Lead(II) complexes of lateral macrobicyclic receptors that incorporate a crown moiety and a pyridine head unit[i]

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Abstract

The coordinative properties towards lead(II) of two lateral macrobicyclic receptors that incorporate either a 1,10-diaza-[15]crown-5 (**L**^{7}) or a 4,13-diaza-[18]crown-6 (**L**^{8}) fragment are reported. Spectrophotometric titrations performed in acetonitrile solution indicate only the formation of mononuclear complexes in solution. The X-ray crystal structures of the two receptors show that the conformation adopted by the ligand is imposed by the presence of intramolecular hydrogen-bonding interactions that involve the secondary amine groups and the pivotal nitrogen atoms. The solid-state structure of [Pb(**L**^{7})(NCS)](SCN)·0.5H_2O shows that the metal ion is asymmetrically coordinated inside the macrobicyclic cavity. The Pb^{II} ion is coordinated to the nitrogen atom of the pyridine unit, the two secondary amine atoms, two oxygen atoms of the crown moiety, and a nitrogen atom of an isothiocyanate group. The distances between the Pb^{II} ion and the two pivotal nitrogen atoms as well as one of the oxygen atoms of the crown moiety are too long (>2.92 Å) to be considered unequivocal bonds, and should be regarded only as weak interactions. The protonation constants of **L**^{7} and **L**^{8} as well as the stability constants of their Pb^{II} complexes were investigated by using potentiometric titrations in 95 % methanol (I = 0.1 M, $n$$Bu_4NClO_4$, 25 °C). The two receptors undergo two protonation processes in the pH range investigated (2.0 < pH < 12.0), which correspond to the protonation of the nitrogen atoms of the oxa–aza moiety. The log K_{PbL} value obtained for **L**^{7} [9.906(1)] is approximately 1.1 log K units higher than the one determined for **L**^{8} [8.75(1)].

Keywords: macrocycles; N,O ligands; lead; crown compounds; cryptands

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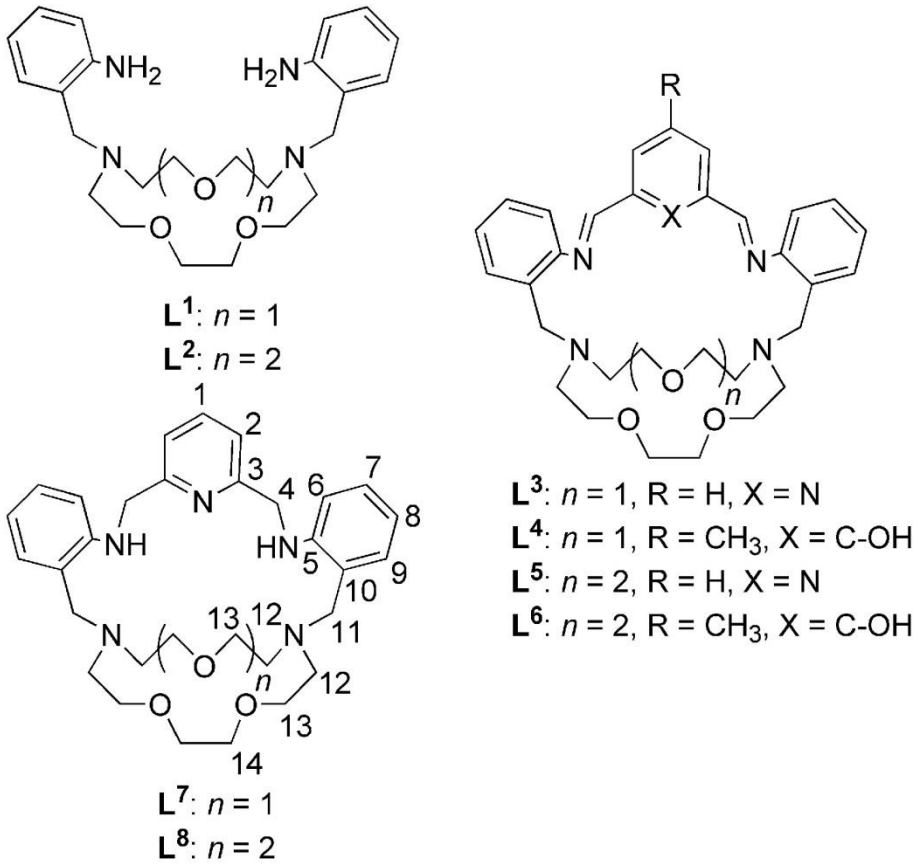
Introduction

The interest in the coordination chemistry of lead(II) is related to its inherent toxicity and health effects and to the widespread industrial uses of its compounds.[1,2] Lead poisoning particularly affects young children, who can absorb up to 50 % of ingested lead.[3] Once ingested through the gastrointestinal tract, lead accumulates in soft tissues, including vital organs such as the kidneys, liver, or brain, where it is bound to thiol and phosphate groups in proteins, nucleic acids, and cell membranes,[4,5] ultimately resulting in severe neurological and/or hematological effects.[6,7] Among the different platforms used for lead(II) complexation, macrocyclic receptors such as crown ethers and related systems,[8] calixarenes,[9] or cryptands[10] play an essential role. These receptors possess a high level of preorganization that often results in superior selectivities of their complexes with metal ions in comparison to those of acyclic ligands.[11]

Lateral macrobicycles are dissymmetrical molecules that are structurally based on the combination of two different binding subunits, a chelating one and a macrocyclic one.[12] Considering the peculiar structural features shown by lateral macrobicycles, one could anticipate that this type of macropolycyclic architectures offers a range of interesting and potentially useful molecular recognition properties, as they offer the advantage of being preorganized and therefore capable of profiting from the thermodynamic macrobicyclic effect. Moreover, they contain convergent binding groups that can be especially designed to match the functionality of the guest molecule. It has been shown that lateral macrobicycles behave as very versatile receptors that can be used as platforms to obtain mono-[13-16] and bimetallic[17] complexes with many different aims (i.e., to induce processes of "push-pull" dimetallic substrate activation)[18] and as receptors for organic molecules,[19] anions,[20] or contact-ion pairs.[21,22]



Scheme 1. Receptors discussed in the present work.

We are interested in the relation between structure and stability of lead(II) complexes with macrocyclic ligands derived from crown ether platforms, as well as in the role of the lone-pair activity of Pb^{II} in these kind of compounds.[23,24] In previous works, we have carried out studies to asses the different complexation capabilities towardslead(II) of the bibracchial lariat ethers **L**[1][16,25] and **L**[2][14] and the related Schiff base lateral macrobicycles **L**[3],[16,24] **L**[4],[26] **L**[5],[15] and **L**[6][25] (Scheme **1**). These macrobicyclic receptors contain two different binding units: a rigid and unsaturated N_2X set (X: N, O) and a flexible and cyclic N_2O_n (n = 3 or 4) set linked by aromatic bridges. As a continuation of these works, in this paper we report the complexation properties of lateral macrobicycles **L**[7] and **L**[8] toward Pb^{II}. These receptors (Scheme **1**) are expected to be more flexible than the parent Schiff base macrobicycles **L**[3] and **L**[5], which could result in a better fit of the coordinative requirements of the metal ion. We have selected the poorly coordinating perchlorate and the strongly coordinating thiocyanate groups as the anions of the metal salt, which allows us to study the effect that the different nature of the counterion may have on the metal coordination environment. The X-ray crystal structures of the two receptors as well as that of a Pb^{II} complex with the receptor **L**[7] have been obtained. The structure of the complexes in acetonitrile has been investigated by means of ^1H and ^{13}C NMR spectroscopy. Finally, the thermodynamic stability of the complexes in MeOH/H_2O (95:5, *v*:*v*) mixtures has been investigated by using potentiometric titrations.

Results and discussion

Synthesis and characterization of the complexes

The macrobicyclic receptors **L**[7] and **L**[8] were prepared by reduction of the corresponding Pb^{II} perchlorate complexes of the Schiff base macrobicyclic precursors **L**[3] and **L**[5] (Scheme **1**) with sodium borohydride.[27] Reaction of **L**[7] or **L**[8]with of lead(II) salts (perchlorate or thiocyanate; 1 equiv.) in absolute ethanol gives complexes [Pb(**L**[7])]$(SCN)_2$ (**1**), [Pb(**L**[7])]$(ClO_4)_2$·MeOH (**2**), [Pb(**L**[8])]$(SCN)_2$·H_2O (**3**), and [Pb(**L**[8])]$(ClO_4)_2$·H_2O (**4**) in good yields (79–87 %). The IR spectra (KBr disks) of **2** and **4** display bands that correspond to the ν_{as}(ClO) stretching and δ_{as}(OClO) bending modes of the perchlorate groups without splitting at approximately 1095 and 624 cm^{-1}, respectively, as befits uncoordinated anions.[28] The IR spectra of **1**and **3** exhibit the thiocyanate stretch at around 2040 cm^{-1}. Upon coordination to Pb^{II} the C=N stretching band of the pyridine moiety in **L**[7] and **L**[8] shifts by 3–15 cm^{-1} to lower wavenumbers, thereby suggesting that the pyridine nitrogen atom is coordinating to the metal ion in the complexes. The FAB mass spectra, obtained using 3-nitrobenzyl alcohol as the matrix, display intense peaks due to [Pb(**L**^{n}–H)]$^+$and [Pb(**L**^{n})X]$^+$ (n = 7, 8; X = ClO_4^-, SCN^-), which confirms the formation of the desired complexes.

X-ray crystal structures

The solid-state structures of compounds **L**[7], **L**[8], and **1** were determined by single-crystal X-ray diffraction analyses. The structures of **L**[7] and **L**[8] are shown in Figure **1** and Figure **2**, respectively. The bond lengths and angles do not show any significant deviation from the expected values. In both **L**[7] and **L**[8], the tertiary amine nitrogen atoms adopt an *endo–endo* conformation with their lone pairs pointing inside the macrobicyclic cavity. This conformation is probably imposed by the presence of intramolecular hydrogen-bonding interactions that involve the pivotal nitrogen atoms and NH groups of the ligand. In the case of **L**[7], the asymmetric unit contains two ligand molecules with only slightly different bond lengths and angles, and therefore we will focus the following discussion on one of these molecules. The secondary amine nitrogen atoms of **L**[7] (N3 and N5) are involved in hydrogen-bonding interactions with the pivotal nitrogen atoms N1 and N2: [N1···N3 2.869(2) Å; N1···H3N–N3 2.19(3) Å, N1–H3N–N3 139(3)°; N2···N5 2.923(2) Å; N2···H5N–N5 2.27(3) Å, N2–H5N–N5 135(2)°]. The secondary amine groups of **L**[8] are also involved in weak intramolecular hydrogen-bonding interactions: the pivotal nitrogen N5 interacts with N3 [N5···N3 2.955(3) Å; N5···H3AN3 2.31(4) Å, N5–H3A–N3 135(3)°], whereas N2 is involved in a bifurcated

hydrogen-bonding interaction[29] with N4 and O4 [N2···N4 2.831(3) Å; N2–H2A···N4 2.12(4) Å, N2–H2A–N4 142(3)° and N2···O4 3.320(3) Å; N2–H2A···O4 2.65(4) Å, N2–H2A–O4 138(3)°]. The five nitrogen atoms of **L**[8] are essentially coplanar [root-mean-square (rms) deviation from planarity 0.0949 Å], as well as the four oxygen atoms of the crown moiety (rms deviation from planarity 0.0351 Å). On the other hand, the different size of the crown moiety fragment in receptors **L**[7] and **L**[8]results in different conformations of the macrobicyclic chain that contain the three aromatic units. Indeed, the angles between the pyridine planes and each benzyl rings amount to 50.4 and 56.4° (**L**[7]), and 59.7 and 86.4° (**L**[8]), whereas the angles between the least-square planes defined by the benzyl rings are 77.4° (**L**[7]) and 38.9° (**L**[8]).

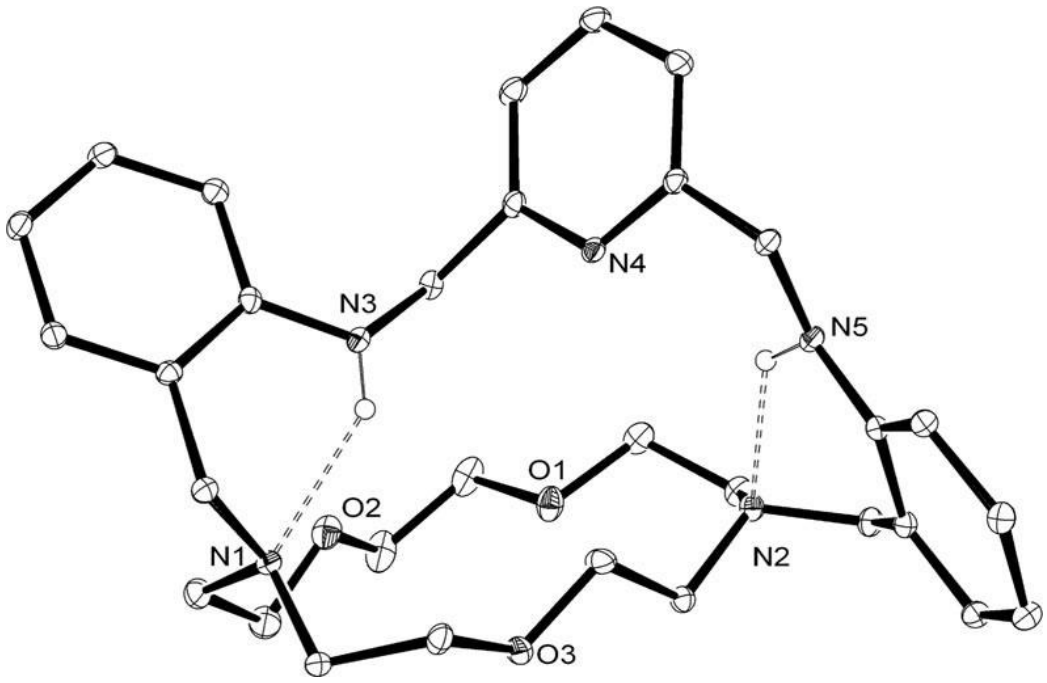


Figure 1. Crystal structure of **L**[7]. Only one of the molecules present in the asymmetric unit is shown for the sake of clarity. The ORTEP plot is drawn at the 30 % probability level. Hydrogen atoms, except those involved in intramolecular hydrogen-bonding interactions, are omitted for clarity.

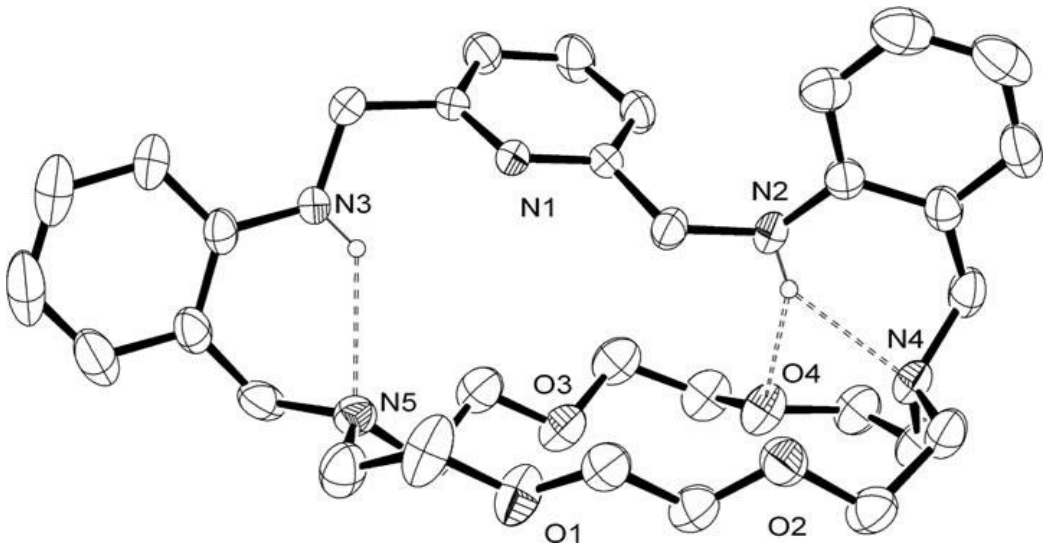


Figure 2. Crystal structure of **L**[8]. The ORTEP plot is drawn at the 30 % probability level. Hydrogen atoms, except those involved in intramolecular hydrogen-bonding interactions, are omitted for clarity.

Crystals of **1** contain the cation $[Pb\mathbf{L}^7(NCS)]^+$ and a noncoordinated thiocyanate anion. Figure **3** displays a view of the structure of the cation, whereas selected bond lengths and angles of the metal-coordination environment are given in Table **1**. The lead(II) ion is asymmetrically placed inside the macrobicyclic cavity. The metal ion is six-coordinate, being bound to the pyridyl nitrogen N3; both secondary amine nitrogen atoms, N2 and N4; two oxygen atoms of the crown moiety, O2 and O3; and a nitrogen atom of the coordinated isothiocyanate group (N2S). Both *N*-[24,30] and *S*-bonded[24,31] Pb^{II} thiocyanate complexes have been reported in the literature, in line with the classification of this metal ion as intermediate in Pearson's hard and soft (Lewis) acids and bases (HSAB).[32] The presence of an *N*-bonded SCN^- ligand in **1** is probably the consequence of the steric hindrance caused around the metal ion by the coordination of the macrobicyclic ligand.[33] The distances between the lead(II) ion and the two pivotal nitrogen atoms [Pb1–N5 2.939(5) and Pb1–N1 2.990(6) Å] are considerably longer than unequivocal Pb–N bonds. The Pb1–O1 distance [2.924(5) Å] is also too long to be considered as an unequivocal Pb–O bond [the sum of the ionic radius of nonacoordinated Pb^{II},[34] and the van der Waals radii of N or O[35] amount to 2.90 and 2.87 Å, respectively]. The secondary amine nitrogen atom N2 is involved in weak intramolecular hydrogen-bonding interaction with one of the oxygen atoms of the crown moiety: [N2···O1 3.099(7) Å; N2–H2N···O1 2.51(5) Å, N2–H2N–O1 129(6)°]. This intramolecular hydrogen-bonding interaction may be responsible for the long Pb1–O1 and Pb1–N5 distances observed. Alternatively, these long bond lengths could be attributed to the stereochemical activity of the Pb^{II} lone pair,[36] which causes a nonspherical charge distribution around the Pb^{II} cation. However, the lengthening of these bond lengths is expected to be accompanied by a concomitant shortening of the bond lengths to donor atoms placed away from the site of the stereochemically active lone pair. The Pb1–N4 distance [2.723(5) Å] is not particularly short, and thus we conclude that the Pb^{II} lone pair is not stereochemically active in **1**.

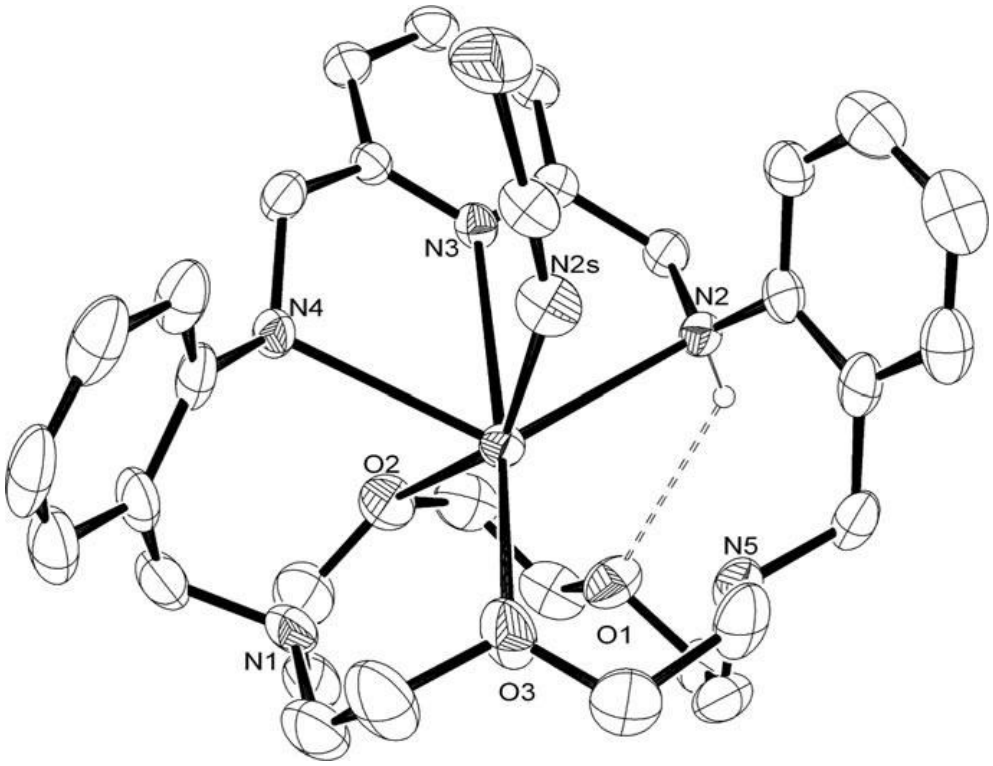


Figure 3. X-ray crystal structure of the cation $[Pb\mathbf{L}^7(NCS)]^+$ in compound **1** with atom labeling. Hydrogen atoms, except those involved in intramolecular hydrogen-bonding interactions, are omitted for simplicity. The ORTEP plot is drawn at the 30 % probability level.

Table 1. Bond lengths [Å] of the metal-coordination environment in compound **1**; see Figure 3 for labeling.

Pb1–N2S	2.450(7)	Pb1–O2	2.810(5)
Pb1–N3	2.675(5)	Pb1–N5	2.939(5)
Pb1–N4	2.723(5)	Pb1–N1	2.990(6)
Pb1–O3	2.686(5)	Pb1–O1	2.924(5)
Pb1–N2	2.784(6)		

The conformation of the macrobicycle in **1** is such that the two benzyl rings are folded toward the crown moiety chain that contains O3, with the angle between the least-square planes defined by the benzyl rings amounting to 67.6(3)°. Angles between the pyridine planes and each of the benzyl rings amount to 68.7(2) and 88.6(2)°; these values are considerably different than those found for the free receptor (see above). Moreover, the distance between both pivotal nitrogen atoms in **1** [4.789(9) Å] is much shorter than that found for $\mathbf{L}^{7}$ [6.008(2) Å]. Thus, the conformation adopted by the macrobicyclic receptor in **1** is considerably different than that observed for uncoordinated $\mathbf{L}^{7}$.

A comparison of the bond lengths of the Pb^{II} coordination environment in **1** with those observed previously for $[Pb(\mathbf{L}^{3})(ClO_4)]^{+}$[16] shows that the reduction of the imine groups of $\mathbf{L}^{3}$ causes an important lengthening of the distances between the metal ion and donor atoms of the crown moiety (0.02–0.25 Å). Conversely, the Pb–N3 and Pb–N4 distances are reduced by approximately 0.03 and 0.11 Å. Thus, the reduction of the imine groups of $\mathbf{L}^{3}$ weakens the interaction between the donor atoms of the crown moiety and the metal ion, which in turn strengthens the bonds formed between the Pb^{II} and N_3 donor set of the macrobicyclic chain that contains the pyridine moiety. We attribute this effect to intramolecular hydrogen-bonding interaction that involves the secondary amine nitrogen atom N2 and one of the oxygen atoms of the crown moiety in $[Pb\mathbf{L}^{7}(NCS)]^{+}$.

Solution properties

The formation of the Pb^{II} complexes of $\mathbf{L}^{7}$ and $\mathbf{L}^{8}$ was investigated by using spectrophotometric titrations in acetonitrile. The UV/Vis spectrum of the free receptor $\mathbf{L}^{7}$ recorded in this solvent features two absorption bands with maxima at 252 nm (ϵ_0 = 24000 $dm^3\,mol^{-1}\,cm^{-1}$) and 291 nm (ϵ_0 = 8500 $dm^3\,mol^{-1}\,cm^{-1}$), which correspond to E_2 and B charge-transfer bands of the aromatic rings, respectively.[37] The spectrum of $\mathbf{L}^{8}$ is nearly identical to that of $\mathbf{L}^{7}$, with bands at 252 nm (ϵ_0 = 27000 $dm^3\,mol^{-1}\,cm^{-1}$) and 296 nm (ϵ_0 = 8100 $dm^3\,mol^{-1}\,cm^{-1}$). Upon complexation to Pb^{II}, the absorption that appears at lower energies experiences a blueshift, and the band at 252 nm splits into two bands at around 240 and 264 nm, thus enabling the formation of the complexes in solution to be monitored (Figure **4**). The spectrophotometric titrations of $\mathbf{L}^{7}$ and $\mathbf{L}^{8}$ (1.00×10^{-5}M) with $Pb(ClO_4)_2{\cdot}3H_2O$ were performed in acetonitrile with Pb^{II}/**L** molar ratios of 0–4.2. The data displayed a single inflection point when the Pb/**L** molar ratio is close to 1 for both titrations, thereby indicating the existence of only one complex species in solution with a 1:1 (Pb/**L**) stoichiometry. This is confirmed by the presence of isosbestic points at approximately 264 and 285 nm (Figure **4**). These results indicate that both receptors form mononuclear complexes with Pb^{II}. This is in contrast to the behavior of the Schiff base analogue $\mathbf{L}^{5}$ (Scheme **1**), for which spectrophotometric titrations suggested the formation of both 2:1 and 1:1($\mathbf{L}^{5}$/Pb) complexes in solution.[15] The steep curvature of the titration profiles of $\mathbf{L}^{7}$ and $\mathbf{L}^{8}$correspond to especially high equilibrium constants. In particular, the *p*parameter [*p* = (concentration of the complex)/(maximum possible concentration of the complex)] was found to be higher than 0.8 in both cases, a condition that does not allow the determination of a reliable equilibrium constant.[38]

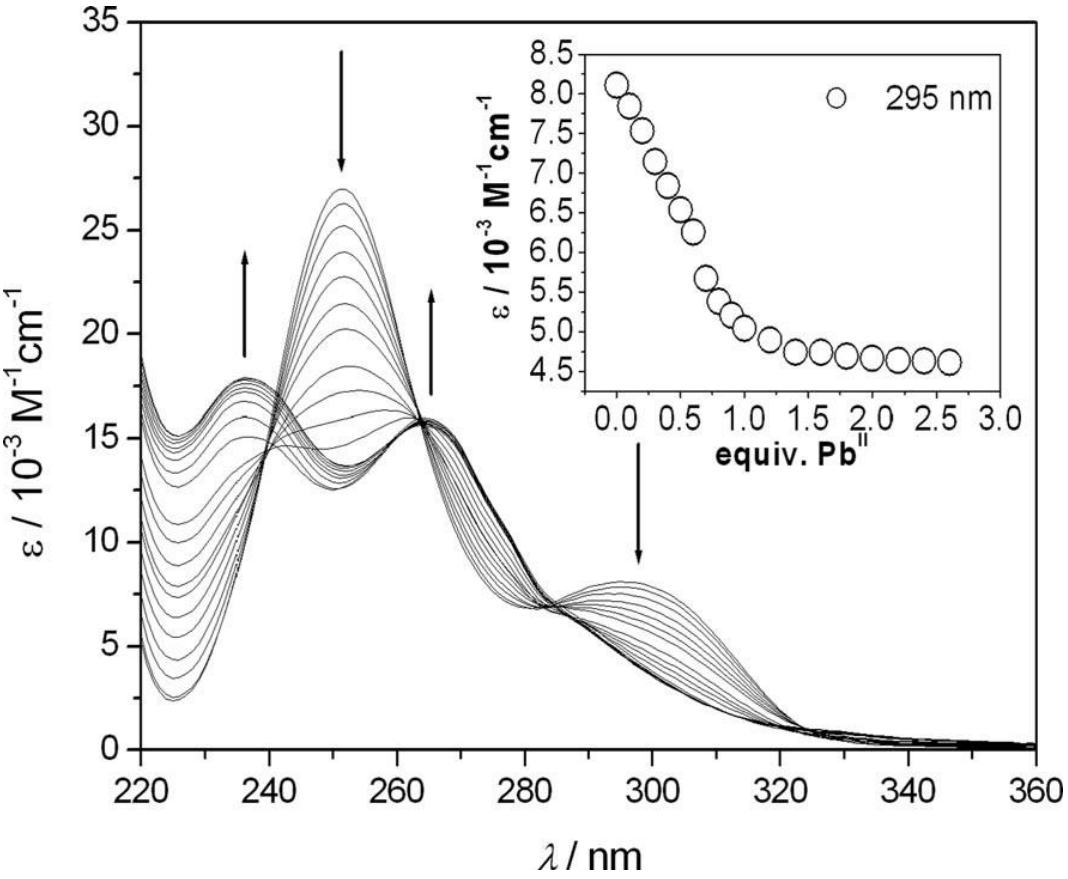


Figure 4. UV/Vis spectrum of **L**[8] in CH_3CN and spectral changes upon addition of aliquots of a solution of $Pb(ClO_4)_2 \cdot 3H_2O$ in the same solvent. Inset: titration profile at 295 nm.

The behavior of the complexes in [D_3]acetonitrile was investigated by ^{1}H and ^{13}C NMR spectroscopy. Assignments were achieved with the aid of 2D H,H COSY, heteronuclear multiple quantum coherence (HMQC) and heteronuclear multiple-bond correlation (HMBC) experiments (see Tables S1 and S2 in the Supporting Information). The poor solubility of **1** in this solvent prevented us from obtaining NMR spectroscopic data for this compound. The ^{13}C NMR spectrum of compound **2** displays 16 signals for the 31 carbon atoms of the ligand backbone, in agreement with an effective C_s symmetry in acetonitrile, whereas the spectra of compounds **3** and **4** show 14 ^{13}C NMR spectroscopic signals (effective C_{2v}symmetry).

Upon coordination to Pb^{II}, the signals that correspond to the protons of the pyridine moiety of **L**[7], H1 and H2, shift downfield by 0.39 and 0.23 ppm, respectively. A similar behavior is observed for the complexes of **L**[8]. The signals that correspond to the protons of the pyridine moiety, H1 and H2, shift downfield by 0.35–0.50 ppm upon coordination (Table S1 in the Supporting Information, Figure **5**). These results are indicative of the coordination of the pyridine moiety to Pb^{II} in the complexes. The aromatic protons of the benzyl rings (H6–H9) and the methylenic protons H4 and H11 undergo substantial downfield shifts upon coordination to the metal ion. Metal-ion complexation also provokes important shifts of most ^{13}C NMR spectroscopic signals of the three compounds (Table S2 in the Supporting Information). Particularly important shifts upon complexation are observed for C2, C5, C6, C8, and C10, in agreement with the coordination to the metal ion of the three nitrogen atoms of the tridentate unit that contains the pyridyl moiety.

The ^{1}H NMR spectrum of **L**[8] shows a broad peak at δ = 7.59 ppm that is attributable to the N–H protons of the secondary amine groups (Figure **5**), whereas for **3** and **4** this resonance appears at higher fields than in the free ligand (δ = 5.68 and 5.14 ppm, respectively). In principle, no distinct region on the δ scale can be assigned to the resonances of exchangeable protons since the position of these resonance signals is strongly

dependent upon the medium and temperature. However, it has been suggested that the formation of hydrogen bonds leads to significant shifts to lower fields.[39] In the case of the **L**[7] complex, metal-ion binding also results in very important shifts to higher fields of the resonance due to N–H protons, which points that in both **L**[7] and **L**[8] the secondary amine protons and the pivotal nitrogen atoms are involved in an intramolecular hydrogen-bonding interaction in acetonitrile, as observed in the solid-state structures of the two receptors (vide supra). This hydrogen-bonding interaction is either not present in the complexes or it is weaker than in the free ligands, thereby resulting in important upfield shifts of the signals due to N–H protons. A comparison of the ^{1}H NMR spectra recorded for compounds **3** and **4** shows that the nature of the counterion substantially affects the chemical shifts of the proton nuclei of the ligand (Figure **4** and Table S1 in the Supporting Information). Thus, thiocyanate coordination appears to provoke substantial changes in the structure of the complex.

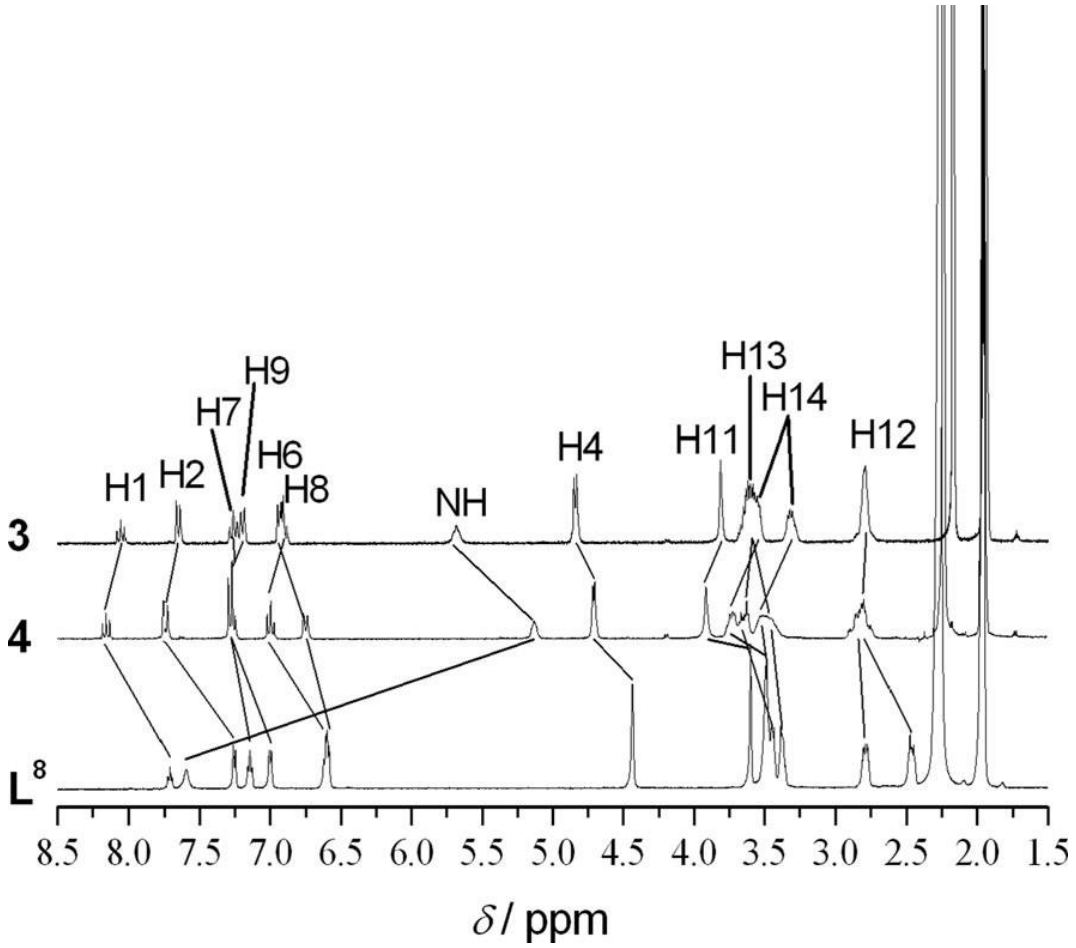


Figure 5. ^{1}H NMR spectra of **L**[8] and compounds **3** and **4** recorded in CD_3CN at 298 K. See Scheme 1 for labeling.

The protonation constants of **L**[7] and **L**[8] as well as the stability constants of their complexes formed with Pb^{II} were determined by potentiometric titrations in 95 % methanol; the constants and standard deviations are given in Table **2**. For comparative purposes, the protonation constants of **L**[1] and **L**[2] (Scheme **1**) and the stability constants of their Pb^{II} complexes are also reported. All the four ligands undergo two protonation processes in the pH range investigated (2.0 < pH < 12.0), which correspond to the protonation of the nitrogen atoms of the oxa–aza moiety. Protonation of these nitrogen atoms has been observed in the solid-state structure of $(H_2\mathbf{L}^5)(ClO_4)_2$.[40] The protonation constants determined for **L**[2] and **L**[8]are lower than those

reported for the parent crown ether 4,13-diaza-[18]crown-6 ($\log K_1 = 9.40$ and $\log K_2 = 7.47$ in 95 % methanol, $I = 0.1$ M Et_4NClO_4, 25 °C).[41] This is in accordance with previous observations in which a diminution of the amine basicity has been observed upon N-alkylation of oxa–aza crown ligands.[42] Both **L**[7]and **L**[8] show lower protonation constants than the parent receptors **L**[1] and **L**[2].

Table 2. Ligand protonation constants and stability constants of their metal complexes.[a]

	L[1]	**L**[2]	**L**[7]	**L**[8]
$\log K_1$[b]	7.680(3)	8.025(2)	6.661(7)	6.865(4)
$\log K_2$[b]	6.160(3)	5.591(1)	5.684(6)	5.435(4)
$\log K_{PbL}$[c]	8.55(1)	10.63(3)	9.906(1)	8.75(5)
$\log K_{Pb(H)L}$[d]	4.30(1)	4.01(2)	2.734(3)	3.37(7)

[a] In 95 % methanol (I = 0.1 M, $n$$Bu_4NClO_4$, 25 °C). [b] $H_{i-1}\mathbf{L} + H^+ \leftrightarrows H_i\mathbf{L}$, i = 1, 2. [c] $Pb^{2+} + \mathbf{L} \leftrightarrows [Pb\mathbf{L}]^{2+}$. [d] $[Pb\mathbf{L}]^{2+} + H^+ \leftrightarrows [PbH\mathbf{L}]^{3+}$.

The $\log K_{PbL}$ values reported in Table **2** show that the four ligands investigated form moderately strong complexes with Pb^{II}. The $\log K_{PbL}$ value obtained for **L**[7] is approximately 1.4 $\log K$ units higher than that determined for the parent receptor **L**[1]. However, the Pb^{II} complex formed by the macrobicyclic receptor **L**[8] is less stable than that formed with the **L**[2] precursor. This is in line with the solid-state structure of the Pb^{II} complex of the macrobicyclic receptor of similar size **L**[5],[15] which shows that the large macrobicyclic cavity of the receptor does not provide an optimum fit for the complexation of Pb^{II}. Receptor **L**[2] provides the highest complex stability among the four receptors investigated, in line with the optimum match between the binding sites offered by the ligand and the Pb^{II} ion.[14] All four Pb^{II} complexes undergo protonation at low pH values. This protonation process probably occurs on one of the nitrogen atoms of the aza-crown moiety, as observed in the solid-state structure of the $[Pb(H\mathbf{L}^5)(NO_3)]^{2+}$ complex.[15]

Conclusion

Lateral macrobicyclic receptors **L**[7] and **L**[8] form moderately strong mononuclear complexes with Pb^{II}. The stability of these complexes is similar to that observed for the complexes of the parent lariat ethers **L**[1] and **L**[2]. The solid-state structure of $[Pb(\mathbf{L}^7)(NCS)](SCN)\cdot 0.5H_2O$ shows that the metal ion is coordinated inside the cavity of the macrobicyclic receptor. However, several donor atoms of the macrocycle remain uncoordinated, which is attributed to the relatively large cavity of the receptor and to the presence of a hydrogen-bonding interaction that involves one of thepivotal nitrogen atoms and an NH group of the receptor. Thus, N-alkylation of these receptors is expected to increase the stability of the corresponding Pb^{II} complexes.

Experimental section

Solvents and starting materials: Receptors **L**[1],[16] **L**[2],[43] **L**[7],[27] and **L**[8] [27] were prepared as described previously. Single crystals suitable for X-ray crystal diffraction of receptors **L**[7] and **L**[8] were grown from a solution of the receptor in acetonitrile. All other chemicals were purchased from commercial sources and used without further purification. Solvents were of reagent grade purified by the usual methods, unless otherwise stated.

Caution! *Although we have experienced no difficulties with the perchlorate salts, these should be regarded as potentially explosive and handled with care.*[44]

Physical methods: ^{1}H and ^{13}C NMR spectra were carried out with a Bruker Avance 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) with respect to TMS. Spectral assignments were based on two-dimensional COSY, HSQC, and HMBC experiments. Elemental analyses were carried out with a Carlo–Erba 1108 elemental analyzer. FAB mass spectra were recorded with a FISONS QUATRO mass spectrometer with Cs ion gun and 3-nitrobenzyl alcohol as matrix. IR spectra were recorded, as KBr discs, with a Bruker Vector 22 spectrophotometer. Electronic spectra were recorded at 20 °C with a Perkin–Elmer Lambda 900 UV/Vis spectrophotometer using 1.0 cm quartz cells. Spectrophotometric titrations were performed in the latter spectrometer connected to an external computer. Typically, a 10^{-5} M solution of the ligand (**L**^{7}or **L**^{8}) in acetonitrile (50 mL) was prepared, and then aliquots (25–300 μL) of a 10^{-3}M solution of $Pb(ClO_4)_2 \cdot 3H_2O$ in the same solvent were successively added. The ionic strength was adjusted to $I = 10^{-3}$ M with tetrabutylammonium perchlorate for each titration.

Potentiometry: Ligand protonation constants and stability constants with Pb^{II}were determined at 25 °C by pH-potentiometric titration in methanol/water mixtures (95 % v/v). A correction was made for the small decrease in volume as a consequence of mixing methanol and water. Atmospheric CO_2 was excluded from the cell during the titration by constant passage of Ar through the solution. The ionic strength was kept at 0.1 M with tetrabutylammonium perchlorate. The titrations were carried out by adding a standardized tetrabutylammonium hydroxide solution with a Metrohm Dosimat 794 automatic burette. A glass electrode filled with LiCl in ethanol was used to measure pH. The stock solutions were prepared by dilution of the appropriate standards. The exact amount of acid present in the standard solutions was determined by pH measurements. Tetrabutylammonium hydroxide was standardized by potentiometric titration against potassium hydrogen phthalate. The ligands were checked for purity by NMR spectroscopy and elemental analysis before titration. The ligand and metal–ligand (1:1) solutions were titrated over the pH range 2.0 < pH < 12.0. The titration data for Pb^{II} complexation were successfully refined assuming the presence of only 1:1 metal–ligand species in solution; in all cases only data that correspond to the lower portions of the titration curves were employed for the calculations in order to avoid complications that arise from competing hydrolysis/precipitation at higher pH values. The protonation and stability constants were calculated from simultaneous fits of two independent titrations with the program HYPERQUAD.[45] The errors given correspond to one standard deviation.

X-ray crystal structures: Three-dimensional X-ray data were collected with Bruker X8 APEXII CCD (**L**^{7}) or Bruker SMART 1000 CCD (**L**^{8}, **1**) diffractometers by the φ/ω scan method. Reflections were measured from a hemisphere of data collected of frames, each covering 0.3° in ω. Of the 52158, 40582, and 41992 reflections measured for **L**^{7}, **L**^{8}, and **1**, all of which were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections, 6939, 4522, and 3919 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 2.0$, respectively. The structures were solved with SHELXS-97[46] by direct methods and refined by full-matrix least-squares methods on F^2 (SHELXL-97)[46] under WINGX.[47] The hydrogen atoms were included in calculated positions and refined by using a riding mode. Minimum and maximum final electronic density: –0.321 and 0.375 e Å^{-3} for **L**^{7}, –0.170 and 0.196 e Å^{-3} for **L**^{8}, and –1.079 and 2.023 e Å^{-3} [next to Pb1] for **1**. Crystal data and details on data collection and refinement are summarized in Table **3**.

CCDC-779434 (for **L**^{7}), -779435 (for **L**^{8}), and -779433 (for **1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 3. Crystal data and structure refinement for compounds **L**^{7}, **L**^{8}, and **1**.

	L^{7}	**L**^{8}	**1**
Formula	$C_{31}H_{41}N_5O_3$	$C_{33}H_{45}N_5O_4$	$C_{33}H_{41}N_7O_3PbS_2$
M_r [g mol^{-1}]	531.69	575.74	855.04
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*P*21	*Pbca*	*Pbca*
T [K]	100.0(2)	298.0(2)	298.0(2)
a [Å]	9.7318(4)	22.6248(9)	18.5899(8)
b [Å]	11.8580(5)	8.9650(4)	12.9940(6)
c [Å]	24.126(1)	31.2078(1)	28.154(1)
α [°]	90	90	90
β [°]	92.465(3)	90	90
γ [°]	90	90	90
V [Å^3]	2781.6(2)	6329.9(4)	6800.8(5)
Z	4	8	8
$\rho_{calcd.}$ [g cm^{-3}]	1.270	1.208	1.670
μ [mm^{-1}]	0.083	0.080	5.129
R_{int}	0.031	0.0556	0.0565
R_1[a]	0.0304	0.0802	0.0376
wR_2 (all data)[b]	0.0903	0.1819	0.1025

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(||F_o|^2 - |F_c|^2|)^2]/\Sigma[w(F_o^4|)]\}^{1/2}$.

[Pb(L^{7})](SCN)$_2$ (1): $Pb(SCN)_2$ (0.0231 g, 0.071 mmol) in absolute ethanol (5 mL) was added to a solution of **L**^{7} (0.0400 g, 0.075 mmol) in the same solvent (10 mL). The resultant solution was heated at reflux with stirring for 2 h and then allowed to cool. The white precipitate formed was filtered and dried under vacuum over $CaCl_2$ (yield: 0.0550 g, 86 %). $C_{31}H_{41}N_7O_3PbS_2$ (855.05): calcd. C 46.35, H 4.83, N 11.47, S 7.50; found C 46.58, H 4.43, N 11.77, S 7.83. MS (FAB, 3-nba): *m*/*z* = 532 [**L**^{7}+ H]$^+$, 739 [Pb(**L**^{7}–H)]$^+$, 797 [Pb**L**^{7}(SCN)]$^+$. IR (KBr): $\tilde{\nu}$ = 3369 (NH), 3219, 1596 [δ(NH)], 1585 [ν(C=N)$_{py}$, ν(SCN)] 2049 cm^{-1}. Solution ^{1}H and ^{13}C NMR spectra: Tables S1 and S2 in the Supporting Information. Slow diffusion of diethyl ether into a solution of the complex in methanol/acetonitrile gave crystals of formula [Pb(**L**^{7})](SCN)$_2$·0.5H$_2$O suitable for X-ray crystallography.

[Pb(L^{7})](ClO$_4$)$_2$·MeOH (2): $Pb(ClO_4)_2$·3H$_2$O (0.0330 g, 0.072 mmol) in absolute ethanol (5 mL) was added to a solution of **L**^{7} (0.0402 g, 0.0.076 mmol) in the same solvent (10 mL). The resultant solution was heated at reflux with stirring for 2 h and then allowed to cool. The white precipitate formed was filtered and dried under vacuum over $CaCl_2$ (yield: 0.0554 g, 79 %); m.p. 270 °C (decomp.). $C_{32}H_{45}Cl_2N_5O_{12}Pb$ (969.83): calcd. C 39.63, H 4.68, N 7.22; found C 39.31, H 4.80, N 7.05. MS (FAB, 3-nba): *m*/*z* = 532 [**L**^{7} + H]$^+$, 739 [Pb(**L**^{7}–H)]$^+$, 838 [Pb**L**^{7}(ClO$_4$)]$^+$. IR (KBr): $\tilde{\nu}$ = 3479 (NH), 3409, 3265, 1599 [δ(NH)], 1589 [ν(C=N)$_{py}$], 1092 [ν_{as}(Cl–O)] cm^{-1}.

[Pb(L^{8})](SCN)$_2$·H$_2$O (3): The white complex was prepared as described for **1** by using $Pb(SCN)_2$ (0.0160 g, 0.049 mmol) and **L**^{8} (0.0201 g, 0.035 mmol) (yield: 0.0278 g, 87 %); m.p 222 °C (decomp.). $C_{35}H_{47}N_7O_5PbS_2$ (917.12): calcd. C 45.84, H 5.17, N 10.69; found C 46.01, H 4.89, N 10.55. MS (FAB, 3-nba): *m*/*z* = 576 [**L**^{8} + H]$^+$, 782 [Pb(**L**^{8}–H)]$^+$, 841 [Pb**L**^{8}(SCN)]$^+$. IR (KBr): $\tilde{\nu}$ = 3254 (NH), 1592 [δ(NH)], 1579 [ν(C=N)$_{py}$], 2040 [ν(SCN)] cm^{-1}.

[Pb(L^8)](ClO_4)$_2$·H_2O (4): The white complex was prepared as described for **1** by using Pb(ClO_4)$_2$·3H_2O (0.0160 g, 0.035 mmol)and **L^8** (0.0201 g, 0.035 mmol) (yield: 0.0280 g, 80 %). $C_{33}H_{47}Cl_2N_5O_{13}Pb$ (999.86): calcd. C 39.64, H 4.74, N 7.00; found C 39.80, H 4.66, N 6.83. MS (FAB, 3-nba): *m*/*z* = 576 [**L^8** + H]$^+$, 782 [Pb(**L^8**–H)]$^+$, 882 [Pb**L^8**(ClO_4)]$^+$. IR (KBr): $\tilde{\nu}$ = 3310 (NH), 1605 [δ(NH)], 1589 [ν(C=N)$_{py}$], 1095 &ν_{as}(Cl–O); cm^{-1}.

Supporting information

^{1}H and ^{13}C NMR spectral data for **L^7**, **L^8**, **2**, **3** and **4**. See also the footnote on the last page of this article.

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