

# Synthesis, solid-state structures and metal ion complexation behavior of 2-picolylxy lariat ethers

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**Abstract**—Three new 2-picolylxy lariat ether compounds are prepared and solid-state structures are determined for two of them. Complexation behavior for a series of lariat ethers with pyridyl-containing side arms toward alkali metal cations and Ag<sup>+</sup> is assessed by two-phase metal picrate extraction from aqueous solutions into chloroform and in homogeneous solutions by isothermal titration calorimetry in methanol. © 2007 Elsevier Ltd. All rights reserved.

## 1. Introduction

For four decades, macrocyclic polyether compounds (crown ethers) have been prepared and utilized in alkali and alkaline earth metal cation determinations due to their superior binding ability for these metal ions.<sup>1</sup> Attachment of a side arm with one or more potential metal ion binding sites produces a complexing agent called lariat ether.<sup>2,3</sup> Such lariat ethers are designed to increase the cation binding ability or selectivity of crown ethers by providing a potential for three-dimensional complexation.

Pyridine is an excellent solvent for neutral and charged inorganic and organic molecules due to its high donicity and solvation ability.<sup>4</sup> The ambivalent hydrophobic–hydrophilic character of the pyridine moiety is of importance in selective extraction and transport of cations through hydrophilic bilayers and in inter- and intramolecular interactions. Therefore, the pyridine moiety is an effective binding site in large number of molecules.<sup>5</sup>

Several reports have appeared in which pyridine-containing side arms have been attached to ring nitrogen atoms of mono-, di-, tri- or tetraazacrown ethers by reactions with 2-, 3-, and 4-picolyl chlorides [2-, 3-, and 4-(chloromethyl)pyridines].<sup>6–12</sup> Metal ion complexation involving coordination with the pyridyl nitrogen was demonstrated in several

instances. Compounds with a pyridine-containing side arm attached to a crown ether ring are rare. Previously, we published the synthesis of *sym*-(2-picolylxy)dibenzo-13-crown-4 (**1**) and its solid-state structure.<sup>13</sup> We now report the synthesis of three analogs in which the crown ether portion of the ligand has been modified to produce *sym*-(2-picolylxy)dibenzo-14-crown-4 (**2**), -dibenzo-16-crown-5 (**3**), and -dicyclohexano-16-crown-5 (**4**) (Fig. 1). Solid-state structures of **2** and **3** are reported and compared with that of **1**. Also monovalent metal ion complexation behavior of lariat ethers **1–4** as determined by picrate extraction and by isothermal titration calorimetry is described.

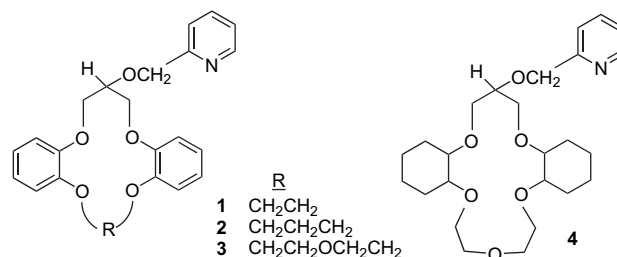


Figure 1. Structures of 2-picolylxy lariat ethers.

## 2. Results and discussion

### 2.1. Synthesis of new 2-picolylxy lariat ethers 2–4

Following the published procedure for the synthesis of the *sym*-(2-picolylxy)dibenzo-13-crown-4 (**1**),<sup>13</sup> the

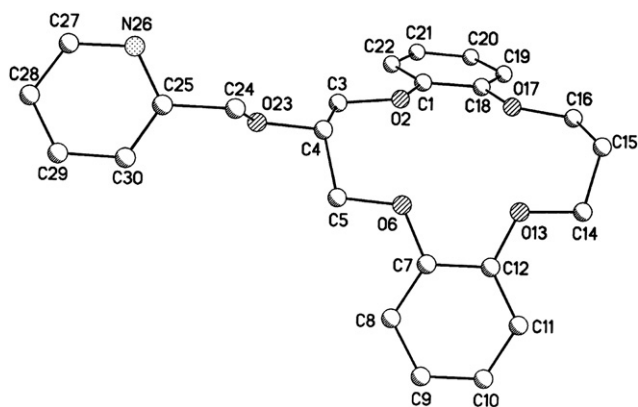
**Keywords:** Lariat ethers; Solid-state structures; Picrate extraction; Isothermal titration calorimetry.

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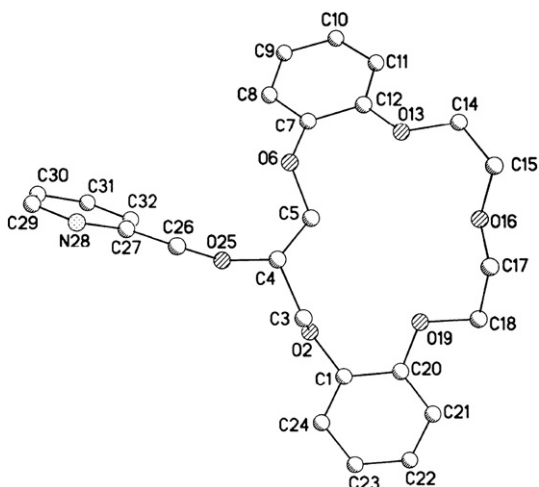
larger-ring analogs **2** and **3** were prepared in good yield by reactions of 2-picolyl chloride with the sodium alkoxides of *sym*-(hydroxy)dibenzo-14-crown-4 and -16-crown-5,<sup>14</sup> respectively. The *sym*-(2-picolyl)oxy)dicyclohexano-16-crown-5 (**4**) was prepared similarly from the potassium alkoxide of *sym*-(hydroxy)dicyclohexano-16-crown-5.<sup>15</sup> New compounds were characterized by NMR and IR spectroscopies and by combustion analysis.

## 2.2. Solid-state structures of *sym*-(2-picolyl)oxy)dibenzo-14-crown-4 (**2**) and -16-crown-5 (**3**)

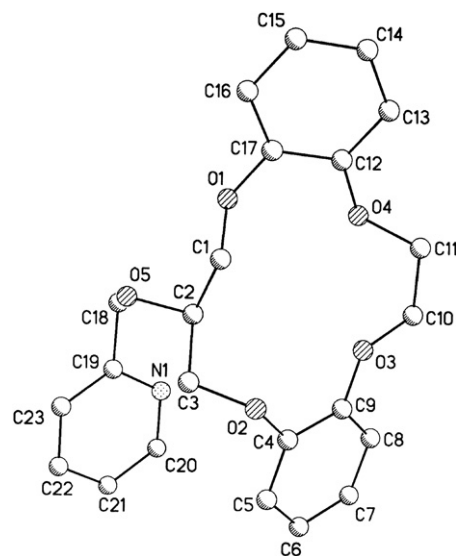
To gain insight into the spatial arrangement of the functional side arm and the polyether ring cavity in lariat ethers **2** and **3**, their solid-state structures were determined (see Figs. 2 and 3, respectively). Orientation of the side arm away from the polyether cavity is clearly evident for both the structures. The calculated angles between the planes defined by the polyether ring oxygens and the plane of the pyridine ring in the side arms are 21.9° and 89.5° in the solid-state structures of lariat ethers **2** and **3**, respectively. For comparison, the structure of molecule A of *sym*-(2-picolyl)oxy)dibenzo-13-crown-4 (**1**) is shown in Figure 4. For this structure, the calculated angle between the plane of the polyether ring oxygens and the plane of the pyridine ring is 33.0°.



**Figure 2.** Solid-state structure and numbering scheme for *sym*-(2-picolyl)oxy)dibenzo-14-crown-4 (**2**).



**Figure 3.** Solid-state structure and numbering scheme for *sym*-(2-picolyl)oxy)dibenzo-16-crown-5 (**3**).



**Figure 4.** Solid-state structure for molecule A of *sym*-(2-picolyl)oxy)dibenzo-13-crown-5 (**1**).<sup>11</sup>

CIF files for lariat ethers **2** and **3** have been deposited with the Cambridge Crystallographic Data Center (CCDC, 12 Union Road, Cambridge CB2 1E2, UK) with identification numbers CCDC-649256 and CCDC-649255, respectively.

## 2.3. Metal ion complexation by lariat ethers 1–4

The monovalent metal ion complexation propensities of 2-picolyl)oxy lariat ethers **1–4** were probed qualitatively by two-phase metal picrate extractions and quantitatively by isothermal titration calorimetry using homogeneous methanol solution.

### 2.3.1. Extractions of alkali metal and silver picrates.

Metal picrate extractions from aqueous solutions into chloro-carbon solvents are frequently used to screen the metal ion binding properties of macrocyclic ligands.<sup>16–18</sup> As normally practiced, this is a qualitative technique for the assessment of metal ion binding.

For the alkali metal cations, aqueous solutions (5.0 mM in the alkali metal picrate and 50.0 mM in the corresponding alkali metal chloride) were extracted with 5.0 mM solutions of lariat ethers **1–4** in chloroform. (These conditions are designed to maximize the extraction of the alkali metal picrate.) Results are recorded in Table 1. As can be seen, ligands **1** and **3** are weak extractants of all the alkali metal picrates. Dibenzo-14-crown-4 ligand **2** gave higher extraction levels with an ordering of  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+$ ,  $\text{Cs}^+$ . The highest extraction of  $\text{Li}^+$  is consistent with a dibenzo-14-crown-4 polyether ring.<sup>19</sup> For the dicyclohexano ligand **4**, the alkali metal picrate extraction percentages are markedly enhanced. This is consistent with the presence of only dialkyl ether oxygens in the crown ether ring of **4**, but could also result from different polyether ring conformations. The extraction order of  $\text{Na}^+ \gg \text{K}^+ > \text{Rb}^+ > \text{Li}^+ > \text{Cs}^+$  is as expected for a lariat ether with a 16-crown-5 ring.<sup>20</sup>

For  $\text{Ag}^+$ , aqueous solutions (5.0 mM) in silver picrate were extracted with 5.0 mM solutions of lariat ethers **1–4** in

**Table 1.** Alkali metal picrate extractions from aqueous solutions into chloroform by 2-picolylxy liariet ethers **1–4**

Lariat ether	Ring <sup>a</sup>	Percentage of picrate extracted (%)				
		Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
<b>1</b>	DB13C4	2.8±0.8 <sup>b</sup>	2.4±0.4	1.6±0.6	BDL <sup>c</sup>	BDL
<b>2</b>	DB14C4	7.2±0.4	3.9±0.5	2.8±0.6	BDL	BDL
<b>3</b>	DB16C5	1.6±0.3	2.6±0.3	1.4±0.7	1.1±0.5	BDL
<b>4</b>	DC16C5	9.8±0.3	49.9±0.8	18.0±1.0	11.7±1.2	7.8±1.5

<sup>a</sup> DB=dibenzo and DC=dicyclohexano.

<sup>b</sup> Average and standard deviation for five samples.

<sup>c</sup> BDL=below detection limit.

chloroform. Results are presented in Table 2. Dibenzo liariet ethers **1–3** exhibited good extraction of silver picrate with little apparent variation as the crown ether ring size was varied. This suggests primary interaction of Ag<sup>+</sup> with the pyridyl nitrogen. This situation changed markedly for the dicyclohexano liariet ether **4**, which showed much higher extraction of silver picrate. Thus increase of the basicity of the oxygen atoms and/or changes in the conformation of the crown ether ring were found to enhance the extraction of Ag<sup>+</sup> indicating that the metal ion interacts with both the pyridyl nitrogen and the polyether ring oxygens in **4**.

**2.3.2. Isothermal titration calorimetric measurements for complexation of monovalent cations.** In contrast to the qualitative data obtained by two-phase metal picrate extractions by ligands, more sophisticated isothermal titration calorimetry (ITC) is performed in a single solvent and yields quantitative thermodynamic data.

To investigate monovalent metal ion complexation by the 2-picolylxy liariet ethers under homogeneous conditions, interactions of Ag<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> with ligands **1–4** in methanol were assessed by ITC. In Table 3 are listed the calculated values for the thermodynamic parameters of association constants (log *K*), enthalpy of complexation ( $\Delta H$ ), and entropy of complexation ( $\Delta S$ ), as well as the metal ion: ligand stoichiometry (*N*).

Focusing attention first upon the interaction of Ag<sup>+</sup> with ligands **1–4**, it is noted that the curve fitting of the calorimetric data gave 1:1 stoichiometries for the complexation of Ag<sup>+</sup> by ligands **2–4**. For ligand **1**, the *N* value of 0.5 is consistent with a 1:2 (metal ion:ligand) stoichiometry. Interaction of Ag<sup>+</sup>

**Table 2.** Silver picrate extractions from aqueous solutions into chloroform by 2-picolylxy liariet ethers **1–4**

Lariat ether	Ring <sup>a</sup>	Percentage of picrate extracted (%)
<b>1</b>	DB13C4	36.4±0.5 <sup>b</sup>
<b>2</b>	DB14C4	32.1±1.1
<b>3</b>	DB16C5	37.0±1.4
<b>4</b>	DC16C5	68.6±0.5

<sup>a</sup> DB=dibenzo and DC=dicyclohexano.

<sup>b</sup> Average and standard deviation for five samples.

with the pyridyl nitrogens of two molecules of **1** is supported by the large negative values for the complexation enthalpy and entropy. For ligands **2–4**, the association constants for Ag<sup>+</sup> complexation decrease in the order **4**>**2**>**3**. Both the complexation enthalpy and the entropy become more negative on going from **4** to **2** to **3**, providing another example of enthalpy–entropy compensation for 1:1 complexation.<sup>21</sup>

Interactions of K<sup>+</sup> with ligands **1–3** were too weak to be measured by the ITC technique. Similarly interaction of Na<sup>+</sup> with ligand **1** was too weak to be measured. Presumably, the latter is due to the constraint in the molecular structure of **1** that prevents a preorganized conformation of the four ring ether oxygens as a basis for a square pyramid.<sup>13</sup>

For 1:1 complexation of Na<sup>+</sup> by ligands **2** and **3**, the stability constants, enthalpies, and entropies are nearly the same. Comparison of the enthalpies and entropies for 1:1 complexation of Na<sup>+</sup> and Ag<sup>+</sup> by ligands **2** and **3** reveals entropy control for the former and enthalpy control for the latter monovalent metal ion species. This difference is attributed to the change from a hard to a soft metal cation.

The observed 1:2 (metal ion:ligand) stoichiometries for complexation of Na<sup>+</sup> and K<sup>+</sup> by the dicyclohexano-16-crown-5 liariet ether **4** were unexpected. Presumably, there are conformational constraints in the polyether ring that prevent 1:1 complexation.

## 2.4. Conclusions

Three new 2-picolylxy liariet ethers **2–4** have been prepared and characterized. Comparison of the solid-state structures for two of them with that reported previously for **1** reveals changes in orientation of the 2-picolylxy side arm with respect to the crown ether cavity, as the latter is expanded

**Table 3.** Thermodynamic parameters for interactions of Ag<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> with 2-picolylxy liariet ethers **1–4** in methanol at 25.0 °C

Lariat ether	Ring <sup>a</sup>	Metal ion	<i>N</i> <sup>b</sup>	log <i>K</i>	− $\Delta H$ (kcal mol <sup>−1</sup> )	$\Delta S$ (cal K <sup>−1</sup> mol <sup>−1</sup> )
<b>1</b>	DB13C4	Ag <sup>+</sup>	0.5	3.56±0.01	11.02±0.09	−20.8±0.3
		Na <sup>+</sup>	—	<2.5		
		K <sup>+</sup>	—	<2.5		
<b>2</b>	DB14C4	Ag <sup>+</sup>	1	4.04±0.01	8.62±0.01	−10.5±0.1
		Na <sup>+</sup>	1	3.18±0.03	1.85±0.09	8.3±0.6
		K <sup>+</sup>	—	<2.5		
<b>3</b>	DB16C5	Ag <sup>+</sup>	1	3.64±0.01	10.01±0.04	−17.3±0.1
		Na <sup>+</sup>	1	3.23±0.01	1.08±0.08	11.1±1.4
		K <sup>+</sup>	—	<2.5		
<b>4</b>	DC16C5	Ag <sup>+</sup>	1	4.85±0.01	7.07±0.01	−1.6±0.1
		Na <sup>+</sup>	0.5	3.27±0.02	4.43±0.25	0.2±0.1
		K <sup>+</sup>	0.5	2.98±0.04	4.67±0.85	−2.1±0.5

<sup>a</sup> DB=dibenzo and DC=dicyclohexano.

<sup>b</sup> *N*=metal ion:ligand stoichiometry.

from dibenzo-13-crown-4 to dibenzo-14-crown-4 to dibenzo-16-crown-5. Complexation studies of monovalent cations by the ligand series **1–4** using picrate extraction and isothermal titration calorimetry have been used to probe the sites of metal ion complexation in the lariat ether ligands.

### 3. Experimental

#### 3.1. General

Melting points were determined with a Fisher–Johns melting point apparatus. Infrared (IR) spectra were recorded with a Perkin–Elmer Model 1600 FTIR spectrometer as deposits from  $\text{CHCl}_3$  on NaCl plates for solids or as films between NaCl plates for liquids. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Varian Unity INOVA 500 MHz FT-NMR ( $^1\text{H}$  500 MHz and  $^{13}\text{C}$  126 MHz) spectrometer in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as internal standard. Chemical shifts ( $\delta$ ) are given in parts per million downfield from TMS and coupling constant ( $J$ ) values are in hertz. Isothermal titration calorimetry was performed with a Microcal MCS isothermal titration calorimeter. Titration runs were monitored by Microcal Observer 3.0 and data analysis was performed using Origin 4.2. Elemental analysis was performed by Desert Analytics Laboratory of Tucson, Arizona.

#### 3.2. Synthesis

Reagents were obtained from commercial suppliers and used directly, unless otherwise noted. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled just before use. *sym*-(Hydroxy)dibenzo-14-crown-4, *sym*-(hydroxy)dibenzo-16-crown-5, and *sym*-(hydroxy)-dicyclohexano-16-crown-5 were prepared by the reported methods.<sup>14,15</sup> *sym*-(2-Picolyl)oxy)dibenzo-13-crown-4<sup>22</sup> was synthesized by the published procedure.<sup>13</sup> Silver picrate was prepared by a reported method.<sup>23</sup>

**3.2.1. *sym*-(2-Picolyl)oxy)dibenzo-14-crown-4 (2).** Under nitrogen, 2-picolyl chloride hydrochloride (0.26 g, 1.58 mmol) and 0.060 g (1.58 mmol) of 60% dispersion of NaH in mineral oil were added to 80 mL of THF. The mixture was stirred for 2 h at room temperature. The insoluble material was removed by filtration through a bed of Celite on a sintered glass funnel. The filtrate was added dropwise to a mixture of *sym*-(hydroxy)dibenzo-14-crown-4 (0.49 g, 1.58 mmol) and 60% dispersion of NaH in mineral oil (0.12 g, 3.16 mmol) in 60 mL of THF. The reaction mixture was stirred for 24 h at room temperature and quenched with 20 mL of water. The THF was removed in vacuo and the aqueous residue was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 50$  mL). The combined extracts were dried over  $\text{MgSO}_4$  and evaporated in vacuo. The residue was chromatographed on alumina with  $\text{EtOAc}$  as eluent to give 0.40 g (63%) of a white solid with mp 97–98 °C. IR  $\nu_{\text{max}}$  (deposit from  $\text{CHCl}_3$  on NaCl plate): 1114 (C–O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.20–2.40 (m, 2H), 4.18–4.38 (m, 11H), 6.81–6.99 (m, 8H), 7.19–7.23 (m, 1H), 7.56 (d,  $J=8.0$  Hz), 7.72 (dt,  $J=7.5$  and 1.5 Hz), 8.56–8.59 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  29.3, 67.0, 70.0, 73.2, 76.9, 115.9, 117.5, 121.6, 122.0, 122.5, 122.7, 136.7, 148.8, 149.1, 149.7, 158.4. Anal. Calcd for  $\text{C}_{24}\text{H}_{25}\text{NO}_5$ : C, 70.74; H, 6.18. Found: C, 70.76; H, 6.14.

**3.2.2. *sym*-(2-Picolyl)oxy)dibenzo-16-crown-5 (3).** In the procedure given above for the preparation of **2**, *sym*-(hydroxy)-dibenzo-14-crown-4 was replaced by *sym*-(hydroxy)-dibenzo-16-crown-5 to give 0.39 g (56%) of **3** as a white solid with mp 41–43 °C. IR  $\nu_{\text{max}}$  (deposit from  $\text{CHCl}_3$  on NaCl plate): 1111 (C–O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.89–3.99 (m, 4H), 4.14–4.19 (m, 4H), 4.25–4.33 (m, 3H), 4.39–4.42 (m, 2H), 5.01 (s, 2H), 6.83–6.88 (m, 4H), 6.93–7.00 (m, 4H), 7.17–7.22 (m, 1H), 7.67 (d,  $J=7.5$  Hz), 7.72 (dt,  $J=7.0$  and 1.5 Hz), 8.55–8.58 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  67.6, 69.6, 71.5, 73.4, 77.6, 113.1, 118.6, 121.1, 122.3, 123.0, 136.6, 148.3, 148.9, 150.4, 59.0. Anal. Calcd for  $\text{C}_{25}\text{H}_{28}\text{NO}_6 \cdot 0.1\text{CH}_2\text{Cl}_2$ : C, 67.43; H, 6.34. Found: C, 67.66; H, 6.00.

#### 3.2.3. *sym*-(2-Picolyl)oxy)dicyclohexano-16-crown-5 (4).

In the procedure given above for the preparation of **2**, *sym*-(hydroxy)dibenzo-14-crown-4 was replaced by *sym*-(hydroxy)dicyclohexano-16-crown-5 (a mixture of at least two stereoisomers),<sup>13</sup> NaH dispersion in mineral oil was replaced by KH dispersion in mineral oil, and the scale was increased to 3.93 mmol. The reaction gave 1.00 g (56%) of **4** as a colorless oil. IR  $\nu_{\text{max}}$  (deposit from  $\text{CHCl}_3$  on NaCl plate): 1107 (C–O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.20–1.95 (m, 16H), 3.39–4.00 (m, 17H), 4.83–4.90 (m, 2H), 7.13–7.18 (m, 1H), 7.64–7.69 (m, 2H), 8.50–8.54 (m, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.5, 21.9, 22.3, 22.6, 27.0, 27.1, 27.3, 28.2, 28.3, 28.5, 28.6, 67.7, 67.9, 68.5, 68.8, 68.9, 70.7, 70.8, 71.1, 72.2, 72.7, 73.2, 78.1, 78.7, 79.4, 121.4, 121.5, 121.6, 122.0, 122.1, 136.5, 148.5, 148.6, 148.7, 159.6, 159.7, 159.8. Anal. Calcd for  $\text{C}_{25}\text{H}_{39}\text{NO}_6$ : C, 66.79; H, 8.74. Found: C, 67.93; H, 8.49.

#### 3.3. Solid-state structure determinations of lariat ethers **2** and **3**

Crystals suitable for structure determinations of **2** and **3** were grown from acetonitrile. Crystal and intensity data for the structural studies were obtained with a Nicolet R3m/V automated diffractometer with Mo  $K\alpha$  radiation ( $\lambda=0.71073$  Å).

**Table 4.** Crystallographic data for 2-picolyl lariat ethers **2** and **3**

	<b>2</b>	<b>3</b>
Formula	$\text{C}_{24}\text{H}_{25}\text{NO}_5$	$\text{C}_{25}\text{H}_{27}\text{NO}_6$
FW ( $\text{g mol}^{-1}$ )	407.45	437.48
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
$a$ (Å)	13.6570(2)	7.891(2)
$b$ (Å)	5.018(2)	11.674(3)
$c$ (Å)	30.0427(2)	24.440(7)
$\beta$ (°)	96.22(2)	90
Volume (Å <sup>3</sup> )	2046.7(0.8)	2251.4(1.0)
$Z$	4	4
$\mu$ ( $\text{mm}^{-1}$ )	0.093	0.092
$F(000)$	864	928
Crystal size (mm)	0.6 × 0.15 × 0.15	0.55 × 0.35 × 0.25
$\theta$ Range for data collection	2.13–25.07	2.41–25.05
Reflections collected	2917	2332
Reflections observed	2791	2296
Number of parameters	272	290
Goodness-of-fit on $F^2$	0.985	1.029
$R$ ( $I > 2\sigma(I)$ )	0.0809	0.0461
Largest difference peak and hole ( $\text{e Å}^{-3}$ )	0.295, −0.439	0.159, −0.146

The solutions of structures **2** and **3** were made using SHELXLS-97<sup>24</sup> and SHELXTL, 4th revision,<sup>25</sup> respectively. For refinement and graphics, SHELXL-97<sup>26</sup> and SHELXTL-PC, version 5.03<sup>27</sup> were utilized. Crystal data and experimental details are presented in Table 4.

### 3.4. Metal picrate extractions into chloroform

Extraction of the alkali metal picrates from aqueous solutions into chloroform solutions of the ligands was performed as before.<sup>16</sup> The silver picrate extractions were performed similarly with the exception that the aqueous solutions contained only 5.00 mM silver picrate.

### 3.5. Assessment of metal ion complexation by isothermal titration calorimetry

Lariat ethers **1–4** were dissolved in dry methanol to give final concentrations of 1.0 mM. From AgNO<sub>3</sub>, KCl and NaCl, 10–90 mM solutions in dry methanol were prepared. The ITC cell temperature was set at 25.0 °C and the water jacket bath temperature was 20.0 °C. In the experiment, the metal salt solution was titrated into the ligand solution. A 250- $\mu$ L syringe was used for the titration. A total of 100 2.0- $\mu$ L injections were made with 100 s elapsed time between the injections. Control experiments were performed under the same conditions by injection of the metal salt solution into dry methanol alone.

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- For **1**, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.08–4.14 (m, 1H), 4.28–4.43 (m, 10H), 6.92–6.99 (m, 4H), (7.00–7.04, m, 2H), 7.08 (dd,  $J=8.0$  and 1.5 Hz, 2H), 7.16 (m, 1H), 7.52 (d,  $J=7.5$  Hz), 7.69 (dt,  $J=7.5$  and 2.0 Hz, 1H), 8.52–8.54 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  68.5, 72.4, 73.1, 77.2, 115.7, 120.5, 121.5, 122.2, 122.3, 123.7, 136.6, 149.0, 149.2, 150.8, 158.6.
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