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Modulating the Hydration Behaviour of Calcium Chloride by Lactam Complexation

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Complexation of calcium chloride with bis(lactam) ligand **L1** allows the formation of both an unstable anhydrous complex, an aqua complex $\{[Ca_2(\mu\text{-}\textbf{L1})_2(H_2O)_9]Cl_4]\}_n$ (**1**) and a related hydrate incorporating additional lattice water of crystallization $\{[Ca(\mu\text{-}\textbf{L1})(H_2O)_5]Cl_2 \cdot H_2O\}_n$ (**2**). Related mono(lactam) **L2** does not form aqua complexes but the anhydrous complex $\{[CaCl_2(\mu\text{-}\textbf{L2})_2]\}_n$ (**3**), is highly deliquescent. An unusual ethanol solvate is also reported $\{[CaCl_2(\textbf{L2})(EtOH)]\}_n$ (**4**).

Introduction

Calcium chloride (CaCl$_2$) is hygroscopic and reacts exothermically with water; a property exploited by the cement industry in accelerating the drying process.[1] This hydrophilicity may be attributed to the 'hard' oxophilic nature of the Ca^{2+} cation and its tendency towards high coordination number.[2] Addition of CaCl$_2$ at a 1-2 weight% dosage is known to significantly reduce cement setting time, and as such the metal salt has become one of the most widely used accelerators.[3-5] However, the performance of calcium chloride within dry mortar systems is limited as a result of its hygroscopicity.[6] In addition, the deliquescent nature of this material causes handling issues. Complexation of calcium chloride with suitable ligand systems may prolong the hydration process or bring about fine control and improved handling characteristics and thereby enhance performance. Suitable ligands for this purpose should form stable anhydrous coordination complexes with CaCl$_2$ with maximum water uptake potential that hydrate exothermically at a controlled rate.

We hypothesise that complexation of the hygroscopic metal salt with oxophilic lactam ligands may delay water uptake and hence prolong the activity of the species. The high polarity of the lactam amide carbonyl functionality enables complexation of a range of oxophilic metal ions such as alkali metals.[7] Englert and coworkers have analysed the calcium chloride complexes reported in the Cambridge Structural Database (CSD) and found a high proportion of Ca-O contacts in 6-coordinate complexes, and therein provided additional support for the oxophilic nature of the metal centre.[8]

Reports of calcium coordination complexes with DMF[9] and N-methylacetamide[10, 11] ligands provide support for the suitability of amide containing ligands for complexation and stabilisation of calcium chloride. Interestingly, the DMF-CaCl$_2$ complex contains two ligand molecules and two water molecules in the metal coordination sphere, highlighting the propensity of the metal salt for binding water despite the inert atmosphere used for the reaction.[9] There are, however, very few cyclic lactam complexes of calcium chloride. Of most relevance to this work is the calcium chloride complex with ε-caprolactam, reported by Khrustalev in 2003.[12] The structure of the complex contains octahedral calcium with chloride ligands bound to the metal centre, in addition to two bound water molecules. The polarity of the amide moiety within caprolactam is illustrated by the short carbonyl-calcium bond distances (2.25 Å) in contrast to the calcium-oxygen distances to the aqua ligand (2.34 Å).

We now report our initial investigations into the generation of slowly hydrating forms of calcium chloride stabilised by lactam ligands **L1** and **L2**.[13]
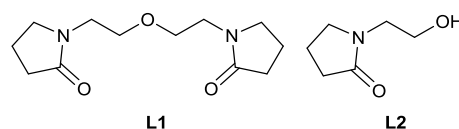
Results and Discussion

Reaction of ligand **L1** with anhydrous CaCl$_2$ in a 1:1 ratio, in ethanol, results in the crystallization of two coordination complexes following solvent evaporation at room temperature over 2-4 days. The X-ray crystal structures of both complexes were determined, showing them to be an aqua complex with a 1D coordination polymer structure $\{[Ca_2(\mu\text{-}\textbf{L1})_2(H_2O)_9]Cl_4]\}_n$ (**1**) and a related hydrated coordination polymer incorporating

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additional lattice water of crystallization {[Ca(μ-**L1**)(H$_2$O)$_5$]Cl$_2$·H$_2$O}$_n$ (**2**). Both complexes form under similar conditions from a stoichiometric mixture but were not found to form concomitantly. In repeated experiments, crystals of complex **2** were isolated more frequently than complex **1** with evaporation rate being the only apparent difference in conditions determining which material is obtained. Like calcium chloride itself, both coordination complexes are hygroscopic, with prolonged absorption of atmospheric moisture resulting in their transformation to an oily residue and samples for detailed further study were stored under a nitrogen atmosphere.

The asymmetric unit of complex **1** contains two ligand molecules bound to two different calcium centres by the carbonyl oxygen atoms (Figure 1). The ether oxygen atoms of both ligands do not coordinate to the Ca^{2+} centres but instead the metal coordination sphere is completed by bound water molecules, illustrating the hygroscopicity of these species. This structure is in contrast to the alkali metal complexes of **L1** in which the ether oxygen atoms chelate the metal centres.[7] The pentagonal bipyramidal Ca(1) ion binds two oxygen atoms from ligand molecules in addition to five bound water molecules, giving an overall coordination number of seven. The geometry at the metal centre is slightly distorted in the axial direction with a O(1)-Ca(1)-O(6) angle of 171.98(7)^o. In contrast, Ca(2) adopts a distorted octahedral geometry, binding two ligand oxygen atoms in addition to four water molecules. The carbonyl oxygen-metal bond distances are shorter for Ca(2) than Ca(1) at 2.2977(17) Å and 2.2962(18) Å compared to 2.3129(18) Å and 2.3134(18) Å for the seven coordinate ion. The carbonyl oxygen-calcium bond distances are considerably shorter than the calcium-aqua bond distances as a result of the high polarity of the amide moiety. The key difference between the 5-coordinate Ca(1) and four coordinate Ca(2) is that in the latter one of the bound water molecules engages in an intramolecular hydrogen bond to the ether oxygen atom of the ligand **L1** O6(s)···O2 2.84 Å. This interaction is absent in the coordination sphere of Ca(1). The chloride anions are not coordinated to the metal ions and bind *via* hydrogen bonding interactions with coordinated water molecules, with an average Cl···O distance of 3.18 Å.

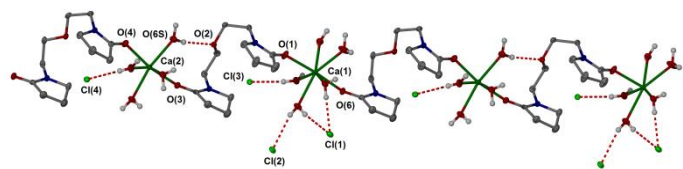Figure 1. X-ray structure of {[Ca$_2$(μ-**L1**)$_2$(H$_2$O)$_9$]Cl$_4$}$_n$ (**1**). CH hydrogen atoms omitted for clarity. Selected bond lengths (Å): Ca(1)-O(1) 2.3138(14), Ca(1)-O(1S) 2.4217(18), Ca(1)-O(2s) 2.4355(16), Ca(1)-O(3s) 2.4121(15), Ca(1)-O(4s) 2.4408(17), Ca(1)-O(5s) 2.4503(16), Ca(1)-O(6) 2.3122(14), Ca(2)-O(3) 2.2964(14), Ca(2)-O(4) 2.2957(15), Ca(2)-O(6s) 3.3288(16), Ca(2)-O(7s) 2.3433(16), Ca(2)-O(8s) 2.3601(16), Ca(2)-O(9s) 2.3601(16). Hydrogen bond: O(6s)···O2 2.854(2).

Like **1**, hydrated complex **2** comprises a one dimensional coordination polymeric chain of calcium ions linked by bridging ligand **L1** bound to the metal centres by the carbonyl oxygen

atoms. A section of the polymer chain is shown in Figure 2. The metal-carbonyl bond distances are longer than those in complex **1** (Ca(1)-O(1) 2.3530(14) Å and Ca(1)-O(3) 2.3222(15) Å), and again are considerably shorter than the calcium-aqua distances. The single unique metal centre adopts a seven coordinate distorted pentagonal bipyramidal geometry, binding five water molecules in addition to the carbonyl oxygen atoms from two different lactam ligands in a similar way to Ca(1) in **1.** Also like Ca(1) in **1** it lacks intramolecular hydrogen bonding to the ether oxygen atom. Instead there is a longer intermolecular OH···O interaction from coordinated water; O(2s)···O(2) 2.94 Å. A further non-coordinated water molecule is held in the lattice *via* hydrogen bonding interactions to aqua ligand O(5s), with an O···O distance of 2.741(2) Å and interacts with a chloride anion.

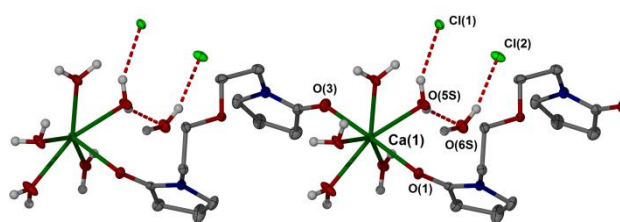Figure 2. X-ray structure of {[Ca(μ-**L1**)(H$_2$O)$_5$]Cl$_2$·H$_2$O}$_n$ (**2**). CH hydrogen atoms omitted for clarity. Selected bond distances (Å): Ca(1)-O(1) 2.3530(14), Ca(1)-O(3) 2.3222(15), Ca(1)-O(5s) 2.4237(15), Ca(1)-O(1s) 2.3888(15), Ca(1)-O(2s) 2.4444(15), Ca(1)-O(3s) 2.4111(16) and Ca(1)-O(4s) 2.4148(15).

The X-ray crystal structures show that lactam **L1** binds readily to Ca^{2+}, and demonstrates that the calcium centres retain the ability to bind water despite the coordination of the ligand. These products represent likely end products of the hydrolysis of a putative anhydrous "CaCl$_2$·**L1**" precursor and suggest that such an anhydrous complex may indeed have application in cement drying. We therefore sought to prepare an anhydrous complex of CaCl$_2$ and ligand **L1** with the potential to hydrate exothermically in a controlled fashion in order to produce products such as **1** and **2**.

Thermogravimetric analysis (TGA) confirms that dehydration of complex **1** occurs upon heating between 68 – 190 ^{o}C, as shown in Figure 3. There is an initial weight loss of 1.4% upon heating to 68 ^{o}C thought to arise from the loss of surface water, present as a result of the hygroscopicity of the complex. The main mass loss of 19 % occurs upon heating between 68 – 190 ^{o}C, corresponding to the loss of all nine water molecules in a two-stage process (calculated 18.75 %). Stage one (68 – 130 ^{o}C) corresponds to the loss of 1.5 water molecules, while stage two (130 – 190 ^{o}C) results in loss of the remaining 7.5 water molecules. The reasonably high temperature required for removal of the 9 water molecules confirms complexation to the metal centre; surface and lattice water would be likely to be removed at lower temperatures. Subsequent mass loss beyond 225 ^{o}C is assigned to decomposition. Hence there is a temperature window between 190 and 225 ^{o}C in which the complex is stable in a dehydrated state. Careful heating of the sample to within this temperature range may enable isolation of the desired anhydrous complex (*vide infra*).
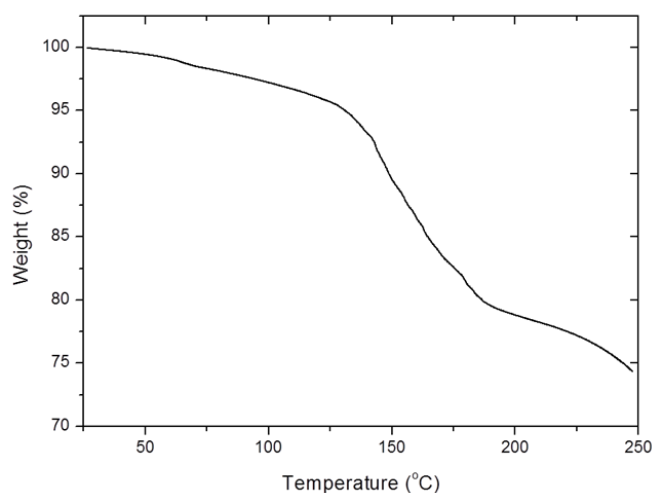
Figure 3. Thermogravimetric trace for $\{[Ca_2(\textbf{L1})_2(H_2O)_9]Cl_4\}_n$ (**1**). 19 % weight loss when heating 68 – 190 °C, attributed to the nine bound water molecules.

Similarly, TGA of complex **2** shows a three-step mass loss profile (supplementary information Figure S1). An initial mass loss of 3.94 % upon heating to 111 °C is thought to arise from the loss of the unbound lattice water molecule (calculated 3.92 %). This is followed by a further mass loss of 19.18 % upon heating to 197 °C, attributed to the removal of the five metal bound water molecules (calculated 19.61 %). Further mass loss upon heating above 225 °C is thought to be a consequence of decomposition. The high temperatures required for dehydration shows the strong interactions between the water molecules and calcium ion. In both complexes **1** and **2** heating to approximately 200 °C is associated with complete dehydration and may enable isolation of the desired anhydrous calcium coordination complex.

While solution crystallization from ethanol enables the isolation of hydrated material in the form of single crystals suitable for analysis, the recovered product yields are reasonably low (40 – 70%) and solvent mediated synthesis is not economically desirable. Solvent-free grinding of the two reactants (ligand **L1** and CaCl₂) offers many advantages to conventional solution-phase processes for the synthesis of coordination complexes, most notably potentially higher yields, increased reaction efficiency and the elimination of organic solvent waste.[14] In addition, the solventless approach eliminates the presence of excess solvent water and may enable the direct synthesis of an anhydrous complex. Mechanically mixing a stoichiometric ratio of ligand **L1** and anhydrous CaCl₂, in a pestle and mortar for 5 minutes, results in the immediate formation of a tacky material, which upon oven-drying at 100 °C forms a cream crystalline powder.

The solid-state IR spectrum of the mechanically prepared powder confirms complexation of ligand **L1**, identified by a shift in the C=O stretching mode to 1648 cm⁻¹ from 1674 cm⁻¹ in the uncomplexed ligand.[7] This wavenumber is very similar to those observed in complexes **1** and **2** and confirms complexation. In addition, the IR spectrum for the mechanochemically prepared powder also contains a broad O-H stretch (3000 – 3500 cm⁻¹) suggesting that the complex is

hydrated even after drying. X-ray powder diffraction establishes that the mechanochemically prepared material is in fact a mixture of **1** and **2**. It fully converts to the hydrated **2** upon exposure to atmosphere over a period of two weeks (Figure 4).
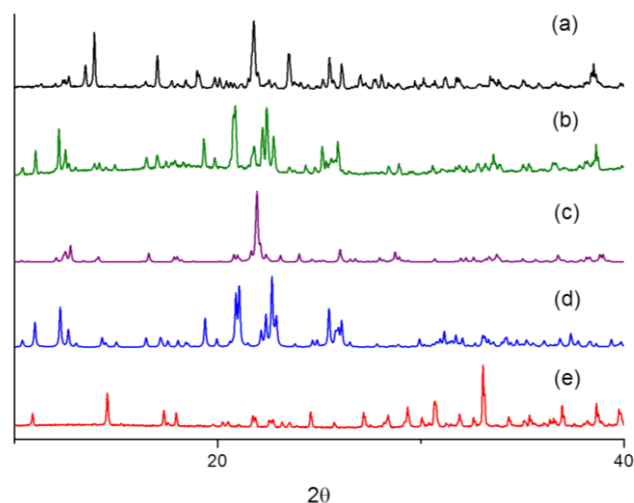

Figure 4. XRPD patterns for (a) mechanochemically prepared mixture of **1** and **2** (dried at 110 °C followed by cooling and exposure to atmospheric moisture); (b) mechanochemically prepared sample after two weeks under ambient conditions (sealed vial) showing transformation to **2**; (c) calculated XRPD pattern for **1**; (d) calculated XRPD pattern for **2**; and (e) anhydrous CaCl₂

A sample of the mechanochemically prepared powder was dried in an oven at 70 °C for 3 hours and then analysed by TGA. The TGA thermogram (supplementary information Figure S2), confirms a weight loss of 12.87 % upon heating from room temperature to 170 °C, with TGA-MS confirming loss of water. The lower temperature required for complete dehydration of this sample is likely to be a result of the finely powdered nature of the material enabling more efficient heat transfer, as opposed to the block crystals of **1** and **2**.

While the TGA thermogram indicates full sample dehydration upon heating to 170 °C, visual monitoring the sample reveals a transition to an orange oil upon heating in air above 130 °C. Therefore, the mechanochemically prepared material was heated at the lower temperature of 110 °C for a prolonged period of 36 hours to isolate the dehydrated complex. IR spectroscopy was used to monitor the hydration state of the mechanically prepared sample prior to, and during, the drying process. Figure 5a shows the IR spectrum of the material immediately following synthesis; sample hydration is evident in the occurrence of an O-H stretching band occurring between 3200 and 3400 cm⁻¹. Figure 5b shows the IR spectrum recorded immediately after heating of the sample at 110 °C for 36 hours; disappearance of the broad O-H band confirms dehydration and indicates formation of the desired anhydrous complex CaCl₂·**L1**. During the heating process the powdered material becomes a viscous oil, which then transforms back to a solid upon cooling to room temperature. The material rehydrates over a period of an hour when exposed to the atmosphere, observed by the reappearance of the O-H band in the IR spectrum. The

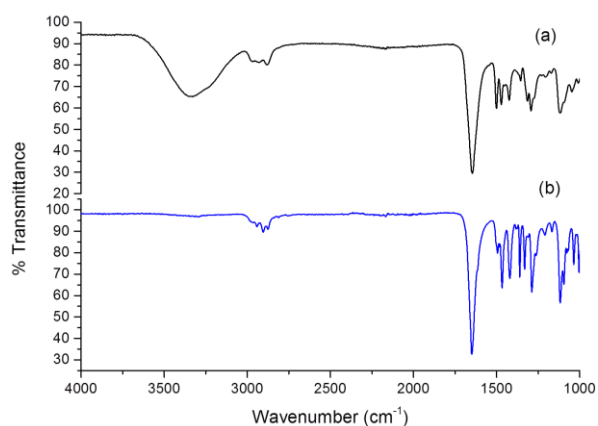anhydrous material rehydrates too readily to allow collection of XRPD data.

Figure 5. IR spectra of mechanochemically prepared "CaCl$_2$·L1" (a) immediately following synthesis and (b) after heating at 110 °C for 36 hours.

Figure 6 shows a series of photomicrographs charting the absorption of atmospheric moisture by the dried mechanochemically prepared sample in comparison to anhydrous CaCl$_2$, highlighting the hygroscopicity of both of these species. Both samples were held in the oven at 110 °C for 36 hours prior to imaging. Images were recorded over a 90 minute period following removal from the oven and exposure to ambient lab conditions at 22 °C. Figure 6(a-d) shows hydration of the CaCl$_2$·L1 complex, with some deliquescence. For comparison, Figure 6(e-h) shows the deliquescence of anhydrous calcium chloride over the same time period. The pure calcium chloride is notably more deliquescent.
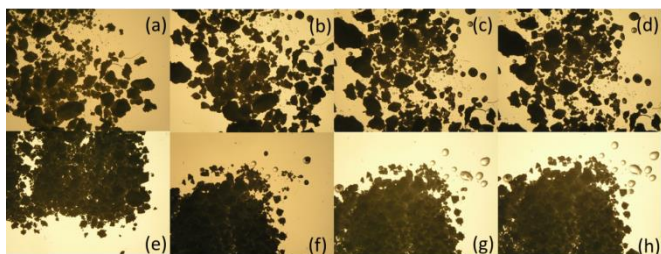

Figure 6. Time-lapse microscopy images showing mechanochemically prepared CaCl$_2$·L1 (a-d) and dried CaCl$_2$ (e-h) following removal from the oven (110 °C) after (a)(e) 0 minutes; (b)(f) 30 minutes; (c)(g) 60 minutes and (d)(h) 90 minutes.

Re-hydration of the dried mechanochemically prepared sample was monitored over a period of 4 days exposure to ambient lab conditions, during which time the mass of the powder increased to 137.5% of the original. In contrast, the mass of CaCl$_2$ increased to 287.5% of the original mass, corresponding to eleven water molecules per CaCl$_2$ confirming the less hygroscopic nature of the L1 complex, although this mass gain corresponds to a similar number of water molecules per Ca^{2+} centre.

The CaCl$_2$ coordination chemistry of hydroxyethylpyrrolidinone (L2) was also investigated in the hope that the reduced ligand size and presence of a hydrogen bond donor OH group may enable greater access to the metal

centre and hence allow for improved water uptake while reducing deliquescence in comparison to the bulky ligand L1 complexes. Reaction of L2 and CaCl$_2$, in a 1:1 ratio in ethanol, results in the crystallization of an anhydrous 1D coordination polymer, namely {[CaCl$_2$(μ-L2)$_2$]}$_n$ (3), and an ethanol solvate {[CaCl$_2$(L2)(EtOH)]}$_n$ (4). Complex 3 comprises a one–dimensional coordination polymeric chain of calcium ions situationed on a crystallographic twofold axis linked by bridging ligand L2 bound to the metal centres *via* both the lactam carbonyl and the alcohol functionalities, Figure 7. Unlike complexes 1 and 2, the chloride anions are bound to the metal centres and hydration does not occur. The chloride anions undergo hydrogen bonding interactions with the alcohol groups on the ligands, with an O(1)···Cl(1) distance of 3.1198(9) Å (DĤA 167(1) °). The metal centre is held in a distorted octahedral geometry, with a Cl(1)-Ca(1)-Cl(1) angle of 101.94(2)°. In contrast, the angle subtended at the metal centre between the alcohol groups of two ligand molecules (O(1)-Ca(1)-O(1)) is relatively low, 81.53(4)°. As expected given the polarity of the lactam group, the carbonyl-calcium bond distance is considerably shorter than the alcohol-calcium bond distance, with distances of 2.2832(9) Å and 2.3957(9) Å, respectively. Ligand L2 is considerably shorter than bis(lactam) ligand L1, resulting in a significant reduction in the calcium-calcium distance (5.93 Å in 3 and 10.56 Å in 2).
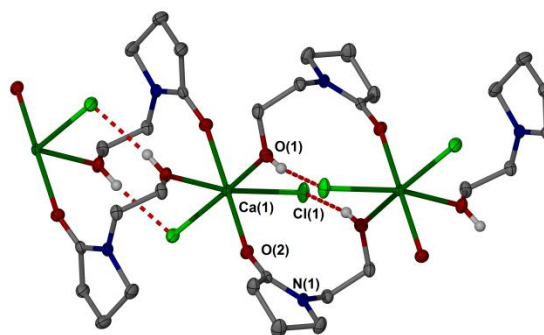

Figure 7. X-ray structure of {[CaCl$_2$(L2)$_2$]}$_n$ (3). Selected hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Ca(1)-O(1) 2.3957(9) and Ca(1)-O(2) 2.2832(9).

While it was not possible to isolate a hydrated calcium chloride complex of ligand L2, the formation of the ethanol solvate (4) is encouraging as this shows that the calcium centre retains the ability to bind solvent and hence may be expected to coordinate to water, and indeed 3 is hygroscopic. The asymmetric unit of complex 4 contains two distinct calcium environments with chloride ligands bridging the metal centres, as seen in Figure 8. One calcium centre (Ca(1)) possesses three bridging chloride atoms in addition to a terminal chloride (Cl(1)). The terminal chloride ligand hydrogen bonds to the ethanol molecule (Cl(1)···O(5) distance 3.053(3) Å) in addition to the hydroxyl moiety of L2 (Cl(1)···O(2) distance 3.099(3) Å).
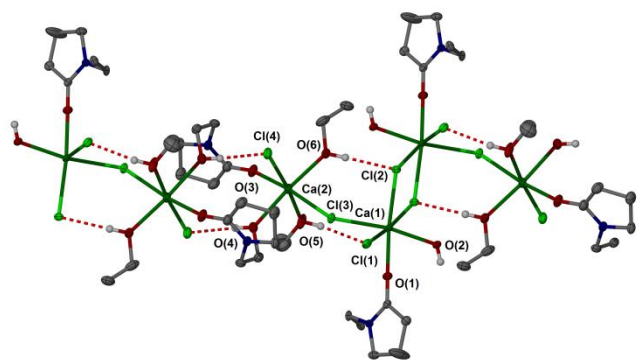
Figure 8. X-ray structure of {[CaCl₂(μ-**L2**)(EtOH)]}ₙ (**4**). Selected hydrogen atoms omitted for clarity. Selected bond distances (Å): Ca(1)-O(1) 2.273(3), Ca(1)-O(2) 2.351(3), Ca(2)-O(3) 2.293(3), Ca(2)-O(4) 2.351(3), Ca(2)-O(5) 2.363(3) and Ca(2)-O(6) 2.381(2).

The carbonyl oxygen to metal bond distances are significantly shorter than the hydroxyl oxygen–calcium distances in a similar way to **3**, with Ca(1)-O(1) 2.273(3) Å and Ca(2)-O(3) 2.293(3) Å, in contrast to Ca(1)-O(2) 2.350(3) Å and Ca(2)-O(4) 2.351(3) Å. The second calcium centre (Ca(2)) binds to two different molecules of ligand **L2**, one *via* the hydroxyl moiety (O(4)) and the other by the carbonyl group (O(3)), in addition to binding two ethanol molecules. The TGA thermogram indicates that loss of the bound ethanol does not occur in a single process, and a steady mass loss is observed on heating from room temperature to 230 ^{o}C (see supplementary information, Figure S3).

Solvent-free grinding of a stoichiometric mixture of ligand **L2** and CaCl₂ results in the formation of a cream powder. However this material is highly deliquescent and XRPD data could not be obtained. The solid-state IR spectrum for the mechanochemically prepared sample is in agreement with that for complex **3** (see supplementary information, Figure S4). The absence of the ethanol or water O-H stretch in the spectra for complex **3** and in the mechanochemical powder is consistent with the anhydrous nature of these complexes. The observed sharp band between 3200 – 3400 cm^{-1} is assigned to the O-H stretch of the alcohol functionality of the ligand. The O-H region is more complicated for complex **4** due to the O-H stretching mode of the ethanol ligand.

A sample of the mechanochemically prepared **3** was dried in the oven at 110 ^{o}C for 36 hours, and the IR spectrum quickly recorded on the hot material (see supplementary information Figure S5). The sample was then removed from the oven and allowed to return to room temperature in an open vial. IR spectra were recorded at intervals over a period of 1 hour. A broad O-H stretch (3200 – 3600 cm^{-1}) increases in intensity during this time period, indicating the absorption of atmospheric moisture. Sample deliquescence is observable as a transition from crystalline material to a liquid as shown in the time-lapsed images in Figure 9, with (a) showing the sample taken straight from the oven as a powder, to the mostly liquid sample (h) taken 2 hours later.
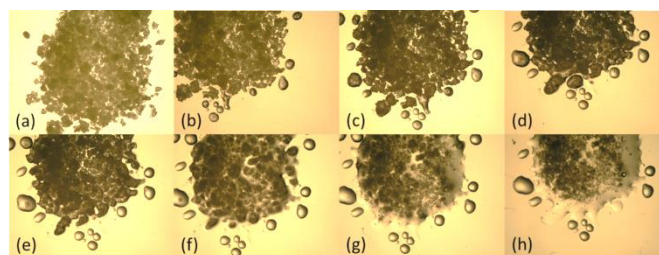

Figure 9. Time-lapse photographs following removal of the mechanochemically prepared complex of CaCl₂ and ligand **L2** from the oven at the following times (minutes): (a) 0; (b) 10; (c) 20; (d) 30; (e) 45; (f) 60; (g) 90 and (h) 120.

Conclusions

The high basicity of the pyrrolidinone carbonyl moiety enables effective calcium binding for both ligands **L1** and **L2**. X-ray crystal structures of metal complexes with the bis(pyrrolidinone) ether ligand are hydrated, whilst those containing ligand **L2** are anhydrous. The ease of synthesis of the complexes has been proven through simple mechanical grinding of reactants, enabling product preparation in a quantitative yield. Thorough drying at 110 ^{o}C allows the preparation of anhydrous CaCl₂(**L1**) which rehydrates to aqua complex **1** over a period of minutes-to-hours and ultimately to pure hydrate **2** after two weeks. The mono(pyrrolidinone) complexes based on **L2** proved less stable to hydration and their deliquescence made them quite difficult to handle without their forming a well-defined aqua complex or hydrate phase. In terms of industrial applicability complexation of CaCl₂ with **L1** retards the degree of hydration and offers a transition from a well-defined anhydrous to hydrated form. In the present system the anhydrous complex is too unstable for practical utility and the **L1** complexes are less efficient that CaCl₂ itself on a mass basis because of the additional presence of the ligand. However the work demonstrates the practicality of the general concept of a controlled transition from an anhydrous to hydrated CaCl₂ complex.

Experimental

General

1-{2-[2-(2-oxo-pyrrolidin-1-yl)-ethoxy]-ethyl}-pyrrolidin-2-one (**L1**) and 1-(2-hydroxyethyl)-2-pyrrolidinone (**L2**) were supplied by Ashland Inc. and used without further purification.[13] All other solvents and reagents were obtained from standard commercial sources and used without further purification. IR spectra were measured with a Perkin-Elmer 100 FT-IR spectrometer, using an ATR attachment. Thermogravimetric analysis was conducted using a Perkin Elmer Pyris 1 TGA with purge gas specified at 40 mL per minute. TGA temperature was increased at 10 ^{o}C per minute up to the temperature specified. 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 120 K on an Agilent Gemini S-Ultra diffractometer equipped with the Cryostream (Oxford

Cryosystems) open-flow nitrogen cryostats, using graphite monochromated MoKα-radiation (λ = 0.71073 Å). All structures were solved using direct methods and refined by full-matrix least squares on F^2 for all data using SHELXL[15] and OLEX2[16] or X-Seed.[17] 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. Elemental analysis was performed using an Exeter Analytical inc. CE-400 Elemental Analyser. Powder diffraction was performed on glass slides using a Bruker AXS D8 Advance diffractometer, with a Lynxeye Soller PSD Detector, using CuKα radiation at a wavelength of 1.5406 Å.

Synthesis of coordination complexes

{[Ca$_2$(**L1**)$_2$(H$_2$O)$_9$]Cl$_4$}$_n$ **(1)**. 1-{2-[2-(2-oxo-pyrrolidin-1-yl)-ethoxy]-ethyl}-pyrrolidin-2-one (**L1**) (0.110 g, 0.459 mmol) was added to anhydrous calcium chloride (0.0461 g, 0.415 mmol) dissolved in ethanol (2 mL). The resulting mixture was sonicated for 1 minute and allowed to stand partially open to the atmosphere (crystals visible after 4 days). Colourless crystals formed upon slow evaporation of the solvent at room temperature (Yield = 0.143 g, 0.165 mmol, 40 %).
Analysis calc. for C$_{24}$H$_{58}$N$_4$O$_{15}$Ca$_2$Cl$_4$: C 33.33, H 6.77, N 6.48 %, found: C 33.45, H 6.81, N 6.52 %; IR (v/cm^{-1}): 1641 (C=O) and 1126 (C-O). Crystal data for C$_{24}$H$_{58}$N$_4$O$_{15}$Ca$_2$Cl$_4$: M = 864.70, 0.5267 x 0.2548 x 0.1614 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 8.9178(3) Å, b = 16.3074(7) Å, c = 16.3501(6) Å, α = 116.158(4)^o, β = 97.927(3)^o, γ = 99.693(4)^o, V = 2042.36(14) Å^3, Z = 2, D_c = 1.406 g/cm^3, F_{000} = 916, Mo Kα radiation, λ = 0.7107 Å, T = 120K, 2ϑmax = 52.0 ^{o}, 24682 reflections collected, 7994 unique (R_{int} = 0.0429). Final GooF = 1.014, R_1 = 0.0362, wR_2 = 0.0898, R indices based on 6303 reflections with I >2$\sigma(I)$ (refinement on F^2), 451 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.604 mm^{-1}.

{[Ca(**L1**)(H$_2$O)$_5$]Cl$_2$·H$_2$O}$_n$ **(2)**. 1-{2-[2-(2-oxo-pyrrolidin-1-yl)-ethoxy]-ethyl}-pyrrolidin-2-one (**L1**) (0.111 g, 0.46 mmol) was added to anhydrous calcium chloride (0.046 g, 0.414 mmol) dissolved in ethanol (2mL). The resulting mixture was sonicated for 1 minute. The vial was left loosely capped, and colourless crystals formed following slow evaporation of solvent at room temperature (visible after 2 days). (Yield = 0.139 g, 0.3015 mmol, 73 %). The crystals proved to absorb atmospheric moisture over time and elemental analysis on a fully dry material could not be obtained. Crystals were held *in vacuo* for 6 h at 100 ^{o}C resulting in a di-hydrated complex. Analysis calc. for C$_{12}$H$_{20}$N$_2$O$_3$CaCl$_2$·6H$_2$O: C 31.38, H 7.02, N 6.10%, re-calc for C$_{12}$H$_{20}$N$_2$O$_3$CaCl$_2$·2H$_2$O: C 37.21, H 6.25, N 7.23%, found: C 37.74, H 6.37, N 7.01%; IR (v/cm^{-1}) 1641 (C=O) and 1116 (C-O). Crystal data for C$_{12}$H$_{32}$N$_2$O$_9$CaCl$_2$: M = 459.38, colourless block, 0.4521 x 0.3035 x 0.1295 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 8.8007(5) Å, b = 8.9311(5) Å, c =

14.7500(8) Å, α = 99.325(5)^o, β = 95.103(4)^o, γ = 104.163(5)^o, V = 1099.18(11) Å^3, Z = 2, D_c = 1.388 g/cm^3, F_{000} = 488, Mo Kα radiation, λ = 0.7107 Å, T = 120K, 2θ_{max} = 54.0 ^{o}, 8493 reflections collected, 4306 unique (R_{int} = 0.0288). Final GooF = 1.053, $R1$ = 0.0360, w$R2$ = 0.0868, R indices based on 3745 reflections with I >2σ(I) (refinement on F^2), 243 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.571 mm^{-1}.

{[CaCl$_2$(μ-**L2**)$_2$]}$_n$ **(3)**. Anhydrous calcium chloride (0.086 g, 0.77 mmol) was dissolved in absolute ethanol and hydroxyethylpyrrolidinone (**L2**) (0.10 g, 0.77 mmol) was added. The reaction mixture was sonicated for 1 minute. The sample vial lid was left loosened and placed within an evacuated vacuum desiccator. Colourless crystals of the coordination complex were visible after 2 days (Yield = 0.20 g, 0.553 mmol, 72 %). The crystals proved to absorb atmospheric moisture over time and elemental analysis on a fully dry material could not be obtained. Analysis calc. for C$_{12}$H$_{22}$N$_2$O$_4$CaCl$_2$: C 39.03, H 6.00, N 7.59 %, re-calc for C$_{12}$H$_{26}$N$_2$O$_6$CaCl$_2$: C 35.56, H 6.47, N 6.91%, found C 35.50, H 6.75, N 6.86%; IR (v/cm^{-1}) 1649 (C=O). Crystal data for C$_{12}$H$_{22}$N$_2$O$_4$CaCl$_2$: M = 369.30 g mol^{-1}, colourless irregular, 0.4869 x 0.3517 x 0.3486 mm^3, monoclinic, space group C$_2$/c (No. 15), a =12.9663(3) Å, b = 11.8541(3) Å, c = 11.4866(3) Å, α = 90.00^o, β = 105.407(3)^o, γ = 90.00^o, V = 1702.08(7) Å^3, Z = 4, D_c = 1.441 g/cm^3, F_{000} = 776, MoKα radiation, λ = 0.71073 Å, T = 120K, 2ϑ_{max} = 52.0 ^{o}, 15388 reflections collected, 1675 unique (R_{int} = 0.0271). Final GooF = 1.080, $R1$ = 0.0218, w$R2$ = 0.0582, R indices based on 1603 reflections with I >2$\sigma(I)$ (refinement on F^2), 99 parameters, 3 restraints. Lp and absorption corrections applied, μ= 0.697 mm^{-1}.

{[CaCl$_2$(**L2**)·EtOH]}$_n$ **(4)**. Anhydrous calcium chloride (0.086 g, 0.77 mmol) was dissolved in absolute ethanol and hydoxyethylpyrrolidinone (**L2**) (0.1 g, 0.77 mmol) was added. The reaction mixture was sonicated for 1 minute to ensure thorough mixing. The sample vial was left open and placed within an evacuated vacuum desiccator. Colourless crystals of the coordination complex were visible after 2 days under a static vacuum (Yield = 0.1518 g, 0.133 mmol, 17.2 %). IR (v/cm^{-1}) 1655 (C=O). Crystal data for C$_{32}$H$_{64}$N$_4$O$_{12}$Ca$_4$Cl$_8$: M = 1140.79 g mol^{-1}, colourless trapezoid, 0.2903 x 0.2057 x 0.0683 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a =9.2400(6) Å, b = 9.9217(7) Å, c = 15.7248(10) Å, α = 72.942(6)^o, β = 89.180(5)^o, γ = 74.421(6)^o, V = 1324.28(16) Å^3, Z = 1, D_c = 1.430 g/cm^3, F_{000} = 596, MoKα radiation, λ = 0.71073 Å, T = 120K, 2ϑ_{max} = 52.0^o, 11341 reflections collected, 5215 unique (R_{int} = 0.0644). Final GooF = 0.979, $R1$ = 0.0512, w$R2$ = 0.0903, R indices based on 3562 reflections with I >2$\sigma(I)$ (refinement on F^2), 293 parameters, 6 restraints. Lp and absorption corrections applied, μ= 0.865 mm^{-1}.

Acknowledgements

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