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Synthesis and structural characterisation of lead(II) isothiocyanate complexes with receptors derived from 1,10-diaza-15-crown-5

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Abstract

Compounds of formula $Pb(L^1)(SCN)_2 \cdot CH_3CN$ (**1**) and $Pb(L^3)(SCN)_2 \cdot 0.5EtOH$ (**2**) (where $\mathbf{L^1}$ is the lariat crown ether *N*,*N′*-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 and $\mathbf{L^3}$ is a Schiff-base macrobicyclic receptor derived from the condensation of $\mathbf{L^1}$ with 2,6-diformylpyridine) were isolated and structurally characterised both in the solid state and in acetonitrile solution. The X-ray crystal structure of **1** shows the metal ion coordinated to the seven donor atoms of the receptor and to the nitrogen atom of an isothiocyanate group. This structure is different to that found for the previously described perchlorate analogous $[Pb(L^1)](ClO_4)_2$, evidencing that the nature of the anionic group present has an important effect in the conformation and fold of $\mathbf{L^1}$ when coordinated to lead(II). In **2**, the metal ion is nearly centred inside the macrobicyclic cavity of $\mathbf{L^3}$ clearly bound to the three oxygen atoms, to one pivotal nitrogen atom, to one imine nitrogen atom and to the pyridine nitrogen donor of $\mathbf{L^3}$, while the remaining donor atoms of $\mathbf{L^3}$ are only weakly coordinated to the lead(II) ion. The coordination sphere of lead(II) is completed by the nitrogen atom of an isothiocyanate group, and the coordination polyhedron may be described as a distorted tricapped trigonal prism. A comparison between this structure and that previously described for $[Pb(L^3)(ClO_4)]^+$ demonstrates that for the $\mathbf{L^3}$ complexes the different nature of the anion present (thiocyanate or perchlorate) hardly has an effect on the fold and conformation that the macrobicycle adopts when acting as a receptor for lead(II). So, the effect that the anion present has on the structure of the lead(II) complexes of $\mathbf{L^1}$ and $\mathbf{L^3}$ appears to be determined by the degree of flexibility of the organic receptor.

Keywords: Lead(II) complexes; Lariat ether; Macrobicycle; Crystal structures; Template synthesis

1. Introduction

The coordination chemistry of macrocyclic ligands is a fascinating area of intense study for inorganic chemists. One aspect of the interest that macrocyclic ligands have promoted steams from the fact that depending on features such as the nature, number and arrangement of the ligand donors, ligand conjugation, substitution and flexibility, it is possible to tailor-make different types of macrocyclic molecules for specific uses. In particular, macrocycles have been widely studied as complexing agents that may be used for the selective extraction of heavy and precious metals, an area of great interest in environmental chemistry [1–3].

Lead is an environmental pollutant with severe toxic effects that may enter the environment at any stage of mining, melting, and refining, in manufacturing processes and during the use of lead-containing products. Atmospheric lead and lead in food are the two major routes of exposure for the general population [4,5]. The only oxidation state important in biological systems is Pb(II) [6]. Lead is harmful mainly through its neurotoxicological effects. Pb(II) inhibits the synthesis of haemoglobin, causing anaemia and interferes with the metabolism and action of essential metals such as Ca, Fe, and Zn. The permitted free Pb(II) concentrations in body fluids are very low; therefore, any significant quantities of total Pb(II) must be complexed in some way [4,5]. For instance, Pb(II) poisoning has been

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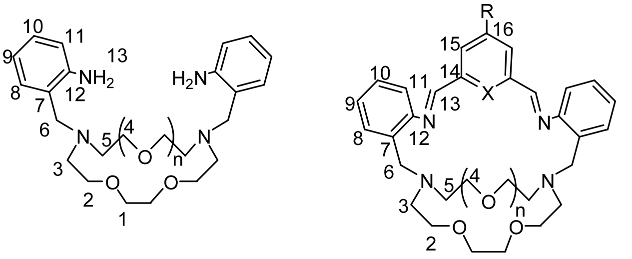
treated by the infusion of $[Ca(EDTA)]^{2-}$ solutions [4]. The design of drugs to counteract the effects of lead poisoning requires establishing the preferred ligands of Pb(II) and their stereochemistry. This caused a resurgence of interest in the coordination chemistry of Pb(II) [7], and in recent years numerous reports concerning chemistry of Pb(II) with chelating ligands [8], macrocycles [9], lariat ethers [10] and cryptands [11] have been published.

In a previous work, we have carried out studies to assess the different complexation capabilities of the bibracchial lariat ethers $\mathbf{L^1}$ and $\mathbf{L^2}$ and the related macrobicycles $\mathbf{L^3}$–$\mathbf{L^6}$ towards lead(II) [12,13]. Structurally, receptors $\mathbf{L^3}$–$\mathbf{L^6}$ belong to the group defined as lateral macrobicycles incorporating an aromatic Schiff-base spacer, and they can only be prepared by using a template procedure [14]. Aiming to understand the structural effect that the nature of the counteranion present in the complex has on the coordination environment around Pb(II), herein we report the synthesis and structural characterization of two novel lead(II) isothiocyanate complexes with the receptors $\mathbf{L^1}$ and $\mathbf{L^3}$ (see Scheme 1). The structures of the complexes are compared to those previously described for their perchlorate analogues $[Pb(L^1)](ClO_4)_2$ and $[Pb(L^3)(ClO_4)](ClO_4)\cdot CH_3CN$ [12].

2. Experimental

2.1. Reagents

2,6-Diformylpyridine was synthesised according to literature methods [15,16]. All other chemicals were purchased from commercial sources and used without further purification. Solvents were of reagent grade purified by the usual methods.



$\mathbf{L^1}$: n = 1
$\mathbf{L^2}$: n = 2

$\mathbf{L^3}$: n = 1, R = H, X = N
$\mathbf{L^4}$: n = 1, R = CH_3, X = C-OH
$\mathbf{L^5}$: n = 2, R = H, X = N
$\mathbf{L^6}$: n = 2, R = CH_3, X = C-OH

Scheme 1.

2.2. Preparation of the ligands

The bibracchial lariat ether *N*,*N*′-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 ($\mathbf{L^1}$) was prepared as previously described by us [12].

2.3. Preparation of the lead(II) complexes

2.3.1. $Pb(L^1)(SCN)_2\cdot CH_3CN$ (**1**)

$Pb(SCN)_2$ (0.037 g, 0.116 mmol) was added to a solution of *N*,*N*′-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 ($\mathbf{L^1}$) (0.050 g, 0.116 mmol) in absolute ethanol (15 ml). The reaction mixture was stirred and refluxed for 4 h. During the reaction, the solution became turbid and a white precipitate appeared which was collected by filtration, washed with absolute ethanol and air-dried. Recrystallisation from acetonitrile gave X-ray quality crystals of **1**. Yield: 0.049 g (56%). *Anal.* Calc. for $C_{26}H_{36}N_6O_3PbS_2\cdot CH_3CN$: C, 42.4; H, 4.9; N, 12.3. Found: C, 42.5; H, 4.9; N, 12.3%. FAB-MS: $m/z = 694$ $[Pb(L^1)(SCN)]^+$, 635 $[Pb(L^1)]^+$. IR (KBr discs): 3259, 3147 $\nu(NH_2)$; 1625 δ (NH_2); 2038, 2049 (SCN) cm^{-1}.

2.3.2. $Pb(L^3)(SCN)_2\cdot 0.5EtOH$ (**2**)

$Pb(SCN)_2$ (0.036 g; 0.109 mmol) was added to a solution of *N*,*N*′-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 ($\mathbf{L^1}$) (0.048 g; 0.109 mmol) in absolute ethanol (120 ml). The mixture was vigorously stirred and heated while a solution of 2,6-diformylpyridine (0.015 g; 0.109 mmol) in absolute ethanol (40 ml) was added dropwise over 1 day. After the addition was complete, the resulting pale yellow solution was stirred and refluxed for 1 day and filtered while hot. Upon cooling the filtrate to room temperature, pale yellow crystals suitable for X-ray diffraction were formed, which were collected by filtration. Yield: 0.285 g (75%). *Anal.* Calc. for $C_{33}H_{37}N_7O_3PbS_2\cdot 0.5EtOH$: C, 46.7; H, 4.6; N, 11.2. Found: C, 46.5; H, 4.6; N, 11.2%. FAB-MS: $m/z = 793$ $[Pb(L^3)(SCN)]^+$, 735 $[Pb(L^3)]^+$. IR (KBr discs): 1630 $\nu(C{=}N)_{imine}$; 1581 $\nu(C{=}N)_{pyridine}$; 2027, 2047 (SCN) cm^{-1}. ^{13}C NMR (acetonitrile-d_3), δ: 163.6, 154.3, 150.5, 141.8, 133.5, 132.3, 131.4, 131.8, 131.4, 129.1, 121.4, 69.3, 68.05, 58.8 and 57.6.

2.4. Measurements

Elemental analyses were carried out on a Carlo Erba 1180 elemental analyser. FAB MS were recorded on a Fisons Quatro mass spectrometer with a Cs ion gun using 3-nitrobenzyl alcohol as matrix. ^1H and ^{13}C NMR spectra were run on a Bruker AC 200F using acetonitrile-d_3 as solvent. IR spectra were recorded, as KBr discs, using a Bruker Vextor 22 spectrophotometer. Conductivity measurements were carried out with a Crison Micro CM 2201 conductivimeter using ca. 10^{-3} M solutions of the complexes in acetonitrile.

2.5. X-ray crystallography

Three dimensional X-ray data for compounds **1** and **2** were collected on a Bruker Smart 1000 CCD operating at 25 °C. Data were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods. Both structures were refined by full-matrix least-squares on F^2. Complex scattering factors were taken from the program package SHELXTL [17]. Hydrogen atoms were included in calculated positions and refined in riding mode. Crystal data and details on data collection and refinement are summarised in Table 1.

3. Results and discussion

3.1. Synthesis

Reaction of $Pb(SCN)_2$ with the bibracchial lariat ether $\mathbf{L^1}$ in absolute ethanol yield compound **1**, with formula $Pb(L^1)(SCN)_2 \cdot CH_3CN$. Compound **2**, with formula $Pb(L^3)(SCN)_2 \cdot 0.5EtOH$, was easily prepared in high yield (75%) by reaction of equimolar amounts of 2,6-diformyl-pyridine and *N*,*N′*-bis(2-aminobenzyl)-1,10-diaza-15-crown-5 ($\mathbf{L^1}$) in the presence of lead(II) thiocyanate in absolute ethanol; the IR and FAB MS confirmed that condensation and [1 + 1] cyclisation had occurred and the lead(II) complex **2** was formed. In a previous paper, we proved that lead(II) perchlorate can act as an effective template in the formation of $\mathbf{L^3}$ [12]. Data here presented demonstrate that the lead(II) thiocyanante is also able to template the formation of $\mathbf{L^3}$, so evidencing that presence of a strongly coordinating anion such as thiocyanate in the reaction medium does not affect to the efficiency of lead(II) as a template in the synthesis of this macrobicycle.

Table 1
Crystal data and structure refinement for **1** and **2**

	1	**2**
Formula	$C_{28}H_{39}N_7O_3PbS_2$	$C_{34}H_{40}N_7O_{3.5}PbS_2$
Molecular weight	792.97	874.04
Crystal system	orthorhombic	monoclinic
Space group	$Pna2_1$	$P2_1/c$
T (K)	298(2)	298(2)
Unit cell dimensions		
a (Å)	16.2938(13)	16.7699(6)
b (Å)	14.1715(11)	14.0394(5)
c (Å)	14.1374(11)	15.6298(6)
β (°)		96.6180(10)
V (Å^3)	3264.4(4)	3655.3(2)
Z	4	4
D_{calc} (g cm^{-3})	1.613	1.588
μ (mm^{-1})	5.336	4.774
$F(000)$	1576	1740
θ	1.90–28.31	1.90–28.31
R_{int}	0.0496	0.0387
Reflections measured	22 155	25 588
Reflections observed	5616	5980
Goodness-of-fit on F^2	1.079	0.963
R_1 [a]	0.0549	0.0330
wR_2 (all data) [b]	0.1514	0.0834
Largest differences peak and hole (e Å^{-3})	2.067 and −3.375	1.097 and −0.630

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.

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

3.2. X-ray crystal structures

Recrystallisation of **1** from acetonitrile gave colourless crystals suitable for single crystal X-ray diffraction. Crystals contain the cation $[Pb(L^1)(NCS)]^+$, a thiocyanate group and an acetonitrile molecule. This is in agreement with the IR spectrum (KBr disc) that displays two bands corresponding to the ν(CN) stretching mode of the thiocyanate groups at 2038 and 2049 cm^{-1}, suggesting the presence of thiocyanate groups with different binding modes. Fig. 1 illustrates the structure of the complex cation. It contains a PbN_5O_3 core with the seven atoms of $\mathbf{L^1}$ coordinated to the lead(II) ion as well as a thiocyanate group coordinated through the nitrogen atom. Bond lengths and angles of the coordination sphere are compiled in Table 2. Distances between the lead(II) ion and the oxygen donors O(3) and O(2) are only slightly longer than the sum of the van der Waals radius of oxygen and the ionic radius of lead(II) of 2.67 Å [18,19], but the considerably long distances Pb–N(3) of 3.038(11) Å and Pb–N(4) of 2.936(13) Å suggest a very weak interaction of the metal ion with both pivotal nitrogen atoms. The coordination polyhedron around the Pb(II) ion can be described as a bicapped distorted octahedron (Fig. 1(b)), where N(3) and N(4) occupy the capping positions. This octahedron can be considered to be comprised by two nearly parallel triangular faces described by atoms N(1S), N(1) and N(2), and O(3), O(1) and O(2). The angle between the planes formed by each of the two triangular faces amounts to 10.2(6)°. The mean twist angle (β) between these two faces (55.8°) is close to the expected value for a regular octahedron (ideal value 60°).

Both pendant aniline arms of the receptor $\mathbf{L^1}$ in **1** are orientated on the same side of the macrocyclic plane, resulting in a *syn* conformation. This conformation was also found in the analogous perchlorate compound $[Pb(L^1)](ClO_4)_2$, where however only one of the aniline groups formed a part of the lead(II) coordination sphere and one perchlorate group acted as a bridge between the metal and the non-coordinated aniline group [12]. A comparison of bond lengths of the coordination sphere for both $[Pb(L^1)](ClO_4)_2$ and $[Pb(L^1)(NCS)](SCN)$ complexes shows that the presence of a different counterion has an important effect on the coordination sphere of the metal ion. Indeed, the distance between lead(II) and the aniline nitrogen atoms are 0.161 (Pb–N(1)) and

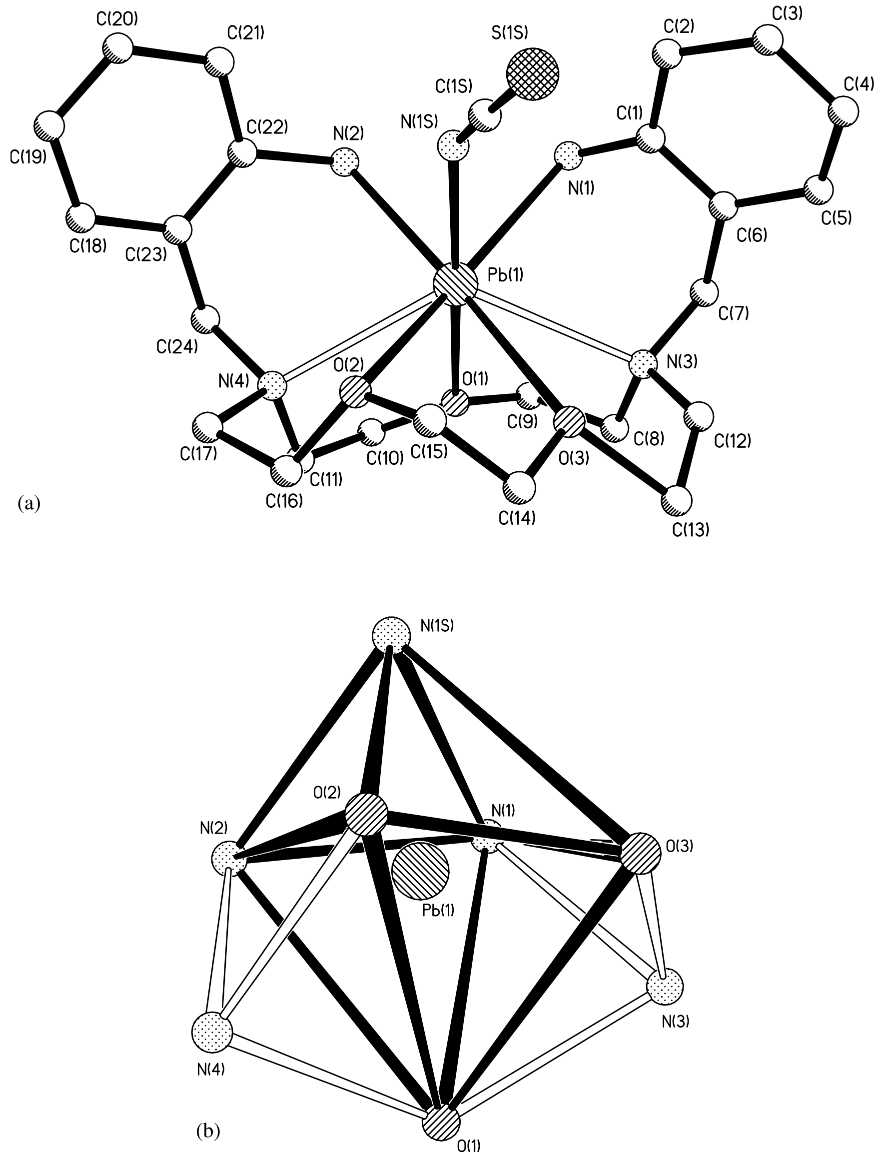


Fig. 1. (a) X-ray crystal structure of the cationic complex $[Pb(L^1)(NCS)]^+$ showing the atomic numbering scheme; hydrogen atoms are omitted for the sake of clarity; (b) coordination polyhedron.

0.069 (Pb–N(2)) Å shorter in **1** than in $[Pb(L^1)](ClO_4)_2$, while the distance between the metal ion and the pivotal nitrogen atoms are 0.281 (Pb–N(3)) and 0.248 (Pb–N(4)) Å longer in **1**. The Pb–O bond distances are also longer in **1** than in $[Pb(L^1)](ClO_4)_2$ by 0.055–0.103 Å. Likewise, in $[Pb(L^1)(NCS)]^+$ the distance between both aniline groups is 3.158(18) Å, ca. 0.5 Å shorter than that found in $[Pb(L^1)](ClO_4)_2$, while the angle N(aniline)–Pb–N(aniline) decreases from 82.1° in the perchlorate complex to 79.2° in **1**. Moreover, the distance between both pivotal nitrogen atoms is longer in **1** [N(3)–N(4) 5.178(16) Å] than in $[Pb(L^1)](ClO_4)_2$ (4.883 Å), whereas the angle formed by the planes containing the aromatic rings changes from 112.1° in $[Pb(L^1)](ClO_4)_2$ to 136.7° in **1**. The presence of an isothiocyanate group in the lead(II) coordination sphere and the relative flexibility of $\mathbf{L^1}$ seem to be the features responsible for all these structural changes. The interaction of the strongly coordinating isothiocyanate group with lead(II) brings the metal ion closer to the aniline groups what, in turn, weakens the interactions of the lead(II) ion with the donor atoms of the crown moiety, especially with the pivotal nitrogen atoms.

The presence of thiocyanate or perchlorate groups in the complexes of $\mathbf{L^1}$ also causes important differences in the crystal packing. Thus, the non-coordinated perchlorate group interacts with the cations through electrostatic interactions as shown in Fig. 2(a) [12], whereas hydrogen-bonding interactions are present in the case of thiocyanate complex. In fact, inspection of the crystal packing of **1** (Fig. 2(b)) reveals that both the coordinated and the uncoordinated thiocyanate groups are

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

1		**2**	
Bond lengths			
Pb(1)–N(1S)	2.496(11)	Pb(1)–N(1S)	2.537(4)
Pb(1)–O(1)	2.671(11)	Pb(1)–O(1)	2.689(4)
Pb(1)–N(3)	3.038(11)	Pb(1)–N(3)	2.725(4)
Pb(1)–N(2)	2.583(11)	Pb(1)–N(2)	2.749(4)
Pb(1)–O(3)	2.787(12)	Pb(1)–O(3)	2.798(3)
Pb(1)–O(2)	2.777(9)	Pb(1)–O(2)	2.824(4)
Pb(1)–N(1)	2.731(17)	Pb(1)–N(1)	2.844(3)
Pb(1)–N(4)	2.936(13)	Pb(1)–N(4)	2.912(4)
		Pb(1)–N(5)	2.708(3)
Bond angles			
N(1S)–Pb(1)–N(2)	80.6(5)	N(1S)–Pb(1)–O(1)	77.39(13)
N(1S)–Pb(1)–O(1)	174.9(4)	N(1S)–Pb(1)–N(5)	74.59(12)
N(2)–Pb(1)–O(1)	94.9(3)	O(1)–Pb(1)–N(5)	142.53(11)
N(1S)–Pb(1)–N(1)	82.5(5)	N(1S)–Pb(1)–N(3)	78.77(12)
N(2)–Pb(1)–N(1)	72.9(4)	O(1)–Pb(1)–N(3)	65.70(12)
O(1)–Pb(1)–N(1)	93.8(4)	N(5)–Pb(1)–N(3)	130.47(11)
N(1S)–Pb(1)–O(2)	79.0(4)	N(1S)–Pb(1)–N(2)	83.43(13)
N(2)–Pb(1)–O(2)	112.3(3)	O(1)–Pb(1)–N(2)	138.64(11)
O(1)–Pb(1)–O(2)	105.2(4)	N(5)–Pb(1)–N(2)	61.33(11)
N(1)–Pb(1)–O(2)	159.5(5)	N(3)–Pb(1)–N(2)	74.86(12)
N(1S)–Pb(1)–O(3)	92.5(5)	N(1S)–Pb(1)–O(3)	135.82(12)
N(2)–Pb(1)–O(3)	170.8(3)	O(1)–Pb(1)–O(3)	98.40(11)
O(1)–Pb(1)–O(3)	92.2(4)	N(5)–Pb(1)–O(3)	119.04(11)
N(1)–Pb(1)–O(3)	112.5(6)	N(3)–Pb(1)–O(3)	60.33(10)
O(2)–Pb(1)–O(3)	59.9(3)	N(2)–Pb(1)–O(3)	71.05(10)
N(1S)–Pb(1)–N(4)	117.2(6)	N(1S)–Pb(1)–O(2)	158.35(13)
N(2)–Pb(1)–N(4)	73.5(4)	O(1)–Pb(1)–O(2)	120.32(11)
O(1)–Pb(1)–N(4)	63.3(3)	N(5)–Pb(1)–O(2)	83.95(11)
N(1)–Pb(1)–N(4)	137.0(6)	N(3)–Pb(1)–O(2)	118.68(11)
O(2)–Pb(1)–N(4)	61.2(3)	N(2)–Pb(1)–O(2)	88.88(12)
O(3)–Pb(1)–N(4)	104.7(4)	O(3)–Pb(1)–O(2)	58.46(10)
N(1S)–Pb(1)–N(3)	120.9(6)	N(1S)–Pb(1)–N(1)	78.17(12)
N(2)–Pb(1)–N(3)	127.9(3)	O(1)–Pb(1)–N(1)	90.85(11)
O(1)–Pb(1)–N(3)	60.0(3)	N(5)–Pb(1)–N(1)	59.47(11)
N(1)–Pb(1)–N(3)	65.2(4)	N(3)–Pb(1)–N(1)	150.14(12)
O(2)–Pb(1)–N(3)	117.9(3)	N(2)–Pb(1)–N(1)	120.68(11)
O(3)–Pb(1)–N(3)	61.0(3)	O(3)–Pb(1)–N(1)	145.94(10)
N(4)–Pb(1)–N(3)	120.2(4)	O(2)–Pb(1)–N(1)	88.59(11)
		N(1S)–Pb(1)–N(4)	126.11(14)
		O(1)–Pb(1)–N(4)	62.75(12)
		N(5)–Pb(1)–N(4)	117.37(11)
		N(3)–Pb(1)–N(4)	112.10(11)
		N(2)–Pb(1)–N(4)	150.10(12)
		O(3)–Pb(1)–N(4)	86.98(11)
		O(2)–Pb(1)–N(4)	61.94(13)
		N(1)–Pb(1)–N(4)	68.28(11)

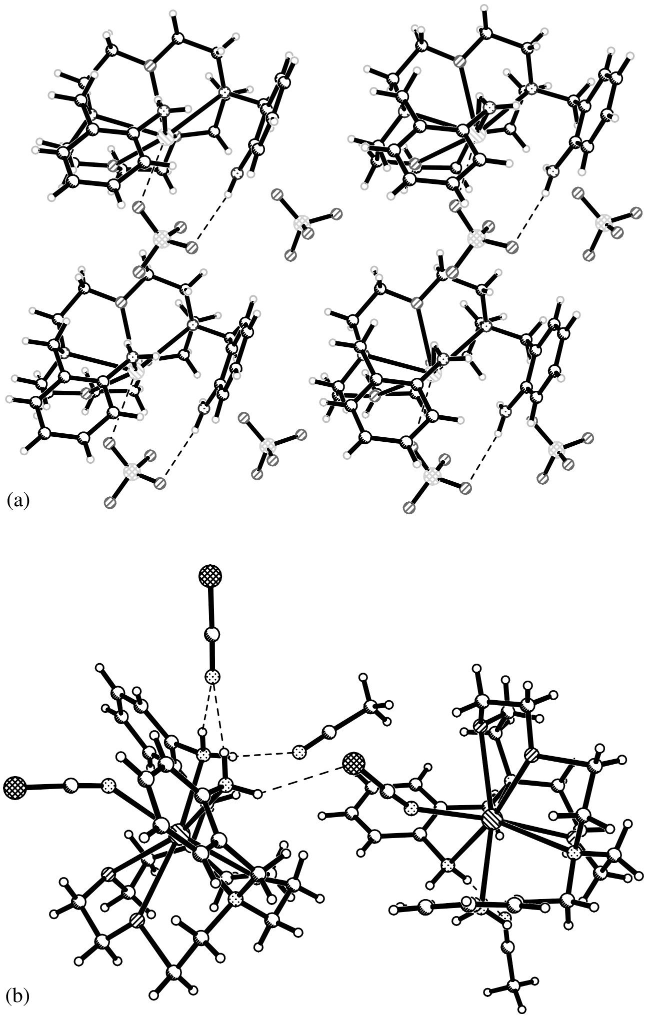


Fig. 2. Crystal packing of compounds $[Pb(L^1)](ClO_4)_2$ (a, Ref. [12]) and $[Pb(L^1)(NCS)](SCN)$ (b).

involved in hydrogen-bonding interactions with the aniline groups. The uncoordinated thiocyanate group interacts with the two aniline groups of the same molecule [N(2)–N(2S) 3.09(2), H(2A)–N(2S) 2.20, N(2)–H(2A)–N(2S) 170.2; [N(1)–N(2S) 3.09(3), H(1B)–N(2S) 2.20, N(2)–H(1B)–N(2S) 173.1], while the coordinated one interacts with the aniline group of a neighbour molecule [N(1)–S(1S) 3.573(19), H(1A)–S(1S) 2.20, N(1)–H(1A)–S(1S) 145.4]. As shown in Fig. 2(b), the acetonitrile molecule is also involved in hydrogen-bonding interaction with an aniline group [N(2)–N(1W) 3.00(2), H(2B)–N(1W) 2.10, N(2)–H(2B)–N(1W) 172.9].

Fig. 3(a) shows the structure of the cation $[Pb(L^3)(NCS)]^+$ present in crystals of **2**, while selected bond lengths and angles are given in Table 2. This structure is very similar to that previously described for the related $[Pb(L^3)(ClO_4)]^+$ complex [12]. The metal ion is found into the macrobicyclic cavity, slightly displaced from the centre, and clearly bound to the three oxygen atoms, to one pivotal nitrogen atom, to one imine nitrogen atom and to the pyridine nitrogen donor of $\mathbf{L^3}$. All these Pb-donor distances are similar to those found in $[Pb(L^3)(ClO_4)]^+$ [12], and fall within the range found for lead(II) crown-ether complexes [20] and lead(II) imine complexes [11,21]. The other imine and pivotal nitrogen atoms of $\mathbf{L^3}$ remain only weakly coordinated through long interactions with the lead(II) ion [Pb–N(1) 2.844(3), Pb–N(4) 2.912(2) Å]. The coordination sphere of lead(II) is completed by the nitrogen atom of a

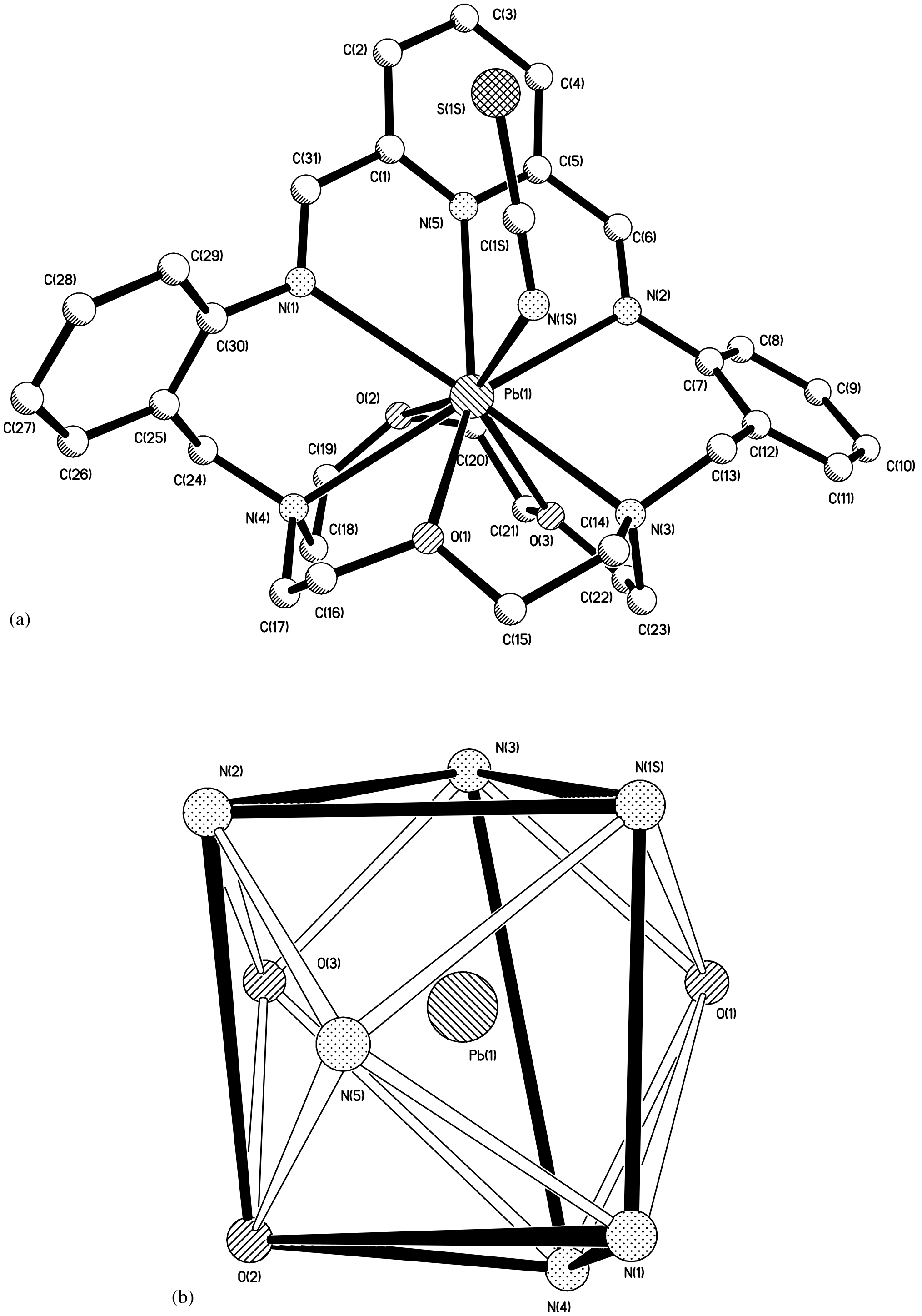


Fig. 3. (a) X-ray crystal structure of the cation $[Pb(L^3)(NCS)]^+$ showing the atomic numbering scheme; hydrogen atoms are omitted for simplicity; (b) coordination polyhedron.

thiocyanate group. The IR spectrum of **2** (KBr disc) displays two bands at 2027, 2047 cm^{-1} corresponding to the ν(CN) stretching mode of the thiocyanate groups, which agrees with the presence of the different binding modes for both thiocyanate groups evidenced in the X-ray crystal structure. The coordination polyhedron may be described as a distorted tricapped trigonal prism comprised by three tripods: N(2), N(3) and N(1S) form the upper tripod; N(1), N(4) and O(2) delineate the lower one, whereas O(1), O(3) and N(5) represent the capping tripod (Fig. 3(b)). The lead atom and the three capping donor atoms are essentially coplanar (mean deviation from plane 0.0122 Å). This plane forms an angle of 5.50(6)° with the upper face of the prism and of

18.67(9)° with the lower one. The degree of distortion of the tricapped trigonal prism has been investigated quantitatively using a geometric analysis based on the determination of three angles, ϕ, θ_i, and ω_i (Fig. 4) [22]. The average bending of the upper ($vs(j)$) and lower ($vi(j)$) tripods is measured by the angle ϕ between the sum vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ ($\mathbf{R}_1 = \Sigma_{j=1}^{3}\, Pb - vs(j)$, $\mathbf{R}_2 = \Sigma_{j=1}^{3} Pb - vi(j)$, $\phi = 180°$ for an ideal trigonal prism), while the angles θ_i reflect the flattening of the coordination polyhedron along the pseudo-C_3 axis, defined as $\mathbf{R}_2$–$\mathbf{R}_1$. Finally, the angles ω_i show the deformation of the distal tripods from the trigonal prism (ideal value 0°) toward an octahedron (ideal value 60°). For **2**, the ϕ angle amounts to 173.9°, pointing to a somewhat distorted trigonal prism, which is also evident from the angle between the planes described by the upper and lower tripods (24.17(19)°). Analysis of the θ_i angles involving donor atoms of the upper tripod discloses that individual values, which are in the range 43.7–51.6°, do not deviate much from their mean value. However, larger deviations from the mean value are observed for θ_i angles involving the donor atoms of the lower tripod, with values ranging from 31.8° to 50.2°. This points again to a somewhat distorted polyhedron. The angles ω_i between projection vectors of the two distal tripods (19.1–33.2°) indicate some distortion from a trigonal prism (ideal value 0°) toward an octahedron (ideal value 60°).

The lateral aromatic rings of the receptor $\mathbf{L^3}$ in **2** are in different planes, which intersect at 87.4(1)°. This angle is slightly larger than the one found in $[Pb(L^3)(ClO_4)]^+$, probably due to the presence of an isothiocyanate group in the coordination sphere of **2**, that causes less steric hindrance than a perchlorate group. The plane of the pyridine ring forms dihedral angles of 45.5(2)° with the plane containing the benzene ring bound to N(2) and 54.0(2)° with the plane containing the other aromatic ring. Dihedral angles N(1)–C(31)–C(1)–N(5) (−6.2°) and N(5)–C(5)–C(6)–N(2) (−6.7°) indicate that both imine groups are slightly rotated from coplanarity with the pyridine ring. This planarity loss is related with the structure of the receptor and the coordinative requirements of the metal guest that forces the receptor to fold increasing the stress of its structure. Distance between both imine nitrogen atoms is 4.861(5) Å, whereas the distance between both pivotal nitrogen atoms amounts to 4.677(5) Å. These distances are very similar to those found in $[Pb(L^3)(ClO_4)]^+$, where they amount to 4.856 and 4.687 Å, respectively [12]. Inspection of crystal packing reveals that both in the perchlorate and thiocyanate complexes the non-coordinated anion group interacts with the cation through electrostatic interactions.

In the light of all of these structural data it can be stated that the different nature of the anion present in the complex (thiocyanate or perchlorate) has an important effect in the conformation that $\mathbf{L^1}$ adopts when acting as a receptor for lead(II), but hardly has an effect on the fold and conformation adopted by $\mathbf{L^3}$. This is probably because: (i) $\mathbf{L^3}$ is relatively rigid compared to $\mathbf{L^1}$; and (ii) the lead(II) ion fits well into the cavity of $\mathbf{L^3}$, limiting conformational changes and any substantial modification in the position of the metal ion with respect to the donor atoms of the macrobicycle.

Both complexes **1** and **2** present the thiocyanate group bound through the nitrogen atom in the so-called

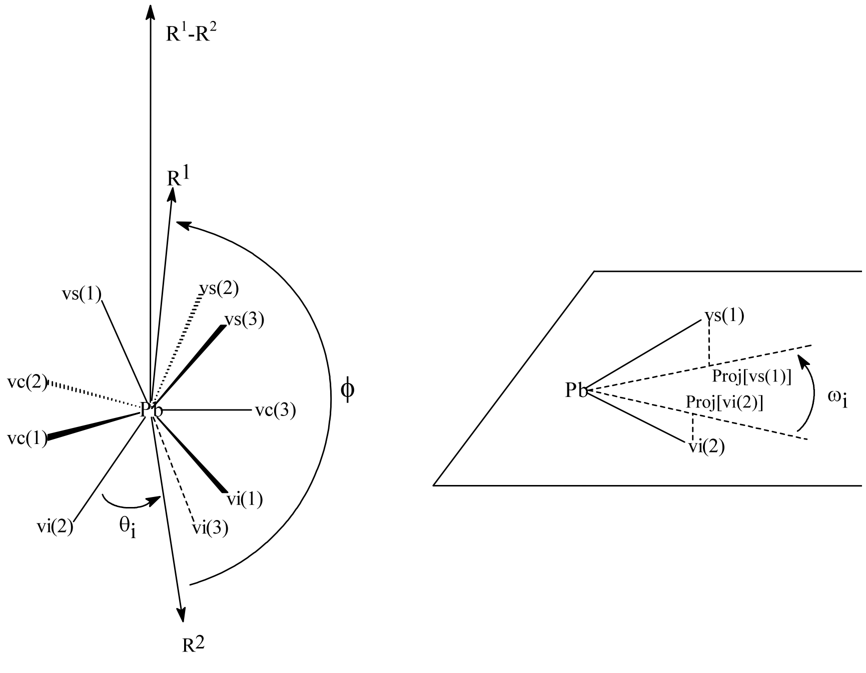


Fig. 4. Definition of the angles and vectors used in the analysis of the coordination polyhedron of **2**.

isothiocyante binding mode. Phenomenologically, it is observed that hard metals tend to be N-bonded whereas soft metals tend to be S-bonded, though kinetic and solubility factors as well as relative thermodynamic stability seem to be also implicated. Lead(II) is intermediate and forms both types of complexes, and this subject continues still being matter of debate. In fact, lead(II) complexes of crown ethers with N-bonded [23], S-bonded [24] or even both N- and S-bonded [25] thiocyanate ligands have been reported. Most likely steric effects are responsible for the N-coordination of the thiocyanate group in the case of compound **2**, as pointed previously for other lead(II) cryptates [26]. For compound **1,** the presence of hydrogen-bonding interactions involving the thiocyanate group and/or steric effects could be responsible for the N-coordination of this ligand.

3.3. Solution properties

Conductivity measurements for 10^{-3} M solutions in acetonitrile at 20 °C ($\Lambda_M = 168$ cm^2 Ω^{-1} mol^{-1} for **1** and 144 cm^2 Ω^{-1} mol^{-1} for **2**) reveal that both compounds behave as 1:1 electrolytes in this solvent [27], which confirms the presence of one thiocyanate group in the coordination sphere of lead(II) in acetonitrile solution as it does in the solid state (vide supra).

The ^{1}H NMR spectrum of **1** recorded in CD_3CN solution (Table 3, Scheme 1) is quite similar to that of the analogous perchlorate complex. It shows a group of complicated signals in the region 2.6–4.2 ppm due to the ethylenic and methylenic protons, while the aromatic protons appear between 7.0 and 7.5 ppm. Even so, there is a significant difference between the spectrum of **1** and that of the perchlorate complex that comes from the position of the peak due to the amine protons H13 (Table 3). Indeed, this signal is shifted to lower field by ca. 0.4 ppm in **1** compared to the perchlorate analogous [12]. In principal, 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 low field [28]. These results suggest that the amine protons of **1** are involved in hydrogen-bonding interaction in acetonitrile solution, in agreement with the X-ray crystal structure.

The ^{1}H NMR spectrum of **2** recorded in acetonitrile solution (Table 3, Scheme 1) shows at high field complicated multiplets due to the ethylenic protons of the crown moiety, as the result of the coordination of the metal by the oxygen atoms of the crown. The signal due to the pyridine protons H16 is shifted to higher fields by 0.08 ppm with respect to the analogous perchlorate complex [12], while the signal due to the imine protons is shifted to lower fields by 0.06 ppm. The overall spectrum is consistent with an effective C_s symmetry of the complex in acetonitrile solution. The spectrum of the perchlorate complex shows the signal due to the imine protons flanked by satellites due to proton coupling to ^{207}Pb [12], while this coupling is not observed for **2**.

Table 3
^{1}H NMR data for compounds **1** and **2** [a]

Proton	**1** [b]	Proton	**2** [c]
H1, H2, H4	3.57(m), 12H	H1, H2, H4	3.0–3.8(m), 12 H
H3, H5	2.87(m), 8 H	H3, H5	2.50(m), 8 H
H6	3.96(m), 4H	H6	4.00(b), 4H
H8	7.25(d), 2H	H8, H9, H11	7.40(m), 6H
H9, H11	7.03(m), 4H	H10	7.59(t), 2H
H10	7.37(t), 2H	H13	9.15(s), 2H
H13	4.61(s), 4H	H15	8.23(d), 2H
		H16	8.44(t), 1H

[a] See Scheme 1 for labeling.

[b] Conditions: $T = 293$ K, 200 MHz. $J_{11,10} = 7.32$; $J_{9,10} = 7.32$; $J_{11,9} = J_{9,11} = 1.47$; $J_{6a,6b} = J_{6b,6a} = 12.95$ Hz.

[c] Conditions: $T = 293$ K, 200 MHz. $J_{16,15} = 6.86$; $J_{15,16} = 7.32$; $J_{10,9} = J_{10,11} = 7.33$; $J_{10,8} = 1.46$ Hz.

4. Concluding remarks

We have tried to understand the structural effect that the nature of the counteranion present in the complex has on the coordination environment around Pb(II) in complexes with receptors of different degree of rigidity. The X-ray crystal structure of compound **1** shows that the interaction of the strongly coordinating isothiocyanate group with lead(II) brings the metal ion close to the aniline groups what, in turn, weakens the interactions of the lead(II) ion with the donor atoms of the crown moiety. This results on a different fold and conformation of the lariat ether **L^1** and, consequently, also on a different coordination environment around the lead(II) ion compared to that observed in the analogous perchlorate complex. The presence of thiocyanate or perchlorate groups in the complexes of **L^1** also causes important differences in the crystal packing and whereas the non-coordinated perchlorate group interacts with the cations through electrostatic interactions, hydrogen-bonding interactions are present in the case of thiocyanate complex. On the contrary, the nature of the counteranion hardly affects the coordination environment of the metal ion in the lead(II) complexes of the relatively rigid Schiff-base macrobicycle **L^3** because the lower degree of flexibility of the ligand allows little adjustment of the metal coordination sphere.

Both in **1** and **2** complexes the thiocyanate group is bound through the nitrogen atom. In principal, steric effects seems to be responsible for this feature, although in case of complex **1** the presence of hydrogen-bonding interactions involving the thiocyanate groups should be also considered.

5. Supplementary material

Crystallographic data for crystal structures of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre as CCDC206817 and CCDC206818, respectively. Copies of the data can be obtained free of charge upon application to The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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