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Synthesis and Reactivity of Nickel(II) Complexes of the Pyridine-Based Phosphorus-Containing Macrocycle 6-Phenyl-15-aza-6-phospha-3,9-dithiabicyclo[9,3,1]pentadeca-1(15),11,13-triene

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The reactivity of the phosphomacrocycle 6-phenyl-15-aza-6-phospha-3,9-dithiabicyclo[9,3,1]pentadeca-1(15), 11,13-triene (L) toward different Ni(II) salts has been studied. The reaction of L with 1 molar equiv of Ni(II) perchlorate in acetonitrile solution gives the complex $[Ni(L)(CH_3CN)_2](ClO_4)_2$ (**1**), which crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 12.704(2)$ Å, $b = 13.538(2)$ Å, $c = 17.377(2)$ Å, $\beta = 107.554(8)°$, and $Z = 4$. The Ni(II) atom in **1** shows an octahedral environment defined by the four donor atoms of L and two acetonitrile molecules in a cis disposition. The reaction of L with Ni(II) perchlorate in 2:1 molar ratio yields the green complex $[Ni(Lox)_2](ClO_4)_2$ (**2**) in which the phosphine groups of the ligand L are in their phosphine-oxide form (Lox). The same complex is also obtained by adding more ligand L to an acetonitrile solution of **1**. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 10.564(1)$ Å, $b = 11.975(2)$ Å, $c = 9.124(2)$ Å, $\alpha = 109.79(1)°$, $\beta = 95.67(2)°$, $\gamma = 109.19(1)°$, and $Z = 1$. The octahedral coordinated Ni(II) atom in **2** lies on a crystallographic center of symmetry, and it is surrounded by two pyridine nitrogen atoms, two thioether sulfur atoms, and two phosphine-oxide oxygen atoms provided by two facially coordinated Lox ligands. The reaction of L with Ni(II) chloride and Ni(II) thiocyanate yields the complexes $[NiCl_2(L)]$ (**3**) and $[Ni(NCS)_2(L)]$ (**4**), respectively, which are also obtained by adding Me_4NCl or KSCN to an acetonitrile solution of **1**. Complex **4** crystallizes in the monoclinic space group $P2_1/n$ (No. 14), with $a = 11.139(2)$ Å, $b = 13.270(2)$ Å, $c = 14.885(1)$ Å, $\beta = 92.34(1)°$, and $Z = 4$, and its structure is similar to that of complex **1**, simply replacing the two acetonitrile molecules by two SCN^- anions. The reactions of the complex **1** with different chelating (en, bipy, *o*-phen) and nonchelating (py) N-donor ligands have also been carried out. In all cases the two acetonitrile molecules of **1** are easily replaced by the N-donor ligands, but the macrocycle L molecule remains coordinated to the Ni(II) atom. The crystal structure of the complex $[Ni(L)(py)_2](ClO_4)_2$ (**5**) is also elucidated. Crystal data: monoclinic space group $P2_1/c$ (No. 14) $a = 13.063(2)$ Å, $b = 16.615(3)$ Å, $c = 14.973(3)$ Å, $\beta = 91.76(2)°$, $Z = 4$.

Introduction

In the last years we have reported the synthesis and complexing behavior of several macrocyclic and open-chain ligands containing the NS_2 donor group which is present in the 2,6-bis(thiomethyl)pyridine unit.[1,2] In these papers we have demonstrated that some of the studied NS_2-based macrocycles behave as neutral carriers in all-solid-state ion-selective electrodes discriminating Cu(II) from Ni(II) and Co(II).[1d] These results encouraged us to study the coordinating abilities of new macrocycles containing the 2,6-bis(thiomethyl)pyridine unit, and we have recently reported the synthesis of the phosphine containing macrocycle 6-phenyl-15-aza-6-phospha-3,9-dithiabicyclo[9,3,1]pentadeca-1(15),11,13-triene (L in Scheme 1).[3] The chemistry of phosphomacrocycles has been comparatively less developed than that of their oxygen, nitrogen, or sulfur

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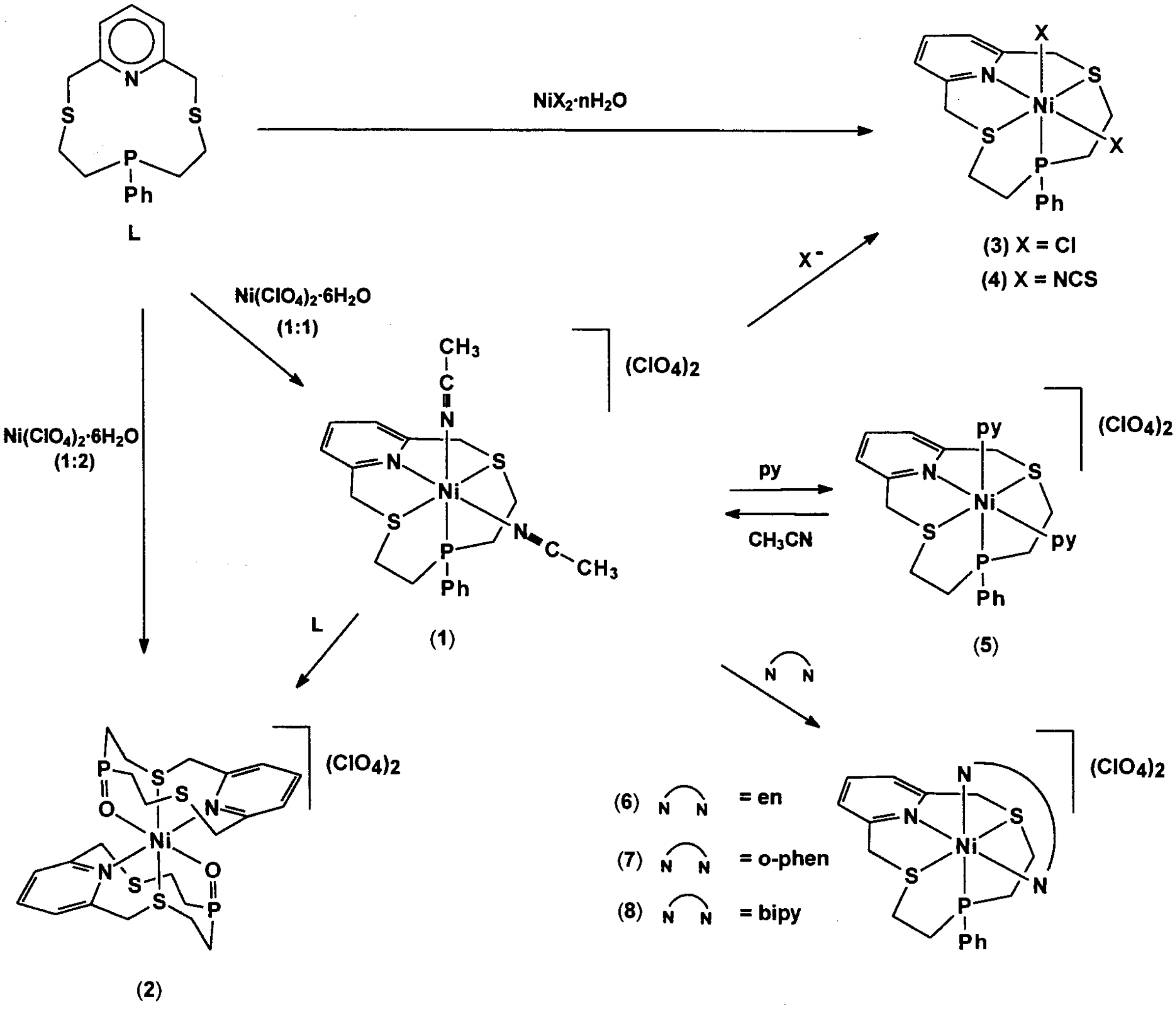
Scheme 1



equivalents.[4] However, the potential catalytic activity of the metal complexes of these ligands and the documented capability of their phosphoryl[5,6] and thiophosphoryl[7] derivatives to interact selectively with ionic species increases the interest in the synthesis of new phosphomacrocycles. In this context we expect that the NS_2P macrocycle L, which combines hard and soft donor atoms, could exhibit interesting coordinating properties toward first and second row transition metal ions. As an additional point of interest, ligands containing N, S, and P mixed donor atoms have been recently used as models in the study of redox processes involved in Ni-containing biological systems.[8]

In this paper we report on the reaction products of the NS_2P macrocyclic ligand L with different Ni(II) salts and their reactivity in front of anionic and neutral N-donor ligands.

Results and Discussion

The syntheses and molecular structures of the new complexes are summarized in Scheme 1.

Reactions of L with $Ni(ClO_4)_2{\cdot}6H_2O$. The reaction at open atmosphere of equimolar amounts of ligand L and $Ni(ClO_4)_2{\cdot}6H_2O$ in acetonitrile solution yields a violet air-stable solution. Addition of diethyl ether to this solution causes precipitation of compound **1** as violet crystals, whose elemental analysis fits the formula $Ni(ClO_4)_2(L)(CH_3CN)_2$. This crystalline material, which slowly turns opaque at room temperature, is soluble in acetonitrile, acetone, and chloroform and behaves as a 2:1 electrolyte in acetonitrile solution. The IR spectrum shows a strong band at 2302 cm^{-1} assigned to the acetonitrile CN stretching. This band position, which is similar to that found in other Ni-acetonitrile complexes,[9,10] proves that the two acetonitrile molecules are directly bound the Ni(II) ion. Therefore, the complex **1** must be formulated as $[Ni(L)(CH_3CN)_2](ClO_4)_2$, as has also been demonstrated by X-ray diffraction analysis.

The reaction at open atmosphere of acetonitrile solutions of ligand L and $Ni(ClO_4)_2{\cdot}6H_2O$ in a 2:1 molar ratio displays a very different behavior to that described before. In this case the reaction mixture turns green and, after addition of diethyl ether, a green, air-stable, crystalline material appears which corresponds to compound **2**. This compound behaves as a 2:1 electrolyte in acetonitrile solution and its elemental analyses indicate that the ligand L and $Ni(ClO_4)_2$ are present in a 2:1

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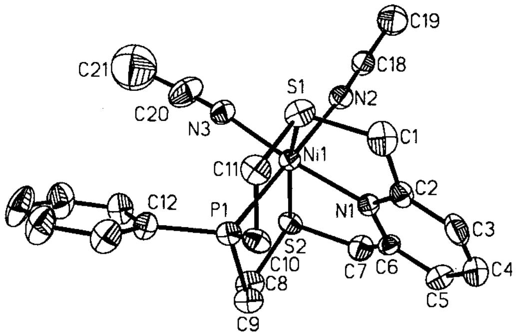

Figure 1. ORTEP plot of complex unit $[\mathrm{Ni(L)(CH_3CN)_2}]^{2+}$ of **1** showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

molar ratio, without any solvent molecules, as it has been confirmed by IR spectroscopy. It is interesting to note that the green, 2:1 complex **2** is also obtained by reaction of equimolar acetonitrile solutions of ligand L and the violet 1:1 complex **1**. Some discrepancies between the calculated and found analysis suggested us that the ligand L in **2** is modified in this complex, as it has been confirmed by X-ray diffraction analysis.

Crystal Structures of 1 and 2. The crystal structure of **1** consists of discrete $[\mathrm{Ni(L)(CH_3CN)_2}]^{2+}$ cations and $\mathrm{ClO_4^-}$ anions without any significant interactions between them. Figure 1 shows the molecular structure and labeling scheme for $[\mathrm{Ni(L)(CH_3CN)_2}]^{2+}$. The coordination sphere of the Ni(II) atom in this complex cation is a distorted octahedron defined by two thioether sulfurs, the phosphine phosphorus and the pyridine nitrogen atoms of the ligand L and two nitrogen atoms from the acetonitrile molecules. The Ni−S distances (2.442(3) Å) are scarcely longer than those found in related Ni(II) macrocyclic complexes containing the 2,6-bis(thiomethyl)pyridine unit[11] (ca. 2.39 Å) and closer to the typical values for Ni(II)-thioether binding (ca. 2.42 Å).[8,10,12] The Ni−N(L) and the Ni−P bond lengths (2.082(6) and 2.342(2) Å, respectively) are not significantly different from the found values in related Ni(II) complexes.[8,11] The two Ni−N(acetonitrile) distances show slightly different values (2.090(7) and 2.023(7) Å), as it has been observed in other bis(acetonitrile)-Ni(II) complexes.[10,13a,b] However, there is no evidence to indicate a different reactivity between the two coordinated acetonitrile molecules, because both are easily replaced by other ligands (see below). The major distortion in the octahedral geometry around the Ni(II) atom is imposed by the meridional coordination of the 2,6-bis(thiomethyl)pyridine unit, as it is observed in the value of the S1−Ni−S2 angle (163.61(9)°). The phosphine-phosphorus atom is located perpendicularly to the plane defined by the Ni(II), the N(L), and the two thioether-sulfur atoms, which provides a folded conformation of the ligand L and leaves the two acetonitrile molecules in a relative cis orientation. There are in the literature several reported cases of bis(acetonitrile)-Ni(II) complexes with tetradentate ligands showing the acetonitrile molecules in a trans orientation;[11a,13] however, the cis disposition of these molecules seems to be less frequent.[10]

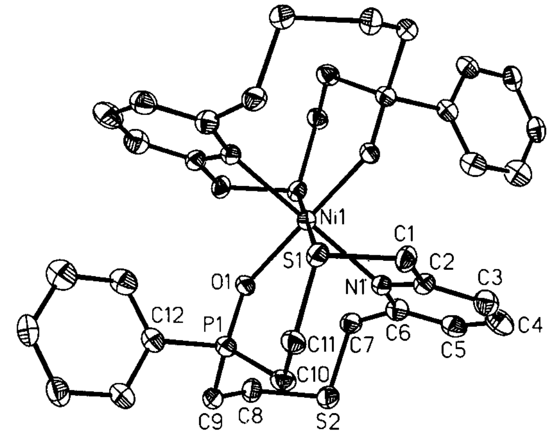

Figure 2. ORTEP plot of the complex unit $[\mathrm{Ni(Lox)_2}]^{2+}$ of **2** showing 30% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

The crystal structure of **2** consists of discrete $\mathrm{ClO_4^-}$ anions and $[\mathrm{Ni(Lox)_2}]^{2+}$ complex cations where the ligand L exists in its phosphine-oxide form (Lox). Figure 2 shows the molecular structure and labeling scheme for $[\mathrm{Ni(Lox)_2}]^{2+}$. The Ni(II) atom occupies a crystallographic inversion center in a distorted octahedral environment of two pyridine nitrogen atoms, two thioether-sulfur atoms and two phosphine-oxide oxygen atoms provided by two facially coordinating Lox ligands. Thus, each Lox macrocyclic unit acts as a tridentate ligand using only three of its four donor atoms and leaving one of the two thioether-sulfur atoms uncoordinated. The Ni−S bond distances (2.451(2) Å) are similar to that found in complex **1**. However, the Ni−N bond lengths (2.189(6) Å) are slightly longer that the average distance found in other reported Ni(II)-pyridine complexes[8,10,11,14] (ca. 2.12 Å). The Ni−O and P−O bond distances (2.022(2) and 1.515(5) Å, respectively) are comparable to those found in the few octahedral Ni(II)-$\mathrm{OPR_3}$ complexes reported yet in the literature.[15] It is interesting to compare the structure of $[\mathrm{Ni(Lox)_2}]^{2+}$ described here with that found in the cation $[\mathrm{Co(Lox)_2}]^{2+}$, which we have previously reported in the double complex salt $[\mathrm{Co(Lox)_2}][\mathrm{CoCl_3(Lox)}]_2$.[3] Both cation complexes are essentially identical with small differences in the M−N and M−S bond distances, which are slightly longer in the Co(II) complex, as it was expected from the different ionic radii of Ni(II) and Co(II).[16] This fact evidences that the noncoordinating behavior of the sulfur S(2) makes the Lox ligand flexible enough to accommodate different metal cations while maintaining the same sandwich-like structure.

As mentioned above, the two macrocyclic ligands in complex **2** are in their phosphine-oxide form (Lox). This can be explained by the reaction of the ligand L and the Ni(II) ion in acetonitrile solution with atmospheric dioxygen, which promotes the oxidation of the phosphine group. The same behavior was observed in the reaction between the ligand L and $\mathrm{CoCl_2}$ in acetonitrile solution, which yields the aforementioned compound $[\mathrm{Co(Lox)_2}][\mathrm{CoCl_3(Lox)}]_2$. However both reactions have different features. The ligand L oxidation in the Co(II) reaction is a slow process (it is easely monitored by UV spectroscopy), and not depends on the L:Co(II) stoichiometric ratio used. The same process in the Ni(II) reaction is very fast, but only occurs when the amount of ligand L exceed the 1:1 ligand-to-metal ratio. Several phosphine-containing Co(II) complexes have been

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reported to display similar behavior toward dioxygen.[17] Even, a mechanism involving the initial formation of a Co(II)-dioxygen adduct has been suggested to explain the observed ligand oxidation.[17b] However, we have not found in the literature examples of this type of oxidation reactions involving phosphine-containing Ni(II) complexes.

Reactions of L with $NiCl_2 \cdot 6H_2O$ and $Ni(SCN)_2 \cdot H_2O$. The reaction of equimolar amounts of ligand L and $NiCl_2 \cdot 6H_2O$ or $Ni(SCN)_2 \cdot H_2O$ in acetonitrile solution gives the air-stable, nonelectrolyte products **3** and **4**, respectively. Both compounds are less solubles in acetonitrile than **1** and **2**, and they are also obtained by adding $(Me_4N)Cl$ and KSCN, respectively, to an acetonitrile solution of **1**. These data suggest that the molecular structure of both compounds is similar to that described for the complex **1** simply replacing the acetonitrile coordinated molecules by the anionic ligands. This assumption has been confirmed by the X-ray diffraction analysis of the compound **4** (see below). It is interesting to note that these reactions seem not to be depending on the used L:Ni(II) stoichiometric ratio. All the experiences made using different metal-to-ligand ratio gave as final products the compounds **3** and **4**, and no evidences of oxidation products have been found. This behavior is in contrast with that described in the reactivity of the ligand L in front of $Ni(ClO_4)_2$. The reason could be the low solubility and neutral character of the compounds **3** and **4** which increase their stability and prevent the oxidation of the ligand L.

Reactions of 1 with N-Donor Ligands. The previously described reactivity evidences the lability of the acetonitrile ligands in complex **1**. In addition, the new complexes seem to retain the macrocyclic ligand L coordinated to the Ni(II) ion which reflects the stability of the (L)Ni(II) coordinated unit. To confirm this assumption, several reactions between the complex **1** and different chelating and nonchelating N-donor ligands have been carried out.

The reaction of equimolar amounts of the complex **1** and pyridine in acetonitrile solution yields the green, air stable complex **5**. The crystal structure of this compound (see below) confirms that the acetonitrile ligands of **1** have been replaced by two pyridine molecules while the (L)Ni(II) unit remains unchanged. The complex **5** redissolves in acetonitrile, producing a violet solution, the electronic spectra of which are coincident with that obtained from acetonitrile solutions of **1**. This fact evidences the lability of the pyridine ligands in **5**, which are displaced to regenerate the complex **1**, in excess of acetonitrile.

A method similar to synthesize the complex **5** has been used to obtain the compounds **6**−**8**. Complex **1** reacts with aliphatic (ethylenediamine) or aromatic (*o*-phenantroline and bipyridine) N-donor chelating ligands, giving the colored, air-stable compounds **6**, **7**, and **8**, respectively. All of them behave as 2:1 electrolytes in acetonitrile solution, and their elemental analysis and IR spectra prove that their molecular structures are similar to that described for **1**, simply replacing the two acetonitrile molecules by the chelating ligand. These complexes are less soluble in acetonitrile than the complex **5**, and no evidence of ligand exchange reactions has been observed in solution. This confirms that the chelating nature of these N-donor ligands stabilizes the complexes **6**−**8** and prevents further reactions.

Crystal Structures of 4 and 5. The crystal structure of the complex **4** consists of discrete $[Ni(NCS)_2(L)]$ molecules, whereas that of the complex **5** contains ClO_4^- anions and $[Ni(L)(py)_2]^{2+}$ complex cations without significant interactions between them. Figures 3 and 4 show the molecular structures and labeling schemes for $[Ni(NCS)_2(L)]$ and $[Ni(L)(py)_2]^{2+}$, respectively. In both cases the coordination geometry of the Ni(II) atom is a distorted octahedron defined by the four donor atoms of the ligand L and the nitrogen atoms of the two SCN^- ions in **4** or the two pyridine molecules in **5**. The arrangement of these ligands around the Ni(II) atoms is similar to that described for the complex **1**, so the two monodentate ligands of each compound have a relative cis orientation. The Ni−N(L) and the two Ni−S distances in **4** (2.108(2), 2.4784(8), and 2.4566(8) Å, respectively) and **5** (2.123(5), 2.515(2), and 2.468(2) Å, respectively) are slightly longer than those for **1**. However, the Ni−P bond distances in **1** and **5** (2.343(2) and 2.342(2) Å, respectively) are equal, whereas in **4** (2.3669(7) Å) it is slightly longer. The Ni−N(pyridine) (compound **5**) and Ni−N(thiocyanate) bond lengths exhibit values comparable to the average distances reported in the literature[12] (*ca.* 2.12 and 2.06 Å, respectively). As in complex **1**, distortion in the Ni(II) octahedral geometry of **4** and **5** is also manifested by the value of the S−Ni−S bond angle (166.33(3) and 159.91(6)°, respectively), which confirms the strain imposed to the ligand L by the meridional coordination of the 2,6-bis(thiomethyl)pyridine unit.

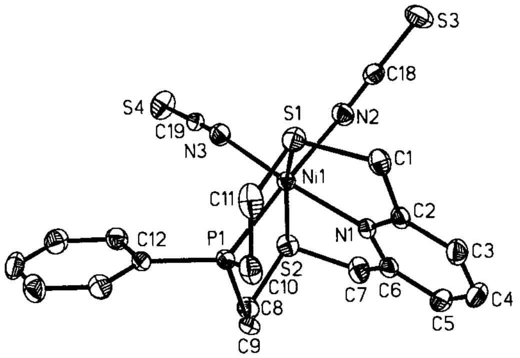

Figure 3. ORTEP plot of the complex $[Ni(NCS)_2(L)]$ **4** showing 20% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

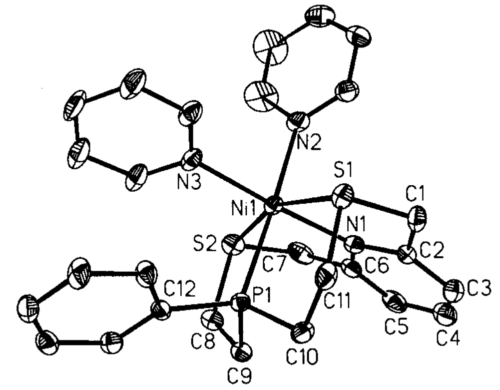

Figure 4. ORTEP plot of the complex unit $[Ni(L)(py)_2]^{2+}$ of **5** showing 20% displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Electronic Spectral Data

complex	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})[a]	Δ_o, cm^{-1}
1	905 (sh), 828 (106), 542 (38)	12 077
2	915 (sh), 844 (65), 539 (30)	11 848
3	970 (sh), 940 (88), 582 (20)	10 638
4	975 (sh), 930 (95), 575 (37)	10 753
6	950 (sh), 918 (62), 592 (25)	10 893
7	983 (sh), 911 (75), 592 (33), 525 (sh)	10 977
8	979 (sh), 915 (60), 594 (43), 531 (sh)	10 929

[a] In CH_3CN.

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Table 2. Crystallographic Data for $[Ni(L)(CH_3CN)_2](ClO_4)_2$ (**1**), $[Ni(Lox)_2](ClO_4)_2$ (**2**), $[Ni(NCS)_2(L)]$ (**4**), and $[Ni(L)(py)_2](ClO_4)_2$ (**5**)

	1	2	4	5
empirical formula	$C_{21}H_{26}Cl_2N_3NiO_8PS_2$	$C_{34}H_{40}Cl_2N_2O_{10}P_2S_4$	$C_{19}H_{20}N_3NiPS_4$	$C_{27}H_{30}Cl_2N_3NiO_8PS_2$
fw	673.15	956.47	508.30	749.25
T,°C	21	21	20	23
λ, Å	0.710 69	0.710 69	0.710 69	0.710 69
a, Å	12.704(2)	10.564(1)	11.139(2)	13.063(2)
b, Å	13.538(2)	11.975(2)	13.270(2)	16.615(3)
c, Å	17.377(2)	9.124(2)	14.885(1)	14.973(3)
α, deg	90.0	109.79(1)	90.0	90.0
β, deg	107.554(8)	95.67(2)	92.34(1)	91.76(2)
γ, deg	90.0	109.19(1)	90.0	90.0
V, Å^3	2849.4(7)	996.6(3)	2198.5(5)	3248(1)
Z	4	1	4	4
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
ρ_{calcd}, g cm^{-3}	1.569	1.594	1.536	1.532
μ, mm^{-1}	1.12	0.97	1.35	0.99
$F(000)$	1384	494	1048	1544
transm coeff	0.90−1.00	0.88−1.11	0.85−1.00	0.80−1.00
R^a	0.070	0.059	0.028	0.046
R_w	0.076^b	0.067^b	0.059^c	0.049^b

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. ^{c} $R_w = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}$.

Electronic Spectroscopy. The electronic spectra of the Ni(II) complexes in acetonitrile solution are consistent with their pseudooctahedral symmetry. The spectra show two d−d bands (ν_1 and ν_2), whereas the third or highest energy band expected for octahedral Ni(II) complexes ($^3A_2 \rightarrow {}^3T_1(P)$, ν_3) is overlapped with a strong charge-transfer band starting around 400 nm, which in the case of **7** and **8** shifts to lower energies and partially overlaps the ν_2 absorption. The spectral data and the ligand field parameter, Δ_o, for all the compounds except **5** (see above) are given in Table 1. Complex **1** has the largest value of Δ_o (12 077 cm^{-1}) in this series. This value is clearly superior to those reported for the octahedral tetrathiomacrocyclic Ni(II) complexes[18] $[Ni([n]aneS_4)(CH_3CN)_2]^{2+}$ {10 810−10 290 cm^{-1}; $[n]$aneS$_4$ = [12]aneS$_4$ (1,4,7,10-tetrathiacyclododecane), [14]aneS$_4$ (1,4,8,11-tetrathiacyclotetradecane), and [16]aneS$_4$ (1,5,9,13-tetrathiacyclohexadecane)}, where the relative disposition of the acetonitrile molecules (cis or trans) is uncertain, and closer to that observed in the complex $[Ni(L1)(CH_3CN)_2]^{2+}$ [11 800 cm^{-1}, L1 = 1,6-bis(2-pyridyl)-2,5-dithiahexane], which contains an N_2S_2 open-chain ligand.[10] Complexes **3**, **4**, and **6**−**8** show Δ_o values ranging from 10 977 to 10 638 cm^{-1}. All these complexes contain the same (L)Ni(II) coordinated subunit so, the differences between their Δ_o values are due to the additional monodentate or N-chelating ligands in the complex. This is confirmed when the values of Δ_o are ordered giving the sequence **7** (*o*-phen) > **8** (bipy) > **6** (en) > **4** (SCN) > **3** (Cl), which fits well with the classical spectrochemical series.[19] The $N_2S_2O_2$ environment of the Ni(II) atom in **2** makes this complex different than the other Ni(II) complexes reported here. This is evidenced by the Δ_o value (11 848 cm^{-1}), which is more like those reported for other N_xS_{3-x} or N_xO_{3-x} (x = 1,2-bismacrocyclic Ni(II) complexes such as $[Ni([9]aneNS_2)_2]^{2+}$ (11 930 cm^{-1}, [9]aneNS$_2$ = 1,4-dithia-7-azacyclononane),[20] $[Ni([9]aneN_2S)_2]^{2+}$ (11 770 cm^{-1}, [9]aneN$_2$S = 1-thia-4,7-diazacyclononane),[21] or $[Ni([9]aneN_2O)_2]^{2+}$ (11 600 cm^{-1}, [9]aneN$_2$O = 1-oxa-4,7-diazacyclononane).[21]

Conclusions

The macrocycle L behaves as a four-coordinate ligand toward Ni(II), leaving free two adjacent coordination sites on the hexacoordinated metal ion in a relative cis orientation, which are filled by anionic ligands (chloride, thiocyanate) or solvent molecules (acetonitrile), depending on the Ni(II) salt used. The reactions described here show that the solvent molecules in the $[Ni(L)(CH_3CN)_2]^{2+}$ complex cation could be easily replaced by different ligands, but maintaining the macrocycle L coordinated to the Ni(II) atom. All of this confirms the key role of the complex **1** in this work and evidences their potential usefulness as starting products in reactions to obtain new Ni(II) macrocyclic complexes.

Experimental Procedures

General Methods. Reagent grade solvents were purified by distillation before use. Commercial grade chemicals were used without purification. The ligand 6-phenyl-15-aza-6-phospha-3,9-dithiabicyclo-[9,3,1]pentadeca-1(15),11,13-triene (L) was obtained by a described procedure.[3] Elemental analyses were performed by the Service of Chemical Analysis of the Universitat Autònoma de Barcelona using a Carlo Erba EA-1108 instrument. Electronic and IR spectra were recorded using Kontron-Uvicon 860 and Perkin-Elmer FT-1710 instruments, respectively.

Safety Note. *Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.*

Synthesis of the Ni(II) Complexes. $[Ni(L)(CH_3CN)_2](ClO_4)_2$ (1). $Ni(ClO_4)_2{\cdot}6H_2O$ (0.219 g, 0.598 mmol) dissolved in acetonitrile (3 cm^3) was added to a solution of L (0.200 g, 0.599 mmol) in dichloromethane (2 cm^3). The violet mixture was stirred for 1 h in air, and then diethyl ether (2 cm^3) was added. The resulting solution was kept at −5 °C overnight. A violet crystalline precipitate (**1**) was formed which was filtered off and vacuum-dried. Yield: 0.310 g (77%). Anal. Found: C, 37.0; H, 3.7; N, 5.9; S, 9.6. Calcd for $C_{21}H_{26}Cl_2N_3NiO_8PS_2$: C, 37.47; H, 3.89; N, 6.24; S, 9.53.

$[Ni(Lox)_2](ClO_4)_2$ (2). Preparation from L. $Ni(ClO_4)_2{\cdot}6H_2O$ (0.109 g, 0.299 mmol) dissolved in acetone (2 cm^3) was added to a solution of L (0.200 g, 0.599 mmol) in acetonitrile (3 cm^3). The green mixture was stirred for 1 h in air, and then diethyl ether (2 cm^3) was added. The resulting solution was stirred for 5 min, and a green precipitate (**2**) was formed, which was filtered off and vacuum-dried. Yield: 0.220 g (82%).

Preparation from 1. A solution of L (0.025 g, 0.074 mmol) in dichloromethane (2 cm^3) was slowly added to a solution of **1** (0.050 g, 0.074 mmol) in acetonitrile (3 cm^3). The violet mixture was stirred

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ni(1)−S(1)	2.442(3)	P(1)−C(10)	1.82(1)
Ni(1)−S(2)	2.442(3)	P(1)−C(12)	1.834(8)
Ni(1)−P(1)	2.342(2)	N(1)−C(2)	1.35(1)
Ni(1)−N(1)	2.082(6)	N(1)−C(6)	1.347(9)
Ni(1)−N(2)	2.090(7)	N(2)−C(18)	1.11(1)
Ni(1)−N(3)	2.023(7)	N(3)−C(20)	1.12(1)
S(1)−C(1)	1.797(9)	C(1)−C(2)	1.51(1)
S(1)−C(11)	1.817(9)	C(6)−C(7)	1.47(1)
S(2)−C(7)	1.811(9)	C(8)−C(9)	1.53(1)
S(2)−C(8)	1.817(9)	C(10)−C(11)	1.55(1)
P(1)−C(9)	1.822(8)		

S(1)−Ni(1)−S(2)	163.61(9)	C(7)−S(2)−C(8)	101.6(4)
S(1)−Ni(1)−P(1)	84.91(8)	C(9)−P(1)−C(10)	109.4(4)
S(1)−Ni(1)−N(1)	84.2(2)	Ni(1)−N(2)−C(18)	174.2(6)
S(2)−Ni(1)−P(1)	85.50(8)	Ni(1)−N(3)−C(20)	172.7(9)
S(2)−Ni(1)−N(1)	83.0(2)	S(1)−C(1)−C(2)	116.4(7)
P(1)−Ni(1)−N(1)	92.4(2)	S(2)−C(7)−C(6)	116.5(5)
P(1)−Ni(1)−N(2)	178.0(2)	S(2)−C(8)−C(9)	115.3(7)
N(1)−Ni(1)−N(3)	172.5(3)	P(1)−C(9)−C(8)	109.5(6)
N(2)−Ni(1)−N(3)	85.8(3)	P(1)−C(10)−C(11)	107.9(6)
C(1)−S(1)−C(11)	100.6(4)	S(1)−C(11)−C(10)	113.5(5)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ni(1)−S(1)	2.451(2)	P(1)−C(10)	1.799(9)
Ni(1)−O(1)	2.022(3)	P(1)−C(12)	1.789(7)
Ni(1)−N(1)	2.189(6)	N(1)−C(2)	1.34(1)
S(1)−C(1)	1.799(7)	N(1)−C(6)	1.35(1)
S(1)−C(11)	1.819(7)	C(1)−C(2)	1.51(1)
S(2)−C(7)	1.827(7)	C(6)−C(7)	1.50(1)
S(2)−C(8)	1.814(8)	C(8)−C(9)	1.51(1)
P(1)−O(1)	1.515(5)	C(10)−C(11)	1.53(1)
P(1)−C(9)	1.809(7)		

S(1)−Ni(1)−O(1)	92.8(2)	C(9)−P(1)−C(10)	109.5(4)
S(1)−Ni(1)−N(1)	79.8(2)	C(9)−P(1)−C(12)	107.4(3)
O(1)−Ni(1)−N(1)	91.5(2)	C(10)−P(1)−C(12)	105.1(4)
Ni(1)−S(1)−C(1)	90.9(3)	Ni(1)−O(1)−P(1)	133.8(3)
Ni(1)−S(1)−C(11)	113.5(3)	S(1)−C(1)−C(2)	114.7(5)
C(1)−S(1)−C(11)	103.5(4)	S(2)−C(7)−C(6)	108.2(6)
C(7)−S(2)−C(8)	102.0(4)	S(2)−C(8)−C(9)	115.4(7)
O(1)−P(1)−C(9)	111.0(4)	P(1)−C(9)−C(8)	116.1(4)
O(1)−P(1)−C(10)	112.8(3)	P(1)−C(10)−C(11)	114.3(6)
O(1)−P(1)−C(12)	110.9(3)	S(1)−C(11)−C(10)	118.2(6)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **4**

Ni(1)−N(1)	2.108(2)	S(2)−C(7)	1.797(3)
Ni(1)−N(2)	2.067(2)	S(2)−C(8)	1.819(3)
Ni(1)−N(3)	2.026(2)	S(3)−C(18)	1.627(3)
Ni(1)−P(1)	2.3669(7)	S(4)−C(19)	1.626(3)
Ni(1)−S(1)	2.4566(8)	P(1)−C(10)	1.829(3)
Ni(1)−S(2)	2.4784(8)	P(1)−C(9)	1.830(3)
S(1)−C(1)	1.810(3)	N(2)−C(18)	1.156(3)
S(1)−C(11)	1.822(3)	N(3)−C(19)	1.161(3)

N(3)−Ni(1)−N(2)	88.84(9)	N(2)−Ni(1)−S(2)	103.79(7)
N(3)−Ni(1)−N(1)	169.60(8)	N(1)−Ni(1)−S(2)	82.39(6)
N(2)−Ni(1)−N(1)	84.16(8)	P(1)−Ni(1)−S(2)	84.21(3)
N(3)−Ni(1)−P(1)	97.52(7)	S(1)−Ni(1)−S(2)	161.33(3)
N(2)−Ni(1)−P(1)	169.67(7)	C(1)−S(1)−C(11)	102.0(2)
N(1)−Ni(1)−P(1)	90.54(6)	C(7)−S(2)−C(8)	100.9(2)
N(3)−Ni(1)−S(1)	103.46(7)	C(10)−P(1)−C(9)	108.8(2)
N(2)−Ni(1)−S(1)	87.35(7)	C(18)−N(2)−Ni(1)	149.5(2)
N(1)−Ni(1)−S(1)	83.93(6)	C(19)−N(3)−Ni(1)	151.1(2)
P(1)−Ni(1)−S(1)	83.27(3)	C(8)−C(9)−P(1)	108.8(2)
N(3)−Ni(1)−S(2)	91.86(7)	C(11)−C(10)−P(1)	108.7(2)

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **5**

Ni(1)−S(1)	2.515(2)	P(1)−C(9)	1.822(6)
Ni(1)−S(2)	2.468(2)	P(1)−C(10)	1.819(6)
Ni(1)−P(1)	2.343(2)	P(1)−C(12)	1.816(6)
Ni(1)−N(1)	2.123(5)	N(1)−C(2)	1.349(7)
Ni(1)−N(2)	2.115(5)	N(1)−C(6)	1.352(8)
Ni(1)−N(3)	2.100(5)	C(1)−C(2)	1.511(9)
S(1)−C(1)	1.799(7)	C(6)−C(7)	1.506(9)
S(1)−C(11)	1.822(7)	C(8)−C(9)	1.526(8)
S(2)−C(7)	1.793(7)	C(10)−C(11)	1.529(9)
S(2)−C(8)	1.821(6)		

S(1)−Ni(1)−S(2)	159.91(6)	C(7)−S(2)−C(8)	102.4(3)
S(1)−Ni(1)−P(1)	83.74(6)	C(9)−P(1)−C(10)	108.0(3)
S(1)−Ni(1)−N(1)	81.4(1)	C(9)−P(1)−C(12)	108.4(3)
S(2)−Ni(1)−P(1)	84.43(6)	C(10)−P(1)−C(12)	107.3(3)
S(2)−Ni(1)−N(1)	82.9(1)	S(1)−C(1)−C(2)	116.1(4)
P(1)−Ni(1)−N(1)	92.1(1)	S(2)−C(7)−C(6)	115.6(4)
P(1)−Ni(1)−N(2)	177.6(2)	S(2)−C(8)−C(9)	116.0(4)
N(1)−Ni(1)−N(3)	176.6(2)	P(1)−C(9)−C(8)	110.6(4)
N(2)−Ni(1)−N(3)	86.8(2)	P(1)−C(10)−C(11)	110.6(4)
C(1)−S(1)−C(11)	99.7(3)	S(1)−C(11)−C(10)	115.5(4)

for 2 h in air. During this time the solution changes from violet to green. The resulting solution was treated with diethyl ether (2 cm^3) and stirred for 5 min. A green precipitate (**2**) was formed, which was filtered off and vacuum-dried. Yield: 0.058 g (82%). Anal. Found: C, 42.5; H, 4.2; N, 2.8; S, 13.2. Calcd for $C_{34}H_{40}Cl_2N_2NiO_{10}P_2S_4$: C, 42.69; H, 4.21; N, 2.93; S, 13.41.

[NiCl$_2$(L)] (3). Preparation from L. $NiCl_2 \cdot 6H_2O$ (0.071 g, 0.300 mmol) dissolved in acetonitrile (2 cm^3) was added to a solution of L (0.100 g, 0.300 mmol) in acetonitrile (2 cm^3). The resulting solution was stirred for 15 min in air, and a green precipitate (**3**) was formed, which was filtered off and vacuum-dried. Yield: 0.108 g (77%).

Preparation from 1. Me_4NCl (8 mg, 0.068 mmol) was slowly added to a solution of **1** (23 mg, 0.034 mmol) in acetonitrile (3 cm^3). The resulting solution was stirred in air for half an hour, and a green precipitate (**3**) was formed, which was filtered off and vacuum-dried. Yield: 0.012 g (76%). Anal. Found: C, 43.9; H, 4.3; N, 2.9; S, 13.5. Calcd for $C_{17}H_{20}Cl_2NNiPS_2$: C, 44.09; H, 4.35; N, 3.02; S, 13.85.

[Ni(NCS)$_2$(L)] (4). Preparation from L. $Ni(SCN)_2 \cdot H_2O$ (0.073 g, 0.410 mmol) dissolved in acetonitrile (2 cm^3) was added to a solution of L (0.127 g, 0.381 mmol) in dichloromethane (2 cm^3). The resulting solution was stirred for half an hour in air, and a blue precipitate (**4**) was formed which was filtered off and vacuum-dried. Yield: 0.120 g (62%).

Preparation from 1. KSCN (17 mg, 0.172 mmol) was slowly added to a solution of **1** (58 mg, 0.086 mmol) in acetonitrile (3 cm^3). The resulting solution was stirred for half an hour in air, and a white precipitate ($KClO_4$) appeared, which was filtered off and discarded. The remaining solution was treated with diethyl ether (10 cm^3) and stirred for 5 min. A blue precipitate (**4**) was formed, which was filtered off and vacuum-dried. Yield: 0.029 g (66%). Anal. Found: C, 44.6; H, 3.8; N, 8.1; S, 25.0. Calcd for $C_{19}H_{20}N_3NiPS_4$: C, 44.97; H, 3.98; N, 8.29; S, 25.23.

[Ni(L)(py)$_2$](ClO$_4$)$_2$ (5). Pyridine (6 mg, 0.074 mmol) was slowly added to a solution of **1** (25 mg, 0.037 mmol) in acetone (3 cm^3). The violet mixture was stirred for 2 h in air. During this time the solution changed from violet to green. The resulting solution was treated with diethyl ether (2 cm^3) and stirred for 5 min. A green precipitate (**5**) was formed, which was filtered off and vacuum-dried. Yield: 0.023 g (82%). Anal. Found: C, 43.3; H, 4.1; N, 5.4; S, 8.5. Calcd for $C_{27}H_{30}Cl_2N_3NiO_8PS_2$: C, 43.37; H, 4.05; N, 5.62; S, 8.56.

[Ni(L)(en)](ClO$_4$)$_2$ (6). Ethylenediamine (3.1 mg, 0.051 mmol) was slowly added to a solution of **1** (35 mg, 0.051 mmol) in acetone (2 cm^3). The green mixture was stirred for 15 min in air. The resulting solution was treated with diethyl ether (2 cm^3) and cooled at 4 °C for 10 h. A green precipitate (**6**) was formed, which was filtered off and vacuum-dried. Yield: 0.031 g (93%). Anal. Found: C, 35.0; H, 4.2; N, 6.1; S, 9.2. Calcd for $C_{19}H_{22}Cl_2N_3NiO_8PS_2$: C, 35.13; H, 4.35; N, 6.47; S, 9.85.

[Ni(L)(*o*-phen)](ClO$_4$)$_2$ (7). *o*-Phenanthroline (8.9 mg, 0.044 mmol) was slowly added to a solution of **1** (31 mg, 0.044 mmol) in acetone (3 cm^3). The resulting solution was stirred for 15 min in air, and a pink precipitate (**7**) formed, which was filtered off and vacuum-dried. Yield: 0.028 g (82%). Anal. Found: C, 44.9; H, 3.5; N, 5.3; S, 8.1. Calcd for $C_{29}H_{28}Cl_2N_3NiO_8PS_2$: C, 45.25; H, 3.67; N, 5.46; S, 8.32.

[Ni(L)(bipy)](ClO$_4$)$_2$ (8). 2,2′-Bipyridine (4.7 mg, 0.030 mmol) was slowly added to a solution of **1** (20 mg, 0.030 mmol) in acetone (3 cm^3). The resulting solution was stirred for 15 min in air, and a dark yellow precipitate (**8**) formed, which was filtered off and vacuum-dried. Yield: 0.013 g (59%). Anal. Found: C, 43.3; H, 3.6; N, 5.6; S, 8.4. Calcd for $C_{27}H_{28}Cl_2N_3NiO_8PS_2$: C, 43.49; H, 3.79; N, 5.64; S, 8.58.

X-ray Data Collections and Structure Determinations of 1, 2, 4, and 5. Single-crystal data collections for **1**, **2**, **4**, and **5** were performed at ambient temperature with a Rigaku AFC5S diffractometer using monochromatized Mo Kα radiation ($\lambda = 0.710\,69$ Å) and $\omega - 2\theta$ scan mode. The unit cell parameters were determined by least-squares refinements of 25 carefully centered reflections. Each set of data was corrected for Lorentz and polarization effects and for absorption (ψ scans). A total of 5251, 3508, 4297, and 5934 unique reflections were collected ($2\theta_{max} = 50°$) for **1**, **2**, **4**, and **5**, respectively, and of those 3087, 2658, 3089, and 3020 were considered as observed. The three check reflections monitored after every 150 reflections showed no decay during the course of data collections.

The structures were solved by direct methods using SHELXS86.[22] Least-squares refinements were performed using the crystallographic software packages of XTAL[23] for **1** and **2**, SHELXL-93[24] for **4**, and TEXSAN[25] for **5**. The structures of **1**, **2**, and **5** were refined on F, and that of **4**, on F^2.

In complex **1**, one of the perchlorate ions exhibits rotational disorder. The two forms of the ion have the oxygen O(5) in common and they differ by rotation around Cl(2)−O(5) bond. The non-hydrogen atoms, except the disordered oxygen atoms and the methyl carbon C(19), were refined with anisotropic displacement parameters. The methyl group containing C(19) was refined as a rigid group with a group isotropic displacement parameter, but the hydrogen atoms connected to C(21) could not be positioned. The rest of the hydrogen atoms were placed at their calculated positions [C−H = 0.95 Å and $U(H) = 1.2U_{eq}$(host atom)].

For **2** and **5**, all non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed at their calculated positions. For **4**, non-hydrogen atoms were refined with anisotropic and hydrogen atoms with fixed isotropic displacement parameters.

Neutral atomic scattering factors were those included in the programs. Crystallographic data are presented in Table 2, and selected bond parameters for complexes **1**, **2**, **4**, and **5** are in Tables 3, 4, 5, and 6, respectively.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of **1**, **2**, **4**, and **5** are available on the Internet only. Access information is given on any current masthead page.

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