



## STUDIES ON THE COORDINATION BEHAVIOUR OF 1,3-PHENYLENEBIS(FORMYLOXYACETYL-4'-BENZO-15-CROWN-5)

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**Abstract**—Yellow solid complexes having the stoichiometric formula  $KLPic$  and  $Na_2L(Pic)_2 \cdot 2H_2O$  ( $L = 1,3$ -phenylenebis(formyloxyacetyl-4'-benzo-15-crown-5),  $Pic =$  picrate anion) were obtained from chloroform–methanol mixtures. The results of the characterization of the two complexes by IR, NMR, UV–vis spectra and molar conductance indicated that a 2:1 complex of crown-separated ion pair (benzo-15-crown-5 unit to  $K^+$ ) and a 1:1 complex of contact ion pair (benzo-15-crown-5 unit to  $Na^+$ ) are formed, respectively.  $^{13}C$  NMR spectra showed that the carbonyl groups on the bridging chain do not take part in the coordination of the picrates. A PVC membrane  $K^+$ -selective electrode based on the title ligand ( $L$ ) was also studied. The 11 kinds of new, coloured, solid rare earth picrate complexes with the stoichiometric formula  $Ln(Pic)_3 \cdot L \cdot nH_2O$  ( $Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Ho, Er, Yb, Y, n = 5$  or  $6$ ) were prepared in an ethanol–chloroform mixture. By elemental analysis, IR, UV–vis spectra, molar conductance and DTA–TG, these complexes were proposed as supermolecules in which the title ligand acts as second-sphere ligand, and  $Ln(Pic)_3$  is associated with the ligand by intermolecular forces.

It is well known that bis(benzo-crown) ethers with various bridge chains exhibit higher coordination ability and selectivity to metal ions than the corresponding monomeric crown ethers because of the cooperative effect of the two crown ether units. In our laboratory bis(benzo-15-crown-5) ethers with various linkages have been synthesized,<sup>1</sup> of which the title ligand with the two benzo-15-crown-5 (B15C5) units situated at the *meta* position of the phenyl ring is expected to possess high coordination selectivity for  $K^+$  over  $Na^+$ .

Trivalent lanthanide ions have a  $4f^n5s^25p^6$  electronic configuration, resulting in weak field and directional effects. In some respects, their chemical properties resemble those of Ia and IIa cations, so that the investigation of their interaction with bis(crown) ethers is a logical extension of the work with alkali and alkaline earth metals. Recently, in the course of our study of the extraction mechanism of benzo-15-crown-5 with lanthanide picrates, a new series of crystal-extracted complexes of

hydrated lanthanide picrates with B15C5 have been obtained, the stoichiometry of the complexes being 1:2:3 (metal:B15C5 unit:Pic), except in the case of  $La(Pic)_3$ . The X-ray structural analysis revealed that the B15C5 acts as a second-sphere ligand, which is associated with the hydrated lanthanide picrate by hydrogen bonding through coordinating water molecules.<sup>2</sup> These interesting results motivated us to investigate the mode of binding interaction between  $Ln(Pic)_3$  and the title ligand. Therefore, a systematic study of the coordination behaviour of the title ligand is reported here.

### EXPERIMENTAL

#### Reagents

All the chemicals used were of analytical grade. The title ligand,  $L$ , as shown in Fig. 1 was synthesized according to the literature method.<sup>1</sup>

#### Preparation of the complexes

*Complexes of potassium picrate (KPic) and sodium picrate (NaPic).* A solution of 0.1 mmol of

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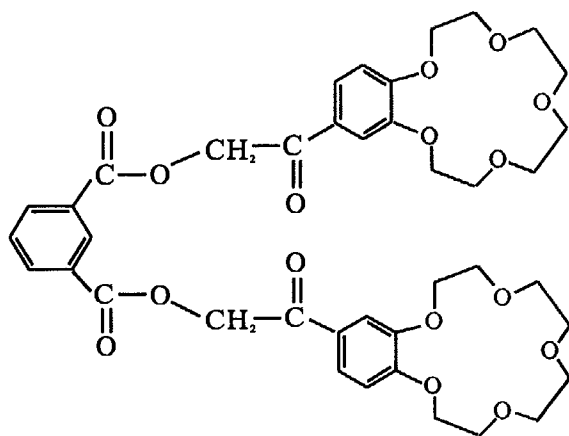


Fig. 1. The title ligand L.

L and 0.1 mmol of KPic (or 0.2 mmol NaPic) in 10 cm<sup>3</sup> of 1 : 1 CHCl<sub>3</sub>-CH<sub>3</sub>OH (v/v) mixed solvent was refluxed for 0.5 h and cooled to room temperature. The yellow solid product was filtered and washed successively in small portions with 1 : 1 CHCl<sub>3</sub>-CH<sub>3</sub>OH mixed solvent and then dried *in vacuo* for 3 days.

**Complexes of the lanthanide picrate.** A solution of L (0.1 mmol) in 5 cm<sup>3</sup> of chloroform was added to an equal volume containing 0.1 mmol of Ln(Pic)<sub>3</sub> in absolute ethanol solution and was refluxed for 4–5 h and then cooled to room temperature. Compared with Ln(Pic)<sub>3</sub>·11H<sub>2</sub>O, the solid products were of different colour (deep yellow or orange) and were collected by filtration, washed twice with small portions of 1 : 1 CHCl<sub>3</sub>-C<sub>2</sub>H<sub>5</sub>OH mixed solvent and dried *in vacuo* for more than 3 days.

#### Preparation of PVC membrane electrode

A PVC membrane K<sup>+</sup>-selective electrode based on the title ligand was prepared according to the usual procedure described in related literature with *o*-nitrophenyloctyl ether used as plasticizer.

#### Chemical and physical measurements

The lanthanide ion contents were determined by a spectrophotometric method using chlorophosphonazo III as photometric reagent. Carbon, nitrogen and hydrogen contents were determined by using a Carlo-Erba 1106 elemental analyser. The IR spectra were recorded as Nujol mulls on a Shimadzu 435 spectrometer. UV-vis spectra were recorded with a Hitachi UV 220A spectrometer. NMR was recorded on a Bruker AC-80 instrument. The DTA-TG curves were obtained using a Shimadzu DT-40 thermal analyser. Conductivity

measurements were performed with a DDS-11A conductometer.

## RESULTS AND DISCUSSION

The elemental analysis, IR and molar conductance data are listed in Table 1, and the ratio of ligand to KPic and NaPic is 2 : 1 and 1 : 1 (B15C5 unit : metal ion), respectively. The obvious absorption peak at 3500 cm<sup>-1</sup> in the NaPic complex is consistent with the results of elemental analysis, and the lack of a ligand absorption band at 980 cm<sup>-1</sup> also indicates that the two complexes are formed. Because the size of K<sup>+</sup> is larger than that of the cavity of the benzo-15-crown-5 units in the ligand, a 2 : 1 intramolecularly crown-separated ion pair, KLPic, is formed, while NaPic forms a 1 : 1 intramolecular contact ion pair Na<sub>2</sub>L(Pic)<sub>2</sub> with L owing to their matching size. UV-vis spectra, molar conductance and <sup>1</sup>H NMR spectra support this conclusion.

Bourgoin *et al.*<sup>3</sup> have reported that the absorption maximum of the picrate anion near 380 nm is indicative of the formation of a loose ion pair, and there are some hypsochromic shifts if the interaction of the picrate anion with a cation or complexed cation exists.<sup>3</sup> Our previous study on the UV-vis spectra of the extracting solution of NaPic or KPic with B15C5 or DB18C6 gave identical results.<sup>4</sup> In this work, we also found that in a mixed 1,2-dichloroethane-acetonitrile (10 : 1) solution, the absorption maxima of the picrate anion at 360 nm for NaPic shifts to 367 nm for Na<sub>2</sub>L(Pic)<sub>2</sub>. Compared with KPic and KLPic, the spectral change is from 365 to 378 nm. That is, in polar media, the formation of a 2 : 1 intramolecular crown-separated ion pair makes the interaction of picrate anion with KL<sup>+</sup> weaker or absent. Therefore, the delocalization of electrons of the picrate anion increases and the absorption maximum nears that of the free picrate anion.<sup>3</sup> On the other hand, in the case of the sodium complex, the ion can fit well into the cavity of B15C5 units in the ligand and a 1 : 1 intramolecular contact ion pair in Na<sub>2</sub>L(Pic)<sub>2</sub> is formed, in which the interaction of complexed cation with the picrate anion cannot be prevented completely. As a result, only a slight bathochromic shift is observed.

The molar conductances of the picrate complexes were determined in acetonitrile (Table 1). The  $\Lambda_M$  value of KLPic is 109.7  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , which can be classified as a 1 : 1 electrolyte according to the literature.<sup>5</sup> This implies that the ligand forms a 2 : 1 crown-separated ion pair with KPic. The  $\Lambda_M$  value of Na<sub>2</sub>L(Pic)<sub>2</sub> (197.2  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) is almost twice that of KLPic. It is evident that the B15C5 unit of

Table 1. Elemental analysis, IR and molar conductance data

Compound	Found, % (Calc.)			IR (cm <sup>-1</sup> )		$\Lambda_m$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
	C	H	N	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O}-\text{C})$	
L	61.3 (61.4)	5.9 (5.9)		1730, 1687	1255, 1138	
Na <sub>2</sub> (Pic) <sub>2</sub> ·L·2H <sub>2</sub> O	47.3 (47.3)	4.1 (4.1)	6.3 (6.4)	1730, 1691	1241, 1123	197.2
KPic·L	52.7 (52.6)	4.7 (4.6)	4.0 (4.0)	1730, 1690	1240, 1125	109.7

the title ligand forms a 1:1 contact ion pair with NaPic, and that one mole of Na<sub>2</sub>L(Pic)<sub>2</sub> may be seen to contain two 1:1 electrolytes.

The determination of <sup>1</sup>H NMR spectra of the ligand and its NaPic and KPic complexes in CDCl<sub>3</sub> shows a dramatic difference of chemical shifts of the phenyl and ether protons of the B15C5 unit. In the case of the NaPic complex, the ether protons shift downfield by ~0.1 ppm relative to those of the free ligand (at 4.17 and 3.96 ppm, respectively), and the phenyl protons of B15C5 unit also show a downfield shift of 0.03–0.06 ppm. It is easy to give an explanation of this phenomenon in terms of the electronic effect caused by the coordination between the B15C5 cavity and the sodium cation, which decreases the electron distribution on the protons of the B15C5 unit and results in the diminishing of their shielding effect. On the contrary, in the <sup>1</sup>H NMR spectrum of the KPic complex, the  $\delta$  values of ether protons shift upfield ~0.2 and ~0.4 ppm relative to those of its free ligand, and similarly, the chemical shifts of the phenyl protons of the B15C5 unit tend to shift upfield by ~0.2 ppm. This interesting result probably arises from the formation of a 2:1 sandwiched structure in the KPic complex, in which the B15C5 units of the ligand have face-to-face structures, thus resulting in an increase of the shielding effect of phenyl and ether protons and the movement of chemical shifts upfield.

In addition, the <sup>13</sup>C NMR and IR spectra confirm that the C=O groups at the linkage of the title ligand do not take part in coordination with the picrates.

An Haoyun *et al.*<sup>6</sup> reported that bis(benzo-15-crown-5) ethers existing in an appropriate V-shape conformation can easily form sandwiched complexes with K<sup>+</sup>, and the electrode based on these bis(crown) ethers is more selective for K<sup>+</sup>. The specific ligand with two B15C5 units situated at the *meta* position of the phenyl linkage mentioned above, which also shows that the V-shape may pos-

sess higher selective coordination with K<sup>+</sup> over Na<sup>+</sup>. The PVC membrane K<sup>+</sup>-selective electrode based on the ligand has thus been studied for this application. The linear response range (M) and detection limit (M) as well as slope (mV) are 10<sup>-4</sup>–10<sup>-1</sup>, 5 × 10<sup>-5</sup> and 50.5 mV, respectively. The electrode is stable at pH 5–11, and the selectivity coefficients  $K_{k^+, M^{n+}}$  of various ions for Na<sup>+</sup>, Li<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> are 5.05 × 10<sup>-4</sup>, 1.64 × 10<sup>-5</sup>, 5.62 × 10<sup>-3</sup>, 3.35 × 10<sup>-6</sup> and 1.35 × 10<sup>-4</sup>, respectively.

The results of elemental analysis and spectrophotometric determination of rare earth ions of the complexes, as shown in Table 2, indicate that in the complexes the ratio of the ligand (B15C5 unit) to lanthanide picrate is 2:1 exclusively, with five or six water molecules.

IR examination on the lanthanide picrate complexes shows that the molecular symmetric vibrational absorption of the ligand at ~980 cm<sup>-1</sup> is absent and the  $\nu(\text{Ar}-\text{O}-\text{C})$  and  $\nu(\text{C}-\text{O}-\text{C})$  absorptions at 1255 and 1138 cm<sup>-1</sup> in L shift to ~1232 and ~1125 cm<sup>-1</sup>, respectively, after the complexes are formed. This is an indication of some kind of interaction between the ligand and lanthanide picrates. The  $\nu(\text{C}=\text{O})$  absorptions of L do not show much difference before and after the formation of the complexes, which implies that the carbonyl groups of the linkage do not take part in coordination.

The measurement of the molar conductance of the lanthanide picrate complexes in acetonitrile (12.7–15.3  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) obviously reveals these complexes to be non-electrolytes. This suggests that in these complexes lanthanide ions do not coordinate with the ligand directly and release the free picrate anion.

The study of the UV-vis spectra of the complexes has shown that the absorption maxima of the picrate anion also undergoes a pronounced hypsochromic shift in 1,2-dichloroethane as compared with that of the corresponding lanthanide picrate (16–25 nm).

Table 2. Analytical data for lanthanide compounds

Compound	Found, % (Calc.)			
	C	H	N	Ln
La(Pic) <sub>3</sub> ·L·5H <sub>2</sub> O	41.0 (41.1)	3.7 (3.7)	7.2 (7.4)	7.7 (8.2)
Pr(Pic) <sub>3</sub> ·L·5H <sub>2</sub> O	40.5 (41.0)	3.6 (3.7)	7.6 (7.4)	8.0 (8.3)
Nd(Pic) <sub>3</sub> ·L·5H <sub>2</sub> O	39.9 (40.9)	3.6 (3.7)	7.2 (7.4)	8.3 (8.5)
Sm(Pic) <sub>3</sub> ·L·5H <sub>2</sub> O	41.1 (41.8)	3.7 (3.7)	7.4 (7.4)	8.5 (8.8)
Eu(Pic) <sub>3</sub> ·L·5H <sub>2</sub> O	39.9 (40.8)	3.6 (3.6)	7.2 (7.4)	8.8 (8.9)
Gd(Pic) <sub>3</sub> ·L·6H <sub>2</sub> O	39.9 (40.2)	3.7 (3.7)	7.2 (7.3)	9.0 (9.1)
Tb(Pic) <sub>3</sub> ·L·6H <sub>2</sub> O	40.5 (40.2)	3.7 (3.7)	7.1 (7.3)	7.6 (9.2)
Ho(Pic) <sub>3</sub> ·L·6H <sub>2</sub> O	40.3 (40.0)	3.7 (3.7)	7.1 (7.2)	9.1 (9.5)
Er(Pic) <sub>3</sub> ·L·5H <sub>2</sub> O	40.1 (40.4)	3.6 (3.6)	7.2 (7.3)	9.7 (9.7)
Yb(Pic) <sub>3</sub> ·L·5H <sub>2</sub> O	40.0 (40.3)	3.6 (3.6)	7.3 (7.3)	10.5 (10.0)
Y(Pic) <sub>3</sub> ·L·6H <sub>2</sub> O	41.5 (41.9)	3.8 (3.8)	7.4 (7.6)	5.1 (5.4)

X-ray structural analysis revealed that in the complexes (Nd, Sm, Er) the two B15C5 molecules act as second-sphere ligands located at the two sides of hydrated lanthanide picrate, which associate with Ln<sup>3+</sup> through hydrogen bonding of the coordinating water molecules.<sup>2</sup> This spatial arrangement of the B15C5 complexes should cause the interaction of B15C5 with picrate anions and, therefore, the delocalization of electrons of picrate anions decreases, and the absorption maxima shift hypsochromically. Although we cannot give an accurate molecular structure of the title ligand complexes as B15C5 complexes, the X-ray determination and characterization of B15C5 complexes inspired us to provide an appropriate model of the complexes which may be speculated as a supermolecule involving Ln(Pic)<sub>3</sub> and the ligand with five or six water molecules. This associate may be governed by intermolecular forces or van der Waals' forces. The thermoanalysis results indicated that the melting point of the ligand is 167 °C, but the complexes decompose at ~200 °C, which implies that the intermolecular forces probably play an important role in the formation of the complexes because the complexes dissociate upon heating before their melting point.<sup>7</sup> The V-shape conformation with two B15C5 units of the ligand which acts as a second-sphere coordination should cause some interaction with the picrate anions, thus

affecting the characterization of the complexes. As a result, it also leads to the hypsochromic shift of absorption maxima of picrate anions.

The study of coordination behaviour of the title ligand provides a higher selective ligand for K<sup>+</sup> over Na<sup>+</sup>, and, furthermore, it also develops an extension of second-sphere coordination of lanthanide crown ether chemistry and offers a supplement of supramolecular chemistry.

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