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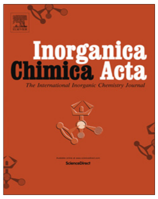

Research paper

Synthesis and structural study of alkali metal complexes derived from 1-phenyl-tetrazole-thiolate and crown ethers

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ABSTRACT

The reaction between 1-phenyl-tetrazole-5-thione (**1**) and the metal hydroxides MOH (M = Li, Na, K, Rb, Cs) in the presence of crown ethers led to the alkali metal complexes, [Li(15-crown-5)(SCN$_4$Ph)] (**2**), [Na(15-crown-5)(SCN$_4$Ph)] (**5**), [K(18-crown-6)(SCN$_4$Ph)] (**4**), [Rb(18-crown-6)(SCN$_4$Ph)] (**5**), [Cs(15-crown-5)$_2$][SCN$_4$Ph] (**6**), [{Cs(15-crown-5)(SCN$_4$Ph)}] (**6a**), [Cs(18-crown-6)(SCN$_4$Ph)] (**7**), [Cs(dibenzo-24-crown-8)(SCN$_4$Ph)] (**8**) and [Cs$_2$(dibenzo-24-crown-8)$_3$(SCN$_4$Ph)$_2$] (**8a**). Compounds **2**–**8** were characterized by physical and analytical methods. X-ray diffraction studies performed on these compounds reveal that crown ether moiety precludes the ionic lattice formation. The tetrazole anion coordinates to the metal cation in a bidentate *N,S* fashion in **3**–**5** with the formation of a four-membered MSCN ring, whereas in **2**, monodentate coordination through a N atom is observed. In contrast, cesium complexes **6**, **6a**, **7**, **8** and **8a** show a variety of structural arrangements including monomeric, dimeric and polymeric species, depending on the size of crown ether employed.

1. Introduction

The structural chemistry of heavy alkali metals, namely rubidium and cesium, is a largely underdeveloped area of coordination chemistry. This despite the ubiquitous use of alkali metal derivatives in the syntheses of organic and inorganic compounds. The main reason for this is the difficulty associated with their structural characterization stemming from their tendency to form polymeric materials.

In this regard, our research group has developed a synthetic strategy designed to control the formation of metal–ligand interactions and thus, able to promote the formation of discrete structural arrangements [1]. This method is based on the design tuning between the host cavity of crown ethers and the guest cation [2]. In general, when the size of the cavity of a crown ether matches the size of the metal center, no metal–ligand interaction is observed, thus producing the separation of the ion-pair. Examples of such systems were observed with imidochalcogenphosphino ligands in [K(18-crown-6)][N{P(E)pH$_2$}$_2$] (E = S, Se) [3,4]. Ion-pair separation also takes place when the size of the crown ether exceeds the cation radii, as demonstrated in the lithium derivatives [Li(15-crown-5)][N{P(E)pH$_2$}$_2$] (E = S, Se) [1]. In contrast, when the metal center is considered large for the cavity of the crown ether, the former tends to complete its coordination sphere through the formation of metal–ligand interactions (v.gr. [Rb(18-crown-6){N(P(S)pH$_2$)$_2$}] [1], [Cs(18-crown-6){N(P(Se)pH$_2$)$_2$}] [1] and [Na(15-crown-5){N(P(E)pH$_2$)$_2$}] (E = S, Se) [5]).

In this regard, our research group has reported on the preparation of alkali metal complexes derived from the 1-phenyl-tetrazole-5-thiolate anion, exhibiting complex polymeric coordination patterns [6]. Indeed, metal complexes derived from 1-organyl-tetrazole-5-thiones exhibit coordination patterns that include monodentate coordination through either a *N* or *S* atom [7–11] or bidentate via *S,N* or *N,N′* atoms yielding a variety of structural arrangements ranging from mono- to multimetallic species [12–20]. Consequently, the control of the aggregation degree of metal derivatives with this ligand constitutes a synthetic challenge. In this regard, our research group briefly explored the formation of discrete sodium and potassium complexes using 1-organyl-tetrazole-5-thiolates and 18-crown-6 ether. The crystal structure of [Na(18-crown-6)(H$_2$O)$_2$][SCN$_4$Ph] [21] reveals no direct interactions between cation and anion, while in [K(18-crown-6)(SCN$_4$Me)] [22] the crown ether precludes the formation of a

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polymeric structure and limits the interaction of the metal center to one ligand unit.

As an extension of this work, we now report on the coordination patterns of the 1-phenyl-tetrazole-5-thiolate anion with alkali metals under a modified chemical environment attributed to the presence of selected crown ethers (Fig. 1).

2. Experimental

2.1. Material and methods

1-Phenyl-1-H-tetrazole-5-thione (**1**) was obtained according to the literature procedure [23], while all the starting materials were purchased from Sigma-Aldrich and used without further purification. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were obtained from $CDCl_3$ solutions on a Jeol Eclipse 300 Delta spectrometer, the experiments were carried out at ambient temperature and TMS was used as an internal reference. The Fast Atom Bombardment (FAB$^+$) mass spectra were obtained on a Jeol JMS-SX 102A spectrometer (operated at an accelerating voltage of 10 kV, using 6 keV and Xe atoms), the samples were dissolved in CH_2Cl_2 and a 3-nitrobencilic alcohol matrix was employed. Elemental analysis (C and H) were performed by Galbraith Laboratories, Inc. (Knoxville, TN). The IR spectra were recorded as KBr pellets on a Nicolet FT-IR Magna 750 spectrometer.

Crystallographic data for structures **2**–**5** and **7** were collected on a Bruker SMART APEX DUO three-circle diffractometer equipped with an Apex II CCD detector using MoK_α (Incoatec IμS microsource with a mirror optic) while the data for **6**, **6a** and **8** and **8a** were collected on an Agilent Technologies SuperNova diffractometer equipped with CCD area detector (EosS2) at 100 K using Mo-Kα radiation (λ = 0.71073) from a microfocus X-ray source. The crystals were coated with a hydrocarbon oil, picked up with a nylon loop, and immediately mounted in the cold nitrogen stream (−173 °C) of the diffractometer. For compounds **2**–**5** and **7**, frames were collected by omega scans, integrated using SAINT program, and semi-empirical absorption correction (SADABS) was applied [24a]. For compounds **6**, **6a**, **8** and **8a**, the frames were collected using omega scans and integrated with CrysAlisPro (Version 1.171.37.35) [24b]. Absorption correction was performed with the SCALE3 ABSPACK implemented in CrysAlisPro (Version 1.171.37.35). The structures were solved by direct methods (SHELXT) [25a], and refined by the full-matrix least-squares on F^2 with SHELXL [25b] using the SHELXLE GUI [26]. Hydrogen atoms were placed in idealized geometrical positions and refined with U_{iso} tied to the parent atom with the riding model, whereas the hydrogen atoms of the H_2O moieties in **5** were localized from the difference electron-density map and refined isotropically with U_{ij} tied to the oxygen atom.

The crystal data and refinement details for these compounds are listed in Tables 1 and 2, and selected bond lengths and angles for these compounds are presented in Tables 3 and 4.

2.2. Preparation of compounds **2**–**8**

2.2.1. [Li(15-crown-5)(SCN$_4$Ph)] (**2**)

LiOH (0.068 g, 2.81 mmol) was added to a solution of 1-phenyl-1-H-tetrazole-5-thione (**1**) (0.50 g, 2.81 mmol) in methanol (40 mL) at ambient temperature. The solution was stirred for 2 h and then 15-crown-5 ether (1,4,7,10,13-Pentaoxacyclopentadecane) (0.62 g, 2.81 mmol) was added. The reaction mixture was stirred for 5 h and the volume of the solution was reduced and allowed to crystallize. Yield: 88%. Mp: 184–186 °C (dec). IR (KBr): $\tilde{\nu}$ 2913, 2881, 1594, 1496, 1098 (C–O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.77 (s, 20H, C*H*$_2$-O), 7.34 (m, 1H, *p*-Ar*H*), 7.44 (t, 2H, *m*-Ar*H*), 8.05 (d, 2H, *o*-Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 69.0 (*C*–O), 124.3 (*o*-*C*), 127.6 (*p*-*C*), 128.8 (*m*-*C*), 137.0 (*i*-*C*), 167.9 (*C*S) ppm. MS (FAB$^+$) *m*/*z* (%): 227 [Li(15-crown-5)$^+$] (1 0 0), 404 [*M*$^+$] (15). Anal. Calcd for $C_{17}H_{25}LiN_4O_5S$ (404.17): C, 50.49; H, 6.19. Found: C, 50.13; H, 6.21.

2.2.2. [Na(15-crown-5)(SCN$_4$Ph)] (**3**)

Compound **3** was prepared using the same procedure outlined for **2** starting from **1** (0.50 g, 2.81 mmol), NaOH (0.110 g, 2.81 mmol) and 15-crown-5 ether (0.62 g, 2.81 mmol). Yield: 73% (0.86 g, 2.05 mmol). Mp: 120–122 °C (dec). IR (KBr): $\tilde{\nu}$ 2907, 2871, 1594, 1496, 1119 (C–O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.66 (m, 20H, C*H*$_2$-O), 7.25 (m, 1H, *p*-Ar*H*), 7.33 (m, 2H, *m*-Ar*H*), 8.00 (m, 2H, *o*-Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 69.3 (*C*–O), 123.6 (*o*-C), 127.7 (*p*-*C*), 128.6 (*m*-*C*), 136.9 (*i*-C), 167.0 (*C*S) ppm. FAB$^+$ *m*/*z* (%): 243 [Na(15-crown-5)$^+$] (1 0 0), 420 [*M*$^+$] (10). Anal. Calcd for $C_{17}H_{25}N_4NaO_5S$ (420.14): C, 48.57; H, 5.95. Found: C, 48.30; H, 6.18.

2.2.3. [K(18-crown-6)(SCN$_4$Ph)] (**4**)

Compound **4** was prepared using the same procedure outlined for **2** starting from **1** (0.30 g, 1.69 mmol), KOH (0.095 g, 1.69 mmol) and 18-crown-6 ether (1,4,7,10,13,16-hexaoxacyclooctadecane) (0.45 g, 1.69 mmol). Yield: 95% (0.77 g, 1.60 mmol). Mp: 173–174 °C (dec). IR (KBr): $\tilde{\nu}$ 2901, 2890, 2827, 1597, 1498, 1106 (C–O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.66 (s, 24H, C*H*$_2$-O), 7.33 (t, 1H, *p*-Ar*H*), 7.43 (t, 2H, *m*-Ar*H*), 8.10 (d, 2 H, *o*-Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 70.2 (*C*–O), 124.4 (*o*-*C*), 127.6 (*p*-*C*), 129.1 (*m*-*C*) ppm. FAB$^+$ *m*/*z* (%): 303 [K(18-crown-6)$^+$] (1 0 0), 480 [*M*$^+$] (10). Anal. Calcd for $C_{19}H_{29}KN_4O_6S$ (480.14): C, 47.50; H, 6.04. Found: C, 47.10; H, 6.24.

2.2.4. [Rb(18-crown-6)(SCN$_4$Ph)(H$_2$O)]·H$_2$O (**5**)

Compound **5** was prepared using the same procedure outlined for **2** starting from **1** (0.30 g, 1.69 mmol), RbOH (0.17 g, 1.69 mmol) and 18-crown-6 ether (0.45 g, 1.69 mmol). Yield: 88% (0.78 g, 1.49 mmol). Mp: 147–149 °C (dec). IR (KBr): $\tilde{\nu}$ 3504 ν(O–H), 2941, 2903, 2865, 1640 δ(H_2O), 1592, 1493, 1121 (C–O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.64 (s, 24H, C*H*$_2$-O), 7.31 (t, 1H, *p*-Ar*H*), 7.43 (t, 2H, *m*-Ar*H*), 8.05 (d, 2H, *o*-Ar*H*) ppm. ^{13}C NMR

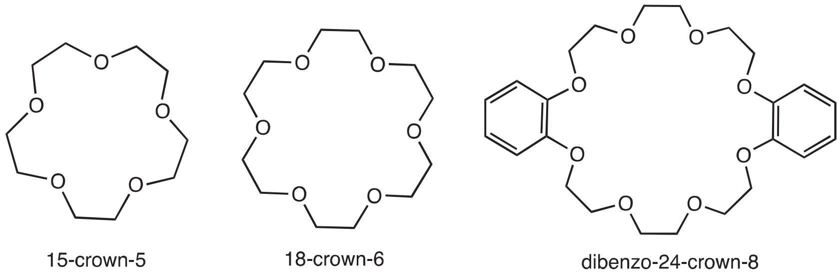

Fig. 1. Crown ethers used in this study.