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A powerful novel strategy for the preparation of discrete inorganic carbon-free rings containing alkaline cations†

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The alkali metal–crown ether 'misfit' is used as a novel synthetic strategy for the preparation of discrete inorganic rings containing the unusual rubidium– and caesium–soft chalcogenide bonds.

The lithium, sodium and potassium salts of the tetraphenylimidodiphosphinochalcogenido ligands have been mainly used to prepare complexes with transition and representative metals.[1] However, there is very little information on these alkaline derivatives. The only known structures containing the symmetric ligands to date are those of the following salts $K[Ph_2SPNPSPh_2]$,[2] $[Na\{Ph_2P(S)NP(S)Ph_2\}(L)]$[3] with L = triglyme or tetraglyme and $[Na\{Ph_2P(Te)NP(Te)Ph_2\}(tmeda)]$.[4] In addition, the structures of two potassium(18crown6) complexes are known, *i.e.* $[K(18C6)][Ph_2EPNPEPh_2]$ with E = O,[5] S,[6] and E = Se.[7]

The purpose of this work is to explore a new synthetic method for the preparation of discrete alkali metal inorganic rings, mainly those containing the unusual, almost unknown, alkali metal–'soft' chalcogen atom bonds. The method consists in the preparation of alkaline crown ether complexes using different sizes of crown ethers in order to control the formation of the alkali metal–chalcogen atom bond interaction.

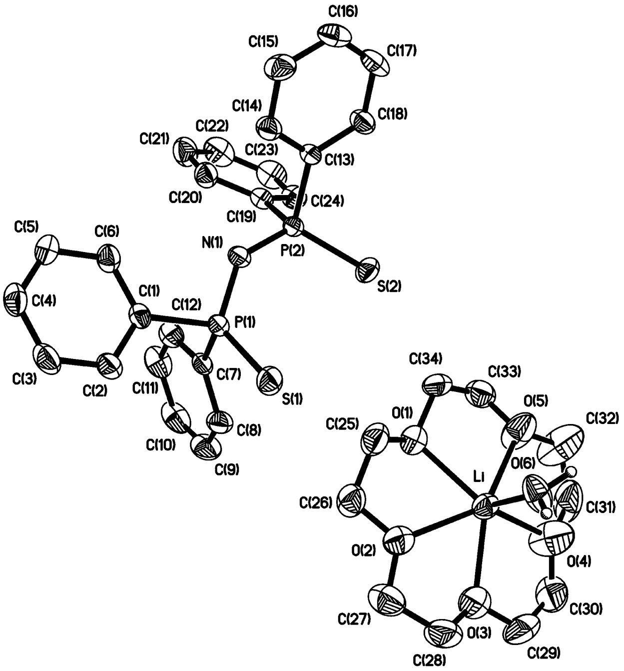

Fig. 1 Selected bond lengths [Å] and bond angles [°] for $[Li(15\text{–}C\text{–}5)][Ph_2SPNPSPh_2]\cdot H_2O$, **2**. P(1)–N(1) 1.593 (3), P(2)–N(1) 1.595 (3), P(1)–S(1) 1.9873 (16), P(2)–S(2) 1.9775 (14), O(6)–Li 1.899 (10), H–S(1) 2.467 (18), H–S(2) 2.384 (17), O(6)–S(1) 3.334 (4), O(6)–S(2) 3.255 (4); P(1)–N(1)–P(2) 136.1 (2), N(1)–P(1)–S(1) 120.83 (15), N(1)–P(2)–S(2) 121.90 (13), O(6)–H–S(1) 163 (4), H–O(6)–S(2) 165 (4).

Herein, we report the syntheses of $[Li(15C5)][Ph_2EPNPEPh_2]$ with E = O (**1**), S (**2**) and Se (**3**); $[Rb(18C6)][Ph_2EPNPEPh_2]$ with E = O (**4**), S (**5**) and Se (**6**) and $[Cs(18C6)][Ph_2EPNPEPh_2]$ with E = O (**7**), S (**8**) and Se (**9**).‡ The X-ray structures of compounds **2** to **9** were obtained. The two oxygen-containing compounds are monohydrate derivatives; the structure of the lithium complex was not determined due to the quality of the crystals. Fig. 1 to 3 show the X-ray structures of compounds **2**, **4** and **9**, respectively.

The fit of the alkali metal cations with specific crown ethers is well known.[8] Usually, if the appropriate crown ether is used, no ligand–cation interactions takes place, as is observed in the reported $[K(18C6)][Ph_2EPNPEPh_2]$ (E = S[6] and Se[7]) compounds. Similar situations occur if larger crown ethers are employed, as we observe in the lithium derivatives with the sulfide and selenide ligands (compounds **2** and **3**) and in $[Na(18C6)][Ph_2EPNPEPh_2]$ (E = S and Se).[9] However, when smaller crown ethers are used, it seems that the large cations need to fulfill their coordination sphere through the formation of alkali metal–chalcogenide bond interactions by ligand chelation. Therefore, this produces chelate ring systems as those observed in the S and Se containing complexes **5**, **6**, **8** and **9**. These compounds contain six-membered inorganic rings that do not exhibit any intermolecular interactions, but the most remarkable feature is that the alkali metal–crown ether 'misfit' promotes the formation of 'hard' Rb and Cs bonded to 'soft' Se and S. These discrete Rb–Se and Cs–Se bonds are Rb–Se 3.483(2), 3.520 (2) Å and Cs–Se 3.720 (2), 3.629 (2) Å.

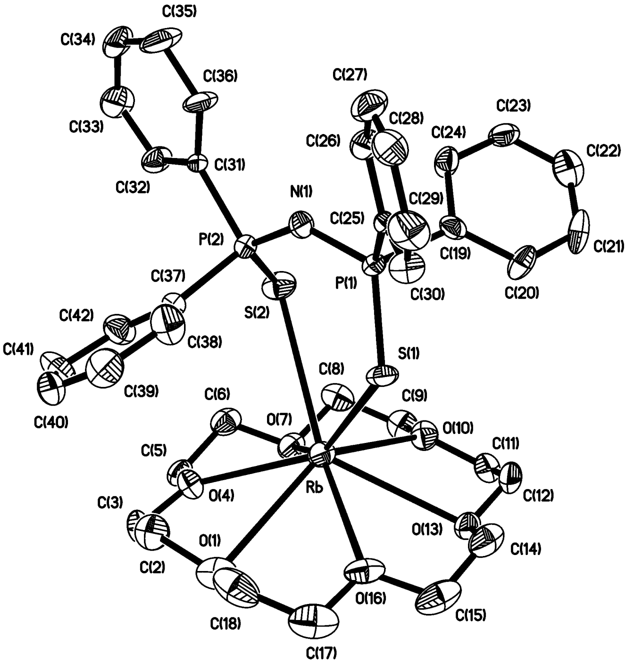

Fig. 2 Selected bond lengths [Å] and bond angles [°] for $[Rb(18\text{–}C\text{–}6)][Ph_2OPNPOPh_2]\cdot H_2O$, **4**. Rb–O(2) 2.931(8), Rb–O(43) 3.205(12), Rb–O(3) 3.049(9), P(1)–N(1) 1.614(10), P(2)–N(1) 1.582(10), P(1)–O(2) 1.494(8), P(2)–O(3) 1.502 (9); P(2)–N(1)–P(1) 129.6(7), O(3)–P(2)–N(1) 120.1(6), O(2)–P(1)–N(1) 118.9(5), O(2)–Rb–O(3) 72.5(2).

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† Electronic supplementary information (ESI) available: experimental data. See http://www.rsc.org/suppdata/cc/b3/b311524k/

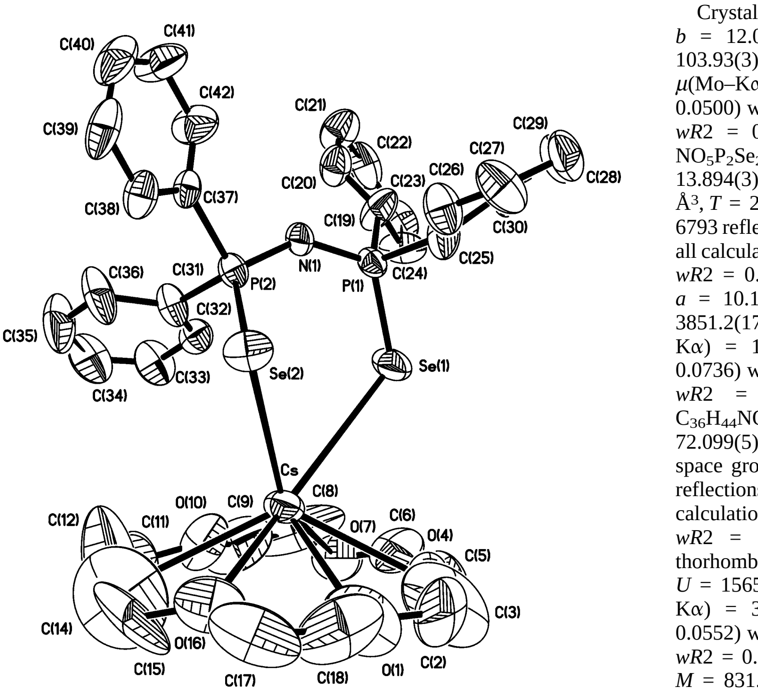

Fig. 3 Selected bond lengths [Å] and bond angles [°] for [Cs(18–C–6)][$Ph_2SePNPSePh_2$], **9**. Cs–Se(2) 3.629(2), Cs–Se(1) 3.720(2), Se(2)–P(2) 2.119(4), Se(1)–P(1) 2.114(4), P(1)–N 1.593(9), P(2)–N 1.584(9); Se(2)–Cs–Se(1) 74.81(4), N(1)–P(1)–Se(1) 122.6(4), N(1)–P(2)–Se(2) 119.9(4), P(2)–N–P(1) 140.9(7).

Concerning the handling of oxygen-containing ligands, it was observed that cation–oxygen atom bond interactions take place in [K(18C6)][$Ph_2OPNPOPh_2$],[5] although a suitable crown ether was used. This could be explained by the great affinity of the 'hard' alkali metals to 'hard' donor atoms such as oxygen. However, we do not know if this interaction would occur even with the usage of a larger crown ether as in [Li(15C5)][$Ph_2OPNPOPh_2$] (**1**), since the structure could, unfortunately, not be determined.

Finally, it is interesting to point out that the formation of ligand–cation bond interactions may be achieved by the alkali metal–crown ether 'misfit' through the employment of smaller crown ethers and that owing to this, the proposed synthetic strategy could be used to produce rare inorganic rings.

Notes and references

‡ The [$Ph_2EPNHPEPh_2$] (E = O, S, Se) ligands were synthesized by published procedures.[10,11] The salts were obtained by stirring an equimolecular methanolic solution of the corresponding acid and MOH (M = Li (when E = 0), Rb and Cs). The mixture was stirred for 2 h at room temperature. The volume of this solution was reduced until precipitation and the solid was filtered and air-dried. The [Li($Ph_2EPNPEPh_2$)] (E = S and Se) were obtained from the reaction of the corresponding acid with metallic lithium in excess (15%) in anhydrous THF under reflux for 1 h. Then, the volume of the solution was reduced until precipitation and the solid was filtered, washed with hexane, and dried in air. The crown ether complexes were obtained by stirring a methanolic solution of the alkaline salt and the selected crown ether in 15% excess for 3 h at room temperature. The volume of this solution was reduced until precipitation and the obtained solid was filtered, washed with hexane, and air-dried. Crystals were obtained by solvent diffusion from dichloromethane–*n*-hexane mixture.

Crystal data: **2**, $C_{34}H_{40}LiNO_5P_2S_2$, M = 693.69, triclinic, a = 11.473(2), b = 12.017(3), c = 13.736(2) Å, α = 96.49(2), β = 90.96(1), γ = 103.93(3)°, U = 1824.4(6) Å^3, T = 273 K, space group $P\bar{1}$ (No. 2), Z = 2, μ(Mo–Kα) = 0.276 mm^{-1}, 6777 reflections measured, 6426 unique (R_{int} = 0.0500) which were used in all calculations. Final R values: $R1$ = 0.0631, $wR2$ = 0.1594, $R1$ = 0.1022, $wR2$ = 0.1788 (all data). **3**, $C_{34}H_{40}LiNO_5P_2Se_2$, M = 787.49, triclinic, a = 11.449(5), b = 12.050(3), c = 13.894(3) Å, α = 97.60(2), β = 91.13(3), γ = 103.26(3)°, U = 1846.9(10) Å^3, T = 273 K, space group $P\bar{1}$ (No. 2), Z = 2, μ(Mo–Kα) = 0.276 mm^{-1}, 6793 reflections measured, 6445 unique (R_{int} = 0.0564) which were used in all calculations. Final R values: $R1$ = 0.0461, $wR2$ = 0.0976, $R1$ = 0.0955, $wR2$ = 0.1111 (all data). **4**, $C_{36}H_{46}NO_9P_2Rb$, M = 784.15, orthorhombic, a = 10.114(4), b = 15.598(2), c = 24.412(3) Å, α, β, γ = 90°, U = 3851.2(17) Å^3, T = 273 K, space group $P2_12_12_1$ (No. 19), Z = 4, μ(Mo–Kα) = 1.420 mm^{-1}, 7620 reflections measured, 6777 unique (R_{int} = 0.0736) which were used in all calculations. Final R values: $R1$ = 0.0844, $wR2$ = 0.1658, $R1$ = 0.2032, $wR2$ = 0.2338 (all data). **5**, $C_{36}H_{44}NO_6P_2RbS_2$, M = 798.25, orthorhombic, a = 23.534(2), b = 72.099(5), c = 9.043(2) Å, α, β, γ = 90°, U = 15344(4) Å^3, T = 273 K, space group $Fdd2$ (No. 43), Z = 16, μ(Mo–Kα) = 1.527 mm^{-1}, 6624 reflections measured, 6424 unique (R_{int} = 0.0635) which were used in all calculations. Final R values: $R1$ = 0.0732, $wR2$ = 0.1184, $R1$ = 0.1617, $wR2$ = 0.1517 (all data). **6**, $C_{36}H_{44}NO_6P_2RbSe_2$, M = 892.05, orthorhombic, a = 23.618(3), b = 72.846(8), c = 9.100(3) Å, α, β, γ = 90°, U = 15656(6) Å^3, T = 273 K, space group $Fdd2$ (No. 43), Z = 16, μ(Mo–Kα) = 3.249 mm^{-1}, 7357 reflections measured, 6891 unique (R_{int} = 0.0552) which were used in all calculations. Final R values: $R1$ = 0.0716, $wR2$ = 0.1271, $R1$ = 0.1542, $wR2$ = 0.1633 (all data). **7**, $C_{34}H_{46}CsNO_9P_2$, M = 831.59, orthorhombic, a = 10.059(1), b = 15.769(3), c = 24.871(3) Å, α, β, γ = 90°, U = 3945.0(10) Å^3, T = 273 K, space group $P2_12_12_1$ (No. 19), Z = 4, μ(Mo–Kα) = 1.070 mm^{-1}, 7784 reflections measured, 6930 unique (R_{int} = 0.0533) which were used in all calculations. Final R values: $R1$ = 0.0586, $wR2$ = 0.1424, $R1$ = 0.0920, $wR2$ = 0.1797 (all data). **8**, $C_{36}H_{44}CsNO_6P_2S_2$, M = 845.69, monoclinic, a = 9.136(3), b = 20.316(3), c = 21.355(2) Å, β = 94.37(2)°, U = 3952.1(15) Å^3, T = 273 K, space group $P2_1/c$ (No. 14), Z = 4, μ(Mo–Kα) = 1.166 mm^{-1}, 7426 reflections measured, 6961 unique (R_{int} = 0.0344) which were used in all calculations. Final R values: $R1$ = 0.0738, $wR2$ = 0.1727, $R1$ = 0.1596, $wR2$ = 0.2268 (all data). **9**, $C_{36}H_{44}CsNO_6P_2Se_2$, M = 939.49, monoclinic, a = 9.232(2), b = 20.359(3), c = 21.385(2) Å, β = 94.80(1)°, U = 4005.3(12) Å^3, T = 273 K, space group $P2_1/c$ (No. 14), Z = 4, μ(Mo–Kα) = 2.864 mm^{-1}, 7512 reflections measured, 7044 unique (R_{int} = 0.0499) which were used in all calculations. Final R values: $R1$ = 0.0808, $wR2$ = 0.1548, $R1$ = 0.1952, $wR2$ = 0.2045 (all data). CCDC 220669–220676. See http://www.rsc.org/suppdata/cc/b3/b311524k/ for crystallographic data in .cif format.

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