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Color Tuning of a Nickel Complex with a Novel N_2S_2 Pyridine-Containing Macrocyclic Ligand

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The novel pyridine-containing 14-membered macrocycle 3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L**), which contains an N_2S_2 donor set, was synthesized, and its protonation behavior was studied by absorption titration with CH_3SO_3H. The reaction of **L** with Pd(II) was studied spectroscopically, and the square-planar complex [Pd(**L**)](BF_4) was isolated and characterized. The reactions between **L** and $NiX_2\cdot 6H_2O$ ($X = BF_4$, ClO_4) in ethanol or acetonitrile afforded the octahedral complexes [Ni(CH_3CN)(H_2O)(**L**)]$(X)_2$ and [Ni$(H_2O)_2$(**L**)]$(X)_2$, respectively. The square-planar complexes [Ni(**L**)]$(X)_2$ were obtained by heating these octahedral complexes. Spectrophotometric titrations of [Ni(**L**)]$(BF_4)_2$ were performed with neutral and negatively charged ligands. The color of nitromethane solutions of this square-planar complex turns from red to cyan, purple, blue, yellow-green, and pink following addition of halides, acetonitrile, water, pyridine, and 2,2′-bipyridine, respectively. X-ray structural analyses were carried out on the {[Ni(ClO_4)(H_2O)(**L**)][Ni$(H_2O)_2$(**L**)]}$(ClO_4)_3$, [Ni(CH_3CN)(H_2O)(**L**)]$(ClO_4)_2$, [{Ni(**L**)}$_2$(μ-Cl)$_2$]$(ClO_4)_2$, and [{Ni(**L**)}$_2$(μ-Br)$_2$]$Br_2\cdot 2CH_3NO_2$ complexes.

Introduction

The *soft*−*hard* nature of donor atoms and the cavity size and flexibility of the molecule are the most important parameters that define the coordination properties of macrocyclic ligands.[1] The introduction of a rigid heterocyclic unit, such as pyridine,[2] 2,2′-bipyridine,[3] or 1,10-phenanthroline,[4] into the skeleton of the macrocycle allows modulation of these parameters and, therefore, selectivity of the resulting ligands. Among these ligands, the most studied to date are those pyridine-containing 14-membered macrocycles with nitrogen or oxygen as donor atoms. The complexes of these compounds have been used in catalysis[5] and in medical and biological studies.[6] They have also proved to be useful for analytical and industrial applications.[7] Despite this, however, the thia-derivatives of these compounds have still not been

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extensively studied.[8] These latter macrocycles are able to coordinate to softer metal ions than those containing nitrogen or oxygen as donor atoms.

The coordination process usually changes the color of the initial solution, and this alteration can be analytically useful. In some cases, the obtained complexes are coordinatively unsaturated or contain labile ligands which can easily be replaced, thus leading to new color changes. It has already been reported that the addition of halide ions into the solutions of some complexes changes either their color or their fluorescence properties,[9] and these features have applications in medicine, analytical measurements, and industrial processes.[10] Many acyclic and macrocyclic ligands have been successfully used in the detection of halide ions,[11] but no macrocyclic nickel complex has been proposed for this purpose.

We report the synthesis and reactivity toward Ni(II) and Pd(II) of the novel pyridine-containing 14-membered macrocycle with an N_2S_2 donor set, 3,11-dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**L**). Additionally, the changes in the UV−visible absorption spectra of nitromethane solutions of $[Ni(\mathbf{L})]^{2+}$ as a function of temperature, as well as the addition of halide and neutral ligands, were studied.

Experimental Section

General Remarks. All syntheses were carried out using standard Schlenk techniques. Solvents were dried by conventional methods and distilled under N_2(g) before being used. Organic reagents and transition metal salts were purchased from Aldrich and used as received. Elemental analyses were performed on a Carlo Erba EA-1108 instrument by the Chemical Analysis Service of the Universitat Autònoma de Barcelona. Mass spectra were recorded using a HP298S GC/MS system. NMR spectra were recorded on a Bruker 250 MHz AC instrument. Conductivity measurements were carried out using a Cyberscan 500 conductimeter. Absorption spectra were recorded on a Shimadzu spectrophotometer UV-2510-PC. Absorption studies at different temperatures were performed using a thermostatic bath. Methanesulfonic acid was used to promote the protonation of the ligand. UV−vis studies in solution were carried out using 10^{-3}−10^{-5} M dichloromethane or nitromethane solutions. *N*,*N*-Bis(3-chloropropyl)amine (**II**), was prepared from 3-amino-1-propanol and 3-chloro-1-propanol, according to the method described in the literature but using chloroform instead of benzene as solvent.[12]

X-ray Crystal Structure Determinations. Single crystals of $[Ni(H_2O)_2(\mathbf{L})][Ni(ClO_4)(H_2O)(\mathbf{L})](ClO_4)_3$ [abbreviated as $\mathbf{2}(ClO_4)_2$], $[Ni(CH_3CN)(H_2O)(\mathbf{L})](ClO_4)_2$ [abbreviated as $\mathbf{3}(ClO_4)_2$], $[\{Ni(\mathbf{L})\}_2(\mu\text{-}Cl)_2](ClO_4)_2$ [abbreviated as $\mathbf{6}(ClO_4)_2$], and $[\{Ni(\mathbf{L})\}_2(\mu\text{-}Br)_2]Br_2{\cdot}2CH_3NO_2$ [abbreviated as $\mathbf{7}(Br)_2{\cdot}2CH_3NO_2$] were mounted on glass fibers and used for data collection. The crystallographic data of $\mathbf{3}(ClO_4)_2$ and $\mathbf{6}(ClO_4)_2$ were collected at 173(2) K on an Enraf Nonius FR590 diffractometer using graphite-monochromated Mo Kα radiation. The data were processed with HKL Denzo and Scalepack.[13] The structures were solved by direct methods, and all non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using SHELXS-97.[14] The crystallographic data of $\mathbf{2}(ClO_4)_2$ and $\mathbf{7}(Br)_2{\cdot}2CH_3NO_2$ were collected at 293(2) K, using a BRUKER SMART CCD 1000 diffractometer. Graphite-monochromated Mo Kα radiation was used throughout. The data were processed with SAINT,[15] and multiscan empirical absorption correction was made using SADABS.[16] These structures were solved by direct methods using the program SIR-92.[17] Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed geometrically, and positional parameters were refined using a riding model. Atomic scattering factors were obtained from the

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International Tables for X-ray Crystallography.[18] Molecular graphics were obtained from ORTEP-3 for Windows.[19]

Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 276449, 263777, 263776, and 263775 for **2**$(ClO_4)_2$, **3**$(ClO_4)_2$, **6**$(ClO_4)_2$, and **7**$(Br)_2{\cdot}2CH_3NO_2$, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

2,6-Bis(mercaptomethyl)pyridine (I). This compound was synthesized by a slight modification of a previously reported method.[20] The product was not extracted with dichloromethane but isolated with a separatory funnel.

3,11-Dithia-7,17-diazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L). A solution of **I** (2.80 g, 16.37 mmol) in DMF (50 mL) and a solution of **II** (2.78 g, 16.37 mmol) in DMF (50 mL) were added simultaneously at 2 mL h^{-1}, to a suspension of CsOH (6.00 g, 36.00 mmol) in deoxygenated DMF (700 mL). After the addition was completed, the reaction mixture was stirred under nitrogen for an additional 24 h. The solvent was removed, and the residue was extracted with diethyl ether (3 × 100 mL). The combined extracts were dried over Na_2SO_4. Evaporation of the solvent yielded a yellow oil which was purified by column chromatography on silica gel using a mixture of $CHCl_3-CH_3OH$ (1:1 v/v ratio) as eluent. Yield 2.38 g, 54%. Anal. Calcd for $C_{13}H_{20}N_2S_2$: C, 58.17; H, 7.51; N, 10.44; S, 23.89. Found: C, 57.90; H, 7.58; N, 10.38; S, 23.64. ^1H NMR (250 MHz, $CDCl_3$): δ 1.74 (m, $^3J_{H,H} = 7.18$ Hz, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 1.91 (s, 1H, $-CH_2-NH-CH_2-$), 2.58 (t, $^3J_{H,H} = 7.18$ Hz, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 2.63 (m, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 3.79 (s, 4H, $-CH_2-Py-CH_2$-), 7.21 (d, $^3J_{H,H} = 7.70$ Hz, 2H, $-CH_2-Py-CH_2-$), 7.62 (t, $^3J_{H,H} = 7.70$ Hz, 1H, $-CH_2-Py-CH_2-$). $^{13}C\{^1H\}$ NMR (250 MHz, $CDCl_3$): δ 27.87 ($-S-CH_2-CH_2-CH_2-NH-$), 28.52 ($-S-CH_2-CH_2-CH_2-NH-$), 37.31 ($-CH_2-Py-CH_2-$), 46.92 ($-S-CH_2-CH_2-CH_2-NH-$), 121.60, 137.44, 158.69 ($-CH_2-Py-CH_2-$). MS-CI (*m/z*): 268.9 $[\mathbf{L} + H]^+$. IR (KBr pellet): 3337, 2923, 2818, 1592, 1571, 1460, 1217, 1148, 660 cm^{-1}.

Synthesis of Metal Complexes. General procedure. A solution of **L** (0.10 g, 0.37 mmol) in dichloromethane (4 mL), was added dropwise to an acetonitrile solution of $M(ClO_4)_n$ or $M(BF_4)_n$ (0.37 mmol, 4 mL). The resulting solution was stirred at room temperature for 2 h, and the solvent was partially removed to ca. 3 mL. Diethyl ether was infused into the solution, producing powdery precipitates. The products were filtered off, washed with diethyl ether, and recrystallized by diffusion of diethyl ether into acetonitrile or ethanol solutions.

[Pd(L)](BF$_4$)$_2$ (1). Yield 0.21 g, 82%. Anal. Calcd for $C_{13}H_{20}N_2S_2PdB_2F_8$: C, 28.47; H, 3.68; N, 5.11; S, 11.69. Found: C, 28.42; H, 3.68; N, 5.13; S, 11.49. Conductivity (CH_3CN, $1{\cdot}10^{-3}$ M): 254 $\mu S\ cm^{-1}$. ^1H NMR (250 MHz, CD_3CN): δ 1.86, 2.49 (m, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 2.00, 3.02 (m, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 3.41, 3.68 (m, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 4.50 (s, 1H, $-S-CH_2-CH_2-CH_2-NH-$), 4.88 (m, 4H, $-CH_2-Py-CH_2-$), 7.66 (m, 1H, $-CH_2-Py-CH_2-$), 8.09 (t, $^3J_{H,H} = 7.96$ Hz, 2H, $-CH_2-Py-CH_2-$). MS-ESI (*m/z*): 186.9 $[Pd(\mathbf{L})]^{2+}$.

[Ni(H$_2$O)$_2$(L)](ClO$_4$)$_2$ [2(ClO$_4$)$_2$] and [Ni(H$_2$O)$_2$(L)](BF$_4$)$_2$ [2(BF$_4$)$_2$]. These compounds were obtained by the general procedure using ethanol as solvent. **2**$(ClO_4)_2$: Yield 0.14 g, 62%. Anal. Calcd for $C_{13}H_{20}N_2S_2NiCl_2O_8{\cdot}2H_2O$: C, 27.78; H, 4.30; N, 4.98; S, 11.41. Found: C, 27.51; H, 4.42; N, 4.91; S, 11.20. Conductivity (CH_3CH_2OH, $1{\cdot}10^{-3}$ M): 78 $\mu S\ cm^{-1}$. Blue crystals suitable for X-ray diffraction with the formula $\{[Ni(ClO_4)(H_2O)(\mathbf{L})][Ni(H_2O)_2(\mathbf{L})]\}(ClO_4)_3$ were obtained by slow diffusion of diethyl ether into an ethanol solution of this complex. **2**$(BF_4)_2$: Yield 0.13 g, 65%. Anal. Calcd for $C_{13}H_{20}N_2S_2NiB_2F_8{\cdot}2H_2O$: C, 29.09; H, 4.51; N, 5.22; S, 11.95. Found: C, 29.37; H, 4.40; N, 5.38; S, 11.79. Conductivity (CH_3CH_2OH, $1{\cdot}10^{-3}$ M): 82 $\mu S\ cm^{-1}$. UV−vis (H_2O) $\lambda = 373$ ($\epsilon = 46$), 592 (16), 836 (19), 953 nm (30 $M^{-1}\ cm^{-1}$). MS-ESI (*m/z*): 163.0 $[Ni(\mathbf{L})]^{2+}$.

[Ni(CH$_3$CN)(H$_2$O)(L)](ClO$_4$)$_2$ [3(ClO$_4$)$_2$] and [Ni(CH$_3$CN)(H$_2$O)(L)](BF$_4$)$_2$ [3(BF$_4$)$_2$]. These compounds were obtained by slow diffusion of diethyl ether into acetonitrile solutions of **2**$(ClO_4)_2$ or **2**$(BF_4)_2$. **3**$(ClO_4)_2$: Anal. Calcd for $C_{13}H_{20}N_2S_2NiCl_2O_8{\cdot}CH_3CN{\cdot}H_2O$: C, 30.79; H, 4.31; N, 7.18; S, 10.96. Found: C, 31.12; H, 4.33; N, 7.48; S, 10.66. Conductivity (CH_3CN, $1{\cdot}10^{-3}$ M): 227 $\mu S\ cm^{-1}$. Lilac crystals suitable for X-ray diffraction with the formula $[Ni(CH_3CN)(H_2O)(\mathbf{L})](ClO_4)_2$ were obtained by slow diffusion of diethyl ether into an acetonitrile solution of this complex. **3**$(BF_4)_2$: Anal. Calcd for $C_{13}H_{20}N_2S_2NiB_2F_8{\cdot}CH_3CN{\cdot}H_2O$: C, 32.18; H, 4.50; N, 7.51; S, 11.45. Found: C, 32.01; H, 4.43; N, 7.74; S, 11.16. Conductivity (CH_3CN, $1{\cdot}10^{-3}$ M): 243 $\mu S\ cm^{-1}$. UV−vis (CH_3CN) $\lambda = 355$ ($\epsilon = 263$), 561 (23), 880 (35), 913 nm (33 $M^{-1}\ cm^{-1}$).

[Ni(L)](BF$_4$)$_2$ [4(BF$_4$)$_2$]. A Schlenck flask charged with **2**$(BF_4)_2$ was kept under oil-pump vacuum at 120 °C for 1 h. The complex turned from blue to red after dehydration. ^1H NMR (250 MHz, CD_3NO_2): δ 1.80, 2.31, 2.55 (m, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 2.03, 2.75, 3.19 (m, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 3.21, 3.37, 3.91 (m, 4H, $-S-CH_2-CH_2-CH_2-NH-$), 4.61 (m, 4H, $-CH_2-Py-CH_2-$), 7.35 (m, 1H, $-CH_2-Py-CH_2-$), 7.83 (t, $^3J_{H,H} = 7.88$ Hz, 2H, $-CH_2-Py-CH_2-$). $^{13}C\{^1H\}$ NMR (250 MHz, CD_3NO_2): δ 25.17, 25.89 ($-S-CH_2-CH_2-CH_2-NH-$), 33.35, 36.78 ($-S-CH_2-CH_2-CH_2-NH-$), 44.64, 44.87 ($-CH_2-Py-CH_2-$), 51.21 ($-S-CH_2-CH_2-CH_2-NH-$), 122.96, 123.08, 141.97, 159.87, 161.52 ($-CH_2-Py-CH_2-$). Conductivity (CH_3NO_2, $1{\cdot}10^{-3}$ M): 156 $\mu S\ cm^{-1}$. UV−vis (CH_3NO_2) $\lambda = 457$ nm ($\epsilon = 165\ M^{-1}\ cm^{-1}$).

Synthesis of Nickel Halide Complexes. General procedure. An acetonitrile solution of the corresponding tetrabutylammonium halide (0.28 mmol in 4 mL), was added dropwise to a solution of **2**$(BF_4)_2$ (75 mg, 0.14 mmol) in acetonitrile (4 mL). The resulting solution was stirred for 2 h and concentrated to ca. 4 mL. The precipitates were filtered off, washed with cold acetonitrile, and dried under vacuum.

[{Ni(L)}$_2$(μ-F)$_2$](BF$_4$)$_2$ [6(BF$_4$)$_2$]. Yield 46 mg, 76%. Anal. Calcd for $C_{26}H_{40}N_4S_4Ni_2B_2F_{10}{\cdot}H_2O$: C, 35.33; H, 4.79; N, 6.34; S, 14.51. Found: C, 35.62; H, 5.12; N, 6.67; S, 14.96. Conductivity (CH_3NO_2, $1{\cdot}10^{-3}$ M): 156 $\mu S\ cm^{-1}$. UV−vis (CH_3NO_2) $\lambda = 386$ ($\epsilon = 56$), 617 (16), 1021 nm (36 $M^{-1}\ cm^{-1}$). MS-ESI (*m/z*): 345.9 $[NiF(\mathbf{L})]^+$.

[{Ni(L)}$_2$(μ-Cl)$_2$](ClO$_4$)$_2$ [6(ClO$_4$)$_2$]. This nickel halide complex was obtained by the general procedure but using **2**$(ClO_4)_2$ (78 mg, 0.14 mmol) as the nickel complex. Yield 46 mg, 82%. Anal. Calcd for $C_{26}H_{40}N_4S_4Ni_2Cl_4O_8{\cdot}2H_2O$: C, 32.53; H, 4.62; N, 5.84; S, 13.36. Found: C, 32.38; H, 4.43; N, 5.76; S, 12.96. Conductivity (CH_3NO_2, $1{\cdot}10^{-3}$ M): 159 $\mu S\ cm^{-1}$. UV−vis (CH_3NO_2) $\lambda = 392$ ($\epsilon = 56$), 631 (23), 888 (25), 990 nm (28 $M^{-1}\ cm^{-1}$). MS-ESI (*m/z*): 360.9 $[Ni(\mathbf{L})Cl]^+$. Green crystals suitable for X-ray structure determination with the formula $[\{Ni(\mathbf{L})\}_2(\mu-Cl)_2](ClO_4)_2$ were obtained by slow evaporation of an ethanol solution of **6**.

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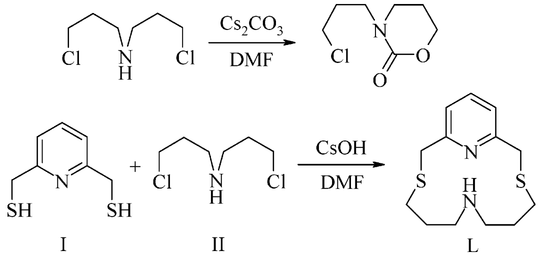
Scheme 1



[{Ni(L)}$_2$(μ-Br)$_2$]Br$_2$ [7(Br)$_2$]. Yield 59 mg, 77%. Anal. Calcd for $C_{26}H_{40}N_4S_4Ni_2Br_4 \cdot 2CH_3CN \cdot 2H_2O$: C, 33.00; H, 4.60; N, 7.70; S, 11.75. Found: C, 33.00; H, 4.23; N, 7.50; S, 12.27. Conductivity (CH_3NO_2, $1 \cdot 10^{-3}$ M): 179 μS cm^{-1}. UV−vis (CH_3NO_2) $\lambda = 399$ ($\epsilon = 80$), 646 (38), 956 nm (26 M^{-1} cm^{-1}). MS-ESI (*m*/*z*): 406.9 [NiBr(**L**)]$^+$, 892.7 [Ni$_2$(**L**)$_2$Br$_3$]$^+$. Green crystals suitable for X-ray structure determination with the formula [{Ni(**L**)}$_2$(μ-Br)$_2$]Br$_2$·2CH$_3$NO$_2$ were obtained from a saturated nitromethane solution of **7**.

[NiI(CH$_3$CN)(L)]I [8(I)]. Yield 57 mg, 71%. Anal. Calcd. for $C_{13}H_{20}N_2S_2NiI_2 \cdot CH_3CN$: C, 28.96; H, 3.73; N, 6.76; S, 10.31. Found: C, 28.64; H, 3.85; N, 6.69; S, 9.90. Conductivity (CH_3NO_2, $1 \cdot 10^{-3}$ M): 74 μS cm^{-1}. UV−vis (CH_3NO_2) $\lambda = 654$ ($\epsilon = 94$), 848 nm (33 M^{-1} cm^{-1}). MS-ESI (*m*/*z*): 452.9 [NiI(**L**)]$^+$.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great caution.

Results and Discussion

Synthesis and Electronic Properties of L. The synthesis of **L** was initially attempted through the slow addition of equimolar amounts of 2,6-bis(mercaptomethyl)pyridine (**I**) and *N*,*N*-bis(3-chloropropyl)amine (**II**) to a suspension of Cs_2CO_3 in DMF, using a similar methodology to that reported by J. Buter and R. M. Kellog for the preparation of thiamacrocycles from $\alpha-\omega$ dithiolates and $\alpha-\omega$ dihalides.[21] However, the ^{1}H and ^{13}C NMR spectra of the reaction mixture showed that the compound obtained was 3-(3-chloropropyl)-[1,3]oxazin-2-one instead of the expected macrocycle **L**. This nonmacrocyclic compound is the result of the reaction between *N*,*N*-bis(3-chloropropyl)amine and carbonate ions (see Scheme 1). This reaction is analogous to those reported for 2-chloroethyl-substituted secondary amines and carbonate ions.[22] The cyclization reaction was performed replacing Cs_2CO_3 with CsOH, which allowed for obtaining the desired macrocycle in a 54% yield.

Ligand **L** has two different protonable groups: an aliphatic secondary amine and a 2,6-disubstituted pyridine ring. To explore the relative basicity of these groups, an absorption titration of a dichloromethane solution of **L** with methanesulfonic acid was performed. The absorption spectrum of the free ligand exhibits a broad band centered at 272 nm ($\epsilon = 5229$ M^{-1} cm^{-1}), assigned to the pyridine $\pi-\pi^*$ transition[23] (see Figure 1A). The addition of 1 equiv of acid leads to a small blue-shift of this absorption band, whereas the rest of the spectrum remains unchanged. This fact reflects that the first protonation process involves the aliphatic amine, which is significantly more basic than the pyridine moiety. Further additions of acid produce the appearance of a new band centered at 302 nm due to the protonation of the pyridine. This new band is commonly assigned to the pyridinium ring, as has been previously reported in the literature for pyridine-containing ligands.[23−25] The inset of Figure 1A shows that an excess of acid is required to achieve the complete protonation of the pyridine moiety due to the lower basicity of this nitrogen atom.

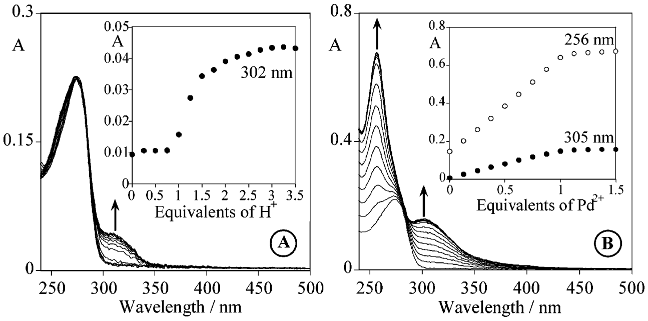


Figure 1. Absorption titrations at room temperature of dichloromethane solutions of **L** ($4.33 \cdot 10^{-5}$ M) with CH_3SO_3H (A), and $Pd(BF_4)_2 \cdot 4CH_3CN$ (B). The insets show the absorbances at different wavelengths.

Reactivity of L with Pd(II). The reaction of **L** with Pd(II) tetrafluoroborate in a 1:1 molar ratio yielded a yellow-orange microcrystalline solid whose elemental analysis fits the formula [Pd(**L**)](BF$_4$)$_2$. This compound behaves as a 2:1 electrolyte in acetonitrile solution, which indicates that it should be formulated as [Pd(**L**)](BF$_4$)$_2$ (**1**). The aliphatic region of its ^{1}H NMR spectrum is significantly more complex than that of the free ligand, since the 16 methylene protons appear as seven complex multiplets instead of four well-defined signals. All proton signals are shifted to a lower field, which suggests that all four donor atoms are involved in the coordination of the metal ion. The limited solubility of this complex makes it difficult to develop further NMR studies. This complexation process was studied by absorption spectroscopy by titrating a dichloromethane solution of **L** with an acetonitrile solution of Pd(BF$_4$)$_2$ (Figure 1B). Complexation of Pd(II) leads to formation of two bands centered at 256 and 305 nm. This increase in the absorbance in the region centered at ca. 300 nm confirms the involvement of the N-pyridine atom in the complexation.[24,25] The inset of Figure 1B shows that the titration is complete after the addition of 1 equiv of metal ion, which is in agreement with the formation of mononuclear species.

Reactivity of L with Ni(II). The reaction between equimolar amounts of **L** and Ni(II) perchlorate or tetrafluoroborate in ethanol yielded blue crystalline products, whose

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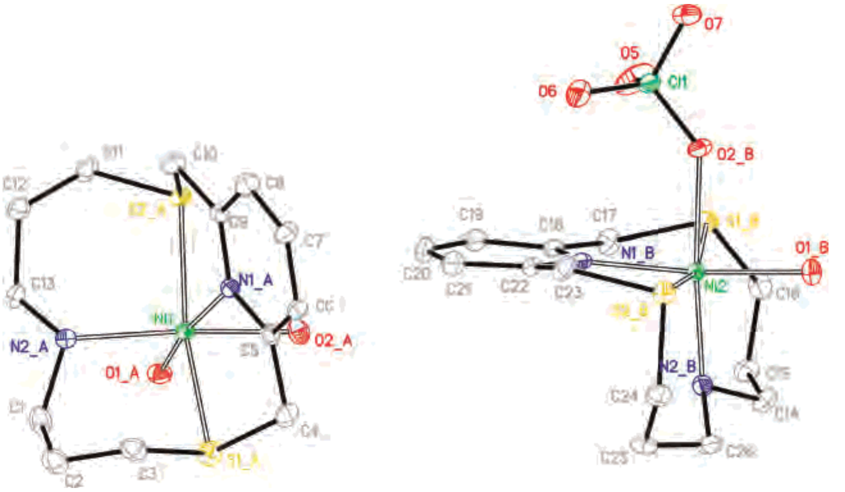

Figure 2. Structure of complexes $[Ni(ClO_4)(H_2O)(\mathbf{L})]^{2+}$ and $[Ni(H_2O)_2(\mathbf{L})]^{2+}$. Ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

elemental analyses agree with the formula $Ni(\mathbf{L})(H_2O)_2(X)_2$ ($X = ClO_4$, BF_4). The thermogravimetric analysis of the perchlorate and tetrafluoroborate complexes show (at around 370 K) clean, two-step weight losses of 6.5% and 6.8%, respectively, corresponding to the loss of two water molecules. Both compounds behave as 2:1 electrolytes in ethanol, which indicates that no counteranion is coordinated to the metal ions. Their electronic spectra in ethanol are the expected ones for nickel ions in distorted octahedral coordination,[26] which suggests that both water molecules and all four donor atoms of **L** are coordinated to the metal ion. These data suggest that these compounds should be formulated as $[Ni(H_2O)_2(\mathbf{L})](ClO_4)_2$ and $[Ni(H_2O)_2(\mathbf{L})](BF_4)_2$.

Dark blue crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into an ethanol solution of $\mathbf{2}(ClO_4)_2$. The crystal structure contains two different complex cations. Each cation has a Ni(II) ion in a distorted octahedral environment, defined by the four donor atoms of a macrocycle **L** and two oxygen atoms provided by two water molecules in one complex cation and one water molecule and one perchlorate ion in the other cation. The structure is completed by three additional perchlorate anions without significant interactions with the above-mentioned cations; therefore, the crystallized compound should be formulated as $\{[Ni(ClO_4)(H_2O)(\mathbf{L})][Ni(H_2O)_2(\mathbf{L})]\}(ClO_4)_3$. Figure 2 shows an ORTEP drawing of the complex cations $[Ni(ClO_4)(H_2O)(\mathbf{L})]^+$ and $[Ni(H_2O)_2(\mathbf{L})]^{2+}$. Crystallographic data and selected bond lengths and angles are summarized in Tables 1 and 2, respectively. The structure of both cations is conditioned by the meridional coordination of the 2,6-bis(thiomethyl)pyridine unit, as is observed in the values of the S−Ni−S angles (163.67(2)° and 164.54(4)°). In both cases, the aliphatic nitrogen is located perpendicular to the pseudo-plane defined by the metal ion, the pyridine ring, and the two thioether sulfur atoms. The folded conformation adopted by **L** leaves the other two coordination sites in a relative cis orientation, which are occupied by water molecules or perchlorate ions.

The $Ni-O_{water}$ and $Ni-O_{perchlorate}$ bond lengths in the $[Ni(ClO_4)(H_2O)(\mathbf{L})]^+$ cation, 2.069(3) and 2.249(2) Å, respectively, are close to the average distances obtained with the Cambridge Structural Database (CSD)[27] for octahedral Ni(II) complexes with $Ni-H_2O$ or $Ni-ClO_4$ bonds (2.077 and 2.294 Å, respectively).[28] The $Ni-O_{water}$ bond lengths in the $[Ni(H_2O)_2(\mathbf{L})]^{2+}$ cation, 2.082(2) and 2.129(2) Å, are slightly longer than the average distance previously mentioned. The Ni−S distances in both complex cations, which range between 2.3877(11) and 2.4216(12) Å, are similar to that found in analogous Ni(II) macrocyclic complexes containing the 2,6-bis(thiomethyl)pyridine unit (ca. 2.39 Å)[29] and those found for other Ni(II) complexes (ca. 2.42 Å).[30] The $Ni-N_{pyridine}$ (2.063(3) and 2.063(3) Å) and the $Ni-N_{aliphatic}$ bond lengths (2.086(3) and 2.120(3) Å) do not differ significantly from those found for related Ni(II) complexes.[31]

When the blue complexes $\mathbf{2}(X)_2$ ($X = ClO_4$, BF_4) were dissolved in acetonitrile, purple solutions were obtained. These solutions yielded purple compounds whose analytical data indicate that one water molecule was replaced by an acetonitrile one; therefore, these new complexes should be formulated as $[Ni(CH_3CN)(H_2O)(\mathbf{L})](ClO_4)_2]$ and $[Ni(CH_3CN)(H_2O)(\mathbf{L})](BF_4)_2$, respectively. The X-ray structure of $\mathbf{3}(ClO_4)_2$ confirms the presence of an acetonitrile molecule in the coordination sphere. Figure 3 shows a drawing of the complex cation **3**. This structure consists of discrete complex cations **3** and ClO_4^- anions without significant interactions between them. The conformation of **L** is analogous to that adopted in the structure of $\mathbf{2}(ClO_4)_2$, so both solvent molecules adopt a cis orientation. The acetonitrile molecule lies in the pseudo-plane defined by the metal ion, the pyridine ring and the two thioether-sulfur atoms, and the water

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Table 1. Crystallographic and Refinement Data

	2(ClO_4)$_2$	**3**(ClO_4)$_2$	**6**(ClO_4)$_2$	**7**(Br)$_2$·2CH_3NO_2
empirical formula	$C_{26}H_{46}Ni_2Cl_4N_4S_4O_{19}$	$C_{15}H_{25}NiCl_2N_3S_2O_9$	$C_{26}H_{40}Ni_2Cl_4N_4S_4O_8$	$C_{14}H_{23}NiBr_2N_3S_2O_2$
fw	1106.12	585.11	924.08	548.00
temp/K	293(2)	173(2)	173(2)	293(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073
cryst size/mm^3	0.48 × 0.36 × 0.10	0.26 × 0.24 × 0.22	0.30 × 0.24 × 0.18	0.25 × 0.14 × 0.07
color/habit	blue/plate	violet/prism	cyan/plate	cyan/prism
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic
space group	$Pca2_1$	$P2_1/a$	$P2_1/n$	$P\bar{1}$
a (Å)	16.408(3)	16.0299(2)	8.1498(1)	8.7603(7)
b (Å)	18.060(3)	8.2335(1)	17.3022(3)	10.3657(8)
c (Å)	13.983(3)	17.9965(2)	12.5813(2)	12.4979(10)
α (deg)	−	−	−	113.368(1)
β (deg)	−	107.187(1)	91.086(1)	95.581(1)
γ (deg)	−	−	−	96.111(1)
V/Å^3	4143.7(13)	2269.15(5)	1773.76(5)	1023.72(14)
Z	4	4	2	2
D_c (Mg m^{-3})	1.773	1.713	1.730	1.778
μ (mm^{-1})	1.448	1.327	1.651	5.066
F(000)	2280	1208	952	548
θ range for data collection (deg)	1.13−27.87	2.99−25.67	2.86−25.02	1.80−26.44
index ranges	$0 \le h \le 21$ $0 \le k \le 23$ $0 \le l \le 18$	$-19 \le h \le 19$ $-10 \le k \le 9$ $-21 \le l \le 21$	$-9 \le h \le 9$ $-19 \le k \le 20$ $-14 \le l \le 14$	$-10 \le h \le 10$ $-12 \le k \le 11$ $0 \le l \le 15$
reflns collected	39 271	7353	5719	11 733
independent reflns	5134 [R_{int} = 0.0464]	4259 [R_{int} = 0.0138]	3092 [R_{int} = 0.0243]	4162 [R_{int} = 0.0366]
max., min. transmission	0.865−0.547	−	−	0.718−0.364
data/restraints/params	5134/1/565	4259/0/301	3092/0/249	4162/0/217
GOF fit on F^2	1.073	1.028	1.037	1.064
final R indices	R1 = 0.0248 wR2 = 0.0544	R1 = 0.0254 wR2 = 0.0599	R1 = 0.0283 wR2 = 0.0566	R1 = 0.0334 wR2 = 0.0638
R indices (all data)	R1 = 0.0288 wR2 = 0.0563	R1 = 0.0304 wR2 = 0.0624	R1 = 0.0415 wR2 = 0.0603	R1 = 0.0632 wR2 = 0.0749
largest diff. peak and hole (e Å^{-3})	0.589 and −0.319	0.484 and −0.397	0.394 and −0.358	0.628 and −0.546

molecule lies perpendicular to this plane. The distances between the metal ion and all donor atoms of the ligand are similar to those previously discussed.

When the reaction between **L** and Ni(II) tetrafluoroborate was carried out in anhydrous nitromethane instead of ethanol, the color of the resulting solution was red instead of blue. This red solution yielded a light red compound which turned blue when exposed to air or by addition of ethanol. Although the electronic spectrum of this compound in ethanol is coincident with those recorded for **2**, the electronic spectrum in anhydrous nitromethane is the one expected for Ni(II) ions in square-planar coordination since it shows only one band in the visible region (λ = 457 nm, ϵ = 165 M^{-1} cm^{-1}).[26] This geometry agrees with the magnetic properties of this compound since it is a diamagnetic species. Its ^{13}C{^{1}H} NMR spectrum shows more signals that the spectrum of **L**, which indicates that the coordination increases the rigidity of the free ligand and, therefore, all its carbon atoms became magnetically nonequivalent. All carbons bonded directly to the donor atoms are shifted to a lower field, which suggests that all four donor atoms are involved in the coordination of the nickel ion. Its ^{1}H NMR spectrum shows nine complex multiplets assigned to the 12 protons of the propyl linkers, which reflects the rigidity of **L** in this complex. This rigidity is also evidenced by the signals of the methylene protons bonded to the pyridine moieties since they appear as a multiplet instead of a singlet. Figure 4 shows the experimental and fitted[32] spectra of these protons. The theoretical fitting agrees well with an ABCD system with chemical shifts δ = 4.49, 4.56, 4.66, and 4.72 ppm, and geminal coupling constants $^2J_{H-H}$ = 15.8 and 16.8 Hz.

This complex behaves as a 1:2 electrolyte in nitromethane solution, which reveals that no counteranion is coordinated to the metal ions; thus, it should be formulated as [Ni(**L**)]-(BF_4)$_2$.

The complex cation **4** can also be obtained by heating nitromethane solutions of **2**(X)$_2$ (X= ClO_4, BF_4). The progress of this reaction can be monitored by UV−vis spectroscopy. Figure 5 shows the electronic spectra of a nitromethane solution of **2**(BF_4)$_2$ at different temperatures ranging from 303 to 343 K. These spectra show that the absorption at 460 nm is a function of the temperature (see inset of Figure 5) since it increases until 335 K. After this point, the spectrum remains unchanged, indicating the total transformation of the hydrated octahedral species into the dehydrated square-planar one. It is interesting to note that this process takes place at a lower temperature in solution than in the solid state, as can be observed by comparing these spectra and the thermogramivetric analysis of **2**(X)$_2$.

Purple solutions were obtained by dissolving the blue complex **2** or the red complex **4** in acetonitrile. The electronic spectra of these solutions are coincident with those recorded for acetonitrile solutions of **3**. The obtention of the same product using different reagents allows the design of two ways to synthesize new **L**-containing Ni(II) octahedral complexes by addition of coordinating molecules: the substitution of the labile water molecules of the octahedral

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(32) *gNMR, 3.6 for Windows*; IvorySoft Scientific Software.

Table 2. Selected Bond Lengths (Å) and Angles (deg)[a]

	$\mathbf{2}(ClO_4)_2$				
	Ni(1)	Ni(2)	$\mathbf{3}(ClO_4)_2$	$\mathbf{6}(ClO_4)_2$	$\mathbf{7}(Br)_2{\cdot}2CH_3NO_2$
Ni−N(1)	2.063(3)	2.026(3)	2.0690(2)	2.0803(19)	2.059(3)
Ni−N(2)	2.120(3)	2.086(3)	2.1115(2)	2.117(2)	2.101(3)
Ni−N(3)			2.0564(2)		
Ni−O(1)	2.082(2)	2.069(3)	2.1388(15)		
Ni−O(2)	2.129(2)	2.249(2)			
Ni−S(1)	2.4216(12)	2.3877(11)	2.4155(5)	2.3868(7)	2.3882(12)
Ni−S(2)	2.3926(11)	2.4051(10)	2.3911(5)	2.3749(7)	2.3718(12)
Ni−X(1)				2.3811(6)	2.5228(6)
Ni−X(1)^i				2.5350(7)	2.7686(7)
S(1)−Ni−S(2)	163.67(4)	164.54(4)	163.70(2)	161.99(3)	163.50(4)
N(1)−Ni−N(2)	103.29(11)	95.43(11)	93.18(6)	97.54(8)	95.44(12)
N(1)−Ni−N(3)			176.06(6)		
N(2)−Ni−N(3)			90.70(7)		
N(1)−Ni−O(1)	170.03(10)	172.52(10)	89.61(6)		
N(2)−Ni−O(1)	86.67(11)	91.42(11)	176.11(7)		
N(3)−Ni−O(1)			86.48(6)		
N(1)−Ni−O(2)	88.55(11)	88.91(10)			
N(2)−Ni−O(2)	167.15(12)	174.83(10)			
O(1)−Ni−O(2)	81.49(10)	84.40(10)			
S(1)−Ni−N(1)	82.58(9)	84.60(9)	85.14(5)	83.78(6)	84.82(10)
S(1)−Ni−N(2)	91.86(9)	92.81(8)	97.57(5)	98.23(7)	100.59(10)
S(1)−Ni−N(3)			94.98(5)		
S(2)−Ni−N(1)	81.27(8)	86.02(8)	83.44(5)	84.18(6)	83.30(10)
S(2)−Ni−N(2)	94.16(9)	100.30(9)	94.63(5)	96.59(7)	91.92(10)
S(2)−Ni−N(3)			95.63(5)		
S(1)−Ni−O(1)	97.52(8)	98.07(7)	85.35(5)		
S(2)−Ni−O(1)	97.97(9)	89.82(9)	82.99(5)		
S(1)−Ni−O(2)	90.09(2)	84.79(7)			
S(2)−Ni−O(2)	87.12(8)	82.77(7)			
Ni−X(1)−Ni^i				93.52(2)	92.94(2)
X(1)−Ni−X(1)^i				86.48(2)	87.06(2)
X(1)−Ni−S(1)				95.30(2)	92.71(3)
X(1)^i−Ni−S(1)				83.60(2)	81.61(3)
X(1)−Ni−S(2)				94.83(2)	96.95(3)
X(1)^i−Ni−S(2)				82.20(2)	85.56(3)
X(1)−Ni−N(1)				172.26(6)	169.73(9)
X(1)^i−Ni−N(1)				85.78(5)	82.72(9)
X(1)−Ni−N(2)				90.21(6)	94.81(9)
X(1)^i−Ni−N(2)				176.36(6)	177.03(10)

[a] Symmetry codes i: $-x, -y, 1 - z$ for $\mathbf{6}(ClO_4)_2$ and $1 - x, 1 - y, -z$ for $\mathbf{7}(Br)_2{\cdot}2CH_3NO_2$.

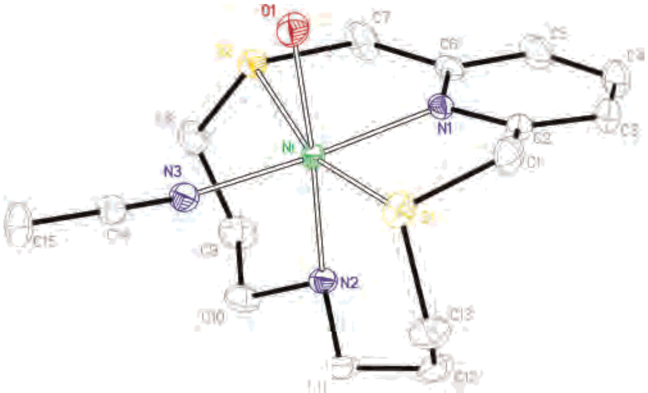


Figure 3. Structure of complex $[Ni(CH_3CN)(H_2O)(\mathbf{L})]^{2+}$. Ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

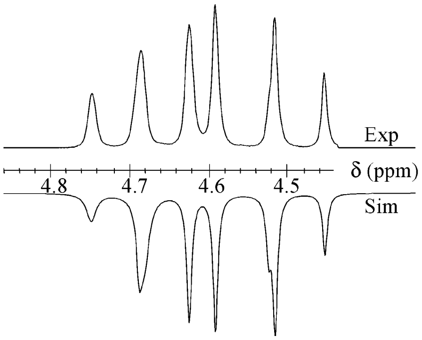


Figure 4. Experimental (top) and simulated (bottom) ^1H NMR spectra of the $-S-CH_2-Py-$ protons of complex **4**.

complex **2** and the expansion of the coordination number of the square-planar complex **4**.

To study the reactivity of the Ni(II)−**L** system, absorption titrations of nitromethane solutions of **4** were performed with different neutral and anionic ligands. The absorption spectra of the pyridine and 2,2′-bipyridine titrations are shown in Figure 6. In both absorption titrations, the addition of increasing amounts of the coordinating agent caused the disappearance of the band assigned to the square-planar complex (460 nm), as well as the formation of the characteristic bands of pseudo-octahedral species (383, 612, and 990 nm for pyridine and 380, 542, and 960 nm for 2,2′-bipyridine).[26] As seen in the insets of Figure 6, the absorbances of the pseudo-octahedral species increase until the addition of 2 and 1 equiv of titrating agent for pyridine and 2,2′-bipyridine, respectively. In the case of the 2,2′-bipyridine titration, the addition of more equivalents of titrating agent was shown to cause significant changes of the absorption

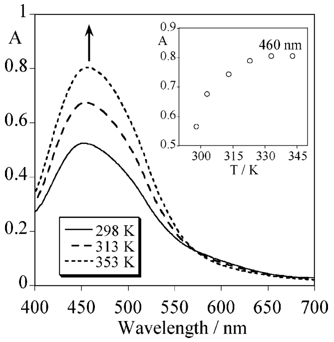


Figure 5. Absorption spectra of a nitromethane solution of **4** at different temperatures. The inset shows the absorbance at 460 nm ([**4**$(BF_4)_2$] = 5.33×10^{-3} M).

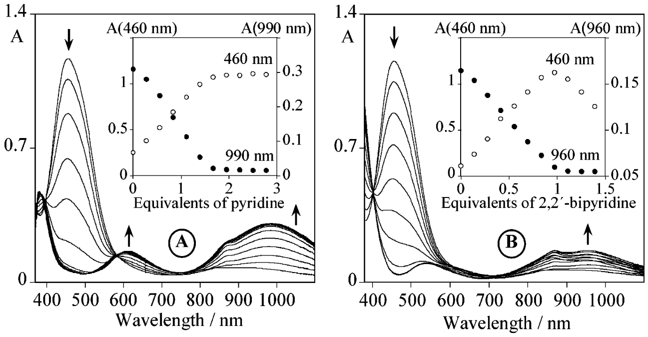


Figure 6. Absorption titrations at room temperature of nitromethane solutions of **4** with pyridine (A) and 2,2′-bipyridine (B). The insets show the absorbances at different wavelengths ([**4**$(BF_4)_2$] = 5.33×10^{-3} M).

spectrum. This fact was attributed to the substitution of **L** molecules by 2,2′-bipyridine which was confirmed by analyzing the red crystals obtained from the reaction between **2**$(BF_4)_2$ and 2,2′-bipyridine in a 1:3 molar ratio since they agree well with the formula [Ni(2,2′-bipyridine)$_3$]$(BF_4)_2$. All attempts to isolate the $[Ni(\mathbf{L})(py)_2]^{2+}$ and $[Ni(\mathbf{L})(bipy)]^{2+}$ complex cations were unsuccessful because all reactions between **2**, **3**, or **4** and pyridine or 2,2′-bipyridine yielded heterogeneous compounds.

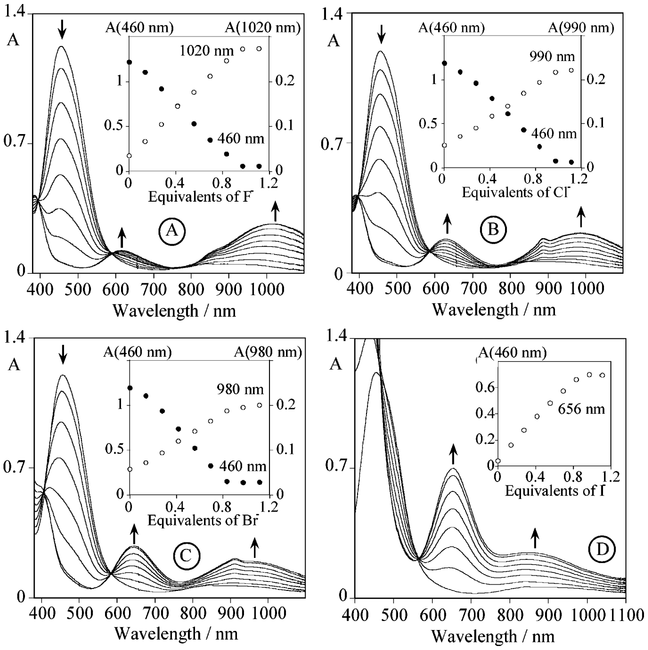
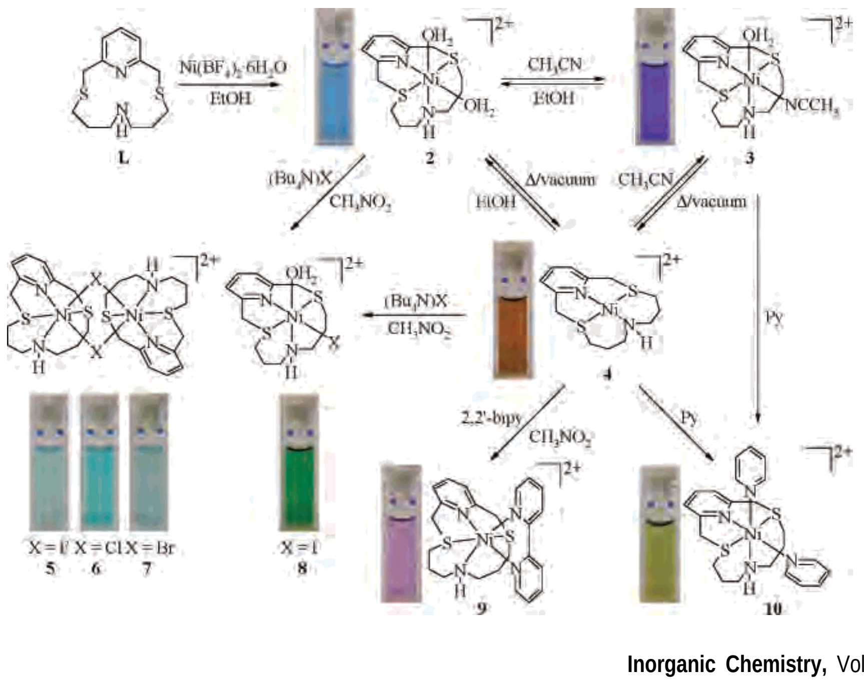


Figure 7. Absorption titrations at room temperature of nitromethane solutions of **4** with tetrabutylammonium fluoride (A), chloride (B), bromide (C), and iodide (D). The insets show the absorbances at different wavelengths ([**4**$(BF_4)_2$] = 5.33×10^{-3} M).

The color of nitrometane solutions of **4** turns from red to cyan by addition of fluoride, chloride, or bromide. In contrast, the color of a nitrometane solution of **4** turns from red to dark green by addition of iodide (see Scheme 2). Figure 7 shows the absorption titrations of nitromethane solutions of **4** with the tetrabutylammonium halides. The addition of fluoride, chloride, or bromide caused a decrease in the intensity of the band assigned to the square-planar complex (460 nm), as well as the development of three new bands around 390, 630, and 980 nm (ϵ = 16 and 56 M^{-1} cm^{-1}), corresponding to the pseudo-octahedral species. In the iodide titration, the disappearance of the band at 460 nm was not

Scheme 2



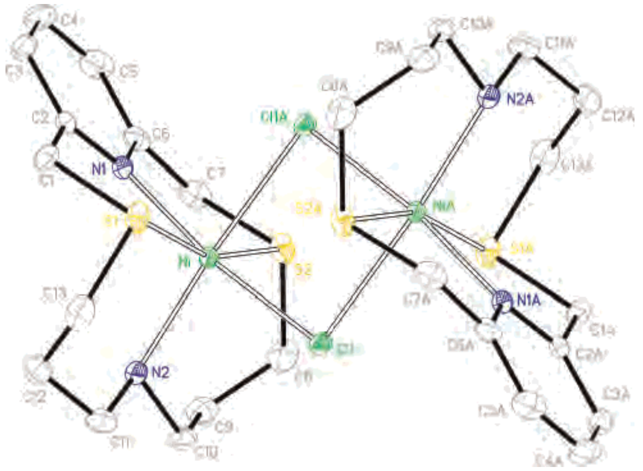


Figure 8. Structure of complex $[\{Ni(\mathbf{L})\}_2(\mu\text{-}Cl)_2]^{2+}$. Ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

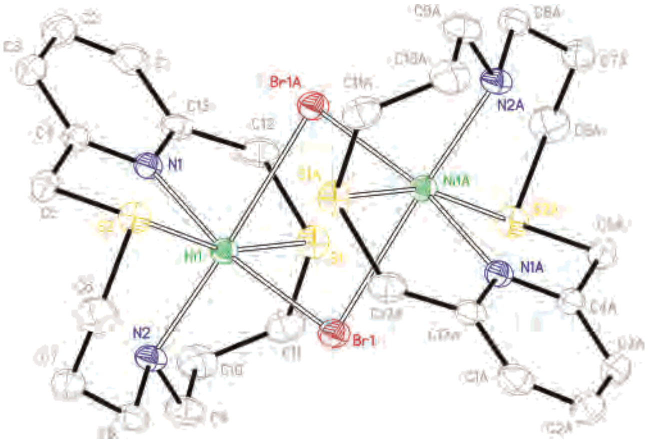


Figure 9. Structure of complex $[\{Ni(\mathbf{L})\}_2(\mu\text{-}Br)_2]^{2+}$. Ellipsoids are shown at the 40% probability level. Hydrogen atoms are omitted for clarity.

observed because it is overlapped by the strong absorption of the iodide ions; however, the addition of increasing amounts of iodide produced the development of two new bands centered at 654 and 848 nm ($\epsilon = 94$ and 33 M^{-1} cm^{-1}, respectively), which suggests the formation of a very distorted octahedral complex.[26] In all these titrations, a plateau was reached after addition of 1 equiv of halide, which indicates that the stoichiometry of the resulting compounds is 1:1. This stoichiometry, together with the pseudo-octahedral geometry of the resulting species, suggests that they could be dimeric compounds with two halide bridges between two Ni**L** moieties, formulated as $[\{Ni(\mathbf{L})\}_2(\mu\text{-}X)_2]^{2+}$, or monomeric compounds with an halide and a solvent molecule coordinated to one Ni**L** moiety, formulated as $[NiX(solvent)(\mathbf{L})]^{2+}$.

The halide complexes were isolated from the reaction between **2**$(X)_2$ ($X = BF_4$, ClO_4) and the corresponding tetrabutylammonium halide. The fluoride, chloride, and bromide complexes behave as 2:1 electrolytes in nitromethane solution, whereas the iodide complex behaves as 1:1 electrolyte in the same conditions. These data, together with the elemental analyses and the ESI-MS spectra of these complexes, suggest that they should be formulated as $[\{Ni(\mathbf{L})\}_2(\mu\text{-}X)_2]^{2+}$ for X = F, Cl, or Br (**5**, **6**, and **7**, respectively) and $[NiX(solvent)(\mathbf{L})]^{+}$ for X = I (**8**). The X-ray data of **6**$(ClO_4)_2$ and **7**$(Br)_2$ confirm the structures assigned on the basis of spectroscopic evidences. Figures 8 and 9 show the molecular structures and numbering schemes of **6** and **7**, respectively.

These structures consist of complex cations **6** and perchlorate counterions in the case of the chloride and complex cations **7**, bromide counterions, and nitromethane molecules in the case of the bromide. Both complex cations consist of two Ni**L** units bridged by two halide ions. The coordination geometry of the nickel atoms is a distorted octahedron defined by two mutually cis halide bridges and the four donor atoms (two S and two N) of one macrocyclic ligand, which adopts a folded conformation similar to those observed in the structures of **2** and **3**. The Ni−N and Ni−S distances are also comparable to those found in the structures of **2** and **3**. The Ni−X distances of each complex ion are 2.3811(6) and 2.5350(7) Å for **6** and 2.5228(6) and 2.7686(7) Å for 7; therefore, there are two significantly different Ni−X distances in each complex ion. This is a common situation, as can be observed by analyzing the 36 previously reported structures of dimeric octahedral nickel complexes with double chloride bridges and the 7 analogous structures with bromide bridges.[28] The average Ni−Cl distance of these previously reported structures (2.44 Å) is almost identical to that found in **6** (2.46 Å). However, the two Ni−Cl distances of this complex are close to the shortest and longest distances of the related reported structures, 2.33 and 2.58 Å, respectively. In fact, the relative difference between both Ni−Cl distances of **6** is the third largest difference of this type of complexes. The average Ni−Br distance of **7** (2.64 Å) is significantly longer than the average distance of the other reported structures of dimeric octahedral nickel complexes with double bromide bridges. In addition, the longest Ni−Br distance of **7** is ca. 0.1 Å larger than the longest distance of the previously reported structures, which makes the relative difference between the Ni−Br distances (0.246 Å) the largest found in this family of dimeric complexes. As stated before, the asymmetry of the bromide bridges is more pronounced than that of the chloride ones; therefore, the larger the size of the halide ion, the greater the asymmetry of its bridges and the weaker its largest bond. This tendency agrees well with the experimental data because, although the formation of the dimeric complex with fluoride ions was observed, the formation of the analogous iodide complex was not observed. Further studies are in progress to determine if the $[Ni(\mathbf{L})]^{2+}$ moiety could be used as a device for detecting iodide ions.

Conclusions

The reaction between the macrocyclic ligand **L** and $Ni(X)_2$ ($X = ClO_4$ or BF_4), leads to formation of the square-planar complex **4** only when no other coordinating species are present in the medium. Addition of coordinating solvent molecules, such as acetonitrile or water, to nitromethane solutions of **4** changes the geometry of the nickel ion from square planar to octahedral. These solvent molecules can be easily removed by heating the resulting solid complexes, which indicates the reversibility of the process. Furthermore, these molecules can also be replaced by adding other neutral or negatively charged ligands. In the octahedral complexes **2**, **3**, **6**, and **7**, **L** adopts a folded conformation and the other two monodentate ligands have a relative cis configuration.

The color of nitromethane solutions of **4** turns from red to blue, violet, pink, and yellow-green by adding water, acetonitrile, 2,2′-bipyridine, and pyridine, respectively. On the other hand, cyan solutions were obtained by adding fluoride, chloride, or bromide; however, the addition of iodide leads to dark green solutions. This behavior encourages further studies in order to develop new devices for detecting iodide ions in solution.

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Supporting Information Available: References and analyses of the crystallographic distances Ni−H_2O and Ni−ClO_4 of octahedral nickel complexes; references and analyses of the crystallographic distances Ni−Cl and Ni−Br of dimeric octahedral nickel complexes with double halide bridges; ^1H, $^{13}C\{^1H\}$, and HMQC NMR spectra of **L** and **4**$(BF_4)_2$; X-ray crystallographic data for **2**$(ClO_4)_2$, **3**$(ClO_4)_2$, **6**$(ClO_4)_2$, and **7**$(Br)_2 \cdot 2CH_3NO_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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