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Complexation of lithium picrate with a novel 12-crown-4 ether: spectrophotometric and quantum-chemical approach ☆

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Abstract

The complexation of lithium picrate (LiPic) with the new crown ether Tetracyclohexan(b,e,h,k)(1,4,7,10)tetraoxacyclododecane (CE) was studied spectrophotometrically in 1,2-dichloroethane and 1% 1,4-dioxane as solvating agent by means of computational methods. The spectra, obtained from the addition of a LiPic solution to a CE solution, showed remarkable overlapping absorption bands and two isosbestic points at 332 and 382 nm resulting from the formation of a LiPic ion pair complex. The complexation occurred instantaneously. The existence of two absorbent species was determined by the TRIANG program. It found experimental evidence for the presence of 1:1 $CELi^{+}Pic^{-}$ ion pair complex. The formation constant value, determined by the SQUAD program, was $\log \beta = 4.68 \pm 0.02$. In addition, the results of conformational studies of this system were performed by the PM3 semiempirical method in gas phase and in the presence of one dioxane molecule. In the gas phase, the most stable complex exhibits three-fold trigonal coordination, while in the presence of one dioxane molecule, four-fold tetrahedral coordination was found. The overall results revealed that the formation of an inclusion complex between the LiPic and the CE due to the presence of the picrate appeared impossible. The PM3 calculations are in good agreement with X-ray reported data in the gas phase and with dioxane. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 12-crown-4 ethers; Lithium picrate; PM3 method; TRIANG and SQUAD Program

1. Introduction

Macrocyclic molecules have considerable application for separation techniques [1,2], non-aqueous catalysis, selective analysis [3] and the design of ion selective electrodes [4]. In the last two decades, there has been increased interest in the synthesis, analysis and modeling of macrocyclic polyethers due to their unusual liganding properties [5]. Particularly because of the selective complexation of alkali and alkaline earth metal ions, macrocyclic polyethers have been investigated in fields of chemistry and biology [6–9]. Moreover, their hydrophilic and lipophilic properties are indispensable to explain the transportation of metal cations through lipophilic biological membranes.

There also has been a growing interest in lithium and lithium ionophores. Lithium has great actual and potential applications in science, medicine and technology [10]. In this sense, lithium selective ionophores present structure–function relationships with possible medical applications. There is need to clarify the mechanisms through which Li^{+} is involved in

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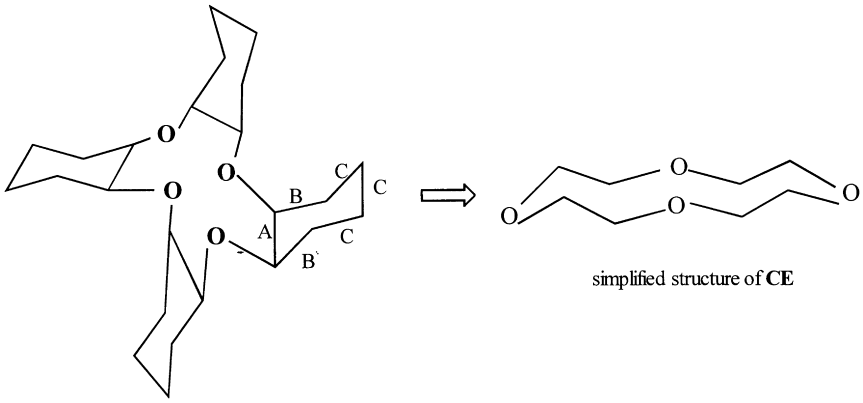

Fig. 1. CE: tetracyclohexan(b,e,h,k)(1,4,7,10)tetraoxacyclododecane.

a biological system. Hence, the elucidation of coordination number and geometry complexes should lead both to improving the understanding of its biological activity, as well as to designing better ionophores for such a function. Crown ethers are among the cyclic synthetic ionophores. Their ethereal oxygen atoms are favorable binding sites for Li^+. Several lithium picrate (LiPic) studies with crown ethers have been reported in the literature [6–9]. Recently, the "Picrate Effect" was related to extraction selectivities of aromatic group containing crown ethers for alkali metal cations in separations [11].

On the other hand, the quantum-mechanical calculation methods allowed us to predict the factors affecting the stability of the ion–macrocycle complexes such as: (i) the probable types and the number of binding sites in the ring; (ii) the relative sizes of the ion and the macrocycle cavity; (iii) the cavity flexibility grade; (iv) the physical binding sites; (v) steric hindrance of the ring; (vi) conformational changes; and (vii) solvent effect [6].

Many synthetic macrocycles, like the crown ethers, contain central hydrophilic cavities and an exterior flexible framework exhibiting a hydrophobic behavior. In many cases, they undergo marked conformational changes during the binding of cations or anions [7].

Conformational studies achieved by X-ray diffraction of LiPic with crown ethers have been reported by other authors about the ionic pairs formed [6–8]. Further, conformational analysis of 12-crown-4 and 15-crown-5 ethers was performed by molecular mechanics calculations with the MM3 program and the results were discussed with respect to experimental data [12,13].

In the present work, the binding of LiPic to the novel 12-crown-4 ether (CE), the tetracyclohexan(-b,e,h,k)(1,4,7,10)tetraoxacyclododecane (Fig. 1), was spectrophotometrically studied in 1,2-dichloroethane solution and by means of the PM3 semiempirical method [14]. The complexation took place spontaneously, resulting in the formation of just one stable ionic pair. The stoichiometry and the formation constant value were calculated by the SQUAD program [15–18]. Conformational studies of this system have been applied to determine the most probable geometry and coordination number of the ionic pair complex.

2. Experimental section

2.1. Apparatus

A Perkin–Elmer Lambda 18 Double-beam Spectrophotometer with 10 mm quartz cells was used for absorbance measurements.

2.2. Reagents

2.2.1. Tetracyclohexan(b,e,h,k)(1,4,7,10) tetraoxacyclododecane

The 12-crown-4 ether used in this experiment was kindly provided by Dr Enrique Angeles, synthesized according to reported procedure [19].

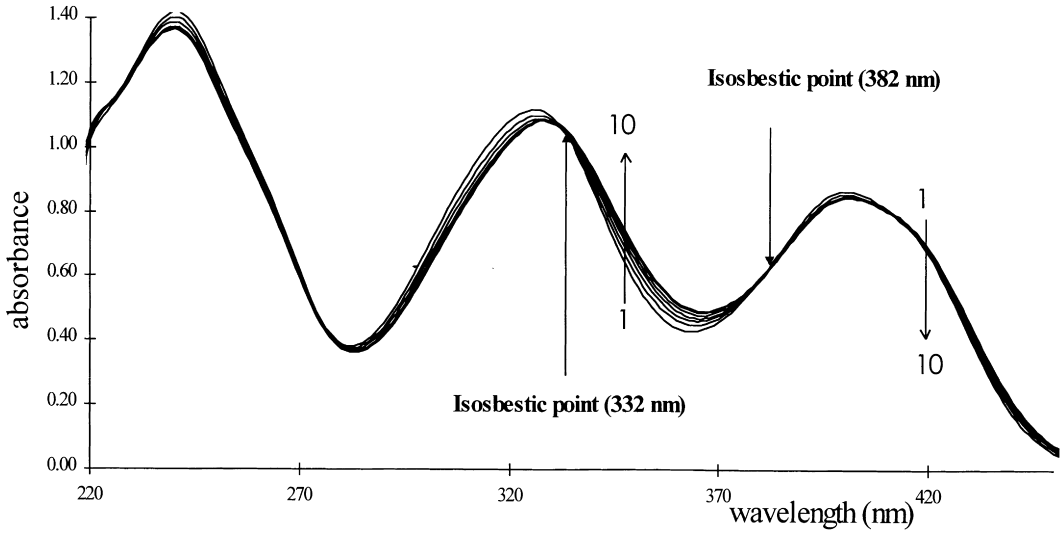

Fig. 2. Absorption spectra obtained from the addition of 10^{-4} M LiPic with 5×10^{-3} M CE.

2.2.2. LiPic

LiPic was obtained by neutralizing of picric acid with monohydrated lithium hydroxide in absolute ethanol. The salt was recrystallized twice from ethyl acetate and hexane and dried under vacuum. The purity was determined by thin-layer chromatography and spectroscopic techniques[1] [1].

2.3. Solutions

A 10^{-2} M LiPic solution: 23.70 mg of LiPic were weighed and dissolved 1,4-dioxane (spectrophotometric grade) and adjusted to a total volume of 10 ml.

A 1.008×10^{-4} M LiPic solution: 100 μl of 10^{-2} M LiPic solution were taken and adjusted to 10 ml with 1,2-dichloroethane (HPLC grade) with 1% dioxane as solvating agent.

A 5.007×10^{-3} M crown ether solution: 19.90 mg of the solid crown ether were weighed and dissolved in hexanes (isomeric mixture HPLC grade) and adjusted to a total volume of 10 ml.

[1] Caution! Metal picrates are potentially explosive hazards, which are sensitive to heat, friction or impact.

2.4. Procedure

The spectrophotometric measurements were carried out by addition of 3.0 ml of 10^{-4} M LiPic 1,2-dichloroethane with 1% 1,4-dioxane solution in a quartz cell by a 5.007×10^{-3} M CE in hexane solution. The complexation took place spontaneously. The spectra were traced against a 1,2-dichloroethane with 1% 1,4-dioxane solution as reagent blank.

3. Results and discussion

3.1. Assays of solvents

In order to bring to completeness the complexation of CE and LiPic, several solvents were assayed for each reactant. The best system of solvents was hexanes and 1,2-dichloroethane and 1% 1,4-dioxane as solvating agent for CE and LiPic, respectively.

3.2. Spectral analysis

Absorption spectra obtained from the titration of 10^{-4} M LiPic with 5×10^{-3} M CE exhibited remarkable overlapping absorption bands with two isosbestic points at 332 and 382 nm resulting from the formation of the LiPic ion pair complex (Fig. 2).

It should be noted that the existence of these

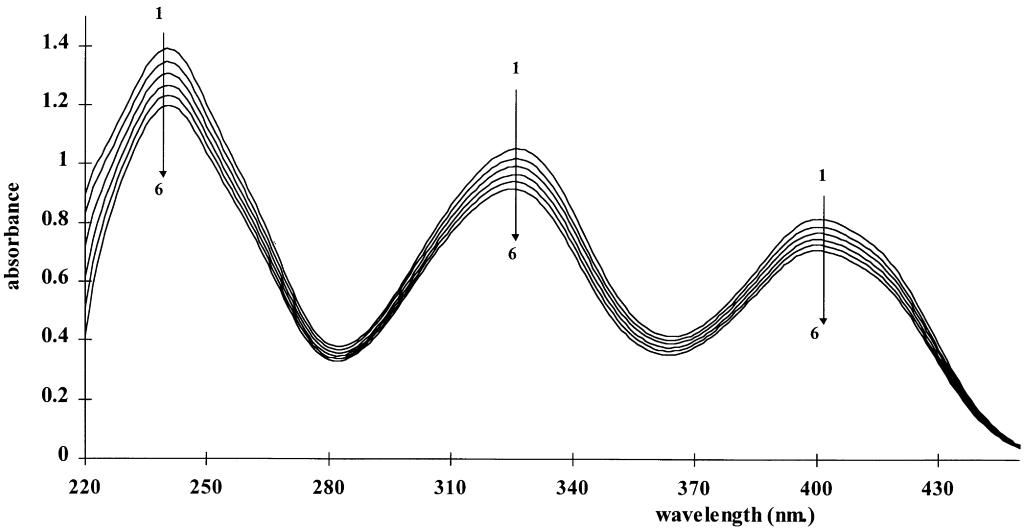

Fig. 3. Absorption spectra obtained from the addition of 10^{-4} M LiPic with hexane solvent.

isosbestic points might be produced by a solvent effect due to the mixture of solvents (1,2-dichloroethane with 1% 1,4-dioxane and hexanes). In order to demonstrate the authenticity of these isosbestic points, the "titration" of this system was carried out by adding just the hexane solvent to a LiPic solution. A dilution effect was observed, but no isosbestic point. This observation confirmed that the existence of isosbestic points was a consequence of the formation of the ionic pair complex (Fig. 3).

3.3. Complex nature

Two absorbing species were determined by means of the TRIANG program [20], one of these species was LiPic and the other one was the ionic pair

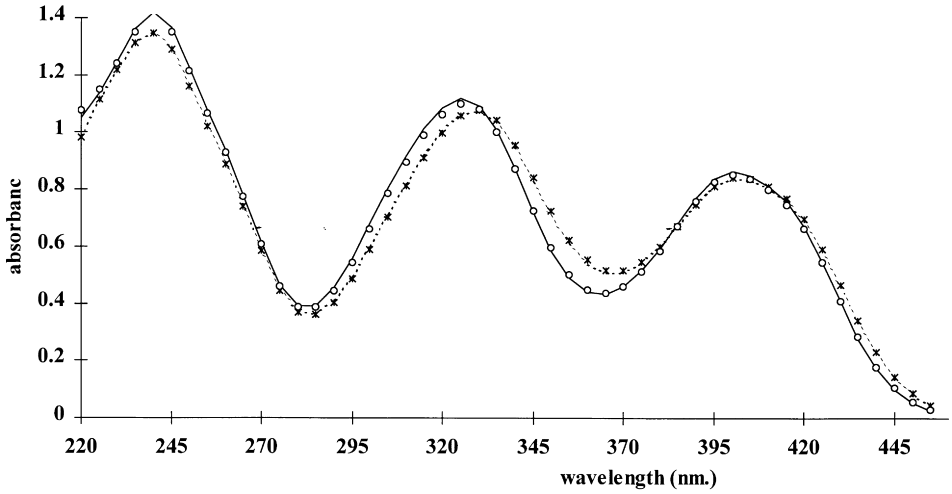

Fig. 4. Simulated absorption spectra for (∗) $CELi^{+}Pic^{-}$ and (○) LiPic and experimental absorption spectra for (- - -) $CELi^{+}Pic^{-}$ and (—) LiPic.

Table 1
Comparison of PM3 calculated and X-ray crystallographic structural features for CE in the gas phase

Bond lengths (Å)				Bond angles (°)				Dihedral angles (°)			
C–O		C–C		C–O–C		C–C–O		C–O–C–C		O–C–C–O	
PM3	X-ray	PM3	X-ray	PM3	X-ray	PM3	X-ray	PM3	X-ray	PM3	X-ray
1.428	1.432	1.557[a] 1.538[a] 1.518[a]	1.519 1.522[b] 1.518[b]	115.4	115.0	110.4 106.2	110.0 107.7	160.0 101.7	160.0 108.2	70.3	67.0

[a] These distances are differentiated length bonds (see Fig. 1).
[b] Average value.

complex. Mole ratio method [21,22] suggested a stoichiometry of 1:1 LiPic:CE ion pair complex, which was confirmed by the SQUAD program. The formation constant and the molar absorptivities were calculated by the SQUAD program. It was refined from input spectra data obtained from the titration LiPic solution with CE and from different hypothetical models, i.e. stoichiometric coefficients and the initial guess of stability constant values of all expected species together with relevant absorptivities. The minimization was accomplished using the sum of squared residuals U with a non-negative least square method (NNLS). The best fit of the analysis of results was obtained by assuming the presence of just one ionic pair $CELi^{+}Pic^{-}$ with a constant value of $\log \beta = 4.68 \pm 0.02$.

In addition, electronic spectra of LiPic and $CELi^{+}$-Pic^{-} were traced from the computed molar absorptivity values. The spectra were simulated and compared with experimental spectra and a good agreement was observed (Fig. 4). In conclusion, despite the big overlapping grade of the spectral bands, the program satisfactorily converged with the statistical parameters.

3.4. Quantum-mechanical calculations

Conformational studies of this system were performed by the PM3 semiempirical method [14]

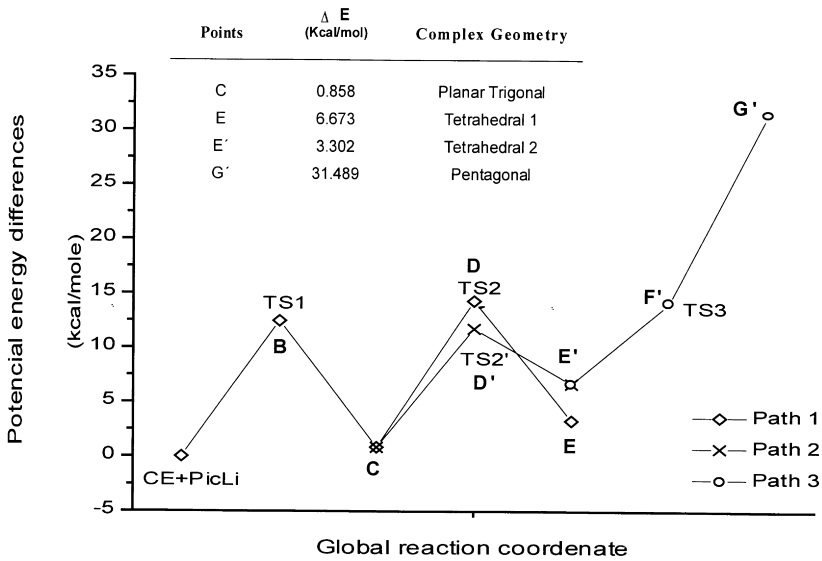

Fig. 5. The reaction profile and complex geometries of $CELi^{+}Pic^{-}$ complexes in the gas phase.

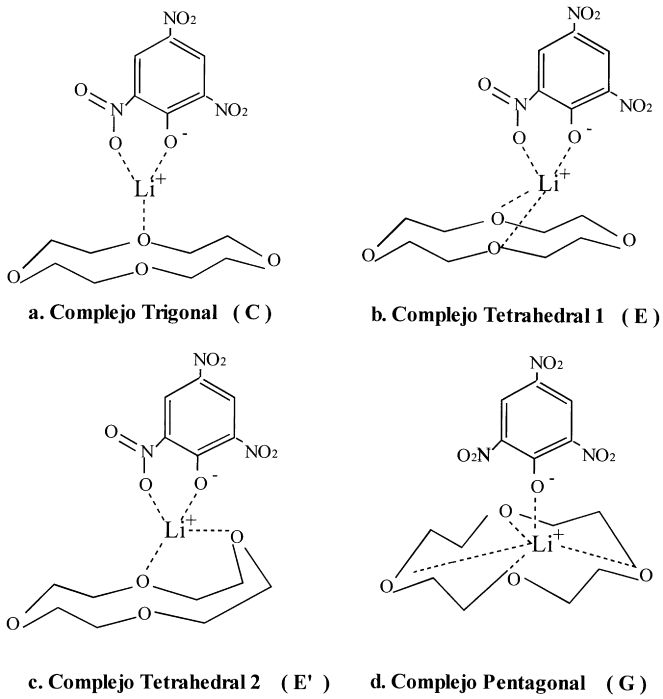

Fig. 6. Geometries of $CELi^{+}Pic^{-}$ in the gas phase.

part of the SPARTAN 4.0.2 package [23]. The geometry of CE was calculated and was found to be very similar to that determined from X-ray analysis [19]. The comparison of these parameters is presented in Table 1.

3.4.1. Complex geometry calculated in the gas phase

In order to establish the most stable geometry of the ionic pair complex in the gas phase, reaction paths were calculated when a LiPic molecule approached CE [24]. The motion of the LiPic molecule was carried out through three different pathways of reaction.

Fig. 5 represents a reaction coordinate diagram for the reaction:

$$CE + LiPic \rightleftharpoons CELi^{+}Pic^{-}$$

which shows the potential energy as a function of interaction distance, i.e. coordinate reaction by three different pathways. The graph presents three minima (points C, E, and E′) and five maxima (points B, D, D′, F′ and G′). While the minima represent probable ternary $CELi^{+}Pic^{-}$ complexes, the maxima B, D and D′ correspond to transition states (TS1, TS2 and TS2′). The F′ and G′ points indicate unstable complex geometries. In all cases, point A means the relative energy point with respect to the reagents.

Fig. 6 shows three probable stable geometries for minima C, E and E′ and one unstable geometry for point G′. The stable complex geometries are trigonal, tetrahedral 1 and tetrahedral 2. The unstable geometry would be that of one pentagonal.

Applying the principle of the least motion [25–27], the most favored geometry corresponds to point C, which has the least energy change, and suggests the existence of a ternary $CELi^{+}Pic^{-}$ complex with a three-fold trigonal geometry (Fig. 6). LiPic seems to be externally bound to one oxygen ether atom and two picrate oxygen atoms with interatomic distances around 2 Å. This complexation proceeds with a conformational change: the plane of one cyclohexane molecule changes from parallel to perpendicular with regard to the other three cyclohexanes (Fig. 6(a)). In this case, a coordination number of three and geometry planar trigonal resulted as the most probable. However, it is important to remark that these

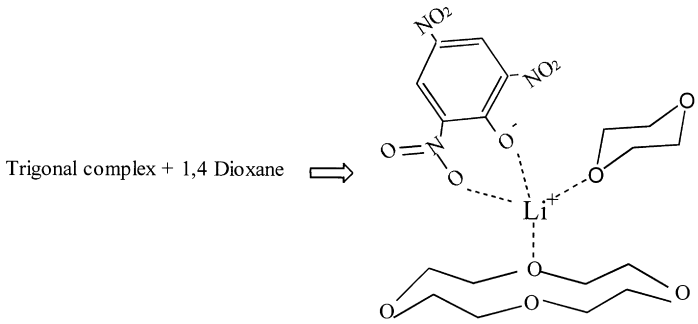

Fig. 7. Tetrahedral geometry of $CELi^{+}Pic^{-}$ in the presence of 1,4-dioxane.

properties are rather rare, because Li^{+} does not necessarily have a single characteristic coordination number and geometry [24]. The small radius of lithium gives the ability for versatile Li^{+} coordination numbers. For this reason, calculations taking into account the solvent effect pointed out other geometries.

In addition, as shown in Fig. 5, the energies $E_D > E_{D'}$ and $E_E < E_{E'}$, so we suggested that the path D–E corresponds to a thermodynamical pathway, and the distance D′–E′ to a kinetical pathway [22].

Since the interaction of Li^{+} with the phenoxide oxygen never got lost during the calculations, the formation of an inclusion complex between the LiPic and the CE was not possible. When the introduction of Li^{+} inside the cavity of crown ether was attempted, the energy increased infinitely.

3.4.2. Complex geometry calculated in the presence of 1,4-dioxane

For this calculation, a similar procedure, previously described, was followed. Among the solvents used, only dioxane presents oxygen donor atoms that act as ion binding sites.

The addition of a dioxane molecule to the trigonal complex produces a new four-fold tetrahedral complex with a tetrahedral 3 geometry (see Fig. 7). The relative energy changes from 0.858 to −2.581 kcal/mol with respect to the initial point, which means the stabilization energy due to the presence of the dioxane molecule is −3.439 kcal/mol. It is assumed that the structures of the complexes in the solid state resemble their structures in solution.

Table 2 presents the comparison of PM3 calculated and X-ray crystallographic reported data for $CELi^{+}$-Pic^{-} in gas phase and with dioxane. As can be observed, the X-ray crystallographic distances of $Li–O_{Ph}$ and $Li–O_{NO_2}$ are closer to a tetrahedral geometry than to a trigonal geometry, not so different from distances of CE geometries. This difference is probably because $Li–O_{NO_2}$ is an average value from different CE geometries and the picrate is a monodentated ligand [24].

Table 2
Comparison of PM3 calculated and X-ray crytallographic structural features for $CELi^{+}Pic^{-}$ in gas phase and 1,4-dioxane (the values between parentheses mean % relative error with respect to X-ray data)

	Bond lengths (Å)			
	$Li–O_{Ph}$	$Li–O_{NO_2}$	$Li–O_{CE}$	$Li–O_{dioxane}$
X-ray data	1.925 [29]	2.040 [29]	2.077 [28][a]	1.94 [30][b]
Trigonal[c]	1.883 (2.18)	1.946 (4.61)	2.114 (−1.78)	–
Tetrahedral 3[d]	1.907 (0.935)	2.008 (1.57)	2.334 (−12.37)	2.102 (−8.35)

[a] Average $Li–O_{CE}$ from different CE geometries.
[b] Average value.
[c] Gas phase calculated by PM3 method.
[d] In the presence of one 1,4-dioxane molecule calculated by PM3 method.

5. Conclusions

There is spectrophotometric evidence of the presence of a LiPic ion pair complex. Despite the notable overlapping of the spectral bands, the SQUAD program is appropriate to calculate the formation constant value of the complex.

To establish the structural features of the possible complexes of the ion pair $CELi^{+}Pic^{-}$, a quantum chemistry strategy is proposed as a very suitable tool in the gas phase and dioxane. The geometries, the bond lengths and the coordination number of these complexes were established. These values are in good agreement with X-ray reported data.

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