Retention of Cs–Cl bond induces coordination polymer formation over trinuclear chiral assembly of copper(II) complexes of L-leucine derived ligand†

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The use of caesium is a less trodden path in terms of the synthesis of coordination polymers. The chemical similarity and mild toxic nature of caesium salts does not provide much impetus to work with these compounds compared to their potassium analogues. However, are the potassium and caesium salts really close in terms of coordination polymer formation? The result presented in this manuscript shows that while neither potassium halides or potassium nitrate inhibit the formation of a trinuclear chiral assembly of a copper(II) complex from a mononuclear Cu(II) complex, caesium chloride preferentially forms a coordination polymer while keeping the Cs–Cl bond intact. Under the same conditions, caesium nitrate does not inhibit the assembly formation. Structural characterization of [{[CsCl{Cu(HL\textsubscript{L-leu})\textsubscript{2}}(H\textsubscript{2}O)}\textsubscript{n}]\textsuperscript{2–} (2) showed it to be a two-dimensional coordination polymer in the ab plane, where penta-coordinated Cu(HL\textsubscript{L-leu})\textsubscript{2} complex units (HL\textsubscript{L-leu} = reduced Schiff base of L-leucine and the salicylaldehyde condensation product) were interconnected through the formation of Cu–Cl–Cs bonds. Multitudes of intermolecular H-bonds were observed as well. The use of KCl, KBr, KI or CsNO\textsubscript{3} in lieu of CsCl to the [Cu(HL\textsubscript{L-leu})\textsubscript{2}(CH\textsubscript{3}CN)] (1) facilitated the formation of the trinuclear assembly, [M{Cu(HL\textsubscript{L-leu})\textsubscript{2}}\textsubscript{3}]X, where M = K\textsuperscript{+} or Cs\textsuperscript{+} and X = Cl, Br, I or NO\textsubscript{3} depending on the salt used. The Cu(HL\textsubscript{L-leu})\textsubscript{2} units in these assemblies are hexacoordinated Cu(II) complexes.

Introduction

The synthesis of coordination polymers and related metal-organic frameworks is under intense scrutiny for their potential use in multiple areas.\textsuperscript{1} While both transition and non-transition metal ions, along with organic molecules acting as ligands, have found wide use in the syntheses of such architecturally beautiful ensembles of molecules, the use of alkali metal ions in such situations are relatively rare.\textsuperscript{2} Alkali metal ions, having a preference for hard oxygen donors and devoid of a crystal field stabilization energy, found more use in crown ethers and their related chemistry due to their biological implication.\textsuperscript{3} Among the alkali metal ions, the case of Cs\textsuperscript{+} is a bit different. It is mildly toxic, not as abundant as Na\textsuperscript{+} or K\textsuperscript{+} and of limited use in biology.\textsuperscript{4} Other than the difference in size (ionic radii: Cs\textsuperscript{+} 1.67 Å, K\textsuperscript{+} 1.38 Å, Na\textsuperscript{+} 0.99 Å), K\textsuperscript{+} can be used in place of Cs\textsuperscript{+} in a synthesis involving a coordination polymer, provided the ligand can supply a large enough number of oxygen donors. Thus, there is little impetus to pursue the use of Cs\textsuperscript{+} in the synthesis of coordination polymers and the literature is limited.\textsuperscript{1a,b,d}

By pursuing chiral recognition using multinuclear molecular assemblies formed using amino acid derived ligands (figure below) and transition metal ions, we found that these ligands support the binding of alkali metal ions rather frequently.\textsuperscript{5} Earlier, we reported the formation of an H-bond stabilized trinuclear assembly of three units of Cu(HL\textsubscript{L-leu})\textsubscript{2} or Ni(HL\textsubscript{L-leu})\textsubscript{2} complexes in the presence of Na\textsuperscript{+} or K\textsuperscript{+}, where the complexes encapsulated an alkali metal ion like a cryptand.\textsuperscript{5a} In order to test the resiliency of the assembly in accommodating a larger central ion, we decided to experiment with Cs\textsuperscript{+} salts. Other than the size, differences between the salts of K\textsuperscript{+} and Cs\textsuperscript{+} were not anticipated. However, to our surprise, we found that unlike K\textsuperscript{+} salts, the use of CsCl severely affected the assembly formation. The results showing the formation of a coordination polymer only in the case of CsCl have been presented in this work.

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Results & discussion

Coordination polymer with CsCl

The simple addition of CsCl to a methanolic solution of the mononuclear copper(II) complex, [Cu(HL-leu)2(CH3CN)] (1), yielded plate-like crystals of the coordination polymer \([\text{[CsCl[Cu(HL-leu)2](H2O)]} \] (2) (Scheme 1). The crystals were of reasonable quality and stability for X-ray data collection and analysis. Complex 2 crystallizes in the space group \(P_{1} \) with one independent asymmetric \([\text{[CsCl[Cu(HL-leu)2](H2O)]}} \) unit per unit cell. This complex is a two-dimensional coordination polymer in the \(ab\) plane where individual \([\text{Cu(HL-leu)2}} \) complex units are connected through CsCl. The Cs(i) is bonded to eleven atoms with bonding distances between 3.18 to 3.72 Å (Fig. 1). These include chloride, two oxygens of one bidentate carboxylate, two oxygens from two carboxylates which are already bound to \(\text{Cu}^{(II)}\), two phenolate oxygens and two water molecules.

The water molecules form bridges between the caesium atoms (Scheme 1). Comparatively, chloride forms only a single bridge between Cs(i) and Cu(II) at an angle of 91.35°. We cannot find any structural report on Cu(II)–Cl–Cs bridging but a Cu(II)–Cl–Cu(II) angle at 91.01(8)°, reported by Wang et al. for a dichloro bridged Cu(II) complex, is about the same as the present case.6

The Cs–Cl distance at 3.46 Å is slightly shorter than 3.55 Å, the combined total of the ionic radii of the individual atoms.7 The number of crystallographic reports where both Cs(i) and chloride is part of an organic or metal–organic network are few.8 Kim et al. reported the structure of a calix[4]-pyrrole containing a CsCl molecule inside the cavity of the

![ORTEP diagram of 2](image-url)
organic entity where the Cs–Cl distance was found to be 3.60 Å. In another example, caesium chloride 2-(N-morpholinio)ethanesulfonate, reported by Milic et al., had a Cs–Cl distance of 3.778 Å and was considered ionic in nature. On the other hand, in CsReCl₄, the Cs–Cl lengths varied from 3.29 to 3.89 Å.

The Cu(HL-leu)₂ units have a slightly distorted (τ = 0.176) square pyramidal geometry around the Cu(ii) atom [τ = (β − α)/60, with α and β being the two largest coordination angles]. The amount of distortion parameter τ is calculated from the structural data, where the value of τ should be 0.0 for perfect square-pyramidal geometry and 1.0 for a perfect trigonal bipyramidal (TBP) structure. The in-plane bond lengths for CuOcarboxylate are within the range of 1.92–1.95 Å, observed for other amino acid or amino acid derived Cu(ii) complexes. The in-plane bond length for CuNamine (Cu1N1) is longer at ~2.00 Å and the Cu1N2 bond length is shorter at 1.96 Å compared to corresponding amino acid complexes (1.96–1.98 Å).

Overall, the assembly is a two-dimensional coordination polymer where the Cs–Cl bond remained intact within the network.

Trinuclear assembly with CsNO₃

In contrast, the addition of CsNO₃ to the Cu(ii) monomeric complex yielded diamond-shaped blue crystals of [Cs(Cu(HL-leu)₂)₃]NO₃ (3). Due to the disordered nature of the structure, it could only be solved without the solvents or counter ion using the SQUEEZE command. The trinuclear core was anisotropically refined‡ with a refinement factor of 10.41% (wR all data, 28.83%). The solvents and some of the aliphatic carbons on the side arm of leucine could not be resolved or refined anisotropically. However, the formation of a trinuclear core identical to the Na⁺ and K⁺ analogues can be observed (Fig. 2a, b). The formation of a trinuclear core is also supported by ESI-mass spectra (Fig. 2c) and the powder diffraction pattern (Fig. S1, ESI†). The experimental isotopic
abundance pattern matches that of the calculated spectra for a trinuclear core (Fig. 2c). The presence of nitrate as a counter ion can be observed in the FTIR spectra (Experimental Section). The trinuclear core, consisting of three Cu(HL\textsubscript{L-leu})\textsubscript{3} units coordinating to a hexacoordinated Cs\textsuperscript{+} through carboxylate oxygen, is similar to a crown ether or cryptate complex. The structure is identical to the other trinuclear assemblies obtained with potassium halides (discussion below).

**Trinuclear assembly with potassium halides**

The addition of KCl, KBr or KI to 1 resulted in distinctive diamond shaped blue crystals similar to 3. The crystals of KCl (4) tend to desolvate faster than 3 and thus, the ESI-mass spectra were compared to prove the formation of the trinuclear assembly (Fig. 2c and d). Powder diffraction patterns (Fig. S2–S5, ESI†) and other characterization data also support the formulation (Experimental Section). The assemblies with KBr (5) diffracted better while the KI analogue (6) was good enough to show the trinuclear formation.‡ Both assemblies are solved in the space group C222\textsubscript{1} with nearly identical crystal parameters.‡ The molecular structures of the assemblies are almost identical to that of 3 (Fig. 2a and 3). The halide counter ion occupies the chiral pockets, formed by the amino acid side chains on the surface of the assembly (Fig. 3). The halide ion acts as a bridge between two neighboring trinuclear assemblies and is H-bonded to the N–H of the ligand. This is similar to the occupation of ClO\textsubscript{4}\textsuperscript{−} in our earlier report. ⁵æ The chirality of all the chiral carbons originating from the amino acid precursors retain their S configuration, while the tertiary amine N atoms have an R configuration after coordination to Cu(II). This opposing configuration on the coordinated amine of the ligand has been observed in all previously reported complexes with the amino acid derived ligands. ⁵æ

Unlike 2, the Cu(II) atoms in the Cu(HL\textsubscript{L-leu})\textsubscript{3} units are hexacoordinated (Fig. 2b). The axial positions are occupied with phenol groups from the ligands. The phenols also form H-bonds with neighboring carboxylate oxygens (Fig. 2b). A total of six such H-bonds encircle the trinuclear unit, acting as a glue stabilizing the trinuclear assembly. ⁵æ

**Conclusions**

Both KCl and CsCl are ionic salts with similar physical and chemical properties. Despite their similarity, they behave differently in trinuclear assembly formation. While KCl and other potassium salts, including halides or nitrates, ⁵æ form trinuclear assemblies with nearly identical structures, CsCl forms a two-dimensional coordination polymer where the Cs–Cl bond remains intact. Cs\textsuperscript{+} alone does not facilitate coordination polymer formation as the formation of 3 shows that the trinuclear assembly is resilient enough to accommodate the Cs\textsuperscript{+} inside its cavity. Although all the reactions are performed under similar reaction conditions, the use of a non-aqueous medium and room temperature may have helped retain the CsCl bond. However, the different behavior of CsCl is quite clear from the observation of 4–6. The only other report containing an intact Cs–Cl bond, that we are aware of, had two recognition sites within a calix[4]pyrrole cavity for both anions and cations next to each other. ⁶æ In contrast, the present system does not impose any such restriction. Furthermore, the coordination polymer of 2 can be converted to a trinuclear assembly in presence of K\textsuperscript{+} salts (Scheme 1, proven using ESI-mass spectroscopy and in comparison with earlier⁵æ results), a fact which highlights the higher stability of the K\textsuperscript{+} containing trinuclear assembly. In conclusion, we have presented results that, somewhat unexpectedly, show the deviant behavior of CsCl, compared to either KCl or NaCl, ⁵æ in retaining this bond within the network, preventing the formation of a trinuclear assembly which otherwise has been shown to be a common occurrence ⁵æ with alkali metal salts. In relation to our earlier report, the formation of a trinuclear assembly with CsNO\textsubscript{3} shows that the assembly is resilient enough to accommodate larger Cs\textsuperscript{+} without rupturing the overall structure.

**Experimental**

**Materials and method**

Methanol was distilled over magnesium methoxide. Anhydrous grade N,N-dimethylformamide (DMF), KBr, CsCl and salicylaldehyde were purchased from Aldrich Chemical Co. L-leucine, KI and KNO\textsubscript{3} were purchased from Sisco Research Laboratories Pvt. Ltd. (SRL), India and used as...
received. The IR spectra were recorded on a Perkin-Elmer Spectrum one FT-IR spectrophotometer with KBr discs in the range 4000–400 cm⁻¹. The solid-state magnetic susceptibility of the complexes at room temperature was recorded using a Sherwood Scientific Magnetic balance MSB-1. Solution electrical conductivity was measured with a Eutech Instruments CON 5/TDS 5 Conductivity Meter. The instrument was calibrated with a standard solution. Elemental analyses were done using a Carlo Erba 1108 and also by using a Perkin-Elmer series II 2400 instrument. X-Band EPR spectra were recorded with a Jeol JES-FA series spectrometer fitted with a quartz Dewar for measurements at liquid nitrogen temperature. The spectra were calibrated with DPPH (g = 2.0037). Electrospray ionization mass (ESI-MS) spectra were recorded on a Micromass Quattro II mass spectrometer. Thermogravimetric analyses were performed with a TA instrument, SDT Q600. Powder X-Ray diffraction patterns were obtained using a MAKE Bruker, D2 phaser with Cu-Κα radiation (λ = 1.5418 Å) equipped with an integrated PC and DIFFRAC. SUITE software. The diffraction patterns were collected over a 2θ range of 5–40° at a step scan rate of 0.02°.

The synthesis and characterization of the ligand H₂L₃-leu and the complex [Cu(HL₃-leu)]₃(CH₃CN) (1) were reported before.²²

**Synthesis of [CsCl{Cu(HL₃-leu)}₂(CH₃CN)] (2)**

Complex [Cu(HL₃-leu)]₂(CH₃CN) (1) (0.050 g, 0.068 mmol) in MeOH (10 mL) was stirred for 15 min and solid CsCl (0.023 g, 0.139 mmol) was added. The stirring was continued. The color of the solution changed from deep blue to blue-green after 10 min. The solution was further stirred for 3 h and left for slow evaporation. Plate-like blue crystals were obtained within six days. Isolated crystals were dried under a vacuum. Yield: 45%. Anal. Calcd. for [CsCl{Cu(C₁₃H₁₈O₃N)₂}Cl(H₂O)]·2H₂O: C, 41.21; H, 5.59; N, 3.70; found C, 41.15; H, 5.13; N, 3.93. IR (KBr, cm⁻¹): ν(OH) 3453 (b), ν(COO)asym 1615 (s), 1604 (s), 1587 (s), other peaks, 1461 (s), 1386 (m), 1277 (m), 1085, 756, 570.

**Synthesis of [K{Cu(HL₃-leu)}₃]I (3)**

The monomer [Cu(HL₃-leu)]₂(CH₃CN) (1) (0.100 g, 0.137 mmol) in MeOH (15 mL) was stirred for 15 min and solid KCl (0.002 g, 0.023 mmol) was added to the stirring solution. The color of the solution changed from deep blue to blue-green after 10 min. The solution was stirred for 2 h and then concentrated in a rotary evaporator. The resulting crude solution was recrystallized by adding a minimum volume of CH₃CN and it was left for slow evaporation. Diamond shaped blue crystals were obtained within four days. Isolated crystals were dried under a vacuum. Yield: 50%. IR (KBr, cm⁻¹): ν(OH) 3421 (b), 2958 (m), ν(COO)asym 1630 (s), 1587 (s), other peaks, 1461 (s), 1386 (m), 1277 (m), 1085, 756, 570. μeff (powder, 298 K): 1.76 μB/Cu.¹⁸ ΛM (Ω⁻¹ cm² mol⁻¹): (MeOH) 115, (DMF) 69.¹⁹

**Synthesis of [K{Cu(HL₃-leu)}₃]Br (5)**

Complex 4 has been prepared by following a similar procedure to that described for 3 using KBr instead of KCl. Diamond shaped blue crystals were obtained within two days. Isolated crystals were dried under a vacuum. Yield: 46%. Anal. Calcd. for [K{Cu(C₁₃H₁₈O₃N)₂}Br·7H₂O]: C, 50.60; H, 6.64; N, 4.54; found C, 50.57; H, 6.70; N, 4.66. IR (KBr, cm⁻¹): ν(OH) 3467 (b), 2958 (m), ν(COO)asym 1633 (s), 1589 (s), other peaks, 1463 (s), 1389 (m), 1279 (m), 1091, 928, 757, 572. μeff (powder, 298 K): 1.71 μB/Cu.¹⁸ ΛM (Ω⁻¹ cm² mol⁻¹): (MeOH) 117, (DMF) 82.¹⁹

**Synthesis of [K{Cu(HL₃-leu)}₃]Br (6)**

Complex 5 has been prepared by following a similar procedure to that described for 3 using KI instead of KCl. Diamond shaped blue crystals were obtained within two days. Isolated crystals were dried under a vacuum. Yield: 42%. Anal. Calcd. for [K{Cu(C₁₃H₁₈O₃N)₂}Br·3CH₃CN·5H₂O]: C, 50.79; H, 6.44; N, 6.35; found C, 50.63; H, 6.39; N, 6.01. IR (KBr, cm⁻¹): ν(OH) 3437 (b), 2956 (m), ν(COO)asym 1632 (s), 1586 (s), other peaks, 1462 (s), 1387 (m), 1278 (m), 1085 (m), 753. μeff (powder, 298 K): 1.74 μB/Cu.¹⁸ ΛM (Ω⁻¹ cm² mol⁻¹): (MeOH) 98, (DMF) 66.¹⁹

**X-ray crystallography**

Crystals of the complexes obtained during the synthesis were used for X-ray analysis. The crystals were mounted on a glass fiber. All geometric and intensity data for the crystals were collected at room temperature using a Bruker SMART APEX CCD diffractometer equipped with a fine focus 1.75 kW sealed tube Mo-Κα (λ = 0.71073 Å) X-ray source, with increasing ω (width of 0.3° per frame) at a scan speed of either 3 or 5 s per frame. The SMART software was used for the data acquisition and the SAINT software for the data extraction. Absorption corrections were done using SADABS only as

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other kinds of absorption did not help.\textsuperscript{15} After the initial solution and refinement with SHELXL, the final refinements were performed on WinGX environment using SHELX97.\textsuperscript{16} All non-hydrogen atoms were refined anisotropically. Whenever possible, the hydrogen atoms were located from the difference Fourier maps and were refined isotropically. Thus, some of the C–H bonds will not be ideal and may vary. Most of the hydrogen atoms attached to the solvent molecules could not be located or fixed, so the molecular weight may not match. Selected crystallographic data have been summarized in the Notes.\textsuperscript{‡} A perspective view of the complex was obtained by ORTEP.\textsuperscript{17}

Complexes 3 and 6 have high R factors. As supporting evidence, the powder diffraction plots of all the compounds along with simulated plots have been provided in the ESI.\textsuperscript{†} These plots show that except for complex 2 (coordination polymer), the rest of them have similar patterns (between 5–10 °C) due to their isostructural nature. The trinuclear complexes desolvate rapidly and have a tendency to form a twinned crystal. For all the structures except complex 5, the refinement used the TWIN command. The presence of water molecules in the lattice, the disordered nature of the isopropyl groups and the twinning perhaps contributed to the high R factor.

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References


