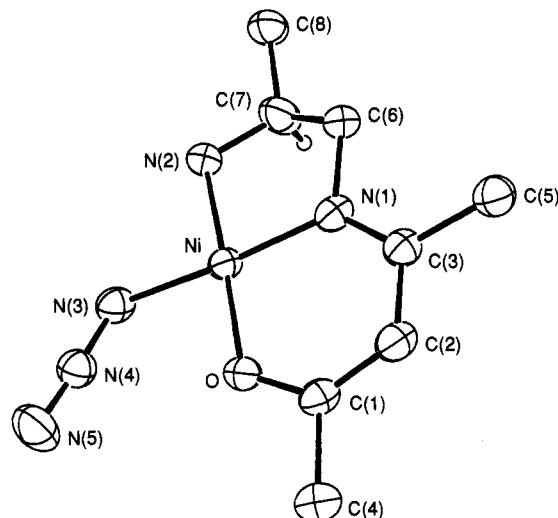**Chart 2.** Schematic Representation of the Four Diastereoisomers Expected for Complexes **3** and **4**

Figure 1. Ortep plot of **3** with the numbering scheme. Hydrogen atoms are omitted for clarity, except for the C(7) H.

Table 3. Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses

Ni–O	1.831(2)	Ni–N(2)	1.893(3)
Ni–N(1)	1.843(3)	Ni–N(3)	1.907(3)
O–C(1)	1.306(5)	N(1)–C(6)	1.462(4)
C(1)–C(2)	1.340(6)	C(6)–C(7)	1.493(6)
C(1)–C(4)	1.520(5)	C(7)–N(2)	1.432(5)
C(2)–C(3)	1.437(5)	C(7)–C(8)	1.519(5)
C(3)–N(1)	1.281(5)	N(3)–N(4)	1.248(5)
C(3)–C(5)	1.508(6)	N(4)–N(5)	1.135(5)
O–Ni–N(1)	96.0(1)	N(1)–Ni–N(2)	85.8(1)
O–Ni–N(2)	178.2(1)	N(1)–Ni–N(3)	173.9(1)
O–Ni–N(3)	89.8(1)	N(2)–Ni–N(3)	88.4(1)
Ni–O–C(1)	123.8(2)	Ni–N(1)–C(6)	112.9(2)
O–C(1)–C(2)	126.6(3)	C(3)–N(1)–C(6)	118.6(3)
O–C(1)–C(4)	112.3(4)	N(1)–C(6)–C(7)	109.0(3)
C(2)–C(1)–C(4)	121.2(3)	C(6)–C(7)–N(2)	106.2(3)
C(1)–C(2)–C(3)	125.0(4)	C(6)–C(7)–C(8)	115.9(4)
C(2)–C(3)–N(1)	120.2(3)	N(2)–C(7)–C(8)	114.9(4)
C(2)–C(3)–C(5)	116.8(3)	Ni–N(2)–C(7)	111.8(3)
N(1)–C(3)–C(5)	123.0(3)	Ni–N(3)–N(4)	118.7(3)
Ni–N(1)–C(3)	128.4(2)	N(3)–N(4)–N(5)	176.0(4)

from Interchim. Elemental microanalysis were performed by the Service de Microanalyse du Laboratorie (C, H, N) and by the Service Central de Microanalyse du CNRS, Lyon, France, (Ni, Cl).

Fourier transform infrared spectroscopy on KBr pellets was performed on a Perkin-Elmer 1725 X FT-IR instrument. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature (295 K) with a Bruker AC200 or Bruker WM250 spectrometer. All chemical shifts (^{1}H and ^{13}C) are given in ppm *versus* TMS using CD_3COCD_3 or CD_2Cl_2 as solvents. Circular dichroism spectra were recorded with an Auto-Dichrograph Mark V spectrometer (Jobin Yvon).

Results and Discussion

The preparative chemistry of ApnH₃ (**1**) and its nickel complexes parallels that previously described in the case of their unsubstituted analogues deriving from AenH₃.[17,18] The main differences between the two series result from the possibility of geometrical and optical isomerism which characterize the substituted species. As will be seen later, geometrical isomerism is restricted to the free ligand ApnH₃ (**1**), which is obtained as a 70/30 mixture of **1r** and **1p** isomers. The r isomer only exists in the nickel complexes **3** and **4**, while this type of isomerism does not occur in **5**. Finally, if the auxiliary ligand B in **3** and **4** is achiral, there are four possible stereoisomers for each of complexes **3–5**. They are labeled: *R*δ, *S*δ, *R*λ, and *S*λ, depending on the chirality (*R* or *S*) of the substituted carbon and on the conformation (δ or λ) of the five-membered ring. They are schematized in Chart 2. These four isomers could be theoretically observed if, as we did in a first series of experiments, *rac*-1,2-diaminopropane is used in the preparation of the complexes. However, to reduce the number of isomers we have performed a second series of preparation starting with (*S*)-1,2-diaminopropane.

Crystals of reasonable size and quality have been obtained in the case of (A(*rac*)-pnH₂)NiN₃, and a structural study has been performed. In the other cases, the stereochemistry is established

from spectroscopic (electronic, circular dichroism, ^{1}H and ^{13}C NMR) data.

Structure of (A(*rac*)-pnH₂)NiN₃ (3). The unit cell comprises four formula weights; one of them is represented in Figure 1. The relevant distances and angles are listed in Table 3. In keeping with the stereochemical problems, we note that (i) the crystal belongs to the space group $P2_1/c$ which is an achiral group so that the unit cell is heterochiral and optically inactive, (ii) each molecule belongs to the point group C_1 and, therefore, is chiral, (iii) the methyl substituent is remote from the acetylacetone moiety so that the (**r**) geometrical isomer alone is present, (iv) the methyl group adopts a pseudo-equatorial orientation, and (v) the azide anion is linear but not included in the coordination plane. It is inclined toward the acetylacetone moiety, and the angle between N_3^- and the coordination plane is 18.5(7)°.

Ignoring item (v), we can conclude that the four molecules of the unit cell form two pairs of enantiomers which can be identified as r *R*λ and r *S*δ (Chart 2). Item (v) deserves interest since it may introduce a supplementary source of dissymmetry. Indeed the helical system formed by N_3^- and, for instance, the perpendicular to the coordination plane may adopt a Δ or Λ configuration.[7] Structural data (heterochiral character of the unit cell, location of N(5) and C(7) on opposite sides of the mean coordination plane, tilting of N_3^- toward the acetylacetone moiety) point to an interdependence between the configuration of N_3^- and the conformation of the five-membered ring or/and the

Table 4. Electronic Spectra of the Nickel(II) Complexes [λ, nm (ϵ_{max})]

(A(S)-pnH$_2$)NiN$_3$	(3)$_S{}^{a,b}$	560,^{c} 475 (280), 350,^{c} 342 (2400), 285 (5310)
	(3)$_S{}^{b,d}$	565, 460, 360, 300
[(A(S)-pnH$_2$)NiPy]ClO$_4$	(4)$_S{}^{a,b}$	455 (170), 340 (2800), 325 (3000), 290 (2750)
(BA(S)-pn)Ni	(5)$_S{}^{b,e}$	566 (53), 450,^{c} 375 (4900), 355 (4700), 300 (5600)
(BA(R)-pn)Ni	(5)$_R{}^{e,f}$	565 (65), 445,^{c} 373 (5200), 356 (5100), 300 (5800)

^{a} MeOH solution. ^{b} This work. ^{c} Shoulder. ^{d} Solid state. ^{e} CH$_2$Cl$_2$ solution. ^{f} From ref 6.

Table 5. CD Spectra of the Nickel(II) Complexes [λ, nm (Δε)]

(A(S)-pn H$_2$)NiN$_3$	(3)$_S{}^{a,b}$	577 (−0.5) (I), 488 (+0.2) (II), 364 (+1.5) (IV)
	(3)$_S{}^{b,c}$	575 (−), 490 (+), 360 (+)
[(A(S)-pnH$_2$)NiPy]ClO$_4$	(4)$_S{}^{a,b}$	525 (−0.7) (I), 445 (−0.6) (III), 355 (+1.3) (IV), 294 (+0.8)
(BA(S)-pn)Ni	(5)$_S{}^{b,d}$	570 (+1.6) (I), 493 (−0.2) (II), 446 (+1.6) (III), 415 (−ε), 381 (−16.1)
(BA(R)-pn)Ni	(5)$_R{}^{d,e}$	575 (−2) (I), 495 (+0.05) (II), 446 (−1.9) (III), 415 (+1.3), 382 (+17.0)

^{a} MeOH solution. ^{b} This work. ^{c} Solid state. ^{d} CH$_2$Cl$_2$ solution. ^{e} From ref 6.

chirality of C(7) so that only two stereoisomers exist in the crystal: r$S\delta\Delta$ and r$R\lambda\Lambda$. Obviously they display an enantiomeric relationship.

Within each molecule, the nickel ion displays the expected square-planar coordination through two nitrogen and one oxygen atoms of the (ApnH$_2$) ligand and one nitrogen atom of the azide ion, the maximum deviation from the plane being 0.018(3) Å.

We have already discussed the δ or λ *gauche* conformation of the five-membered ring formed by the diamine moiety chelating the nickel ion, but one point deserves further comments. The *gauche* conformation displays an important unsymmetrical character. Indeed, while four atoms of the ring, Ni, N(1), C(6), N(2), are approximately coplanar, the fifth one, C(7), is displaced from this mean plane by 0.506(5) Å. This large deviation is likely related to the tetrahedral hybridization of the adjacent nitrogen N(2) which contrasts with the planar geometry around N(1). The six-membered ring defined by the metal and the acetylacetone moiety is almost ideally planar.

The bond lengths between the nickel ion and the donor atoms and the bond lengths and angles within the ApnH$_2$ moiety do not differ significantly from the values reported for similar complexes.[3,10,25,26]

The azide fragment is linear and asymmetric as it is the case in organic azides.[27] The distance between N(3) and N(4) [1.248-(5) Å] is markedly larger than the N(4)–N(5) separation [1.135-(5) Å] suggesting that the major canonical form is Ni—N—N≡N.

Electronic and Circular Dichroism Spectroscopies. The relevant experimental data are reported in Tables 4 and 5. The CD spectra have been obtained with samples (3)$_S$, (4)$_S$, and (5)$_S$ prepared from (S)-diaminopropane. For comparison, we have included in Tables 4 and 5 data related to complex (5)$_R$, prepared from (R)-diaminopropane.

In view of their intensity, the absorptions located at 560–565 nm and 445–450 nm in the electronic spectra of (5)$_S$ and (5)$_R$ may be attributed to d–d transitions.[6,16] A similar assignment may be made for the bands observed at 560 and 475 nm in the spectrum of 3. In the case of 4 only one absorption attributable to a d–d transition is seen at 455 nm in the electronic spectrum, but the related CD spectrum points to the presence of another band at lower energy (∼520 nm). It seems that three bands of d–d origin appear in the CD spectra of (5)$_S$ and (5)$_R$. They are labelled I–III in Table 5. In the same region we observe only two bands for the complexes, 3 and 4, of A(S)-pnH$_3$. However the overall appearance of these spectra suggests that extensive overlapping occurs and, eventually, masks bands of feeble rotational strength. Considering the lower-energy band I, we not that it is negative in the complexes (3)$_S$ and (4)$_S$ deriving

from A(S)-pnH$_3$ as it does in (5)$_R$ while it is positive in (5)$_S$. This correlation can be extended to band IV and to bands II and III if we suppose that, due to overlapping or/and intrinsic low intensity, band III is not observed in the spectrum of 3 and band II is not observed in the spectrum of 4. It is generally admitted[6,11] that, within a series of Schiff-base complexes, the Cotton effect associated with a given transition reflects the conformation of the chelate five-membered ring. This rationale confers preferentially a δ conformation to complex (5)$_R$ and, conversely, a λ conformation to (5)$_S$[6,11] with, in both cases, the methyl substituent in the axial position. As for the complexes (4)$_S$ and (3)$_S$, the same rationale led us to the conclusion that they involve a five-membered ring adopting, at least preferentially, a δ conformation with the methyl substituent taking an equatorial orientation (isomer $S\delta$ in Chart 2). By comparison of the CD spectra of (3)$_S$ in the solid state and in solution, it can be seen that they display the same general pattern suggesting that the same conformation prevails in both states.

^{1}H and ^{13}C NMR Spectroscopy. For the ligands 1 and 2 and their related complexes 3–5, samples prepared from (rac)- and (S)-diaminopropane give superimposable ^{1}H and ^{13}C spectra in achiral media where it is well-known that enantiomers cannot be distinguished.

The relevant parameters are quoted in Tables 6 and 7. As for the free ligand 1, the ^{1}H spectrum is characteristic of the simultaneous presence of two species in a 70:30 ratio. This is supported by selective decoupling experiments which reveal the expected connections (J-effect) between the individual resonances of each species and the lack of interspecies connections. The two species are identified as the geometrical 1p and 1r isomers (Chart 1), the latter being the most abundant. Indeed, while the NH$_2$ resonance appears as one broad signal (δ = 2.41 ppm), two signals of different multiplicities and intensities are observed for the NH resonance. Selective decoupling shows that the triplet structure of the most intense signal (δ = 10.909 ppm) is due to coupling with two equivalent methylenic protons (H$_\alpha$ and H$_\beta$) of the diamino chain N–C(H$_\alpha$)(H$_\beta$)–C(H$_\gamma$)(CH$_3$)–N while the doublet structure of the second signal (δ = 10.815 ppm) results from coupling with H$_\gamma$ in accordance with the overall geometries 1p and 1r, respectively. This attribution is further supported by the multiplicity of the C(8) resonance in the ^{1}H-coupled ^{13}C spectra. Obviously, in both isomers, C(8) is coupled with three protons ($^1J_{C–H}$ = 127.6 Hz) but each component of the resultant quadruplet displays either a doublet (1p) ($^3J_{CNH}$ = 2.7 Hz) or a triplet (1r) ($^3J_{CNH}$ = 5.6 Hz) structure attributable to coupling with the NH group or the NH$_2$ group, respectively.

The ^{1}H and ^{13}C spectra of both complexes (ApnH$_2$)NiN$_3$ (3) and [(ApnH$_2$)NiPy]ClO$_4$ (4) are simple, each of them comprising one set of signals in accordance with the occurrence of one geometrical isomer. From the structural data we may infer that it is the r-isomer. This is supported by the multiplicity of the C(8) resonance in the ^{1}H-coupled ^{13}C spectrum which is almost identical to that observed previously for 1r.

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Table 6. ^{1}H Chemical Shifts $\delta(^1\mathrm{H})$ (ppm) vs TMS (CDCl$_3$ Solution)

	CH$_3$			CH$_2$, CH				NH	NH$_2$
	4^a	5	8	2	H$_\alpha{}^b$	H$_\beta{}^b$	H$_\gamma{}^b$		
ApnH$_3$ (1p)	2.046 (s)^c	1.952 (s)	1.200 (d)	4.996 (s)	2.659 (m)^d	2.659 (m)^d	3.641 (m)	10.815 (d)	2.41^e
ApnH$_3$ (1r)	2.007 (s)	1.961 (s)	1.102 (d)	5.029 (s)	3.184 (m)^d	3.184 (m)^d	2.980 (m)	10.909 (t)	2.41^e
(ApnH$_2$)NiN$_3$ (3)	1.967 (s)	1.800 (s)	1.312 (d)	5.042 (s)	3.330 (m)	2.795 (m)	3.105 (m)		2.45(d)^{c,e} 2.34(dxd)^{c,e}
[(ApnH$_2$)NiPy]ClO$_4$ (4)	2.019 (s)	1.706 (s)	1.283 (d)	5.134 (s)	3.423 (m)	3.032 (m)	3.222 (m)		2.74(d)^e 2.50(dxd)^e
(BApn)Ni (5)	1.864 (s) 1.860 (s)	1.852 (s) 1.811 (s)	1.282 (d)	4.877 (s) 4.834 (s)	3.065 (m)	2.590 (m)	3.226 (m)		

^{a} The numbering scheme is as described in Figure 1. ^{b} The protons of the diamino chain are labeled according to the scheme N–C(H$_\alpha$)(H$_\beta$)–C(H$_\gamma$)(CH$_3$)–N with δ(H$_A$) < δ(H$_B$). ^{c} Multiplicity: s, stands for singulet; d, for doublet; t, for triplet; m, for multiplet (see text). ^{d} H$_\alpha$ and H$_\beta$ equivalent. ^{e} Broad.

Table 7. ^{13}C NMR Data [$\delta(^{13}\mathrm{C})^a$ (Multiplicity,^{b} $^1J_{\mathrm{C-H}}{}^c$]

	CH$_3$			CH$_2$, CH			C	
	4	5	8	2	6	7	1	3
1p^d	28.03 (q, 127.6)	20.65 (q, 125.8)	18.79 (q, 127.6)	94.66 (d, 159.0)	50.79 (d, 135.0)	47.60 (t, 135.0)	193.85 (s)	161.80 (s)
1r^d	28.03 (q, 127.6)	20.65 (q, 125.8)	18.32 (q, 127.6)	94.75 (d, 159.0)	50.61 (t, 136.9)	46.35 (d, 135.0)	193.94 (s)	162.44 (s)
3^e	23.66	20.13	17.31	99.36	59.91	50.80	175.41	168.15
4^d	24.00 (q, 126.9)	21.43 (q, 129.0)	18.05 (q, 129.0)	100.37 (d, 161.1)	59.93 (t, 139.2)	52.05 (d, 144.0)	175.82 (s)	166.00 (s)
5^d	24.33 (q, 126.5)	21.05, 19.77 (q, 126.5)	21.40 (q, 127.1)	99.47 (d, 159.8)	58.92 (139.7)	57.46 (d, 137.7)	176.70 (s)	162.81, 164.87 (s)

^{a} ppm vs TMS. ^{b} s stands for singulet, d for doublet, t for triplet, q for quadruplet. ^{c} Hz. ^{d} CDCl$_3$ solutions. ^{e} (CD$_3$)$_2$CO solution.

Table 8. Coupling Constants $^nJ_{\mathrm{H-H}}$ (Hz) (CDCl$_3$ Solutions)

	$^3J_{\mathrm{HC(8)-H_\gamma}}$	$^3J_{\mathrm{H_\alpha-H_\beta}}$	$^3J_{\mathrm{H_\alpha-H_\gamma}}$	$^3J_{\mathrm{H_\beta-H_\gamma}}$	others
1p	6.5		6.7^a		$^3J_{\mathrm{HN-H_\gamma}}$ = 9.0
1r	6.3		6.2^a		$^3J_{\mathrm{HN-CH_2}}$ = 2.5
3	6.0	13.0	4.2	9.3	$^2J_{\mathrm{HNH}} \sim {}^3J_{\mathrm{HN-H_\gamma}} \sim 9.0^b$
4	5.8	13.1	4.2	9.5	$^2J_{\mathrm{HNH}}$ = 9.0, $^3J_{\mathrm{HN-H_\gamma}}$ = 8.5
5	6.3	12.3	5.6	<0.3	

^{a} H$_\alpha$ and H$_\beta$ equivalent. ^{b} Broad and ill-resolved signals.

In both complexes, the NH$_2$ protons give two separated resonances. This diastereotopicity likely originates in the prochiral character of the related nitrogen atom. In the case of 4 these resonances are well resolved and we observed that the signal centered at δ = 2.74 ppm is a doublet with a separation of 9.0 Hz while the signal at δ = 2.50 ppm is a doublet of doublets with two separations of 9.0 and 8.7 Hz. The 9.0 value has to be attributed to $^2J_{\mathrm{HNH}}$. The 8.7 value is due to coupling of one of the NH$_2$ proton with the adjacent Hγ in the r isomer.

In the r and p isomers of the free ligand, the H$_\alpha$ and H$_\beta$ protons of the diamino chain are isochronous while they are inequivalent in complexes 3 and 4 in accordance with the loss of several degrees of freedom upon complexation.

The ^{1}H and ^{13}C spectra of (BApn)Ni (5) deserve few comments. As previously noted, there is no geometrical isomerism. However, due to the dissymmetry of the diamino bridge, the two terminal acetylacetone moieties are inequivalent, so that two signals are observed for C(8)H and four signals for the methyl groups.

With respect to stereochemical problems, let us consider the vicinal coupling constants $^3J_{\mathrm{H-H}}$ in the N–C(H$_\alpha$)(H$_\beta$)–C(H$_\gamma$)–N fragment. It is generally accepted that these constants depend on the corresponding dihedral angles via the Karplus (or Karplus-like)[28] equations and, in the present case, on the conformation of the five-membered ring. The values observed for 3 and 4 (cf. Table 8) do not greatly differ from the values generally attributed to *gauche* (approximately 3–6 Hz) and *trans* (approximately 9–12 Hz) coupling constants[8,29–31] in accordance with an equatorial orientation of the methyl group (isomers $R\lambda$ and $S\delta$ in Chart 2). In the case of 5 the coupling pattern is almost identical to that

reported for a structurally characterized macrocyclic Ni(II) complex[32,33] with two distorted *gauche* couplings and, therefore, an axial methyl group (isomers $R\delta$ and $S\lambda$ in Chart 2).

In both cases, the slight discrepancies between the actually observed ^3J values and the mean values reported in the literature could be tentatively attributed to a deformation of the chelate ring which is clearly established in the case of 3. Indeed an unsymmetrical *gauche* conformation would correspond to a decrease of both dihedral angles (H$_\alpha$–C–C–CH$_\gamma$) and (H$_\beta$–C–C–H$_\gamma$) with respect to their values in a symmetrical conformation. Due to the mathematical form of the Karplus equations, the net result would be a decrease of the larger $|^3J|$ and an increase of the smaller $|^3J|$, as observed. The existence of a conformational equilibrium with substantial but not complete preference for a given methyl group orientation could be an alternative explanation. This seems to us less likely since, for 3 and 4, the diastereotopicity of the NH$_2$ protons and the large difference of chemical shifts ($\Delta\delta \sim 0.4$–0.5 ppm) between H$_\alpha$ and H$_\beta$ favor the occurrence of a fixed conformation in solution.

As previously noted, in achiral media, superimposable spectra are obtained for samples of 3–5 prepared from (*rac*)- and (*S*)-diaminopropane.

This behavior suggests that diastereoisomeric species are absent from the mixtures prepared from (*rac*)-diaminopropane. However it may be consistent with the presence of enantiomers which could be identified by NMR experiments performed in chiral medium. Indeed a chiral auxiliary is expected to convert a mixture of enantiomers into a mixture of diastereoisomers characterized by chemical shift nonequivalence of (certain) diastereotopic nuclei.[15] Addition of (*S*)-1-(9-anthryl)-2,2,2-trifluoroethanol to acetonic solutions of 3 and 4 results in the observation of two resonances for each proton of the diamino chain. The feeble magnitude of the nonequivalence and the severe overlap of the signals in the 2.3–3.5 ppm region limit any quantitative conclusion to the CH$_3$ group for which we note separations of 1.5 Hz (3) and 6.0 Hz (4).

In the case of 5 nonequivalences are observed for all the protons of the molecule. The chemical shift differences are 3.2 (CH_3), 25.5 (H$_\beta$), 41.2 (H$_\alpha$) and 6.2 Hz (H$_\gamma$) for the diamino H chain and 4.2 and 31.0 Hz for the CH protons of the two inequivalent

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acetylacetone moieties. Eight signals are observed for N–C–CH_3 and O–C–CH_3. Though they are not attributable with certainty, their number supports the presence of two enantiomers in the sample.

Finally, for the three complexes **3–5**, no more than two sets of signals are revealed by the chiral auxiliary, allowing us to conclude that, in each case, the initial sample prepared from (*rac*)-diaminopropane only contains two enantiomeric forms. From the ^{1}H NMR (achiral medium) and CD data and, in the case of **3**, from the structural data, they can be identified as $R\lambda/S\delta$ for **3** and **4** and $R\delta/S\lambda$ for **5**. We note that the general pattern of the CD spectrum of **3** is preserved in changing from the solid state to solution suggesting that the preferential conformation of the five-membered chelate ring is not essentially modified. On the contrary an inversion of conformation occurs in passing from complexes **3** and **4** of the tridentate ligand to the complexes deriving from the related tetradentate Schiff base. It is generally accepted and structurally established in some instances[34–36] that,

in metal complexes of tetradentate Schiff bases, a methyl substituent onto the diamino chain preferably occurs in the axial position. The origin of this arrangement lies in the steric repulsion between the methyl substituent and the hydrogen atoms or the methyl group of the azomethine. As for the complexes of the terdentate ligand, we have shown that only the remote isomer **1r** (cf. Chart 1) is able to complex the nickel(II) ion so that the amount of steric interaction is considerably reduced allowing the methyl substituent to adopt a "more normal"[37–39] equatorial position.

Supplementary Material Available: Tables of hydrogen coordinates, anisotropic thermal parameters, complete distances and angles, and least-squares planes equations and deviations therefrom (5 pages). Ordering information is given on any current masthead page.

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