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Sodium and Potassium Ion Directed Self-Assembled Multinuclear Assembly of Divalent Nickel or Copper and L-Leucine Derived Ligand†

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L-Leucine derived ligand ($H_2L^{L\text{-leu}}$), KOH, and Ni(II) salt in 2:2:1 ratio self-assembled into a rather large (~13 Å) supramolecular assembly with the formula $[K\{Ni(HL^{L\text{-leu}})_2\}_3]^+$ (**1**). Structural characterization showed three $[Ni(HL^{L\text{-leu}})_2]$ units encapsulated K^+ similar to organic crown ethers/cryptand. Substituting Ni(II) with Cu(II) and K^+ with Na^+ in the above reaction resulted in a set of structurally identical assemblies with the general formula $[M'\{M(HL^{L\text{-leu}})_2\}_3]^+$, where M′ is either K^+ or Na^+ and M is either Cu(II) or Ni(II); $[Na\{Ni(HL^{L\text{-leu}})_2\}_3]ClO_4$ (**2**), $Na\{Ni(HL^{L\text{-leu}})_2\}_3]OTf$ (**3**), $[K\{Cu(HL^{L\text{-leu}})_2\}_3]ClO_4$ (**4**), $[Na\{Cu(HL^{L\text{-leu}})_2\}_3]ClO_4$ (**5**), $[K\{Cu(HL^{L\text{-leu}})_2\}_3]NO_3$ (**6**). Electrospray Ionization (ESI)-mass spectra of the assemblies in MeOH showed the retention of assemblies in solution. Visible spectroscopic studies showed retention of assembly **1** in *N*,*N*-dimethylformamide (DMF) which is stable even after the addition of 5 equiv of [18]-crown-6. The assemblies in **2**–**6** show various degrees of dissociation to $[M(HL^{L\text{-leu}})_2]$ and M′, in stronger H-bonding methanol. The dissociation can be reversed upon addition of excess KNO_3/$NaNO_3$ salt. Structural characterization of $[Cu(HL^{L\text{-leu}})_2(MeCN)]$ (**7**) along with its transformation to $[K\{Cu(HL^{L\text{-leu}})_2\}_3]^+$ in the presence of K^+ salt demonstrated that the assembly formation proceeds through an alkali metal ion induced ligand reorientation within the $[Cu(HL^{L\text{-leu}})_2]$ units which is further stabilized by six strong H-bonds holding the assembly. Interestingly, visible spectra of **1** and **2** shows that minor structural changes caused by replacing K^+ with Na^+ is sufficient to shift the d-d transition of Ni(II) by ~70 nm, thereby providing an indirect way of distinguishing K^+ and Na^+, none of which have spectroscopic signature in the visible range.

Introduction

Molecules or molecular assemblies with cavities of different sizes and shapes have been synthesized in view of their potential use as selective hosts for anion sensing, catalysis, selective recognition, and separation of guest molecules.[1−3] Metal complexes of amino acid derived reduced Schiff base ligands generated several interesting architectures including chiral capsule, channels and cavity owing to their flexibility, H-bonding ability, and inherent chirality.[4,5] Earlier, using a L-histidine derivative and Cu(II), we reported a self-assembled octanuclear assembly accommodating four pyridine molecules inside a cavity.[5a]

The L-histidine derivative used earlier was unique in several ways. Being a non planar tetradentate ligand it promoted formation of multinuclear species unless an external ligand blocked the vacant sites.[5a−c] The ambidentate nature of the imidazole arm of L-histidine further increased the difficulty in predicting the final structure.[5c] We decided to reduce the ligand denticity to three by choosing L-leucine over histidine. We expected that this will allow us synthesizing mononuclear bis complexes with Ni(II) leaving the amino acid arms to

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[†] We dedicate this paper to Dr. Prinaki Bandyopadhyay, University of North Bengal, Siliguri, India.

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control steric crowding in case cavities or channels form because of H-bonding between mononuclear units.

In this report, using a L-leucine derivative (Scheme 1), we have characterized a set of spontaneously formed multinuclear assemblies binding both cation and anion of a binary salt in the solid state. Considerable amount of works have been reported on the use of metal complexes as a crown ether/cryptand analogue,[6] as well as organic anion[7] receptor, but few molecular assemblies having both alkali metal ion and an anion binding site exist.[8]

Experimental Section

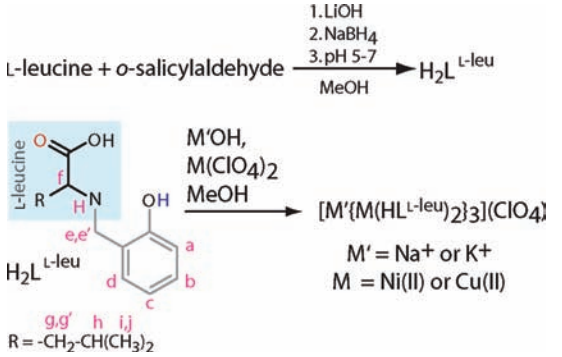
Materials and Methods. Solvents used were purified prior to use following standard literature procedure. *o*-Salicylaldehyde and [18]-crown-6 were purchased from Aldrich Chemical Co. L-Leucine was purchased from Sisco Research Laboratories Pvt. Ltd. (SRL), India, and used as received.

The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer with KBr discs in the range 4000−400 cm^{-1} and electronic spectra on Perkin-Elmer Lambda 25 and Lambda 750 UV−vis spectrophotometers. The ^1H NMR spectrum was recorded using a Varian Mercury plus 400 MHz instrument. 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 Eutech Instruments CON 5/TDS 5 Conductivity Meter. The instrument was calibrated with standard solution. Elemental analyses were performed on a Carlo Erba 1108 and also by using a Perkin-Elmer series II 2400 instrument. Optical rotation of the ligand was measured using a Perkin-Elmer 343 polarimeter. X-Band EPR spectra were recorded with a Jeol JES-FA series spectrometer fitted with a quartz dewar flask 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 Waters (Micromass MS Technologies) Q-Tof Premier mass spectrometer.

Caution! *Perchlorate salts used as starting materials are potentially dangerous as explosives and should only be handled in small quantities.*

Synthesis and Characterization. (*S*)-2-(2-Hydroxybenzylamino)-4-methylpentanoic Acid ($H_2L^{L\text{-leu}}$). A mixture of L-leucine (1.00 g, 7.62 mmol) and $LiOH \cdot H_2O$ (0.323 g, 7.62 mmol) in methanol (25 mL) was stirred for 10 min to dissolve. A methanolic solution of *o*-salicylaldehyde (0.930 g, 7.62 mmol) was added dropwise to the above solution. The color of the solution turned yellow. The stirring was continued for 30 min. The solution was then treated with $NaBH_4$ (0.580 g, 15.3 mmol) with constant stirring. The solution became colorless. The solvent was evaporated under reduced pressure, and the resulting solid was dissolved in water. The clear solution was then acidified with dil. HCl (pH∼5−7). The ligand precipitated as white solid. The solution was filtered, and the residue was washed thoroughly with water. The solid was dried in a vacuum desiccator (yield 1.65 g, 88%). Because of poor solubility, the ^1H NMR spectra for the ligand was recorded for lithium salt of the ligand, prepared by adding 2 equiv of $LiOH \cdot H_2O$ in CD_3OD. ^1H NMR Li_2L (CD_3OD, 400 MHz. ppm) (Scheme 1): 0.76 (d, 3H, H^j), 0.81 (d, 3H, H^i), 1.36 (m, 1H, H^g), 1.41 (m, 1H, $H^{g'}$), 1.67 (m, 1H, H^h), 3.07 (dd, 1H, H^f), 3.65 (d, 1H, H^e), 3.94 (d, 1H, $H^{e'}$), 6.35 (t, 1H, H^c), 6.45 (d, 1H, H^a), 6.94 (m, 2H, $H^{b,d}$). *m*/*z* (ESI-MS,$[LiL]^-$); Calcd: 242.22, found 242.02. IR (KBr, cm^{-1}) $\nu(COO)_{asym}$ 1600 (s), 1593 (s); $\nu(COO)_{sym}$ 1393 (m), cm^{-1}. $[\alpha]_D^{25°} = -15°$ in MeOH, c = 0.2 g/100 mL, in presence of 2 equiv of $LiOH \cdot H_2O$.

Scheme 1. Synthesis of the Assembly along with ^1H NMR Labeling Scheme of the Ligand



$[K\{Ni(HL^{L\text{-leu}})_2\}_3]ClO_4$ (1). Ligand $H_2L^{L\text{-leu}}$ (0.200 g, 0.847 mmol) was deprotonated with KOH (0.047 g, 0.847 mmol) in 10 mL of MeOH which offered a clear colorless solution. After 20 min a methanolic solution (∼5 mL) of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.155 g, 0.424 mmol) was added dropwise to the above solution. The color of the solution changed immediately from green to light blue. The solution was stirred for 2 h and was evaporated to dryness in a rotary evaporator. The resulting crude green solid (0.347 g) was recrystallized by dissolving in minimum volume of MeOH followed by addition of CH_3CN. The diamond shaped purple-blue crystals were obtained after 2 days of slow evaporation. Crystals were dried under vacuum. Yield: 60%. If 2 equiv of base (relative to ligand) is used then the super latent solution is green instead of bluish-green, but the crystals isolated were identical with those using 1 equiv of base. Using 2 equiv of base decreases the yield by ∼20%. Anal. Calcd for $[K\{Ni(C_{13}H_{18}O_3N)_2\}_3]ClO_4 \cdot 3H_2O \cdot 2CH_3CN$: C, 52.71; H, 6.47; N, 5.99; K, 2.09; found C, 52.62; H, 6.28; N, 5.64; K, 2.10. IR (KBr, cm^{-1}): $\nu(COO)_{asym}$ 1594 (s), $\nu(COO)_{sym}$ 1481 (s), ν(phenolic CO) 1289 (s), $\nu(ClO_4^-)$ 1110, 1043, cm^{-1}. μ_{eff} (powder, 298 K); 2.98 μB/Ni. Λ_M (ohm^{-1} cm^2 mol^{-1}): (MeOH) 92, (DMF) 66.

$[Na\{Ni(HL^{L\text{-leu}})_2\}_3]ClO_4$ (2). This has been prepared following a similar procedure to that described for **1** using NaOH instead of KOH. Diamond shaped purple crystals were obtained within 2−5 min after addition of CH_3CN. Yield: 58%. Anal. Calcd for $[Na\{Ni(C_{13}H_{18}O_3N)_2\}_3]ClO_4 \cdot 3H_2O \cdot 2CH_3CN \cdot CH_3OH$: C, 52.90; H, 6.63; N, 5.94, Na, 1.21; found C, 52.46; H, 6.22; N, 5.79; Na, 1.30. IR (KBr, cm^{-1}): $\nu(COO)_{asym}$ 1621 (s), $\nu(COO)_{sym}$ 1460 (s), ν(phenolic CO) 1250 (s), $\nu(ClO_4^-)$ 1088, cm^{-1}. μ_{eff} (powder, 298 K); 3.06 μB/Ni. Λ_M (ohm^{-1} cm^2 mol^{-1}): (MeOH) 116, (DMF) 69.

$[Na\{Ni(HL^{L\text{-leu}})_2\}_3]CF_3SO_3$ (3). Ligand $H_2L^{L\text{-leu}}$ (0.100 g, 0.423 mmol) was deprotonated with NaOH (0.034 g, 0.846 mmol) in 10 mL of MeOH which offered a clear colorless solution. A methanolic solution of (∼5 mL) $Ni(OTf)_2$. (0.075 g, 0.211 mmol) was added dropwise to the above stirring ligand solution. The color of the solution changed from green to light bluish

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green immediately. The solution was stirred for 2 h and was evaporated to dryness in a rotary evaporator. Diamond shaped purple crystals were obtained within 2−5 min after addition of CH_3CN. Yield: 50%. Anal. Calcd for $[Na\{Ni(C_{13}H_{18}O_3N)_2\}_3]CF_3SO_3\cdot 10H_2O\cdot CH_3CN$: C, 48.96; H, 6.64; N, 4.93. found C, 48.60; H, 6.70; N, 4.93. IR (KBr, cm^{-1}): $\nu(COO)_{asym}$ 1596 (s), $\nu(COO)_{sym}$ 1462 (s), $\nu(SO_3^-)$ 1272, ν(phenolic CO) 1254 (s), cm^{-1}. μ_{eff} (powder, 298 K); 2.5 μB/Ni.[9]

$[K\{Cu(HL^{L\text{-}leu})_2\}_3]ClO_4$ (4). Ligand $H_2L^{L\text{-}leu}$ (0.200 g, 0.846 mmol) was deprotonated with KOH (0.047 g, 0.846 mmol) in 25 mL of MeOH. A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.156 g, 0.423 mmol) in MeOH (15 mL) was added dropwise to the ligand solution, and the stirring was continued for 2 h. The color of the solution at this point was deep green-blue. The solution was concentrated to ∼5, and 0.5 mL of CH_3CN was added. The diamond shaped blue crystals were obtained after 2 days of slow evaporation. Crystals were dried under vacuum. Yield: 46%. Anal. Calcd for $[K\{Cu(C_{13}H_{18}O_3N)_2\}_3]ClO_4\cdot 3H_2O\cdot CH_3OH$: C, 51.31; H, 6.54; N, 4.54; found C, 51.44; H, 6.47; N, 4.67. IR (KBr, cm^{-1}): υ(OH) 3444 (b), $\upsilon(COO)_{asym}$ 1633 (s), 1587(s), $\nu(COO)_{sym}$ 1462 (s), 1386 (m), 1086, cm^{-1}. μ_{eff} (powder, 298 K); 1.78 μ_B/Cu. Λ_M (ohm^{-1} cm^2 mol^{-1}): (MeOH) 114, (DMF) 70. EPR: MeOH, 77 K, $g_\parallel = 2.247$, $g_\perp = 2.051$, $A_\parallel = 180$ G.

$[Na\{Cu(HL^{L\text{-}leu})_2\}_3]ClO_4$ (5). This has been prepared following a similar procedure to that described for **4** using NaOH instead of KOH. The solution was concentrated to ∼5, and 0.5 mL of CH_3CN was added. The diamond shaped blue crystals were obtained after 2 days of slow evaporation. Crystals were dried under vacuum. Yield: 46%. Anal. Calcd for $[Na\{Cu(C_{13}H_{18}O_3N)_2\}_3]ClO_4\cdot 4H_2O\cdot 2CH_3OH\cdot CH_3CN$: C, 51.61; H, 6.71; N, 5.14; found C, 51.72; H, 6.87; N, 5.11. IR (KBr, cm^{-1}): υ(OH) 3445 (b), $\upsilon(COO)_{asym}$ 1633 (s), 1588 (s), $\nu(COO)_{sym}$ 1462 (s), 1386 (m), 1277 (m), 1087, cm^{-1}. μ_{eff} (powder, 298 K); 1.72 μ_B/Cu. Λ_M (ohm^{-1} cm^2 mol^{-1}): (MeOH) 118, (DMF) 91.

$[K\{Cu(HL^{L\text{-}leu})_2\}_3]NO_3$ (6). The synthesis and crystallization procedure are identical with that of **4** except $Cu(NO_3)_2\cdot 6H_2O$ was used in place of perchlorate salt. Yield: 54%. Anal. Calcd for $[K\{Cu(C_{13}H_{18}O_3N)_2\}_3]NO_3\cdot 6H_2O$: C, 51.54; H, 6.65; N, 5.39; found C, 51.71; H, 6.40; N, 5.40. IR (KBr, cm^{-1}): υ(OH) 3436 (b), $\upsilon(COO)_{asym}$ 1629 (s), 1588 (s), $\nu(COO)_{sym}$ 1462 (s), 1384 (s), 1277 (m), 1086 (m), cm^{-1}. μ_{eff} (powder, 298 K); 1.69 μ_B/Cu. Λ_M (ohm^{-1} cm^2 mol^{-1}): (MeOH) 118, (DMF) 77.

$[Cu(HL^{L\text{-}leu})_2(CH_3CN)]$ (7). Ligand $H_2L^{L\text{-}leu}$ (0.200 g, 0.846 mmol) was taken in 15 mL of MeOH which offered a white undissolved matter. A solution of $Cu(OAc)_2\cdot H_2O$ (0.082 g, 0.421 mmol) in MeOH (10 mL) was added dropwise to the above ligand solution and stirring continued. The color of the solution changed from green-blue to deep blue immediately. The solution was stirred for 1 h and was evaporated to dryness in a rotary evaporator. The resulting crude solid was dissolved in DMF, crystallized by adding an equal volume of CH_3CN, and left for slow evaporation for 2 days. The rod shaped blue crystals were obtained. Isolated crystals were washed with CH_3CN and dried under vacuum desiccator. Yield (72%). Anal. Calcd for $[Cu(C_{13}H_{18}O_3N)_2CH_3CN]\cdot 4CH_3OH$: C, 54.49; H, 7.85; N, 5.95; found C, 54.45; H, 7.77; N, 5.87. IR (KBr, cm^{-1}): υ(OH) 3461 (b), $\upsilon(COO)_{asym}$ 1626 (s), 1592 (s), $\nu(COO)_{sym}$ 1460 (s), 1382 (s), 1271 (m), cm^{-1}. μ_{eff} (powder, 298 K); 1.64 μ_B. Λ_M (ohm^{-1} cm^2 mol^{-1}): (MeOH) 0.4, (DMF) 3.0. EPR: MeOH, 77 K, $g_\parallel = 2.235$, $g_\perp = 2.039$, $A_\parallel = 183$ G.

X-ray Crystallography. Crystals of the complexes obtained during synthesis were used for X-ray analysis. The crystals were mounted on 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-Kα (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/frame. The SMART software was used for data acquisition, and the SAINT software for data extraction. Absorption corrections were done using SADABS only as either kinds of absorption did not help.[10] After the initial solution and refinement with SHELXL, the final refinements were performed on a WinGX environment using SHELX97.[11] All non-hydrogen atoms were refined anisotropically. Where ever possible, the hydrogen atoms were located from the difference Fourier maps and were refined isotropically. Thus, some of the C−H bond 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 Table 1.

Results and Discussion

Synthesis and Solid State Structures. The diamond shaped crystals of the assemblies **1**−**6** were readily isolated by mixing ligand, metal salt, and alkali metal bases in correct proportions (2:2:1) and standing the solution for 2−3 days. If 2 equiv of base per ligand is used to deprotonate both the phenolic and the carboxylic acid proton, the color of the solution becomes darker and of a different hue (Experimental Section) but eventually yields crystals of **1** to **6** after several days as characterized by comparing FTIR, UV−vis, and structural parameters. Use of extra base decreases the yield. We think the use of 2 equiv of base per ligand initially forms the bis complex, $[M^{II}(L^{L\text{-}leu})_2]^{2-}$, where both the ligand protons have been deprotonated (darker solution) which gradually gets partially protonated by hydrolyzing the water present in methanol. The presence of excess base and the rate of hydrolysis probably delayed the assembly formation, as well as adversely impacted the yield. We are unable to isolate pure $[M^{II}(L^{L\text{-}leu})_2]^{2-}$ species. Crystallographic characterization of **1**−**6** shows the assemblies are isostructural (Table 1).

The **1** crystallizes in the space group $C222_1$, where half of the assembly is identical with the other half connected through symmetry. Thus Ni1 is on the crystallographic 2-fold axis and Ni2 is on the general position. Selected bond distances are in Table 2. In **1**, K^+ is hexa-coordinated by three $[Ni^{II}(HL^{L\text{-}leu})_2]$ units through six carboxylate oxygens (Figure 1a). In each of the $[Ni^{II}(HL^{L\text{-}leu})_2]$, Ni(II) is hexacoordinated by two facial tridentate ligand where the carboxylate groups from the ligands are *cis* to each other (Figure 1b). The carboxylate oxygens are simultaneously coordinated to Ni(II) and K^+ (Figure 1b). Each of the ligands in **1** has one acidic proton which is H-bonded between phenolic oxygen (O1b) and carboxylate oxygen (O3b) from the neighboring $[Ni^{II}(HL^{L\text{-}leu})_2]$ unit (Figures 1b and 2a). Thus there are six such H-bonds in one molecule of $[K\{Ni(HL^{L\text{-}leu})_2\}_3]^+$. These H-bonds are on the short end of the 2.5−3.0 Å range usual for O···O H-bond distances (Table 2).[12] The aromatic rings of the

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[9] Magnetic moment (B.M.) range for Ni(II): 2.9−3.3 and Cu(II) 1.7−2.1. Solid state moment can be lower if weak anti ferromagnetic interaction is present: (a) Figgis, B. N.; Lewis, J. *Prog. Inorg. Chem.* **1964**, *6*, 37. (b) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203. (c) Earnshaw, A. *Introduction to Magnetochemistry*; Academic Press: London, 1968. Molar conductance (ohm^{-1} cm^2 mol^{-1}) range for 1:1 electrolyte in DMF: 65−90, MeOH: 80−115.(d) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

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(11) (a) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structures Refinement*; University of Göttingen: Göttingen, Germany, 1997.(b) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(12) O··O range (2.5 to 3.0) Å: (a) Miyake, R.; Tashiro, S.; Shiro, M.; Tanaka, K.; Shionoya, M. *J. Am. Chem. Soc.* **2008**, *130*, 5646. (b) Desiraju, G. R. *Perspective in Supramolecular Chemistry*; Wiley: New York; Vol. *7*. (c) Ref<mac_bibrefref-style="base-text"=" rid="cit3b"/> (d) Ref .(e) Yang, C. T.; Moubaraki, B.; Murray, K. S.; Vittal, J. J. *Dalton Trans.* **2003**, 880.

Table 1. Crystallographic Data and Refinement Parameters for the Complexes

	1	**2**	**3**	**4**	**5**	**6**
empirical formula	$C_{82}H_{108}ClKN_8Ni_3O_{27}$	$C_{84}H_{116}ClN_8NaNi_3O_{27}$	$C_{87}H_{108}F_3N_{10}NaNi_3O_{22}S$	$C_{84}H_{102}ClCu_3KN_8O_{27}$	$C_{83}H_{114}ClCu_3N_8NaO_{27}$	$C_{80}H_{108}Cu_3KN_7O_{31}$
fw	1888.38	1904.42	1934.01	1920.94	1904.91	1893.45
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$C222_1$	$C222_1$	$C222_1$	$C222_1$	$C222_1$	$C222_1$
a, Å	17.6885(7)	17.7564(8)	17.5336(6)	17.746(2)	17.786(3)	17.8717(16)
b, Å	20.9207(8)	20.9237(10)	21.0148(6)	21.144(3)	21.037(3)	21.262(2)
c, Å	26.7585(10)	26.6820(13)	27.5553(9)	26.968(4)	26.971(4)	26.901(3)
V, Å^3	9902.1(7)	9913.2(8)	10153.2(6)	10119(2)	10092(3)	10222.1(17)
z/ρ	4/1.267	4/1.276	4/1.265	4/1.261	4/1.254	4/1.230
μ	0.706	0.669	0.650	0.764	0.729	0.733
coll. reflns	70786	67506	35518	34073	46466	41985
indep reflns	10098	10833	8146	11573	11948	5180
FLACK para.	−0.004(14)	0.002(10)	−0.005(12)	0.009(16)	0.006(12)	0.00(2)
GOF	1.011	1.031	1.044	0.979	1.020	1.053
R1[a]	0.0466	0.0404	0.0383	0.0634	0.0506	0.0546
wR2[a]	0.1287	0.1102	0.0952	0.1327	0.1173	0.1432
R1[b]	0.0653	0.0510	0.0518	0.1308	0.0874	0.0633
wR2[b]	0.1397	0.1152	0.1035	0.1624	0.1173	0.1485

[a] $I > 2\sigma$. [b] All data.

Table 2. Selected Bond Lengths (Å) for the Assemblies

	1			**2**			**3**		
Ni−O$_{phenol}$	2.162(3)	2.154(3)	2.151(3)	2.147(2)	2.155(2)	2.132(2)	2.150(2)	2.145(3)	2.123(2)
Ni−O$_{carboxy}$	2.021(3)	2.019(3)	2.025(3)	2.015(19)	2.019(19)	2.025(2)	2.012(2)	2.028(2)	2.025(2)
Ni−N$_{amine}$	2.080(3)	2.085(3)	2.077(2)	2.073(2)	2.087(3)	2.085(3)	2.077(3)	2.079(3)	2.087(3)
K/Na−O$_{carboxy}$	2.675(2)	2.650(2)	2.687(3)	2.642(2)	2.550(18)	2.607(2)	2.627(3)	2.548(2)	2.612(3)
OH···O	2.537	2.591	2.541	2.561	2.517	2.514	2.509	2.561	2.497
	4			**5**			**6**		
Cu−O$_{phenol}$	2.487	2.465	2.465	2.451	2.476	2.449	2.504	2.461	2.478
Cu−O$_{carboxy}$	1.964(3)	1.956(3)	1.965(4)	1.967(2)	1.960 (2)	1.967(3)	1.957(5)	1.957(4)	1.963(5)
Cu−N$_{amine}$	2.003(4)	2.020(4)	2.020(5)	2.018(3)	2.013(3)	2.025(3)	2.010(6)	2.015(6)	2.009(6)
K/Na−O$_{carboxy}$	2.743(3)	2.715(3)	2.730(4)	2.598	2.698(3)	2.597(2)	2.666(3)	2.706(4)	2.737(5)
OH···O	2.596	2.621	2.589	2.545	2.545	2.554	2.594	2.644	2.574

ligands completely encapsulate the central potassium ion from both sides in a capsular shape with six amino acid residues protruding on the surface (Figure 2b).

While the *cis* orientation of carboxylates allowed the $[Ni^{II}(HL^{L\text{-}leu})_2]$ unit to bind K^+, similar orientation of amines provided a H-bonding site for oxo anions making the capsular assembly, capable of binding both anion and cation of a salt within the same assembly in solid state (Figure 2a).

The conformation at the chiral carbon of the ligand is *S*. In addition to the asymmetric carbon center in the ligand, the coordination of amine N to the Ni(II) gives rise to an asymmetric secondary nitrogen atom which has the *R* configuration. This phenomenon of opposite conformation preference at chiral carbon and amine N has been observed in all the characterized complexes of this type of ligand.[4,5]

The molecular structures of **2** and **3** showed that overall organization of the assembly is identical with that of **1** differing only by the oxo-anion and central Na^+ ion. Replacement of K^+ with smaller Na^+ reduced the alkali metal to carboxylate length bringing $[Ni^{II}(HL^{L\text{-}leu})_2]$ units closer (Table 2). This in turn shortened the already short inter unit phenol-carboxylate H-bonds (Table 2). The Na−O and K−O lengths are comparable to those found in literature.[13]

Oxo anions form bridges between two neighboring assemblies through two H-bonds between amine NH and two different oxygen atoms of the oxo anion creating an extensively H-bonded three-dimensional network. This might be the reason behind poor solubility of the assemblies' in common organic solvents. **1** and **2** are soluble in polar DMF and only partially soluble in MeOH and water (< 50 mg in 10 mL of MeOH). The presence of additional weak interaction between fluorine and aromatic CH (F1···C18, 3.20 Å) has been observed in **3** which probably reduced the solubility further.[14] **3** is insoluble even in DMF. The lattice also contains acetonitrile and water as solvents of crystallization (Supporting Information, Figure S1).

The molecular structures of Cu(II) assemblies, **4**−**6**, have the identical organization with that of Ni(II) assemblies discussed above. What is notable in these structures

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(13) K−O distance range (2.6 to 2.9) Å: from refs 6a, 6b, and 6d above. A difference of 0.3 Å between K−O and Na−O was observed in two similar crystal where Na^+ or K^+ is bound by DMF. Average Na−O, 2.303, K−O, 2.607 Å(d) Patra, A. K.; Ray, M.; Mukherjee, R. N. *Polyhedron* **2000**, *19*, 1423.

(14) Weak CH···F interaction between aromatic C−H and C−F ranging from 2.1 to 3.1 Å has been reported: Teff, D. J.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1997**, *36*, 4372.

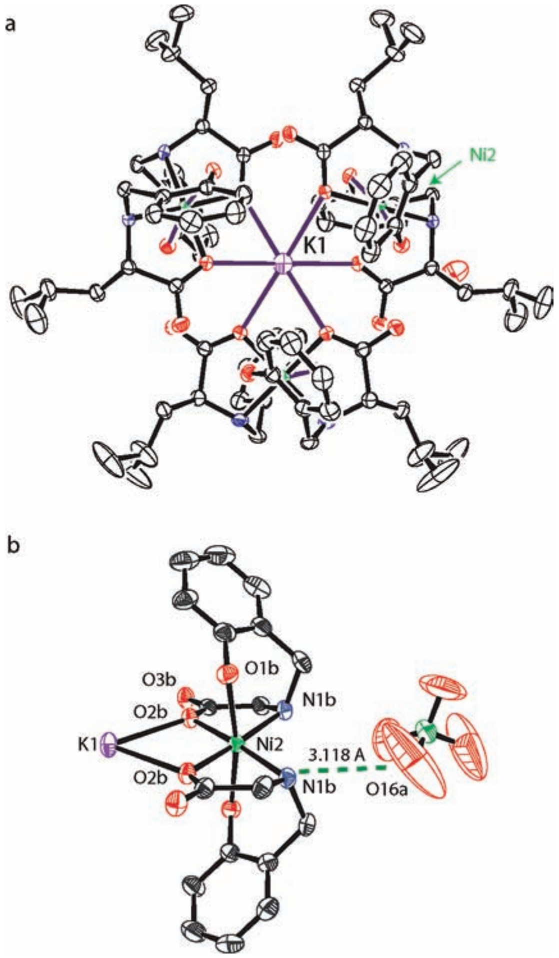

Figure 1. (a) ORTEP diagram of **1** with thermal ellipsoids set to 30% probability level, and (b) coordination around one Ni(II) unit showing the cation and anion binding sites.

is the hexacoordination of Cu(II) which otherwise prefers to be pentacoordinated in almost all the complexes reported so far with similar type of ligands.[4,5,6d] The axial bond lengths (Cu$-$O$_{\text{phenol}}$) are much longer than Ni(II) counterparts because of Jahn$-$Teller distortion (Table 2). In **4**$-$**6**, the in-plane lengths are slightly shorter and K/Na$-$O$_{\text{carboxy}}$ lengths are longer than corresponding bonds in Ni(II) complexes (Table 2).

Overall, the structural characterization of the six structures (**1**$-$**6**) showed that six of L-leucine derived tridentate ligand, three Ni(II) or Cu(II), and one K$^+$ or Na$^+$ self-assemble into a rather large (~1 nm) sized assembly having binding site for one alkali metal ion and three sites for oxo anion (Figure 2). The structures also show that substitution of Ni(II) with Cu(II) is possible without destroying the assembly.

Solid state room temperature magnetic moments of **1**$-$**6** are well within expected range (Experimental Section).[9]

Solution Identity. The solution identities of the assemblies were assessed using solution conductance, ESI-Mass, and electron paramagnetic resonance (EPR) spectroscopy. The solution conductance measurement in methanol and DMF showed the complexes as 1:1 electrolyte (Experimental Section).[9] Thus, the H-bond between the anion and the secondary amines are dissociable in H-bond capable solvent. The ESI-Mass spectra of all the complexes show the molecular ion peak with matching isotopic abundance pattern (Figure 3, Supporting Information, Table S1) supporting the presence of the assemblies in solution.

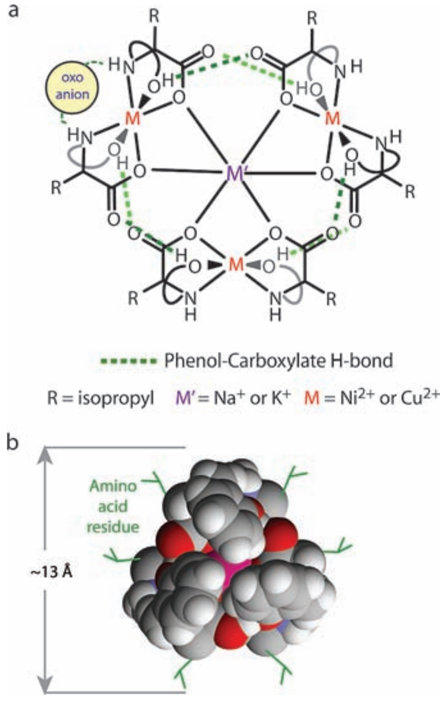

Figure 2. (a) Sketch model of the assembly showing cation as well as anion binding sites and position of the six short hydrogen bonds, and (b) space filling model of the assembly with isopropyl groups shown as sticks.

One notable difference observed between the mass spectra of **2** and **1** was the weak intensity of molecular ion peak for **2** in MeOH (Figures 3a and 4a). The mass spectrum of **2** shows strong enhancement of the intensity of the molecular ion peak after addition of excess $NaNO_3$ (Figure 4b). Excess Na$^+$ perhaps reversed the dissociation of the assembly in MeOH, enhancing the molecular ion peak (Scheme 2). This can be due to the partial dissociation the equilibrium of which shifts toward assembly in the presence of excess Na$^+$ ion causing the enhancement of the molecular ion peak (Scheme 2). This is also supported by the visible spectroscopic measurements described in the next section. Mass spectra of the Cu(II) containing assemblies also show less intense molecular ion peaks suggestive of partial dissociation (Supporting Information, Figure S2). However, higher dissociation of the Cu(II) complexes during the ionization process compared to Ni(II) complexes because of higher lability of the Cu(II) complexes cannot be ruled out. The EPR spectra of the Cu(II) assemblies in methanol at 77 K are all commensurate with their tetragonally distorted structure (Experimental Section, Supporting Information, Figure S3).[15]

Absorption Spectra in DMF. Octahedral Ni(II) and Cu(II) complexes are known to show d-d transition

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[15] (a) Rajendiran, V.; Palaniandavar, M.; Swaminathan, P.; Uma, L. *Inorg. Chem.* **2007**, *46*, 10446. (b) Zurowska, B.; Erxleben, A.; Glinka, L.; Łeczycka, M.; Zyner, E.; Ochocki, J. *Inorg. Chim. Acta* **2009**, *362*, 739.

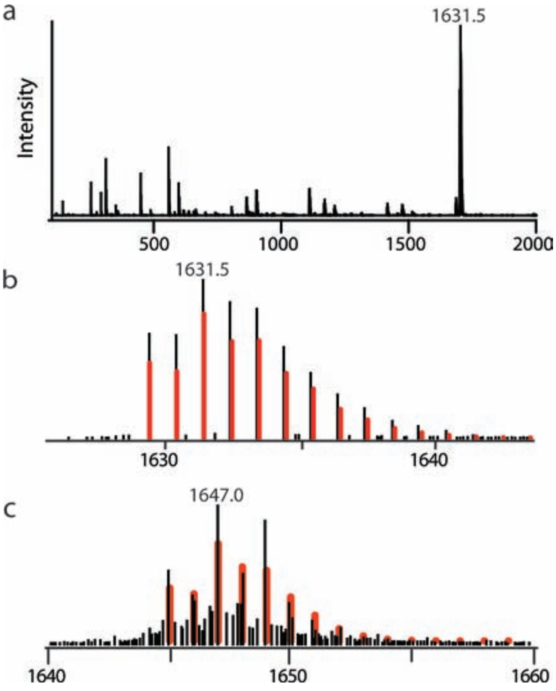


Figure 3. (a) ESI-MS spectrum for **1**, (b) isotopic abundance pattern calculated (red) and experimental (black) of **1**, and (c) the isotopic abundance pattern of **4**.

sensitive to coordination environment.[16] In DMF, both **1** and **2** shows four broad absorptions between 300 and 1600 nm (Figure 5a, Table 3). Six coordinate axially elongated Ni(II)'s are known to show multiple overlapped transitions in this region as lower than octahedral symmetry lifts the degeneracy of the usual three transitions for $^3T_{1g}(P) \leftarrow {}^3A_{2g}$, $^3T_{1g} \leftarrow {}^3A_{2g}$, and $^3T_{2g} \leftarrow {}^3A_{2g}$ typically observed for octahedral Ni(II) complexes.[15] The small sharp absorption maxima at ~755 nm arising from the forbidden singlet state is seen in many other six coordinated Ni(II) complexes.[16] The similarity between the spectra of **1** and **2** indicated their structural similarity in solution. Between **1** and **2**, the absorption maxima at ~1200 nm shows about 70 nm blue-shifted in **2** (Table 3). This peak is usually sensitive ($^3B_{1g} \rightarrow {}^3E_g$ in D_{4h} symmetry) to the relative magnitudes of the axial and equatorial field strengths.[16] The shift does indicate that substitution of Na^+ by K^+ causes minor perturbation in the ligand strengths around the Ni(II). This observation provides an interesting way to distinguish K^+ over Na^+ in the visible region through perturbing a spectroscopically active Ni(II) center. We think that the difference in charge/radius ratio of the two ions binding with the Ni(II) coordinating carboxylates might have influenced the ligand field strength. The spectra remain unchanged upon addition of excess KNO_3 in solutions of **1** (Figure 5a) and $NaNO_3$ in **2** indicating absence of dissociation (Scheme 2). The complex **3** is insoluble in any common solvents. Diffuse reflectance visible spectra of the complexes in the solid state were too noisy for comparison purpose.

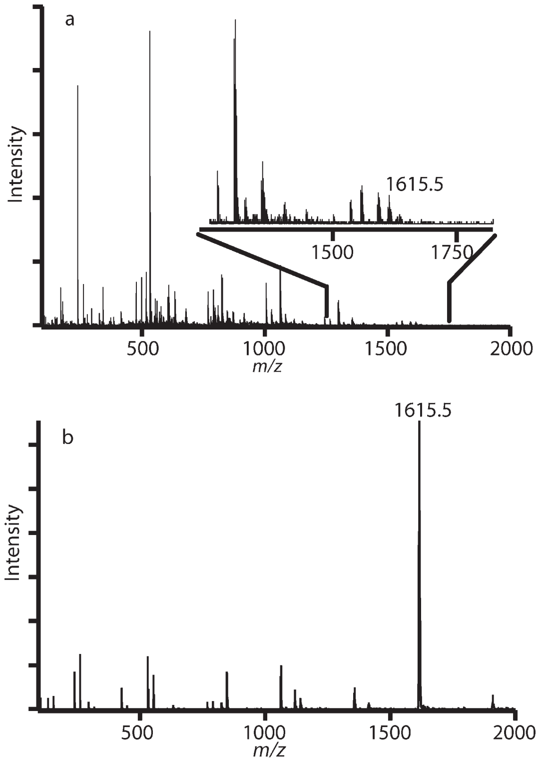
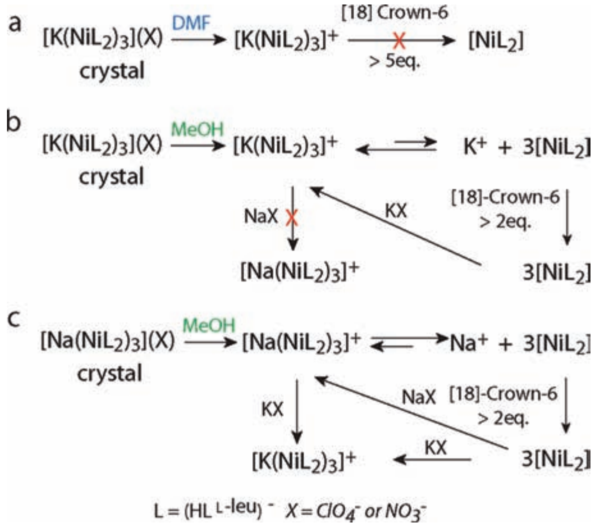


Figure 4. ESI-Mass spectra of **2** in MeOH before (a) and after (b) addition of $NaNO_3$.

Scheme 2. Schematic Representation of the Equilibrium Present in Solution and Inter conversion between the Species Observed Spectrophotometrically



Copper complexes with K^+ as central ion in **4** and **6** show one broad d-d transition in DMF, expected for tetragonally distorted Cu(II) (Table 3, Figure 5b).[16] The spectra of **4** and **6** spectra are identical but appears at lower energy (diff. 30 nm) compared to that of Na^+ containing **5**. Spectrum of **5** is identical with the monomer **7** (Table 3). This indicates some amount of dissociation of the Na^+ containing assembly to $[Cu(HL^{L\text{-leu}})_2]$ units and Na^+. Thus spectra of **5** and **7** are mostly of $[Cu(HL^{L\text{-leu}})_2]$ units. Addition of sodium nitrate to **5** or potassium nitrate to **4** is expected to shift this equilibrium toward multinuclear assembly. As expected, addition of alkali metal salts leads to a sharper peak at ~640 nm for both (Figure 5b and Supporting Information, Figure S4). This

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[16] Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; p 507.

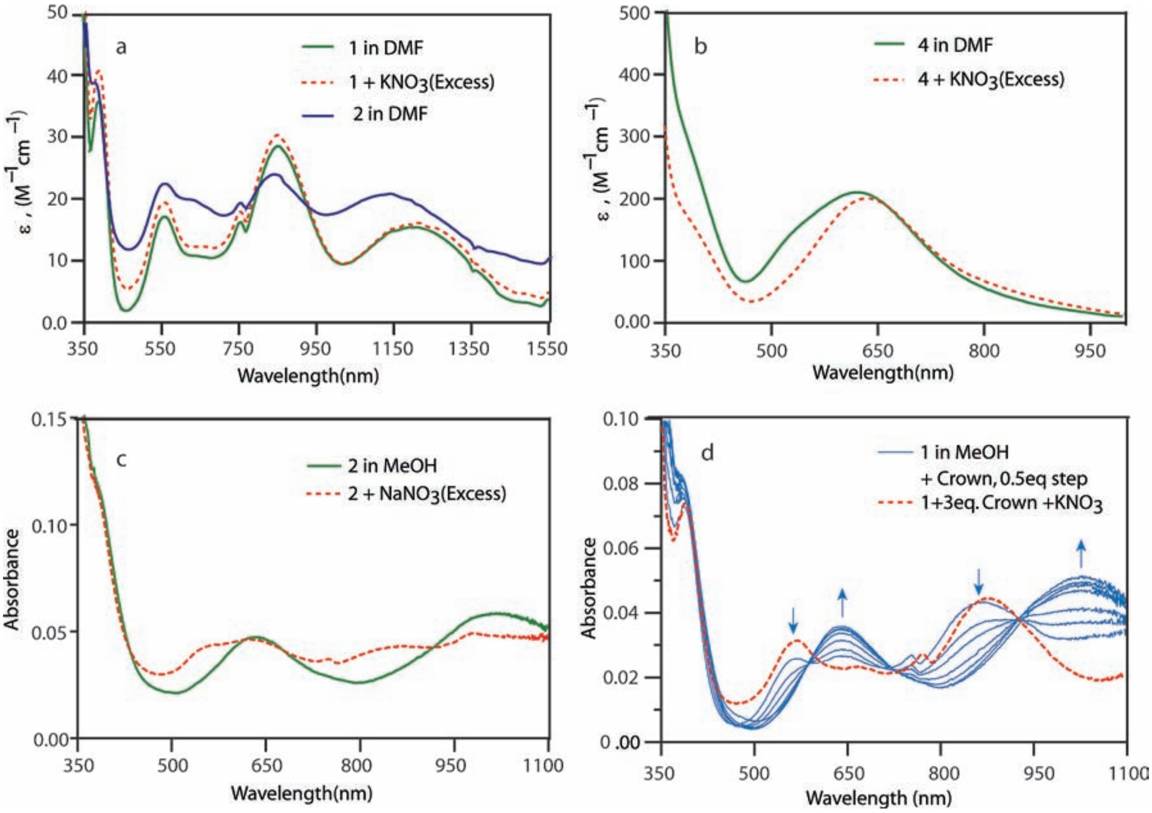

Figure 5. Electronic spectra of the assemblies in different solvents and spectral changes upon addition of salts and [18]-crown-6.

shows that unlike Ni(II) counterparts both the Cu(II) assemblies are partially dissociated in DMF. This is also supported by the structural observation that K/Na$-$O$_{\text{carboxy}}$ and OH$\cdots$O, H-bond lengths in Cu(II) assemblies are slightly longer compared to Ni(II) assemblies thus making them more vulnerable to dissociation.

Dissociation in MeOH and Effect of [18]-Crown-6 Addition. ESI-Mass spectra of **2** (Figure 4) indicated partial dissociation of the assembly to Na$^+$ and [Ni(HL$^{\text{L-leu}}$)$_2$] units in MeOH. To study further, we have recorded the absorption spectra in MeOH (Table 3). Spectra in MeOH were recorded up to 1100 nm because of $-$OH overtone interference beyond this range.

Out of the three bands ~ 550, 850, and 1200 nm observed in DMF, only the first two were visible in MeOH. These two bands were not sensitive to Na$^+$ or K$^+$ in DMF. The spectrum of **1** in both solvents is similar up to the 1100 nm range, but **2** in MeOH showed a substantially different spectrum (Table 3). Suspecting presence of dissociation equilibria, we have recorded spectra after the addition of the respective salts (Figure 5c and Supporting Information, Figure S5). Addition of KNO$_3$ to **1** enhanced the intensity of the peaks slightly, but peak position remains the same indicating very little dissociation of **1** in MeOH (Scheme 2b). This is consistent with the ESI-Mass spectral observation (Figure 3a). Complex **2** on the other hand showed pronounced difference in spectra upon addition of NaNO$_3$ indicating appreciable amount of dissociation in solution. Addition of NaNO$_3$ shifts the equilibrium toward multinuclear species and absorption maxima at 560 and 850 nm increases at the expense of peak at 634 and 1008 nm (Figures 4 and 5c). We think the peaks at 634 and 1008 nm were likely of [Ni(HL$^{\text{L-leu}}$)$_2$] species generated because of dissociation.

Table 3. Electronic Spectral Data[a]

	solvent	$\lambda_{\max}$, nm (ε, M^{-1} cm^{-1})
1	DMF	390(35), 565(20), 755(sh), 865(30), 1230(15)
	MeOH[b]	217(32300), 242(sh), 280(12800), 384 (40), 551 (20), 750 sh, 850 (30)
2	DMF	380(40), 565(22), 755(sh), 855(25), 1160(20)
	MeOH[b]	218(33400), 242(sh), 281(13800), 378 (50), 634 (20), 1008 (30)
4	DMF	625(210)
	MeOH[b]	207(52700), 218(sh), 239(sh), 276(24373), 377 (sh), 616(280)
5	DMF	595(220)
	MeOH[b]	207(51000), 218(sh), 239(sh), 275(24100), 376(sh), 615(280)
6	DMF	625(210)
	MeOH[b]	209(52100), 215(sh), 239(sh), 276(23700), 377(sh), 613(275)
7	DMF	595(100)
	MeOH[b]	225(sh), 244(sh), 277 (12000), 356(sh), 605(100)

[a] Scan range in DMF, 300$-$2000 nm, MeOH, 200$-$1100 nm. [b] ε values were calculated using ~2 mM solution for visible region and 0.01$-$0.02 mM solution for Uv region.

When increasing amounts of [18]-crown-6 are added to methanolic solution of **1** and **2**, the intensity of the peaks at 560 and 850 nm decreases while the peaks at 634 and 1008 nm increases (Figure 5d). The sequestering of K$^+$/Na$^+$ by [18]-crown-6 generates more of [Ni(HL$^{\text{L-leu}}$)$_2$] (Scheme 2). This confirms that the peaks observed at 634 and 1008 nm in the spectrum of **2** are for the [Ni(HL$^{\text{L-leu}}$)$_2$]

species. When excess KNO_3 is added to **2**, the spectrum resembles the spectrum of **1** inferring that Na^+ assembly can be converted to the K^+ containing assembly. The reverse is not observed (Supporting Information, Figure S5b). We conclude that K^+ binds $[Ni(HL^{L\text{-leu}})_2]$ units more strongly compared to Na^+ retaining a multinuclear structure in MeOH.

Addition of [18]-crown-6 (>5 equiv) did not show any changes in the spectrum of either **1** or **2** in DMF indicating the better stability of the Ni(II) assemblies in DMF (Supporting Information, Figure S6). It is likely that MeOH acting both as H-bond donor as well as acceptor interferes with the six H-bonds and facilitates the dissociation of the assembly. On the other hand DMF, which can only act as an H-bond acceptor through the oxygen, is probably unable to dissociate the assembly. These results highlight the role of the six H-bonds in stabilizing the assembly, preventing the sequestration of alkali ion by the [18]-crown-6. Determination of quantitative parameters for these equilibria proved difficult because of low absorbance values along with limited solubility of the complexes.

Copper containing assemblies **4−6** in MeOH show single broad absorption ~615 nm (Table 3) not affected by addition of either corresponding salts or [18]-crown-6. The ESI-mass spectra in MeOH show weak molecular ion peaks (Supporting Information, Figure S2). Together they indicate greater dissociation of the assembly compared to that of the Ni(II) containing assemblies in MeOH.

Structure of 7 and Monomer to Assembly. We attempted synthesizing monomeric $[M(HL^{L\text{-leu}})_2]$ (where M = Ni(II) or Cu(II)) complexes to study the transformation of monomeric units to assemblies. The reaction between divalent Cu(II) acetate and ligand resulted in crystals of $[Cu(HL^{L\text{-leu}})_2(MeCN)]$ (**7**). The complex **7** was crystallized in the space group C_2.[17] Half of the molecule of 7 is symmetrical with the other half through C_2 symmetry. The molecular diagram of **7**, as well as selected bond lengths, is shown in Figure 6a. The square pyramidal geometry around **7** is due to coordination of two $HL^{L\text{-leu}}$ ligands and an acetonitrile coordinated axially. Unlike in **4−6**, the two mono protonated $HL^{L\text{-leu}}$ coordinated in a *trans* N_2O_2 mode and phenols remain uncoordinated to Cu(II). In-plane distances are comparable to corresponding distances in **4−6**. Compared to **4−6**, the axial bond length in **7** is considerably short and might be due to the pentacoordination around Cu(II) as opposed to hexa coordination in **4−6**.

Apart from the coordinated acetonitrile, the crystal contains four acetonitrile molecules. Two of the acetonitriles are symmetrically disposed around **7** showing weak CH···N interaction (C15···N3, 3.342 Å).[18] The other two acetonitriles are disordered over four positions with half occupancy. The phenol, carboxylate, and amine are H-bonded in a linear three center two H-bond (Figure 6b) in a complementary fashion which led to formation of a one-dimensional chain of molecules. This type of linear three centers two H-bond was never reported in any of the complexes with this type of ligands. The H-bond between phenol and carboxylate at 2.635 Å (O2···O3) is longer than the average 2.589 Å observed in **4−6**. One notable feature of the lattice is the formation of two-dimensional channels within the crystal which accommodate four acetonitrile solvents (Supporting Information, Figure S7). The dimensions of the channels (a cuboid space approximately $5 \times 5.7 \times 9.7$ Å^3) are larger than those observed earlier by us in an iron(III) complex with an L-histidine derived ligand.[5b]

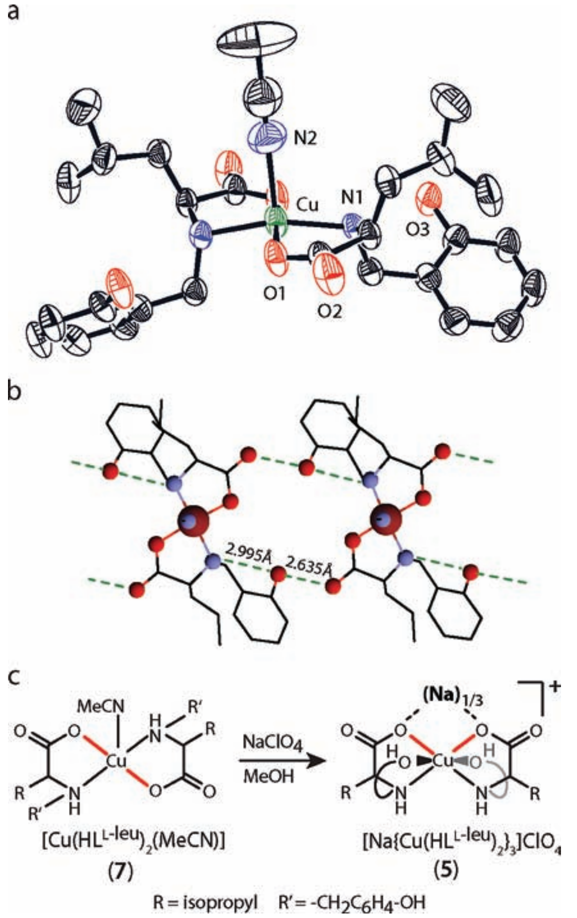

Figure 6. (a) ORTEP diagram of **7** with thermal ellipsoids set to 50% probability level. (b) Intermolecular and intramolecular hydrogen bonding pattern of **7**. (c) Sketch model showing *trans* to *cis* transformation during monomer to assembly conversion. Selected bond distances (Å): Cu1−O1 1.9340(16), Cu1−N1 2.008(2), Cu1−N2 2.332(5), H-bonds: N1···O3 2.995(3), O3···O2 2.635 (3).

The complex is fairly soluble in MeOH. Addition of solid $NaClO_4$ to a methanolic solution of **7** yielded crystals of **5** which was confirmed from FTIR, ESI-Mass, visible spectra, and crystal parameter determinations. Notable in this transformation is the *trans* orientation of the in-plane ligands in **7** to the *cis* orientation in **5** which is necessary for binding the alkali metal ion. This result substantiates that carboxylate groups necessary for alkali metal binding were not predisposed in the Cu(II) monomers but was a result of alkali metal ion influenced reorientation (Figure 6c).

Synthesis of monomeric Ni(II) similar to **7** was attempted, but the resulting complex was insoluble in all

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[17] Crystal data for **7**: $C_{36}H_{45}CuN_7O_6$, Fw 735.34, T (K) 296(2), monoclinic, $C2$, $a = 23.924(2)$ Å, $b = 9.7748(9)$ Å, $c = 8.7819(8)$ Å; $\beta = 92.053°$, $V = 2052.3(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.190$ Mg m^{-3}, $\mu = 0.580$ mm^{-1}, reflections collected 3578, independent 2926, R1 = 0.0374, wR2 = 0.0755 [$I > 2\sigma(I)$]; R1 = 0.0511, wR2 = 0.0804 (all data), GOF = 0.979.

[18] (a) Cotton, F. A.; Daniels, L. M.; Jordan, G. T.; Murillo, C. A. *Chem. Commun*. **1997**, 1673, and references cited therein. (b) Desiraju, G. R. *Crystal Engineering. The Design of Organic Solids*; Elsevier: Amsterdam, 1989; p 166, and references cited therein.(c) Mazik, M.; Blaser, D.; Boese, R. *Tetrahedron* **1999**, *55*, 7835.

the common solvents. Thus, similar conversion experiments could not be performed. The result nonetheless points out the necessity of alkali metal ion forming the assembly.

Conclusions

In this manuscript, we have presented a reaction where a L-leucine derivative, a divalent metal ion, and an alkali metal ion readily self-assembled into a capsular assembly, having sites for both cation and anion of a binary salt. Identical assembly formation was observed irrespective of alkali metal ion (Na^+ or K^+) or divalent metal ion (Ni(II) or Cu(II)) used. In the assembly, three $[M^{II}(HL^{L\text{-}leu})_2]$ units encapsulate alkali metal ion through six oxygen donors forming a cryptate like adduct.[6] The assembly is homochiral with three potential chiral recognition sites on the surface (three pairs of N−H between the isopropyl groups of L-leucine), two of which are occupied by bridging oxo-anions in the present set of complexes. Solution studies using ESI-Mass and visible spectroscopy revealed retention of the cationic capsular assembly in DMF. However, the better H-bonding capability of MeOH was able to partially dissociate the assemblies in solution.

Interestingly, the visibly silent alkali metal ion within the assembly affects the spectral characteristic of Ni(II) (Figure 5a). We have not come across any report where the shift in the visible band of Ni(II) is indirectly influenced by K^+ over Na^+. This perhaps has happened because the bonds and angles in the assembly are interdependent on the bivalent metal ion, alkali ion, and the six strong H-bonds. A change in the size of the alkali ion changes the bond lengths and angles in a way that it caused the shift in the d-d transition of the Ni(II) spectra.[19] This overall interdependence and the short H-bonds perhaps forced the Cu(II) to adopt a not so common octahedral geometry. Further, support comes from the structural characterization of monomeric **7** which showed that without the alkali metal ion, Cu(II) adopts a five coordinate geometry (Figure 6). Thus, it is the alkali metal ion coordination that directs the ligands to adopt *cis* configuration which is further stabilized by the formation of six short H-bonds. Except for four complexes with L-alanine, L-glycine, and L-isoleucine, structurally characterized bis complexes always have *trans* orientation of the two amino acids around Cu(II).[20] These six short H-bonds stabilizes the assembly to such an extent that the assemblies can withstand the sequestration of the alkali metal ion by [18]-crown-6 in weak H-bonding solvent DMF.

While several interesting structural architectures, channels, and capsular motifs have been reported by us and others[4,5] using amino acid derived reduced Schiff base ligands, this work presents the formation of a new multifaceted architecture with easily variable sites for two different types of metal ions and anions. The facile formation and easy transformation from monomeric units increase the potential for future exploitation of the architecture for chiral anion recognition.

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Supporting Information Available: CIF for **1** to **7**, detail synthesis and characterization data along with figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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