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Binding and Ionophoric Properties of Polyamide Compounds. Lead Selectivity

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Abstract. The extraction and transport properties of macrocyclic dioxa-, dithia- and diazatetralactams are reported along with those of open-chain analogous compounds. The preference of three of them for lead over alkali, alkaline-earth or other heavy metal cations is discussed.

Key words: tetralactams, complexation, extraction, transport, formation constants

1. Introduction

Development of lead-specific sequestering agents remains a current challenge with various applications such as (i) therapeutic agents for lead decorporation [1], (ii) neutral ionophores for lead-selective electrodes [2], (iii) sensors for lead-sensitive field effect transistors [3], (iv) carriers for cation selective separations using liquid membranes [4]. Among them, dioxamide compounds exhibit interesting selectivity for Pb^{2+} in ion selective electrodes [5] or extraction processes [6].

Our previous results on cation discrimination by macrocyclic tetralactams have indicated very high selectivities for barium [7], calcium [8] or strontium [9] depending on the ring size and the nature of substituents on the nitrogen atoms. When bibracchial diazatetralactams were used [10] an efficient zinc extraction constitutes the main difference with the dioxatetralactam series.

In this paper we investigate the binding and ionophoric properties of dioxa-, dithia- and diazatetralactams (**3a–c**) and the di- or tetramide open-chain related compounds **1–2** for a large series of cations. A lead-selectivity vs. Na^{+}, Ca^{2+} and other heavy cations is evidenced.

2. Experimental

UV-Vis spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer and infrared spectra on a Perkin-Elmer 883 with KBr discs. Mass spectra were

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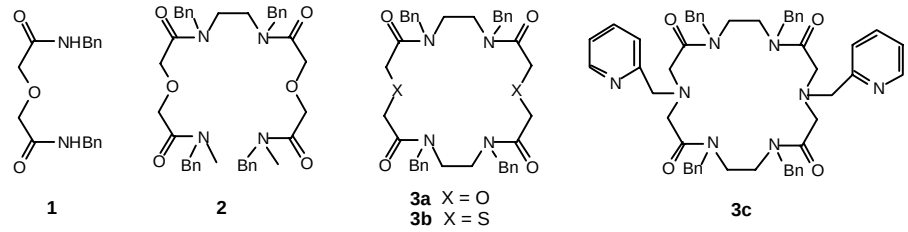

Scheme 1–3c.

performed on a Perkin-Elmer SCIEX API 100 apparatus. Elemental analyses were carried out by the "Service Commun de Microanalyse élémentaire UPS-INPT" in Toulouse. Solvents were purified prior to use by standard methods [11].

2.1. SYNTHESIS OF THE LIGANDS

The ligands were prepared as described previously: diamide **1** [12], tetramide **2** [13], tetralactams **3a–3c** [14].

2.2. PREPARATION OF THE COMPLEXES

The ligand (0.02 mmol) was dissolved in 10 mL of acetonitrile, then stirred for 24 h in the presence of an equimolar quantity of solid lead picrate ($PbPic_2$). After filtration, the solvent was evaporated to give a yellow powder which was washed with acetonitrile.

3a.Pb^{2+}Pic$_2^-$.2H$_2$O. IR (KBr) ν: 3436 (OH), 1629, 1608 (C=O), 1568, 1543 (NO_2 as.), 1364, 1318 (NO_2 s.) cm^{-1}. Anal. calcd. for $C_{52}H_{52}N_{10}O_{22}Pb$: C, 45.38; H, 3.81; N, 10.18. Found C, 45.43; H, 3.44; N, 10.33.

3c.Pb^{2+}Pic$_2^-$.2H$_2$O + 3c.(Pb^{2+}Pic$_2^-$)$_2$.2H$_2$O. IR (KBr): ν 3434 (OH), 1628, 1605 (C=O), 1570, 1547 (NO_2 as.), 1362 (NO_2 s.) cm^{-1}. ES$^+$.MS (CH_3CN): m/z = 1292.6 [M-Pic]$^+$, 1201.3 [M-Pic-C_6H_5N]$^+$, 1110.5 [M-Pic-2C_6H_5N]$^+$, 881.3 [M-1-2Pic-2C_6H_5N]$^+$ with M = **3c**.$PbPic_2$and based on ^{207}Pb.

Anal. calcd. for $C_{64}H_{64}N_{14}O_{20}Pb$ (45%) + $C_{76}H_{68}N_{20}O_{34}Pb_2$ (55%): C, 45.26; H, 3.62; N, 12.61. Found C, 45.14; H, 3.61; N, 12.66.

2.3. FORMATION CONSTANT DETERMINATION

The formation constants for Pb^{2+}-ligand complexes were determined by UV spectrophotometry in tetrahydrofuran solutions as previously reported [10] for Ca^{2+}-ligand complexes.

Table I. Extraction percentages (E) of lead and calcium picrates with tetralactam **3a** at 25 °C and different concentrations[a]

Concentration (M)	1.5×10^{-2}	10^{-3}	5×10^{-4}	3.3×10^{-4}	2.5×10^{-5}
E_{Ca}	78	1	–	0	–
E_{Pb}	100	72	61	45	2
E_{Pb}(calc.)[b]	96	73	58	45.5	<1

[a] Extraction conditions: aqueous phase [picrate] = [ligand], organic phase ($CHCl_3$).
[b] Calculated using log K_{ex} = 10.54.

2.4. EXTRACTION STUDIES

Three 10^{-3} M chloroform solutions of ligand (0.25 mL) and aqueous solutions (0.25 mL) prepared from 2×10^{-3} M picric acid (or 10^{-3} M for the extraction of Na^+) and an excess (5×10^{-2} M) of metal nitrate were magnetically stirred for 15 h in three stoppered glass tubes immersed in a water bath thermoregulated at 25 °C. A blank experiment, without ligand, was run under the same conditions in a fourth tube. After stirring, the aqueous phases were separated and the percent of picrate salt extracted (E%) was determined by UV spectrophotometry as previously reported [9].

In a first set of experiments, the extraction percentages of lead and calcium picrates were measured at different concentrations in dioxatetralactam **3a** (Table I) to determine the best selectivity range.

The results were also used to calculate the extraction constant, K_{ex}, of the lead picrate by tetralactam **3a** with a 1 : 1 metal-ligand stoichiometry. A value of log K_{ex} = 10.54 was determined using the equation $K_{ex} = E/4\ Co^3\ (1 - E)^4$ deduced from the general equations of the liquid-liquid extraction equilibria [16] with Co being the equal ligand and salt concentrations.

2.5. TRANSPORT STUDIES

These were performed [10] at 25 °C in a cell divided into three parts of 11 mL each separated by two Fluoropore membranes of 175 μm thickness and stirred independently and synchronously at 545 rpm. The ionophore (10^{-3} M) in $CHCl_3$ was placed in the middle compartment and the metallic picrate (10^{-3} M) in aqueous phase I. The transport rates were calculated from the quantity of ion transported after 24 h into the aqueous phase II, which was determined by UV-spectrophotometry at the maximum absorbance of the picrate ion (λ_{max} = 355 nm, ϵ = 29 000 M^{-1} cm^{-1}).

Table II. Extraction percentages[a] of metal picrates at 25 °C

	Na^+	Ca^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Co^{2+}	log P[b]
1	1	6	1	2	0	1	2	1.5
2	0	**39**	**48**	2	1	4	4	1.8
3a	5	1	**72**	1	0	2	7	3.0
3b	0	6	1	2	2	1	0	3.2
3c	–	3	**81**	–	11	–	–	5.6
18-crown-6[c]	∼0	4	**86**	–	17	–	–	0

[a] Extraction conditions: aqueous phase [picrate] = 10^{-3} M; organic phase ($CHCl_3$) [ligand] = 10^{-3} M.
[b] Lipophilicity measured by RPTLC technique [15].
[c] Following ref. 16.

3. Results and Discussion

Open-chain or macrocyclic compounds like Schiff bases [17], dioxaoctane diamide [18], dithiocarbamates [19], crown-ethers [20], calix[4]arenes [3a] or dioxadilactams [6] display selective Pb(II) ionophoric properties. These were determined by measuring selectivity coefficients from ion selective electrodes and CHEMFETs or from liquid-liquid extraction percentages and transport ratios through a liquid membrane. We used the two latter techniques for the **1–3** amide containing compounds. An increased selectivity was anticipated for the macrocyclic tetralactams.

3.1. EXTRACTION STUDIES

The extraction results gathered in Table II were obtained following the technique recently used by Nishimura [21] with calix[4]arene derivatives replacing only chloroform by methylene chloride.

In order to select the best concentration of the extractants to ensure the largest selectivity scale, the extraction percentages of lead or calcium picrates with dioxatetralactam **3a** (Table I) were measured at different concentrations. The calcium ion was selected as reference for extraction due to its high affinity for this ionophore [10].

It can be seen, for instance, that the selectivity ratio E_{Pb}/E_{Ca} is very low (1.3) at 1.5×10^{-2} M with E_{Ca} and $E_{Pb} > 78\%$ but high (72) at 10^{-3} M where $E_{Pb} = 72\%$. Considering the great affinity of tetralactams for alkaline-earth cations and particularly for calcium [8] the 10^{-3} M concentration was selected as the best one for the ionophoric properties of our compounds.

Compounds **1**, **2**, **3a**, **3b** extract very poorly Na^+, Zn^{2+}, Co^{2+}, Cu^{2+} and Cd^{2+}. The low extraction of Na^+ and Zn^{2+} has been previously found with dioxatetralac-

tams [9]. The open-chain diamide **1** which does not extract significantly any cation presents an opposite behaviour to that of ETH129 used in calcium selective electrodes, which is selective for alkaline-earth and zinc cations [10]. ETH129 differs from **1** only by substituting cyclohexyl for H and benzyl groups on the nitrogen atoms. The main reason for this difference can be found in the greater lipophilicity of ETH129 (log P = 6.7) compared with that of **1** (log P = 1.5).

The main trends found from Table II are the very good selectivity of tetralactams **3a** and **3c** for the extraction of the lead(II) cation similar to that of 18-crown-6. As a matter of fact, the same selectivity for Pb^{2+} vs. Na^{+} and Ca^{2+} of these two class of compounds is very striking. To rationalize this for the 18-crown-6 ligand Izatt [22] explains the greater binding energy for oxygen-containing compounds with Pb^{2+} than with alkaline or alkaline-earth metals of similar radii (i.e. 1.18 Å for Pb^{2+} and 1.0 Å for Ca^{2+}) by a greater covalent character of the chemical bonds formed with the donor oxygen atom. This feature can be extended to the extraction. Takeda [16] has effectively stated that a complex with a crown-ether as ligand can be extracted more efficiently if it is more stable in an aqueous solvent. The pre-eminence of these energetic considerations versus the concept of complementarity between the ligand and the cation can be also applied to tetralactams.

In the case of 18-crown-6, the complementarity is achieved by a good equivalence between the ligand hole size and the cation diameter; with dioxatetralactams of the same ring size, the coordination of the oxygen atoms of the macrocycle ensures good stability; for instance, log β_{ML} = 5.6 in tetrahydrofuran solution [9] for the complex $Ca^{2+} \subset$ **3a** although the cation is located out of the mean plane of the ring in a conformation where the carbonyl groups point in its direction. However, the previous energetic explanation does not account completely for the results obtained for dioxatetralactam **3a**; for instance, fair Pb^{2+} and Ca^{2+} extractions (respectively 48 and 39%) were observed for the tetramide **2**, the open-chain analogous compound of **3a**. The selectivity ratio E_{Pb}/E_{Ca} shifts from 72 (**3a**) to 1.2 (**2**). This difference accounts for the fact that the most rigid ligand is the most selective following the well known macrocyclic effect [23]. This constitutes the first report of such an effect in the polylactam series. Finally, the advantage of tetralactam **3a** over the 18-crown-6 is related to its higher lipophilicity (log P = 3 vs. 0) and its greater lead selectivity vs. Zn^{2+}.

A comparison can also be carried out with two 15- and 17-membered catechol derived azadilactams [6]. With these two macrocycles the E_{Pb}/E_{Ca} selectivity is also very high, i.e. ∼10 and even ∼100 for the 15- and 17-membered dilactams respectively. However, the extraction percentages of lead picrate by these two compounds is relatively low, i.e. 13.9 and 24.5% respectively at 10^{-2}M concentration. Compared with them the dioxatetralactam **3a** extracts 100% of lead cation at 1.5×10^{-2}M concentration. This increased extraction power can be related to the presence in the macrocycle of four rather than two amide functions and, particularly, their substitution by lipophilic benzyl groups.

When sulfur atoms in the dithiatetralactam **3b** are substituted for the ethereal oxygens atoms of **3a**, the extraction percentage of lead picrate decreases dramatically. This result could indicate an active participation of the ethereal oxygen atoms in the complexation, as Pb(II) has a greater affinity for hard oxygen atoms than for softer sulfur atoms; but this is inconsistent with the molecular structure of the complex that we present in Section 3.5. From MD simulations on ionophores like calix[4]tetramide at a water-chloroform interface Wipff [24] reported that, at 10^{-3} M, the solute remains anchored by its polar carbonyl head to the interface via water fingers. The interface modulates the conformation and the (pre)organization of ionophores. Thus, the explanation of that dramatic diminution of extraction could be related to a less suitable ligand conformation at the interface. Changing the ethereal oxygen atoms in the dioxatetralactam **3a** by sulfur atoms (**3b**) can offer less stabilizing interactions with water in the water finger where **3a** presents the better preorganization for complexing.

On the other hand, the introduction of pyridine ligating side arms into the tetralactam system (compound **3c**) enhances slightly its ionophoric properties, but decreases the selectivity of Pb^{2+} vs. Zn^{2+}.

3.2. TRANSPORT STUDIES

The transport rates of metal picrates across a chloroform membrane were also measured and are reported in Table III. Three features clearly appear. Firstly, the identical behaviour of **3a** and **3b** versus the four investigated cations, i.e. Ca^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+}. The transport rate does not exceeds 10^{-7} mol.h^{-1} but the alkaline-earth Ca(II) is carried ten times less than the heavy metal cations Pb(II), Cd(II) and Zn(II). Secondly, the best transport rate and lead-selectivity are observed for the tetramide **2** in contrast to the extraction results. Thirdly, the bibracchial diazatetralactam **3c** is a poor carrier but a very good extractant for Pb^{2+} and a good carrier but a bad extractant for Zn^{2+}.

These inverted behaviours can be explained by examination of the stability constants. After Izatt [25], it is known that the most efficient transport of cations by an ionophore is reached only for a narrow scale of stability constants related to the carried cation. Here, **3b** transports Pb^{2+} moderately as well as **3a**, and might have also a low stability constant. On the other hand, the stability constant of the $Pb^{2+} \subset$ **3c** complex might be too high for good transport. A formation constant such as $\log \beta_{ML} = 8.2$ was reported for the $Ca^{2+} \subset$ **3c** complex in tetrahydrofuran solution [10] and a greater value could be expected for $Pb^{2+} \subset$ **3c**. The complex lies in the chloroform phase and is not easily dissociated and carried. This is likely the same phenomenon which also intervenes with **3a** and which explains a better transport rate of Pb^{2+} ions by tetramide **2**, $Pb^{2+} \subset$ **2** probably being less stable than $Pb^{2+} \subset$ **3a** and *a fortiori* than $Pb^{2+} \subset$ **3c**.

Table III. Transport[a] rates $\times$ 10^7 (mol.h^{-1}) of metal picrates across $CHCl_3$ at 25 °C

	Na^+	Ca^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}
2	–	0.1	**1.7**	0.1	0
3a	–	0.1	1.0	1.0	0.9
3b	–	0.1	0.9	0.9	1.0
3c	0.06[b]	0.69[b]	0.28	–	**1.25**[b]

[a] Transport conditions: aqueous phase I: 11 mL, guest cation, 10^{-3} M; $CHCl_3$ phase 11 mL, host carrier, 10^{-3} M; aqueous phase II: 11 mL.
[b] Transport conditions: same apparatus; concentrations: 1.2×10^{-3} M; ref. 10.

3.3. ES-MS STUDIES

An indication of the stability difference of complexes $Pb^{2+} \subset$ **3a** and $Pb^{2+} \subset$ **3c** is observed in their ES-MS spectra. In fact, electrospray ionization mass spectrometry (ES-MS) is particularly suitable for the observation of preformed ions in solution and has been applied successfully to the characterization of metal complexes [26]. ES-MS spectra of $Pb^{2+} \subset$ **3a** and $Pb^{2+} \subset$ **3c** were recorded at the same conditions and for a concentration of 10^{-4} M in acetonitrile. The ES^+-MS spectrum of $Pb^{2+} \subset$ **3a** shows only one peak at m/z = 677.5 which is due to the protonated ligand $[H(\mathbf{3a})]^+$. In contrast, the mass spectrum of $Pb^{2+} \subset$ **3c** is dominated by the peaks at m/z = 1292.6, 1201.3, 1110.5, 881.3 which correspond to the expected cation $[Pb(\mathbf{3c})(Picrate)]^+$ and to the successive loss of one, and two methylpyridyl units and the second picrate counter-ion. The isotopic pattern of these peaks is consistent with these formulations. Thus, these observations indicate a high difference between the abilities of **3a** and **3c** tetralactams to complex Pb^{2+} ion.

3.4. FORMATION CONSTANTS

These considerations led us to calculate the formation constants of the $Pb^{2+} \subset$ **3a** complex. Due to the low solubility of $PbPic_2$ in chloroform they were measured in tetrahydrofuran solutions. The progressive addition of dioxatetralactam **3a** to a solution of lead picrate (Figure 1) gave (i) absorption curves with two isosbestic points (ii) two slope modifications at ρ = 0.5 and 1 in the representation of the optical density against the ratio ρ = L/M of the ligand/metal concentrations. These observations suggest the existence of two complexes with 2/1 and 1/1 stoichiometries. The analysis of the complexation equilibrium with the STAR program [27] indicates values of log β_{ML} = 5.9 $\pm$ 0.1 and log β_{M2L} = 9.7 $\pm$ 0.4. At 10^{-3}M concentration the ML complex is pre-eminent (>90%).

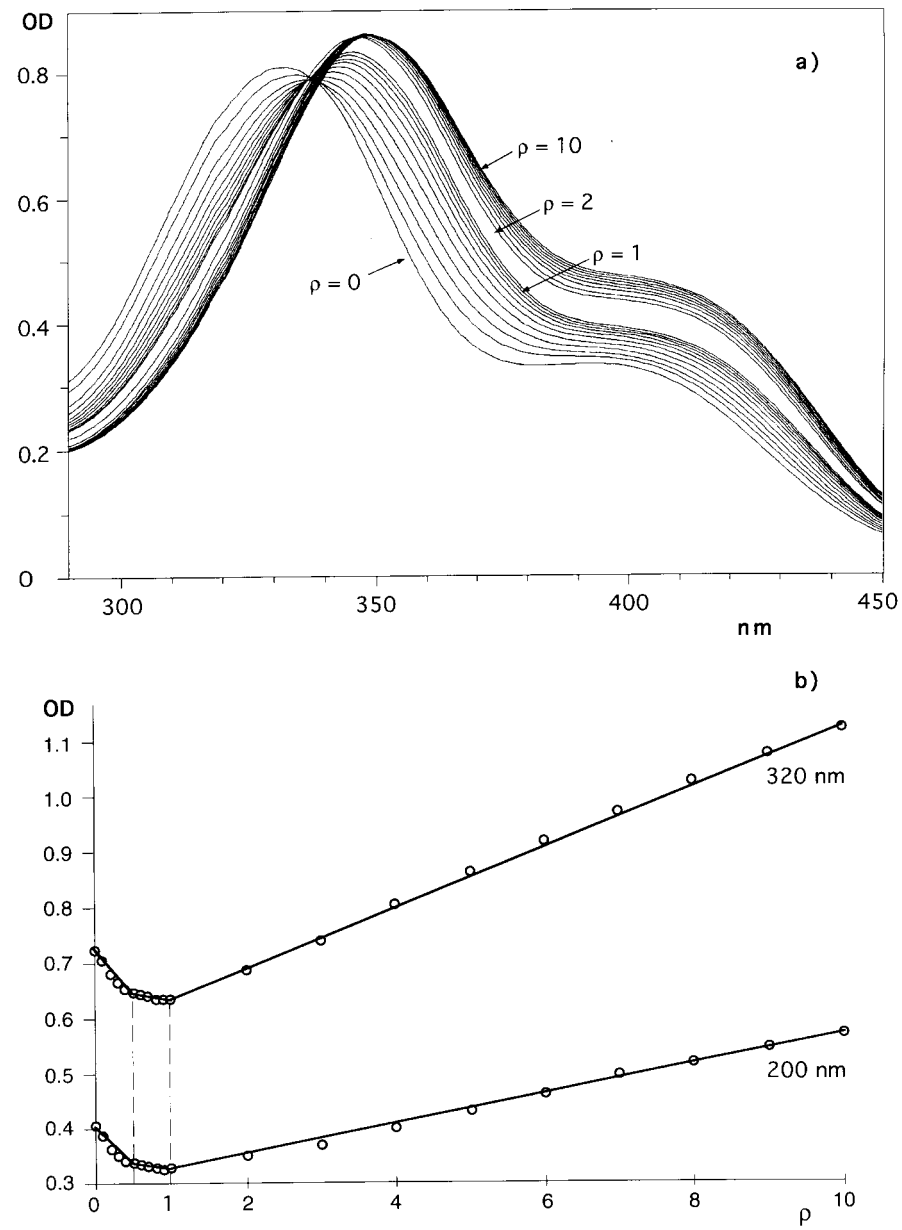

Figure 1. (a) Changes in the UV/Vis. absorption spectrum of $PbPic_2$ upon addition of ligand **3a** in tetrahydrofuran: [**3a**] = 1.68×10^{-3} M, $0 \leq \rho \leq 10$; (b) O.D. variation as a function of ρ = [**3a**]/[$PbPic_2$].

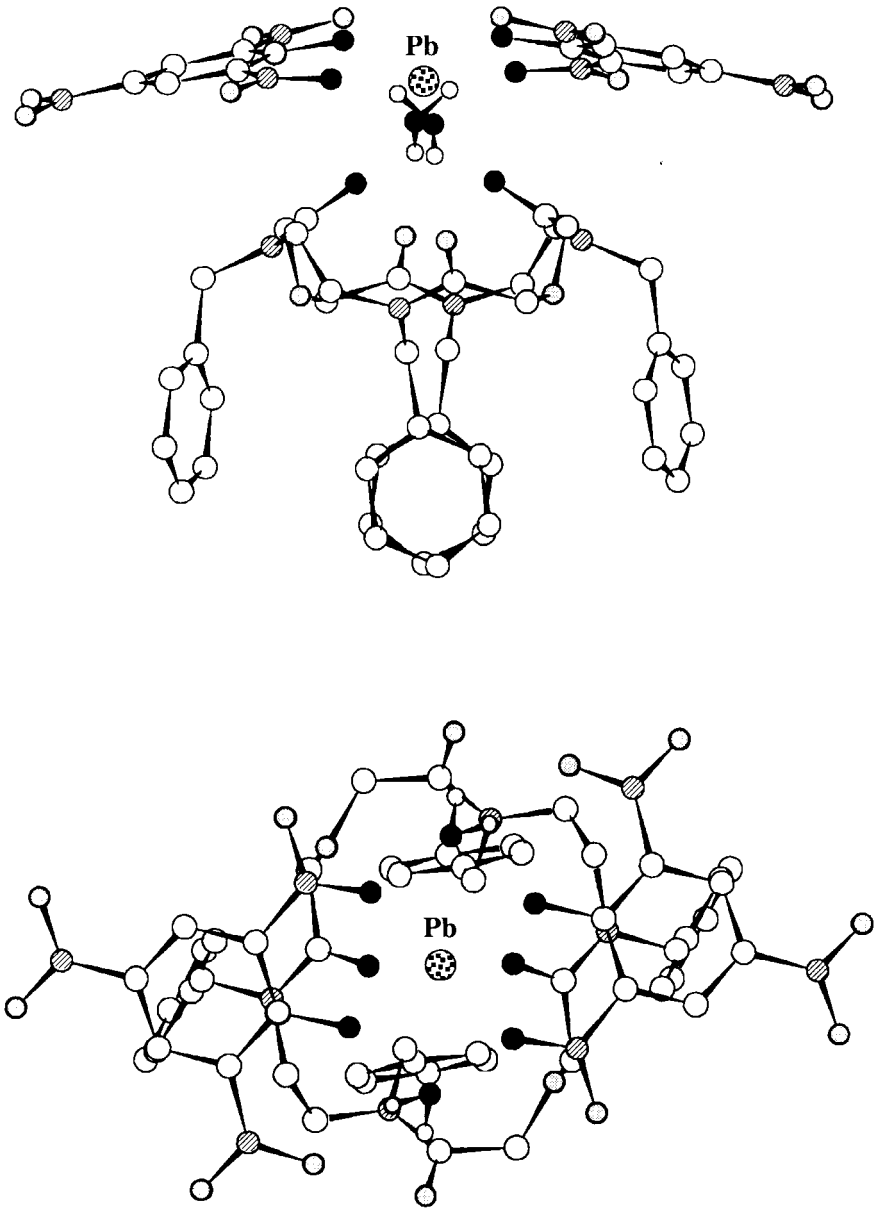

Figure 2. 3D Representation of the $Pic_2Pb \subset$ **3a**, $2H_2O$ complex in two orthogonal views (chelated atoms in black, other oxygen atoms in dotted area, nitrogen atoms in dashed lines).

3.5. STRUCTURE OF THE $PbPic_2 \subset$ **3a** COMPLEX

Information about the structure of this ML complex was obtained from I.R. spectra, elemental analysis of a solid sample and MD simulations in a water box [28]. According to the results, we propose for the $PbPic_2 \subset$ **3a** complex the structure shown in Figure 2. Two carbonyl oxygens only participate in the complexation along with two nitro groups (one of each picrate), two phenoxy oxygens and two water molecules bound to the metal ion to achieve a eight coordination geometry. It is noteworthy that the four phenyl groups are located in head-to-head orientations defining a hydrophobic environment; among them two groups display stabilizing stacking interactions. A similar structure was suggested for the free ligand giving an amphiphilic character to the dioxatetralactam favourable for the contact with the water finger interface and, consequently, to the extraction process.

4. Conclusion

The extraction of a series of cations by some polyamide and tetralactams gives a high selectivity for Pb^{2+} over alkali, alkaline-earth and heavy metal ions like Zn^{2+} for the macrocyclic compounds, namely **3a** and **3c**, while the transport of this ion across a chloroform membrane is more efficient for open-chain tetramide **2** rather than for tetralactams in relation with the stability of the complexes.

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