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ARTICLE TYPE

N-Alkyl Pyrrolidone Ether Podands as Versatile Alkali Metal Ion Chelants

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This work explores the coordination chemistry of a bis(pyrrolidone) ether ligand. Pyrrolidones are commercially important functional groups because of the high polarity and hence high hydrophilicity and surface affinity. An array of alkali metal ion complexes of a podand bearing two pendant pyrrolidone functionalities, namely 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (**1**) are reported. Reaction of this ligand with sodium hexafluorophosphate gives two discrete species of formulae $[Na(\mathbf{1})_2]PF_6$ (**3**) and $[Na_3(H_2O)_2(\mu\text{-}\mathbf{1})_2](PF_6)_3$ (**4**), and a coordination polymer $\{[Na_3(\mu_3\text{-}\mathbf{1})_3(\mu_2\text{-}\mathbf{1})](PF_6)_3\}_n$ (**5**). The same reaction in methanol gives a 1:1 complex, namely $[Na_2(\mu\text{-}\mathbf{1})_2(MeOH)_2](PF_6)_2$ (**6**). Use of tetraphenyl borate as a less coordinating counter ion gives $[Na_2(\mathbf{1})_2(H_2O)_4](BPh_4)_2$ (**7**) and $[Na_2(\mathbf{1})_4](BPh_4)_2$ (**8**). Two potassium complexes have also been isolated, a monomer $[K(\mathbf{1})_2]PF_6$ (**9**) and a cyclic tetramer $[K_4(\mu_4\text{-}H_2O)(\mu\text{-}\mathbf{1})_4](PF_6)_4$ (**10**). The structures illustrate the highly polar nature of the amide carbonyl moiety within bis(pyrrolidone) ethers with longer interactions to the ether oxygen atom. The zinc complex is also reported and $\{[ZnCl_2(\mu\text{-}\mathbf{1})]\}_n$ (**11**) exhibits bonding only to the carbonyl moieties. The ether oxygen atom is not necessary for Na^+ complexation as exemplified by the structure of the sodium complex of the analogue 1,3-bis(pyrrolid-2-on-1-yl)butane (**2**). Reaction of compound **1** with lithium salts results in isolation of the protonated ligand.

Introduction

The extremely polar nature of the amide carbonyl bond makes amides very effective as solvents (as in the classic dipolar aprotic solvent dimethyl formamide) and as ligands for hard metal centres.[1] Incorporation of the amide functionality within a cyclic lactam offers increased control over the amide bond polarity. Pyrrolidone and caprolactam derivatives in particular are common, commercially important functional groups because of the high polarity and hence high hydrophilicity and surface affinity of their amide carbonyl groups.[2] As a result, lactam oligomers and polymers have remarkable properties, such as very high hydrophilicity (including water solubility), and high surface activity such that they find a range of applications, for example polyvinylpyrrolidone and polyvinylcaprolactam in the inhibition of gas hydrate crystallization in the oil industry.[3-5] Other applications include uses in the pharmaceutical, cosmetic and detergent industries and in membranes, glue sticks, hot-melt adhesives, hydrogels and for crop protection.[2] The bis(pyrrolidone) derivative 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (**1**, Fig. 1) and related compounds have been recently reported to have a number of commercially important properties as solvents, solubilising agents, freezing point depressors, dispersants, reaction media and cleaning agents.[6] This versatility means that this type of compound offers a huge range of potential uses in fields such as performance chemicals, personal care and pharmaceutical formulation. The mode of action of these fascinating materials is not fully understood, but interactions of the highly polar amide carbonyl moiety with other formulation components are likely to be core to the materials' properties.

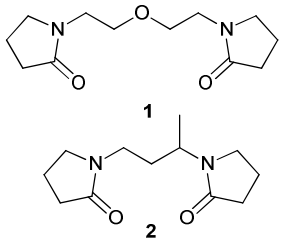

Figure 1. Structures of the bispyrrolidones **1** and **2**.

By analogy to the well-known crown ethers[7-9] and their acyclic podand analogues,[10, 11] we postulate that materials such as compound **1** should act as effective chelants for alkali metal cations. Such complexes should have versatile applications, for example as part of a delivery formulation for drug alkali metal cation salt forms. The high negative charge density on the lactam carbonyl groups is expected to result in particularly strong complexation of hard metal ions, in contrast to crown ethers, for example. Some clue to the likely success of this strategy comes from early work on the coordination of lanthanide and actinide ions by bis(pyridone) and bis(pyrrolidone) ligands in which the twin amide moieties are linked by a single oligomethylene

chain.[12-14] We now report the synthesis and structures of a range of metal ion complexes of compound **1** and its short-chain analogue 1,3-bis(pyrrolid-2-on-1-yl)butane (**2**), model compounds for polyvinylpyrrolidone hydrate crystallization inhibitors.[15]

Results and Discussion

Sodium Salts

Reaction of compound **1** with $NaPF_6$ in acetonitrile followed by solvent evaporation after brief sonication to aid dissolution results in the isolation of three crystalline solids; two discrete complexes of formulae $[Na(\mathbf{1})_2]PF_6$ (**3**) and $[Na_3(H_2O)_2(\mu\text{-}\mathbf{1})_2](PF_6)_3$ (**4**), and a coordination polymer $\{[Na_3(\mu_3\text{-}\mathbf{1})_2(\mu_2\text{-}\mathbf{1})_2](PF_6)_3\}_n$ (**5**), with metal:ligand stoichiometry 1:2, 3:2 and 3:4, respectively. The product obtained is dependent primarily on the ratio of metal salt and ligand added and highlights the extremely versatile coordination behaviour of ligand **1**. The same reaction in methanol or 2,2-dimethoxypropane results in the isolation of a 1:1 complex, namely $[Na_2(\mu\text{-}\mathbf{1})_2(MeOH)_2](PF_6)_2$ (**6**). The new complexes were characterised using elemental analysis, IR spectroscopy, thermogravimetric analysis (TGA) and X-ray crystallography (see experimental section for analytical and crystallographic details). For all complexes a notable shift in the amide carbonyl stretch in the solid state IR spectra is observed upon metal complexation. The carbonyl stretching mode occurs at 1674 cm^{-1} in a thin film of compound **1** shifting to 1650 - 1661 cm^{-1} suggesting a shift towards the enolate resonance form upon complexation. Spectra are reproduced in the supplementary material.

The X-ray molecular structure of **3** is shown in Fig. 2 and comprises a single distorted octahedral Na^+ cation bound between two bis(pyrrolidone) ligands in a sandwich fashion reminiscent of the 1:2 complex of sodium triflate with [12]crown-4,[16] although in the present case the Na^+ cation is bound by relatively unusual seven membered chelate rings, as opposed to 5-membered in crown ether complexes.[17] There is a clear difference in bond lengths to the pyrrolidone groups compared to the ether oxygen atoms, with bond distances to the pyrrolidone units being substantially shorter at 2.36 Å (av.) compared to 2.54 Å consistent with the excellent donor properties of the highly polar lactam carbonyl groups. The hexafluorophosphate anion is disordered and does not make a close approach to the metal cation in either orientation. It is held in a 'pocket' formed by the ligand methylene groups, interacting with the cationic complex by a number of CH···F hydrogen bonds.[18, 19]

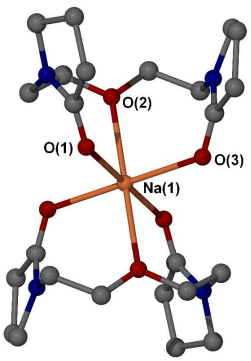

Figure 2. X-ray molecular structure of the cation in $[Na(\mathbf{1})_2]PF_6$ (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Na–O(1) 2.3697(9), Na–O(2) 2.5366(9), Na–O(3) 2.3524(9).

The molecular structure of the 3:2 complex **4** appears to be closely related to **3** in the sense that one Na^+ cation is again sandwiched between two bis(pyrrolidone) ether ligands (Fig. 3). The remaining two Na^+ cations are then coordinated one to each pair of pyrrolidone oxygen atoms of a single ligand as well as a pyrrolidone oxygen atom of the other ligand. The result is that each ligand has one doubly bridging and one triply bridging pyrrolidone oxygen atom. The two bis(pyrrolidone) ether ligands are mutually rotated to an angle of *ca.* 54° instead of *ca.* 180° in **3** in order to face and mutually bridge the two 'incoming' Na^+ ions. These multiple bridging modes highlight just how versatile a ligand the pyrrolidone is. The remaining coordination sites of the two 'extra' (non-sandwiched) sodium ions are occupied by interactions to coordinated water, and one bridging and one terminal PF_6^- anion each. This interesting structure is apparently a response to the presence of excess sodium in the reaction mixture and maximises the donor interactions for a limited number of ligands. Most interestingly the $Na(1)–O_{pyrrolidone}$ distances are very similar to the distances observed in **3** despite the multiple bridging mode of the donor atoms (2.35 Å av.). The distance to the ether oxygen atom is rather shorter than in **3** at 2.418(6) Å.

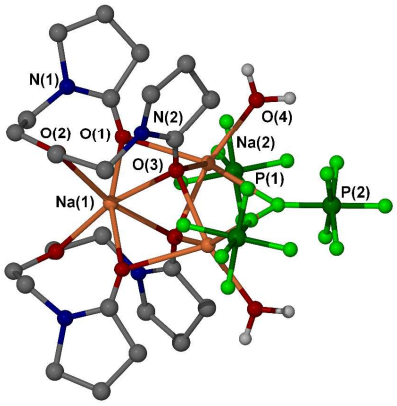

Figure 3. X-ray molecular structure of $[Na_3(H_2O)_2(\mu\text{-}\mathbf{1})_2](PF_6)_3$ (**4**). Hydrogen atoms are omitted for clarity except water molecules. Selected bond lengths (Å): Na(1)–O(1) 2.338(8), Na(1)–O(2) 2.418(6), Na(1)–O3 2.364(6), Na(2)–O(1) 2.509(9), Na(2)–O(3) 2.271(7), Na(2)–O(4) 2.279(10), Na(2)–F(1) 2.418(10), Na(2)–F(7) 2.644(11).

The third structure in this sequence, complex **5** exhibits a 3:4 metal-ligand ratio and hence represents the adaptation of the system to the presence of a dearth of sodium rather than an excess as in the previous case. The structure is again based on the sandwich motif but in this case two Na^+ cations, Na(2) and Na(3), are sandwiched in a similar fashion to **3** by a total of three bis-*N*-ethylpyrrolidone ether ligands. Each of these two Na^+ cations is situated in an environment closely related to the coordination geometry of the sandwiched $Na(1)^+$ ion in **4** and hence also interact with the ether donors with distances of 2.35 – 2.50 Å, comparable to **3** and **4**. The remaining Na^+ cation, Na(1), is

bound to a total of four pyrrolidone oxygen atoms that are part of the sandwiched core; two doubly bridging and two triply bridging. This 'peripheral' sodium ion also binds to two further bis(pyrrolidone) ether ligands solely *via* the pyrrolidone oxygen atoms (the ether groups are uncoordinated, highlighting the better donor properties of the former). Each of these ligands, in turn, binds to adjacent Na_3 clusters to give an infinite 1D coordination polymer with metal clusters arranged like beads on a string, Fig. 4. As with **3** the disordered PF_6^- anions do not make a close approach to the metal centre and are bound in pockets above the ligand again by CH···F interactions.

Changing the solvent from the dipolar aprotic acetonitrile to methanol or dimethoxypropane allows the isolation of a 1:1 complex $[Na_2(\mu\text{-}\mathbf{1})_2(MeOH)_2](PF_6)_2$ (**6**) from an equimolar solution of metal salt and ligand. In the latter solvent the methanol ligand apparently arises from the acid hydrolysis of the 2,2-dimethoxypropane as a result of residual HF in the $NaPF_6$. The structure of **6** (Fig. 5) is related to the 'sandwich' series **3** – **5** obtained from acetonitrile in the sense that each sodium cation is capped by a tridentate bis(pyrrolidone) ligand. The structure comprises a centrosymmetric dimer with each of the two ligands **1** binding to both Na^+ cations *via* a bridging pyrrolidone oxygen atom. The other pyrrolidone oxygen atom and ether donor of each the ligands are bound to only a single metal centre. Each metal coordination sphere is completed by a molecule of methanol, strongly hydrogen bonded to the non-bridging pyrrolidone oxygen atom and by a coordinated PF_6^- anion to give an octahedral coordination geometry. Distances from the Na^+ ion to the pyrrolidone oxygen atoms are again shorter than to the ether donor and interestingly the bond lengths to the bridging and terminal pyrrolidone donors are very similar to one another despite their different coordination modes.

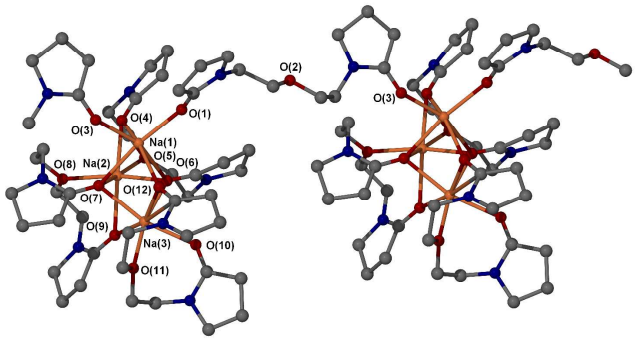

Figure 4. X-ray molecular structure of the cationic coordination polymer $\{[Na_3(\mu_3\text{-}\mathbf{1})_2(\mu_2\text{-}\mathbf{1})_2](PF_6)_3\}_n$ (**5**). Hydrogen atoms and counter ions are omitted for clarity. Selected bond lengths (Å): Na(1)–O(1) 2.2739(19), Na(1)–O(3) 2.287(2), Na(1)–O(4) 2.4719(18), Na(1)–O(6) 2.6537(18), Na(1)–O(7) 2.4392(18), Na(1)–O(12) 2.336(2), Na(2)–O(4) 2.3588(18), Na(2)–O(5) 2.4417(18), Na(2)–O(6) 2.2665(18), Na(2)–O(7) 2.3662(18), Na(2)–O(8) 2.3568(18), Na(2)–O(9) 2.4281(19), Na(3)–O(6) 2.3244(18), Na(3)–O(7) 2.3728(17), Na(3)–O(9) 2.6290(19), Na(3)–O(10) 2.2749(19), Na(3)–O(11) 2.5044(19), Na(3)–O(12) 2.376(2).

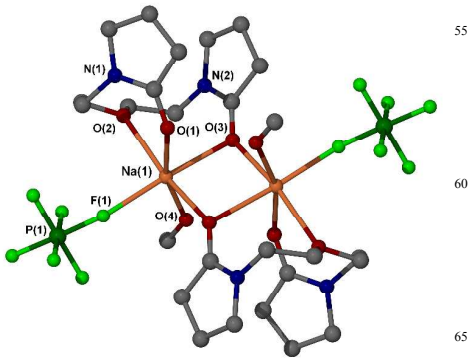

Figure 5. X-ray molecular structure of $[Na_2(\mu\text{-}\mathbf{1})_2(MeOH)_2](PF_6)_2$ (**6**). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Na(1)–O(1) 2.428(2), Na(1)–O(2) 2.496(2), Na(1)–O(3)' 2.322(2), Na(1)–O(3) 2.438(2), Na(1)–O(4) 2.329(3), Na(1)–F(1) 2.295(2).

Since the PF_6^- counter anion is weakly coordinating in complex **6**, use of the alternative sodium tetraphenylborate ($NaBPh_4$) was examined in an attempt to further reduce counter anion coordination to the metal centre. Crystallization of ligand **1** with an equimolar solution of $NaBPh_4$ in water, results in the isolation of a complex of formula $[Na_2(\mu\text{-}\mathbf{1})_2(H_2O)_4](BPh_4)_2$ (**7**) comprising a centrosymmetric dimer containing two metal-bound water molecules per Na^+ cation (Fig. 6). The BPh_4^- counter anion does not coordinate to the sodium ions and effectively sheaths the dimer complex. The water molecules are held in position through hydrogen bonding to the carbonyl moiety and also through OH···π interactions to the anion. Precedence for the unusual occurrence of OH···π interactions can be found within the literature from neutron diffraction data.[20]

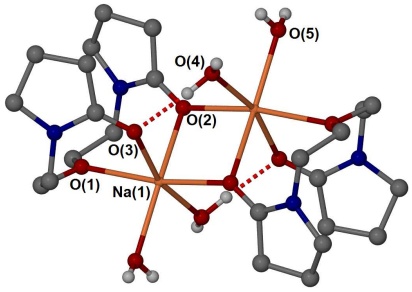

Figure 6. X-ray molecular structure of the cation in $[Na_2(\mu\text{-}\mathbf{1})_2(H_2O)_4](BPh_4)_2$ (**7**). Selected hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Na(1)–O(1) 2.4652(12), Na(1)–O(2) 2.4434(13), Na(1)–O(2)′ 2.3293(13), Na(1)–O(3) 2.3876(13), Na(1)–O(4) 2.3726(15), Na(1)–O(5) 2.3971(17) Å.

The structure of complex **7** is analogous to compound **6**, with

one carbonyl group and the ether oxygen of ligand **1** binding to a single metal centre *via* donor atoms O(1) and O(3), while the remaining carbonyl group, O(2), forms a bridge between the two metal centres. As in the previous structures, the carbonyl oxygen-metal bond distance is slightly shorter than the ether-metal bond distance; see figure caption for detailed bond lengths.

A 1:2 metal:ligand mixture of $NaBPh_4$ with **1** in ethanol allows isolation of $[Na_2(\mathbf{1})_2(\mu\text{-}\mathbf{1})_2](BPh_4)_2$ (**8**). In this complex two ligands are bound to the metal centre through all three oxygen atoms O(1-3), while the remaining two ligands bind through only one carbonyl oxygen atom, O(4). The remaining two oxygen atoms, O(5) and O(6), surprisingly are not coordinated. The sodium cation is five coordinate and has considerably shorter bond distances to the carbonyl oxygen atoms than the ether donor, Figure 7.

Both complexes **7** and **8** show two quite distinct carbonyl absorptions in their solid state IR spectra (*e.g.* 1668 and 1643 cm^{-1} in **7**), consistent with the presence of two different carbonyl groups in each complex.

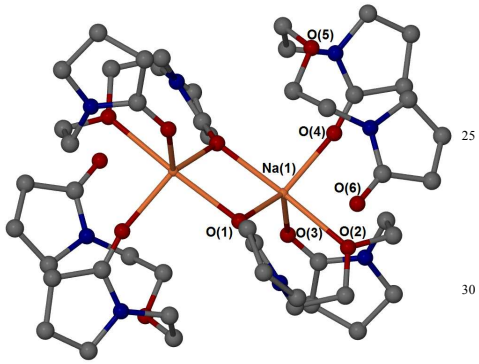

Figure 7. X-ray molecular structure of $[Na_2(\mathbf{1})_2(\mu\text{-}\mathbf{1})_2](BPh_4)_2$ (**8**). Hydrogen atoms and counter ions are omitted for clarity. Selected bond lengths (Å): Na(1)-O(1) 2.3033(15), Na(1)-O(2) 2.4976(14), Na(1)-O(3) 2.2769(15) and Na(1)-O(4) 2.2363(16) Å.

Potassium Salts

Reaction of ligand **1** with KPF_6 in acetonitrile results in two complexes of metal:ligand stoichiometry 1:2 and 1:1, namely a monomer $[K(\mathbf{1})_2]PF_6$ (**9**) and a cyclic tetramer $[K_4(\mu_4\text{-}H_2O)_2(\mu\text{-}\mathbf{1})_4](PF_6)_4$ (**10**), again determined by the stoichiometry of the reaction mixture. The tetrameric complex **10** can also be isolated from methanol as a slightly different polymorphic modification (see experimental section). As with the sodium complex, IR spectroscopy shows a shift in the carbonyl frequency on complexation from 1674 cm^{-1} in the free ligand to 1650 – 1666 cm^{-1} in the complexes. The coordination mode of ligand **1** in both **9** and **10** is very similar and comprises the same tridentate, face-capping arrangement observed in the sodium complexes. Indeed the 1:2 sandwich complex **9** is isomorphous with the sodium analogue **3** (Fig. 2), and hence is not pictured. The $K–O_{pyrrolidone}$ bond distances of 2.64 Å (av.) are significantly longer than the sodium analogue (2.36 Å av.) consistent with the larger ionic radius of K^+, but as in **3** the bond to the central ether unit is longer and hence likely to be weaker coordinated than the pyrrolidone groups. The structures of both solid forms of **10** (Fig. 8) proved to be disordered with the pyrrolidone rings adopting two positions; however, the gross structural features can be readily distinguished. Moreover, the structure of the cation and coordination mode of the bis(pyrrolidone) ligand in each case is essentially identical with an unusual quadruply bridging water molecule in the centre of the cluster disordered over two positions. The tetrameric complexes of type **10** appear to be in the same 'series' as the sodium complexes **3** – **6** in the sense that pyrrolidone oxygen atoms bridge between pairs of metal cations. However, the larger ionic radius of K^+ allows the cluster to open up into a higher nuclearity species. As with **9**, the bond distances are generally significantly shorter to the pyrrolidone oxygen atoms than to the ether units in both structures of type **10**, although the poor precision of the data limits the value of detailed quantitative comparisons. Crystallographic disorder takes the form of 'up-down' disorder of the bridging water molecule which caps a square face of K^+ ions but can be on either side of the metal square. As a result there is void space within the ligand pocket on the other face that is occupied by an additional, partially occupied water molecule. $K^+–OH_2$ distances are unreliable because of disorder but appear to be of a similar length to the pyrrolidone oxygen bonds to the K^+ cations.

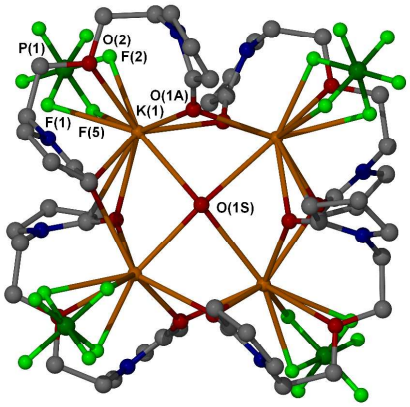

Figure 8. X-ray molecular structure of one of the crystallographically unique tetranuclear complexes $[K_4(\mu_4\text{-}H_2O)_2(\mu\text{-}\mathbf{1})_4](PF_6)_4$ of **10**.

Protonation

A number of attempts were made to isolate Li^+ complexes of ligand **1**; however, no crystalline products were obtained using the same kinds of approaches adopted for sodium and potassium with $LiPF_6$, $LiNO_3$, LiCl, LiBr or LiI. A crystalline solid isolated from a 1:1 mixture of $LiPF_6$ and ligand **1** in methanol proved to be a surprising monoprotonated complex of the ligand that did not contain any Li^+. The structure of this protonated species $\mathbf{1}{\cdot}HPF_6$ is shown in Fig. 9 and the fact that a stable acid addition salt can be isolated represents *de facto* evidence of the highly basic nature of the pyrrolidone oxygen atoms. The lack of Li^+ incorporation is attributed to the highly solvated nature of the lithium cation in methanol. The structure of $\mathbf{1}{\cdot}HPF_6$ comprises a zigzag 1D chain of monoprotonated ligands linked by very short and therefore presumably strong hydrogen bonds from the

protonated carbonyl group on one ligand to the unprotonated carbonyl on the next. The hydrogen bonded O···O distance of 2.443(2) Å is consistent with strongly hydrogen bonded oxonium ion species such as $H_5O_2^+$.[21, 22] Precedent for the protonation of polar carbonyl moieties comes from the ionic co-crystal of *N*-methylpyrrolidone with protonated *N*-methylpyrrolidonium tribromide, and a similar protonated *N*-methylpyrrolidone dimer in the structure of a polyoxomolybdate cluster, both of which exhibit very similar O···O distances to the present case.[23, 24]

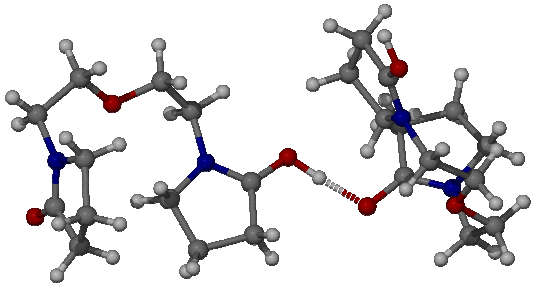

Figure 9. X-ray crystal structure of the protonated species **1**·HPF_6. Hydrogen bond distance O···O 2.443(2) Å

Other metal salts

Attempts to prepare crystalline complexes of ligand **1** with a range of transition and alkaline earth metal salts generally resulted in non-crystalline compounds that proved difficult to characterise. In the case of zinc(II) chloride, however, a crystalline coordination polymer of formula $\{[ZnCl_2(\mu\text{-}\mathbf{1})]\}_n$ (**11**) was isolated by slow evaporation of an equimolar mixture of $ZnCl_2$ and **1** in acetone. The structure of **11** is shown in Fig. 10 and is based on tetrahedral Zn(II) cations each coordinated to two chloride ligands and the pyrrolidone oxygen atoms of two different ligands. Hence each ligand **1** links a pair of zinc ions together. The Zn–O distances are short at 1.995(2) Å, consistent with the small size of the Zn^{2+} ion. The ether functionality is uncoordinated. The solid state IR spectrum of this material shows a carbonyl stretching mode at 1611 cm^{-1}, markedly shifted from the free ligand at 1674 cm^{-1} consistent with the strongly polarising nature of the zinc(II) dication.

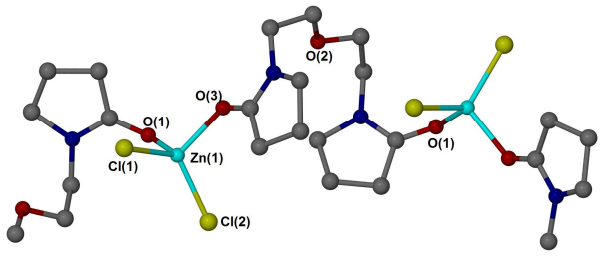

Figure 10. X-ray crystal structure of coordination polymer $\{[ZnCl_2(\mu\text{-}\mathbf{1})]\}_n$ (**11**) (H atoms are omitted for clarity). Selected bond lengths (Å): Zn(1)–Cl(1) 2.2368(7), Zn(1)–Cl(2) 2.2116(7), Zn(1)–O(1) 1.9958(18), Zn(1)–O(3) 1.9952(18).

Addition of compound **1** directly to $ZnCl_2$ in the same proportions, followed by addition of solvent, results in the immediate formation of a white crystalline powder upon sonication. Examination of the resultant powder using PXRD, and comparison to the predicted powder pattern based on the single crystal data for **11** (see supplementary data) indicates the formation of a new material. Elemental analysis is consistent with a 1:1 formulation and hence this material must be an isomer or polymorph of **11**. The IR spectrum shows only a slight difference in the pyrrolidone carbonyl band compared to **11** (1615 cm^{-1} *cf.* 1611 cm^{-1} in **11**) suggesting a similar coordination mode. In the absence of structural data no further conclusions can be reached regarding this material.

1,3-Bis(pyrrolid-2-on-1-yl)butane

In all of the complexes **3** – **10**, coordination of ligand **1** occurs *via* both the pyrrolidone and ether oxygen atom donor groups, albeit with significantly longer bonds to the ether unit. For comparison we attempted the reaction of alkali metal salts with 1,3-bis(pyrrolid-2-on-1-yl)butane (**2**)[15, 25] which does not contain an ether group. We were successful in isolating the fascinating 2:3 trigonal 1D coordination polymer complex $\{[Na_2(\mu\text{-}\mathbf{2})_3](PF_6)_2\}_n$ (**12**) by reaction of **2** with $NaPF_6$ in a *ca.* 1:2 metal to ligand ratio by slow evaporation of a methanol solution (Fig. 11). The crystal structure comprises two independent polymeric chains both based on unusual trigonal antiprismatic Na^+ cations coordinated to the pyrrolidone oxygen atoms of **2**. Each ligand bridges a pair of Na^+ cations. Alternating sodium ions are either coordinated to the same three ligands, or situated in the void in between adjacent ligand trigonal antiprismatic trimers. The groups of three ligands arranged around a single sodium ion as a trigonal prismatic trimer are all homochiral but the configuration at the asymmetric carbon atom alternates along the chain to give an achiral but polar structure. Na–O distances are in the range 2.43 – 2.57 Å, rather longer than the distances in **3** for example, reflecting steric strain in the smaller ligand.

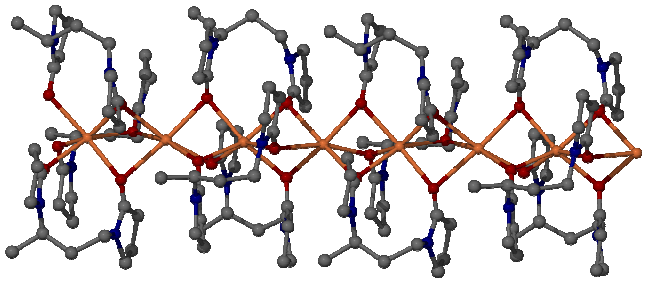

Figure 11. X-ray crystal structure of the coordination polymer $\{[Na_2(\mu\text{-}\mathbf{2})_3](PF_6)_2\}_n$ (**12**). Hydrogen atoms and counter ions are omitted for clarity.

Conclusions

The bis(pyrrolidone) ether ligand **1** is an effective metal ion chelant for sodium and potassium ions, forming significantly shorter bonds *via* the pyrrolidone oxygen atoms than the ether donor, highlighting the highly basic nature of the pyrrolidone carbonyl groups. This characteristic is also exemplified by the isolation of the protonated form of the ligand in the presence of $LiPF_6$. No lithium complexes were isolated, which is attributed to the higher solvation energy of the Li^+ cation. The ether oxygen atom is not necessary to bring about metal ion complexation as

exemplified by the structure of complex **12** involving the shorter bis(pyrrolidone) ligand **2** and coordination to zinc(II) occurs without the involvement of the ether oxygen atom in **11**. The ligand **1** is extremely versatile in its coordination modes because of the ability to form both bridging and terminal interactions. As a result a wide variety of stoichiometries are encountered with the product, and hence coordination cluster nuclearity is determined mainly by the ratio of reactants introduced. Solvent also plays some role with alcohols and aqueous media resulting in different species to those observed in acetonitrile. Complexes containing bound protic solvent are extensively hydrogen bonded and the hydrogen bonding interactions may well act to stabilise the crystal and hence determine the particular species isolated as a result of solubility effects in these labile systems. The identity of the metal ion does not appear to be critical in determining coordination behaviour as may be anticipated from the ligand's high degree of flexibility although bond distances to K^+ are slightly longer than those to Na^+ as would be expected. The sheer versatility of the alkali metal ion complexation properties of ligand **1** coupled with its high solubility and facile synthesis suggests that it may have applications as a delivery agent for alkali metal salts of materials such as drug substances, for example.

Experimental

General

1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (**1**) and 1,3-bis(pyrrolid-2-on-1-yl)butane (**2**) were supplied by Ashland Inc., and used without further purification. Sodium hexafluorophosphate, sodium tetraphenylborate, potassium hexafluorophosphate, lithium hexafluorophosphate and zinc chloride were purchased from Sigma-Aldrich and used without further purification.

IR spectra were measured with a Perkin-Elmer 100 FT-IR spectrometer, using an ATR attachment. Crystals suitable for single crystal X-ray diffraction structure determination were selected, soaked in perfluoropolyether oil and mounted on a preformed tip. Single crystal X-Ray data were collected at 120K on an Agilent Gemini S-Ultra diffractometer equipped with the Cryostream (Oxford Cryosystems) open-flow nitrogen cryostats, using graphite monochromated MoKα-radiation (λ = 0.71069 Å). All structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXL[26] and OLEX2[27] software. All non-hydrogen atoms were refined with anisotropic displacement parameters. CH hydrogen atoms were placed in calculated positions, assigned an isotropic displacement factor that is a multiple of the parent carbon atom and allowed to ride. H-atoms attached to oxygen were located on the difference map when possible, or placed in calculated positions. In some cases disordered H atoms could not be included in the model.

Synthesis of Coordination Compounds

$[Na(1)_2]PF_6$ (3). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.286 g, 1.19 mmol) was added to $NaPF_6$ (0.1 g, 0.595 mmol) dissolved in acetonitrile (2 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.276 g, 0.425 mmol, 71%). Analysis calc. for $C_{24}H_{40}N_4O_6NaPF_6$: C 44.45, H 6.22, N 8.64%, found: C 44.38, H 6.26, N 8.57%; IR (υ/ cm^{-1}): 1661 (C=O), 1120 (C-O, ether). Crystal data for $C_{24}H_{40}N_4O_6NaPF_6$: M = 648.56 g mol^{-1}, colourless plate, 0.497 × 0.2891 × 0.1196 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 7.0768(4) Å, b = 8.5945(5) Å, c = 12.9170(7) Å, α = 77.011(5)°, β = 77.346(4)°, γ = 74.071(5)°, V = 725.67(7) $Å^3$, Z = 1, D_c = 1.484 g cm^{-3}, F_{000} = 340, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, $2\theta_{max}$ = 55.0°, 12472 reflections collected, 3330 unique (R_{int} = 0.0337). Final *GooF* = 1.064, *R1* = 0.0377, *wR2* = 0.0956, *R* indices based on 2945 reflections with $I>2\sigma(I)$ (refinement on F^2), 212 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.194 mm^{-1}.

$[Na_3(\mu\text{-}1)_2(H_2O)_2](PF_6)_3$ (4). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.0487 g, 0.202 mmol) was added to $NaPF_6$ (0.0511 g, 0.304 mmol) dissolved in acetonitrile (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.0481 g, 0.0471 mmol, 23%). Analysis calc. for $C_{24}H_{44}N_4O_8Na_3P_3F_{18}$: C 28.26, H 4.35, N 5.49%, found: C 28.38, H 4.18, N 5.58%; IR (υ/ cm^{-1}): 1650 (C=O), 1123 (C-O, ether). Crystal data for $C_{24}H_{44}N_4O_8Na_3P_3F_{18}$: M = 1020.51 g mol^{-1}, colourless irregular, 0.2738 × 0.1334 × 0.0759 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 13.848(2) Å, b = 17.969(3) Å, c = 16.913(3) Å, α = 90°, β = 107.686(18)°, γ = 90°, V = 4009.8(11) $Å^3$, Z = 8, D_c = 1.690 g cm^{-3}, F_{000} = 2080, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, $2\theta_{max}$ = 58.6°, 32122 reflections collected, 5004 unique (R_{int} = 0.1991). Final *GooF* = 1.310, *R1* = 0.1745, *wR2* = 0.4286, *R* indices based on 2014 reflections with $I>2\sigma(I)$ (refinement on F^2), 274 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.314 mm^{-1}. The poor residuals arise from the overlap of numerous plate-shaped crystals. While the precision is poor, the gross structural details are unequivocal.

$\{[Na_3(\mu_3\text{-}1)_2(\mu_2\text{-}1)_2](PF_6)_3\}_n$ (5). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.0975 g, 0.406 mmol) was added to $NaPF_6$ (0.0511 g, 0.304 mmol) dissolved in acetonitrile (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.1291 g, 0.088 mmol, 29%). Analysis calc. for $C_{48}H_{80}N_8O_{12}Na_3P_3F_{18}$: C 39.35, H 5.50, N 7.65%, found: C 39.33, H 5.61, N 7.69%; IR (υ/ cm^{-1}): 1655 (C=O), 1117 (C-O, ether). Crystal data for $C_{48}H_{80}N_8O_{12.28}Na_3P_3F_{18}$: M = 1469.61 g mol^{-1}, colourless plate, 0.7422 × 0.4462 × 0.1434 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 13.2010(4) Å, b = 13.6768(4) Å, c = 18.1009(5) Å, α = 85.700(2)°, β = 84.890(2)°, γ = 88.882(2) °, V = 3245.65(16) $Å^3$, Z = 2, D_c = 1.504 g cm^{-3}, F_{000} = 1525, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, $2\theta_{max}$ = 55.0°, 76405 reflections collected, 14788 unique (R_{int} = 0.0868). Final *GooF* = 1.029, *R1* = 0.0563, *wR2* = 0.1197, *R* indices based on 10349 reflections with $I>2\sigma(I)$ (refinement on F^2), 894 parameters, 0 restraints. Lp and absorption corrections applied, μ

= 0.226 mm^{-1}.

[Na$_2$(μ-1)$_2$(MeOH)$_2$](PF$_6$)$_2$ (6). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.05 g, 0.208 mmol) was added to $NaPF_6$ (0.035 g, 0.208 mmol) dissolved in 2,2-dimethoxypropane (1 mL). The resulting mixture was sonicated for 1 minute. Pale yellow crystals formed upon evaporation of the solvent at room temperature (Yield = 0.0654 g, 0.0743 mmol, 36%). The sample for analysis was dried *in vacuo* for 2h at 110 ^{o}C resulting in loss of the coordinated methanol. Analysis calc. for $C_{12}H_{20}N_2O_3NaPF_6$: C 35.30, H 4.94, N 6.86%, found: C 35.62, H 5.06, N 6.78%; IR (υ/ cm^{-1}): 1650 (C=O), 1123 (C-O, ether). Crystal data for $C_{26}H_{48}N_4O_8Na_2P_2F_{12}$, M = 880.60 g mol^{-1}, colourless plate, 0.2888 × 0.1892 × 0.0992 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.1886(5) Å, b = 13.3508(5) Å, c = 13.6275(6) Å, α = 90˚, β = 111.547(5)˚, γ = 90º, V = 1893.37(14) Å^3, Z = 2, D_c = 1.545 g cm^{-3}, F_{000} = 912, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, 2θ_{max} = 55.0º, 13061 reflections collected, 4262 unique (R_{int} = 0.0515). Final *GooF* = 1.043, *R1* = 0.0618, *wR2* = 0.1266, *R* indices based on 2880 reflections with $I>2\sigma(I)$ (refinement on F^2), 248 parameters, 2 restraints. Lp and absorption corrections applied, μ = 0.247 mm^{-1}.

[Na$_2$(μ-1)$_2$(H$_2$O)$_4$](BPh$_4$)$_2$ (7). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.05 g, 0.20 mmol) was added to $NaBPh_4$ (0.071 g, 0.20 mmol) dissolved in water (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed within 24 hours at room temperature (Yield = 0.0807 g, 0.065 mmol, 33%). Analysis calc. for $C_{72}H_{88}B_2N_4Na_2O_{10}$: C 69.90, H 7.18, N 4.53 %, found: C 70.06, H 7.11, N 4.64 %; IR (υ/ cm^{-1}): 1668, 1643 (C=O), 1120 (C-O, ether). Crystal data for $C_{72}H_{88}B_2N_4Na_2O_{10}$: M = 1237.06 g mol^{-1}, colourless block, 0.5581 × 0.241 × 0.1241 mm^3, triclininc, space group P-1 (No. 2), a = 11.9380(5) Å, b = 12.1701(5) Å, c = 13.1018(7), α = 67.444(4)˚, β = 75.171(4)˚, γ = 78.989(3)˚, V = 1690.16(13) Å^3, Z = 1, D_c = 1.215 g cm^{-3}, F_{000} = 660, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, 2θ_{max} = 55.0º, 28252 reflections collected, 7743 unique (R_{int} = 0.0612). Final *GooF* = 1.023, *R1* = 0.0502, *wR2* = 0.1006, *R* indices based on 5539 reflections with $I>2\sigma(I)$ (refinement on F^2), 422 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.091 mm^{-1}.

[Na$_2$(1)$_2$(μ-1)$_2$](BPh$_4$)$_2$ (8). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.1 g, 0.41 mmol) was added to $NaBPh_4$ (0.071 g, 0.20 mmol) dissolved in ethanol (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed within 4 days at room temperature (Yield = 0.1339 g, 0.0814 mmol, 39%). Analysis calc. for $C_{96}H_{120}B_2N_8Na_2O_{12}$: C 70.07, H 7.35, N 6.81 %, found: C 69.87, H 7.26, N 6.89 %; IR (υ/ cm^{-1}): 1666, 1642 (C=O), 1116 (C-O, ether). Crystal data for $C_{96}H_{120}B_2N_8Na_2O_{12}$: M = 1645.60 g mol^{-1}, colourless block, 0.4125 x 0.2418 x 0.1581 mm^3, triclinic, space group P-1 (No. 2), a = 11.5127(6) Å, b = 13.7549(9) Å, c = 15.9209(7) Å, α = 71.514(5)˚, β = 79.756(4)˚, γ = 66.772(5) º, V = 2193.2(2) Å^3, Z = 1, D_c = 1.246 g cm^{-3}, F_{000} = 880, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120K, 2θ_{max} = 54.0º, 31465 reflections collected, 9579 unique (R_{int} = 0.0578). Final *GooF* = 1.032, *R1* = 0.0513, *wR2* = 0.1090, *R* indices based on 6919 reflections with $I>2\sigma(I)$ (refinement on F^2), 541 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.090 mm^{-1}.

[K(1)$_2$]PF$_6$ (9). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.1000 g, 0.40 mmol) was added to KPF_6 (0.038 g, 0.2 mmol) dissolved in acetonitrile (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.09 g, 0.135 mmol, 68%). The crystals proved to absorb atmospheric moisture over time and elemental analysis data on a fully dry material could not be obtained. Analysis calc. for $C_{24}H_{40}N_4O_6KPF_6$: C 43.37, H 6.07, N 8.43%, re-calc for $C_{24}H_{40}N_4O_6KPF_6{\cdot}2H_2O$: C 41.14, H 6.34 and N 7.99 %, found: C 41.19, H 6.37, N 7.92 %; IR (υ/ cm^{-1}): 1650 (C=O), 1121 (C-O, ether). Crystal data for $C_{24}H_{40}N_4O_6KPF_6$: M = 664.67 g mol^{-1}, colourless block, 0.5484 × 0.4243 × 0.1448 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 7.0028(2) Å, b = 8.6199(3) Å, c = 13.2814(4) Å, α = 79.410(3)˚, β = 79.591(3)˚, γ = 74.036(3)º, V = 750.45(4) Å^3, Z = 1, D_c = 1.471 g cm^{-3}, F_{000} = 348, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, 2θ_{max} = 55.0º, 19534 reflections collected, 3441 unique (R_{int} = 0.0431). Final *GooF* = 1.041, *R1* = 0.0357, *wR2* = 0.0871, *R* indices based on 2977 reflections with $I>2\sigma(I)$ (refinement on F^2), 193 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.312 mm^{-1}.

[K$_4$(μ_4-H$_2$O)$_2$(μ-1)$_4$](PF$_6$)$_4$ (10). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.1318 g, 0.548 mmol) was added to KPF_6 (0.1007 g, 0.547 mmol) dissolved in acetonitrile (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.20 g, 0.115 mmol, 21%). Analysis calc. for $K_4P_4F_{24}C_{48}H_{84}N_8O_{14}$: C 38.19, H 5.61, N 7.42%, found C 38.11, H 5.62, N 7.51%; IR (υ/ cm^{-1}): 1666 (C=O), 1121 (C-O, ether). Crystal data for $C_{48}H_{84}F_{24}K_4N_8O_{14}P_4$: M = 1733.51 g mol^{-1}, colourless block, 0.941 x 0.6432 x 0.3017 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 28.4413(11) Å, b = 12.8337(3) Å, c = 23.8944(8) Å, α = 90˚, β = 120.757(5)˚, γ = 90˚, V = 7494.9(4) Å^3, Z = 4, D_c = 1.536 g cm^{-3}, $F000$ = 3568, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, 2θ_{max} = 55.0º, 57703 reflections collected, 8606 unique (R_{int} = 0.0386). Final *GooF* = 1.046, *R1* = 0.0677, *wR2* = 0.1611, *R* indices based on 7330 reflections with $I>2\sigma(I)$ (refinement on F^2), 561 parameters, 0 restraints. Lp and absorption corrections applied, μ= 0.443 mm^{-1}. The pyrrolidone rings of one ligand are disordered across two positions, occupancy refined to approximately 50%.

A second polymorph was obtained as follows: 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.050 g, 0.208 mmol) was added to KPF_6 (0.038 g, 0.206 mmol) dissolved in methanol (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.04 g, 0.231 mmol, 11%). Analysis calc. for $C_{48}H_{84}F_{24}K_4N_8O_{14}P_4$: C 33.26, H 4.89, N 6.46%, found: C 33.37, H 4.71, N 6.61%; IR (υ/ cm^{-1}): 1666

(C=O), 1122 (C-O, ether). Crystal data for $C_{48}H_{84}F_{24}K_4N_8O_{14}P_4$: M = 1733.49 g mol^{-1}, colourless prism, 0.6726 × 0.1765 × 0.0362 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 41.2572(13) Å, b = 12.8318(4) Å, c = 45.5789(17) Å, α = 90˚, β = 111.458(4)˚, γ = 90 º, V = 22457.2(13) Å^3, Z = 12, D_c = 1.538 g cm^{-3}, F_{000} = 10704, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, $2\theta_{max}$ = 55.0º, 118863 reflections collected, 25414 unique (R_{int} = 0.2077). Final *GooF* = 0.998, *R1* = 0.0973, *wR2* = 0.2059, *R* indices based on 10209 reflections with $I>2\sigma(I)$ (refinement on F^2), 1387 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.443 mm^{-1}.

Protonation (1·HPF$_6$). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.1580 g, 0.657 mmol) was added to $LiPF_6$ (0.0998 g, 0.657 mmol) dissolved in methanol (2 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.03 g, 0.078 mmol, 12%). Analysis calc. for $C_{12}H_{21}N_2O_3PF_6$: C 37.31, H 5.48, N 7.25%, found: C 37.12, H 5.25, N 7.12%; IR (υ/ cm^{-1}): 1642 (C=O), 1116 (C-O, ether). Crystal data for $C_{12}H_{21}N_2O_3PF_6$: M = 386.28 g mol^{-1}, colourless block, 0.6976 × 0.1279 × 0.1267 mm^3, orthorhombic, space group *Pbca* (No. 61), a = 11.6287(6) Å, b = 13.8824(7) Å, c = 20.0682(10) Å, α = 90˚, β = 90˚, γ = 90º, V = 3239.7(3) Å^3, Z = 8, D_c = 1.584 g cm^{-3}, F_{000} = 1600, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, $2\theta_{max}$ = 55.0º, 30797 reflections collected, 3708 unique (R_{int} = 0.1202). Final *GooF* = 1.060, *R1* = 0.0618, *wR2* = 0.1604, *R* indices based on 2595 reflections with $I>2\sigma(I)$ (refinement on F^2), 221 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.249 mm^{-1}.

{[ZnCl$_2$(μ-1)]}$_n$ (11). 1-{2-[2-(2-oxo-pyrrolid-1-yl)-ethoxy]-ethyl}-pyrrolid-2-one (0.1823 g, 0.786 mmol) was added to $ZnCl_2$ (0.0517 g, 0.379 mmol) dissolved in acetone (2 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.0951 g, 0.253 mmol, 67%). Analysis calc. for $C_{12}H_{20}N_2O_3ZnCl_2$: C 38.27, H 5.35, N 7.44%, found: C 38.25, H 5.26, N 7.47%; IR (υ/ cm^{-1}): 1611 (C=O), 1128 (C-O, ether). Crystal data for $C_{12}H_{20}N_2O_3ZnCl_2$: M = 376.57 g mol^{-1}, colourless plate, 0.4654 × 0.197 × 0.0541 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 11.3180(6) Å, b = 8.6628(3) Å, c = 16.7004(9) Å, α = 90˚, β = 107.888(6)˚, γ = 90º ,V = 1558.26(13) Å^3, Z = 4, D_c = 1.605 g cm^{-3}, F_{000} = 776, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, $2\theta_{max}$ = 55.0º, 15272 reflections collected, 3543 unique (R_{int} = 0.0560). Final *GooF* = 1.042, *R1* = 0.0370, *wR2* = 0.0712, *R* indices based on 2795 reflections with $I>2\sigma(I)$ (refinement on F^2), 181 parameters, 0 restraints. Lp and absorption corrections applied, μ = 1.926 mm^{-1}.

{[Na$_2$(μ-2)$_3$](PF$_6$)$_2$}$_n$ (12). 1,3-Bis(pyrrolid-2-on-1-yl)butane[15] (0.2672 g, 1.191 mmol) was added to $NaPF_6$ (0.1041 g, 0.6198 mmol) dissolved in methanol (1 mL). The resulting mixture was sonicated for 1 minute. Colourless crystals formed upon evaporation of the solvent at room temperature (Yield = 0.2744 g, 0.544 mmol, 88%). Analysis calc. for $C_{18}H_{30}N_3O_3NaPF_6$: C 42.86, H 5.99, N 8.33%, found: C 42.88, H 6.09, N 8.37%; IR (υ/ cm^{-1}): 1645 (C=O). Crystal data for $C_{18}H_{30}N_3O_3NaPF_6$: M = 504.41 g mol^{-1}, colourless plate, 0.2116 × 0.1894 × 0.09 mm^3, trigonal, space group $P3_1c$ (No. 159), a = 23.9245(6) Å, b = 23.9245(6) Å, c = 13.3123(4) Å, α = 90˚, β = 90˚, γ = 120º, V = 6598.9(3) Å^3, Z = 12, D_c = 1.523 g cm^{-3}, F_{000} = 3156, Xcalibur, Sapphire3, Gemini ultra, Mo Kα radiation, λ = 0.7107 Å, T = 120 K, $2\theta_{max}$ = 55.0º, 104425 reflections collected, 10093 unique (R_{int} = 0.2215). Final *GooF* = 1.079, *R1* = 0.1126, *wR2* = 0.2853, *R* indices based on 5779 reflections with $I>2\sigma(I)$ (refinement on F^2), 574 parameters, 7 restraints. Lp and absorption corrections applied, μ = 0.221 mm^{-1}. The poor residuals arise from twinning of the overlap of numerous plate-shaped crystals. While the precision is poor the gross structural details are unequivocal.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full IR spectral data and additional data on zinc complexation of ligand **1**. Crystallographic data has been depositied in the Cambridge Crystallographic Data Centre CCDC 965875–965885. See DOI: 10.1039/b000000x/

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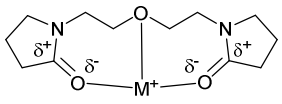
Graphical Abstract



The highly polar nature of lactam carbonyl groups makes them potent chelators of alkali metal ions as part of a flexible podand ligand.