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CRYSTAL GROWTH & DESIGN
2009
VOL. 9, NO. 8
3603–3608

Cocrystallized Dinuclear−Mononuclear $Cu^{II}_3Na^I$ and Double-Decker−Triple-Decker $Cu^{II}_5K^I_3$ Complexes Derived from *N,N′*-Ethylenebis(3-ethoxysalicylaldimine)

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Received March 26, 2009; Revised Manuscript Received June 10, 2009

ABSTRACT: The syntheses and structures of a [2×1+1×2] cocrystal **[{**$Cu^{II}L^1Na^I(H_2O)_2$**}**$\{Cu^{II}L^1\}_2$**]**(NO_3) (**1**) and [3×1+5×1] cocrystal $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**2**) derived from the hexadentate Schiff base compartmental ligand *N,N′*-ethylenebis(3-ethoxysalicylaldimine) (H_2L^1) are described. Compounds **1** and **2** crystallize in triclinic $P\bar{1}$ and monoclinic $P2_1/c$ systems, respectively. The structure of **1** consists of the $[Cu^{II}L^1Na^I(H_2O)_3]^+$ cation and two mononuclear $[Cu^{II}L^1]$ moieties. In the dinuclear $[Cu^{II}L^1Na^I(H_2O)_3]^+$ cation, the metal centers are doubly bridged by the two phenolate oxygen atoms. Each of the two coordinated water molecules of the dinuclear unit is encapsulated in the O_4 cavities of the two mononuclear $[Cu^{II}L^1]$ moieties resulting in the formation of a [2×1+1×2] cocrystal. In compound **2**, one trinuclear double-decker system $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]$ and one pentanuclear triple-decker system $[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]$ are cocrystallized. Evidently, compound **2** is a [3×1+5×1] cocrystal. Structural resemblance of 3d metal ions with Na(I) and a rare example of double-decker−triple-decker cocrystal are the major outcomes of the present investigation.

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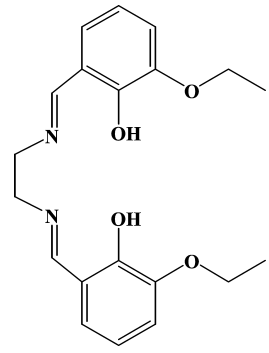
Introduction

Studies of self-assembled organic and metal−organic systems have attracted vast fascination in recent years.[1−3] Because of extensive developments in recent years, it has been possible in many cases for the designed synthesis of a target assembly which, in turn, may be useful as functional materials.[1−3]

Multicomponent crystals, which are known as cocrystals, are important due to their applications as pharmaceuticals, nonlinear optical materials, and charge-transfer solids.[4] Although the formation of cocrystals can be designed in some cases, many times it is accidental. The organic cocrystals,[4−6] in particular, can be designed by utilizing the concepts of intermolecular interactions. However, the formation of cocrystals containing metal complexes[7] as the components are usually accidental and the reason of coexistence therein cannot be understood in most cases. It should also be noted that, in comparison to the large number of organic cocrystals, there are only a few metal-containing cocrystals.[7]

Sandwich systems are well-known in coordination and organometallic chemistry. Ferrocene and other metallocenes are well-studied examples in this area.[8] The sandwich complexes may be double-decker,[9−12] triple-decker,[13−16] or multiple-decker.[17,18] There are also examples of double-decker and triple-decker based polymeric compounds which are formed due to inherent self-assembly or the interlinking of the individual units by inorganic bridging anions.[19] To the best of our knowledge, there is only one example of the coexistence of double-decker and triple-decker systems in a single crystal.[20] It may also be noted that, although there are examples of the sandwich complexes of 3d or main group metal ions,[9,10,12−14,17,18] this family is dominated by lanthanide ions.[11,15,21]

Chart 1. Chemical Structure of H_2L^1



H_2L^1

The Schiff base ligands obtained by condensation of 3-ethoxysalicylaldehyde and diamines are known to stabilize discrete dinuclear 3d-4f complexes[22] in which a 3d metal ion occupies the N_2O_2 cavity and a 4f metal ion occupies the O_4 cavity. In the course of exploring the 3d-3d complexes derived from this type of ligand environment, we have previously used *N,N′*-ethylenebis(3-ethoxysalicylaldimine) (H_2L^1; Chart 1) and *N,N′*-*o*-phenylenebis(3-ethoxysalicylaldimine) and observed that potential encapsulation of a water molecule results in the formation of tetranuclear or heptanuclear systems consisting of cocrystals of dinuclear and mononuclear moieties.[7a,b] As the compositions of 3d-4f and 3d-3d systems are entirely different, we were interested in the nature of the products obtained by reacting a mononuclear 3d complex with alkali metal ions; will these be 3d-4f like dinuclear[22] or 3d-3d like cocrystals[7a,b] as observed in systems derived from 3-ethoxysalicylaldehyde-diamine ligands or dinuclear, double-decker trinuclear and sandwich-based polynuclear as observed in 3d-alkali metal systems[23] derived from 3-methoxysalicylaldehyde-diamine ligands?

To address the above-mentioned queries, we have reacted the mononuclear inclusion product $[Cu^{II}L^1\subset(H_2O)]$[7a] with alkali

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10.1021/cg900341r CCC: $40.75 © 2009 American Chemical Society
Published on Web 07/06/2009

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Table 1. Crystallographic Data for 1 and 2

	1	2
empirical formula	$C_{60}H_{70}N_7O_{17}Cu_3Na$	$C_{100}H_{110}N_{13}O_{29.2}Cu_5K_3$
fw	1374.84	2396.21
crystal color	dark red	dark red
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	12.1509(13)	21.756(2)
b, Å	15.284(2)	25.229(2)
c, Å	17.597(2)	18.377(2)
α, deg	87.531(9)	90.00
β, deg	83.906(7)	94.654(7)
γ, deg	69.005(6)	90.00
V, Å^3	3033.7(6)	10053.5(16)
Z	2	4
T, K	120(2)	120(2)
2θ	2.86−60.00	7.04−50.06
μ, mm^{-1}	1.126	1.252
ρ_{calcd}, g cm^{-3}	1.505	1.583
$F(000)$	1426	4946
absorption-correction	multiscan	multiscan
T_{min}	0.694	0.712
T_{max}	0.798	0.882
index ranges	$-14 \le h \le 16$	$-25 \le h \le 25$
	$-21 \le k \le 21$	$-29 \le k \le 30$
	$-22 \le l \le 24$	$-21 \le l \le 21$
reflections collected	31665	74755
independent reflections (R_{int})	16391(0.0308)	17701(0.0305)
$R_1{}^a/wR_2{}^b$ ($I > 2\sigma(I)$)	0.0473/0.1238	0.0404/0.1047
$R_1{}^a/wR_2{}^b$ (for all $F_o{}^2$)	0.0697/0.1378	0.0609/0.1200

^{a} $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$. ^{b} $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$.

metal salts and have been able to crystallize two complexes containing sodium and potassium. Herein, we report the syntheses and structures of these two compounds.

Experimental Section

Materials and Physical Measurements. All the reagents and solvents were purchased from commercial sources and used as received. The mononuclear inclusion product $[Cu^{II}L^1\subset(H_2O)]$ was synthesized by the reported procedure.[7a] Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400−4000 cm^{-1} on a Perkin-Elmer RXIFT spectrophotometer with samples as KBr disks. Magnetic susceptibility measurements at 300 K were carried out with a Sherwood Scientific Co., U.K. magnetic susceptibility balance. Electronic spectra were obtained with a Hitachi U-3501 spectrophotometer.

Syntheses. $[\{Cu^{II}L^1Na^I(H_2O)_2\}\{Cu^{II}L^1\}_2](NO_3)$ (1). To a stirred suspension of $[Cu^{II}L^1\subset(H_2O)]$ (0.218 g, 0.5 mmol) in acetone (20 mL) was added finely powdered sodium nitrate (0.17 g, 2 mmol). After being stirred for 1 h, the mixture was filtered to remove the unreacted $NaNO_3$ and the clear red colored filtrate was kept for slow evaporation. After a few hours, dark red crystalline compounds containing diffractable single crystals that deposited were collected by filtration. Yield: 0.195 g (85%). Anal. Calcd for $C_{60}H_{70}N_7O_{17}Cu_3Na$: C, 52.42; H, 5.13; N, 7.13. Found: C, 52.50; H, 5.04; N, 7.20. IR (cm^{-1}, KBr): $\nu(H_2O)$, 3476m; ν(C=N), 1630vs; ν(nitrate), 1450s, 1324s. μ_{eff}, 3.08 μ_B.

$[\{(Cu^{II}L^1)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (2). This compound was prepared in the same way as described above for **1** except using KNO_3 instead of $NaNO_3$. Color: dark red. Yield: 0.192 g (80%). Anal. Calcd for $C_{100}H_{110.4}N_{13}O_{29.2}Cu_5K_3$: C, 50.12; H, 4.64; N, 7.60. Found: C, 50.20; H, 4.71; N, 7.52. IR (cm^{-1}, KBr): $\nu(H_2O)$, 3461w; ν(C=N), 1629vs; ν(nitrate), 1455s, 1345s. μ_{eff}, 3.95 μ_B.

Crystal Structure Determination of 1 and 2. Crystallographic data are summarized in Table 1. X-ray diffraction data for **1** and **2** were collected at 120 K on Bruker Smart 1K/APEX CCD diffractometers, respectively, using Mo Kα radiation. Data were processed using SAINT.[24] The structures were solved by direct methods in SHELXS and refined by full matrix least-squares on F^2 in SHELXL.[25] The structure of **2** contained some disorder including two positions for K(3), and the occupancies of the two atomic sites were constrained to equal one, since the isotropic displacement parameters are closely linked to site occupancy the displacement parameters were constrained to be the same but allowed to refine. This gave a value of 0.803(2) for the occupancy of K(3A), and the occupancies of K(3A) and K(3B) were fixed at 80% and 20% respectively in all further refinement cycles with the anisotropic displacement parameters constrained to be the same but refining throughout. The presence of a water oxygen atom attached to K(3B) was determined on the basis of a q-peak in the difference Fourier map consistent with the presence of ∼1/5 of an oxygen atom in a geometrically sensible location. The occupancy of this oxygen was fixed to be the same as K(3B). In view of the fact that K(3B) is too far away to bind strongly to the oxygen atoms of the mononuclear moieties (in the same manner as seen for K(3A)), it seems chemically reasonable that the O_4 ligand cavity may contain a water molecule (as seen in other examples of similar compounds where hydrogen-bonded waters are frequently found, e.g., in **1**). However, hydrogen atoms were unable to be located probably due to their low occupancy. The disorder in the bound nitrate (N(11)) was identified on the basis of residual peaks in the Fourier difference map. The occupancies were determined by setting the sum of the occupancies for the two nitrate groups [N(11A), O(21A), O(22A), and O(23A)] and [N(11B), O(21B), O(22B), and O(23B)] to be 1. During this the displacement, parameters were allowed to refine, but the two nitrogen atoms were constrained to have the same displacement parameters as were the six oxygen atoms. The occupancy for the first nitrate group (N(11A)) refined to 0.757(4); however, the occupancies for the two groups were fixed at 80:20, consistent with the potassium atom to which they were attached. In addition to achieving consistency with the potassium atom occupancies, part of the reason for fixing the occupancies at 80:20 was that the Fourier difference map in this region is slightly noisy and there may be some additional disorder of the nitrate groups (which have relatively large anisotropic displacement parameter) that could not be sensibly modeled. In relation to this, the second nitrate group (N(11B)) required restraints to keep the N−O and O···O distances consistent with those found in the first nitrate group (N(11A)) when an anisotropic refinement was carried out. The occupancies of the oxygen atoms for the free nitrates (N(12) and N(13)) were determined using the same refinement strategy as described above for K(3) and the nitrate group N(11), with the oxygen atoms linked in groups of 3. Here each set of three oxygen atoms were constrained to have the same occupancy, with the sum of the occupancies constrained to be 1 and the isotropic displacement parameters constrained to be the same. The site occupation for O(25A), O(26A), and O(27A) refined to 0.548(5) and was fixed at 0.55, while the site occupation for O(28A), O(29A), and O(30A) refined to 0.668(5) and was fixed at 0.67. All hydrogen atoms, except the solvent water hydrogen atoms in **1**, were positioned geometrically (aromatic C−H 0.95 Å, ethyl C−H 0.99 Å, and methyl C−H 0.98 Å) and refined using a riding model with the isotropic displacement parameters fixed at $U_{iso}(H) = 1.2$ times U_{eq} of the parent carbon atom for the aromatic and ethyl hydrogens and $U_{iso}(H) = 1.5$ times U_{eq} of the parent carbon atom for the methyl hydrogens. The solvent water O−H atoms were located in the Fourier difference map, the O−H distances were restrained to 0.86 Å and the isotropic displacement parameters were fixed to $U_{iso}(H) = 1.2$ times U_{eq} of the parent oxygen atom. The final least-squares refinements (R_1) based on $I > 2\sigma(I)$ converged to 0.0473 and 0.0404 for **1** and **2**, respectively.

Results and Discussion

Syntheses and Characterization. The reaction between the mononuclear inclusion compound $[Cu^{II}L^1\subset(H_2O)]$ and sodium(I) nitrate produces the red-colored heteronuclear compound $[\{Cu^{II}L^1Na^I(H_2O)_2\}\{Cu^{II}L^1\}_2](NO_3)$ (**1**). Similar reaction of the mononuclear compound with potassium(I) nitrate produces the red-colored heteronuclear compound $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**2**). The IR spectrum of $[Cu^{II}L^1\subset(H_2O)]$ exhibits one strong absorption at 1620 cm^{-1} due to $\nu_{C=N}$ vibration. In comparison, the vibration due to $\nu_{C=N}$ appears at slightly higher energy (ca. 1630 cm^{-1}) for both the complexes **1** and **2**. The water stretchings in compound **1** appear as a medium intensity band at 3476 cm^{-1}. As will be discussed below, per molecule of compound **2** contains 0.2 H_2O. However, the presence of water in this compound can be evidenced by a weak intensity infrared band at 3461 cm^{-1}. The signals for the nitrate ions are observed at 1450 and 1324 cm^{-1}

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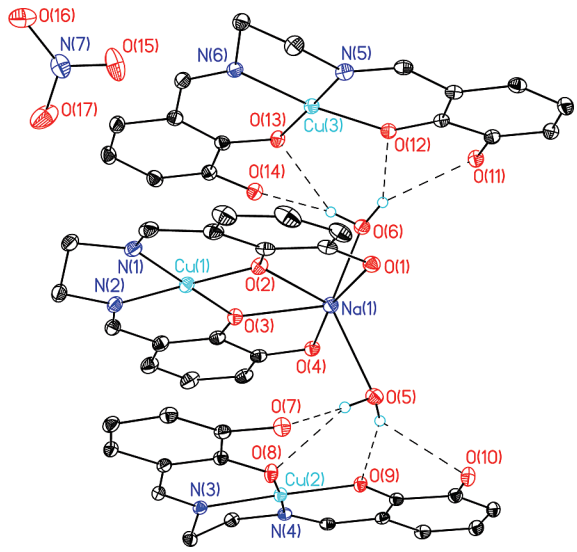

Figure 1. Crystal structure of $[\{Cu^{II}L^{1}Na^{I}(H_2O)_2\}\{Cu^{II}L^{1}\}_2](NO_3)$ (**1**).

for compound **1** and 1455 and 1345 cm^{-1} for compound **2**. The values of magnetic moment at 300 K of **1** and **2** are 3.08 and 3.95 μ_B, respectively, which are very close to the theoretical magnetic moments (3.0 and 3.87 μ_B, respectively) for three (in **1**) and five (in **2**) noncorrelated copper(II) centers. The absorption behavior of $[Cu^{II}L^{1}\subset(H_2O)]$, **1**, and **2** are compared in Figure S2, Supporting Information. The electronic spectrum of the mononuclear compound $[Cu^{II}L^{1}\subset(H_2O)]$ is characterized by a broadband at 575 nm and a sharper signal at 373 nm, which arise due to d-d transition and Cu^{II}−O(phenolate) charge transfer transition, respectively. In **1** and **2**, the Cu^{II}−O(phenolate) charge transfer is slightly shifted to 371 nm. Similarly, the d-d band is slightly shifted to 565 and 570 nm, respectively for **1** and **2**. The molar extinction coefficient (ε; M^{-1} cm^{-1}) per mole of copper(II) ion for these two types of bands in $[Cu^{II}L^{1}\subset(H_2O)]$, **1**, and **2** are not very different; 691, 656, and 667, respectively, for the d-d band and 16939, 15911, and 16079, respectively, for the charge transfer band.

Description of Structure of $[\{Cu^{II}L^{1}Na^{I}(H_2O)_2\}\{Cu^{II}L^{1}\}_2](NO_3)$ (1). As shown in Figure 1, the structure of **1** consists of the heterotetranuclear $[\{Cu^{II}L^{1}Na^{I}(H_2O)_2\}\{Cu^{II}L^{1}\}_2]^{+}$ cation and one nitrate anion. In the tetranuclear cation, the diphenoxo-bridged $[Cu^{II}L^{1}Na^{I}(H_2O)_2]^{+}$ cation is interlinked with two mononuclear $[Cu^{II}L^{1}]$ species by hydrogen-bonding interactions (vide infra). In the $Cu^{II}Na^{I}$ dinuclear core, one copper(II) ion (Cu(1)) occupies the N_2O_2 cavity, and the second compartment of $[L^{1}]^{2-}$ is occupied by one sodium(I) ion (Na(1)), which is coordinated to the two bridging phenoxo oxygen atoms, two ethoxy oxygen atoms, and two water molecules.

The selected bond lengths and angles of the coordination environment of three copper(II) centers (Cu(1), Cu(2), and Cu(3)) in the N_2O_2 compartment are summarized in Tables S1 and S2, Supporting Information, respectively. The Cu−N and Cu−O bond lengths lie in the ranges 1.930(2)−1.949(2) Å and 1.897(2)−1.914 (2) Å, respectively. As in the inclusion compound $[Cu^{II}L^{1}\subset(H_2O)]$ (**3**) and [2×1+1×2] tetranuclear compounds $[\{Cu^{II}L^{1}M^{II}(H_2O)_3\}\{Cu^{II}L^{1}\}_2](ClO_4)_2$ (M = Cu (**4**), Co (**5**) or Mn (**6**)) derived from H_2L^{1}, each of the Cu−N bond lengths are slightly longer than its respective *trans* Cu−O distance.[7a] The ranges of the *cisoid* (84.33(9)−94.06(9)°) and *transoid* (172.84(8)−178.93(8)°) angles, the average deviation (0.02−0.08 Å) of the donor atoms, and the displacement (0.00−0.03 Å) of the copper(II) center from the corresponding least-squares N_2O_2 plane indicate that the coordination environment of these metal ions deviates only by a small amount from the ideal values.

Table 2. Geometries (Distances in (Å) and Angles in (°)) of the Hydrogen Bonds in 1

D−H····A	D····A	H····A	D−H····A
O(5)−H(5A)····O(7)	2.921	2.083	166.2
O(5)−H(5A)····O(8)	2.942	2.389	122.9
O(5)−H(5B)····O(9)	2.935	2.123	158.4
O(5)−H(5B)····O(10)	3.178	2.538	132.4
O(6)−H(6B)····O(11)	3.106	2.393	141.4
O(6)−H(6B)····O(12)	2.883	2.121	148.4
O(6)−H(6A)····O(13)	2.955	2.365	126.3
O(6)−H(6A)····O(14)	3.034	2.198	164.6

As already mentioned, the second metal center (Na(1)) in the dinuclear $[Cu^{II}L^{1}Na^{I}(H_2O)_2]^{+}$ core is hexacoordinated (Figure 1 and Tables S1 and S2, Supporting Information) with two bridging phenoxo oxygen atoms (O(2)) and O(3)), two ethoxy oxygen atoms (O(1) and O(4)), and two water oxygen atoms (O(5) and O(6)). The bond distances involving the bridging phenoxo oxygen atoms (Na(1)−O(2) = 2.373(2) Å, Na(1)−O(3) = 2.344(2) Å) and those involving the water oxygen atoms (Na(1)−O(5) = 2.361(2) Å, Na(1)−O(6) = 2.327(2) Å) are significantly shorter than the two M−O(ethoxy) distances (Na(1)−O(1) = 2.692(2) Å, Na(1)−O(4) = 2.674(2) Å). The O−Na(1)−O angles in the coordination environment of sodium(I) lie in the range 61.06(6)−133.24(8)°. The coordination environment cannot be modeled with any of the regular or distorted polyhedra. It may be mentioned that the Cu−O(phenoxo)−Na bridge angles (Cu(1)−O(2)−Na(1) = 102.62(8)°, Cu(1)−O(3)−Na(1) = 103.68(8)°) lie in the range (91.82(12)−105.29(14)°) of the Cu−O(phenoxo)−M bridge angles observed in the dinuclear $[Cu^{II}L^{1}M^{II}(H_2O)_3]^{2+}$ cores of the tetranuclear compounds **4**−**6**. However, the metal···metal separation in **1** (Cu(1)···Na(1) = 3.3509(11) Å) is significantly longer than the Cu···M distances (3.09−3.22 Å) in **4**−**6**.[7a]

Similar to that in $[Cu^{II}L^{1}\subset(H_2O)]$ (**3**) and $[\{Cu^{II}L^{1}M^{II}(H_2O)_3\}\{Cu^{II}L^{1}\}_2](ClO_4)_2$ compounds (**4**−**6**), water encapsulation through bifurcated hydrogen bonds also occurs in **1**. Both the two coordinated water molecules in **1** are encapsulated in the O_4 cavity of two $[Cu^{II}L^{1}]$ species (Figure 1). The geometries of the hydrogen bonds are summarized in Table 2. The O(water)··· O(phenoxo/ethoxy) contacts and the O−H···O angles lie in the ranges 2.88−3.18 Å and 122.9−166.2°, respectively, indicating that some hydrogen bonds are moderately strong and some are weak. The extent of encapsulation of water can be understood from the displacement of the water oxygen from the least-squares $O(phenoxo)_2O(ethoxy)_2$ plane. The displacement of O(5) and O(6) from the corresponding O_4 planes are 1.31 and 1.30 Å, respectively. In the case of the previously reported compound $[Cu^{II}L^{1}\subset(H_2O)]$ (**3**), the oxygen atom of the encapsulated water lies on the least-squares $O(phenoxo)_2O(ethoxy)_2$ plane, while the oxygen atoms of the encapsulated and coordinated water molecules in $[\{Cu^{II}L^{1}M^{II}(H_2O)_3\}\{Cu^{II}L^{1}\}_2](ClO_4)_2$ (**4**−**6**) are displaced by 0.92−1.23 Å from the corresponding $O(phenoxo)_2O(ethoxy)_2$ plane, indicating that the extent of encapsulation in the mononuclear inclusion product **3** is much greater than that in compounds **1** and **4**−**6**. It is also evident that the extent of encapsulation in the previously reported 3d-3d series **4**−**6** is almost similar to that in compound **1**.[7a]

Description of the Structure of $[\{(Cu^{II}L^{1})_2K^{I}\}(NO_3)]\cdot[\{(Cu^{II}L^{1})_3K^{I}_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (2). The crystal structure of **2** is shown in Figure 2, while the selected bond lengths and angles are listed in Table S3 and Tables S4−S5, respec-

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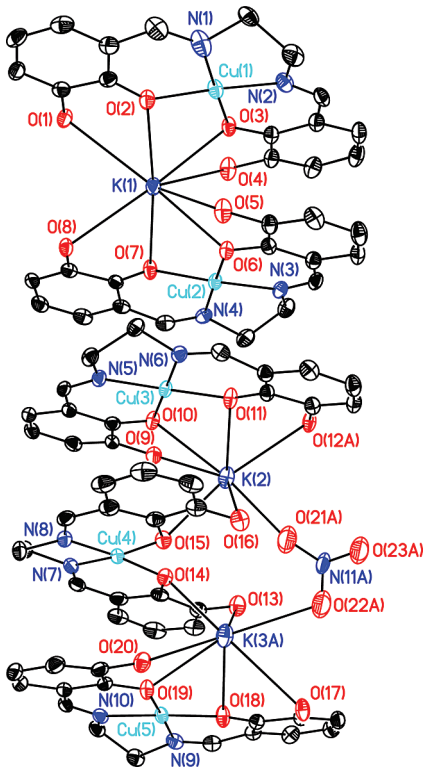

Figure 2. Crystal structure of $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**2**).

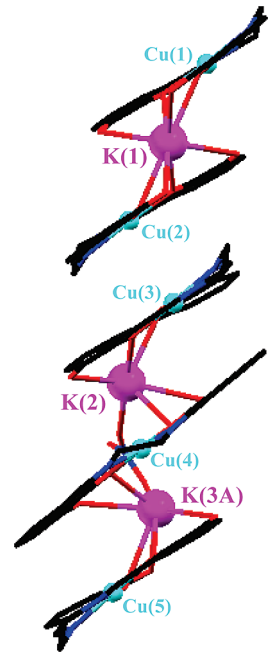

Figure 3. A perspective view down the crystallographic *b* axis for better understanding of the double-decker and triple-decker nature of the two species in $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**2**).

tively. The structure shows that compound **2** consists of two different species, one trinuclear double-decker system $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]$ and one pentanuclear triple-decker system $[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]$. Double-decker and triple-decker topologies of the two moieties can be better understood from Figure 3. As was already mentioned, compound **2** contains some disorder, and hence for clarity only the major components are depicted in Figures 2 and 3. Both positions of major (K(3A)) and minor (K(3B)) occupancies of the potassium(I) ion are shown in Figure S1, Supporting Information.

The trinuclear double-decker system $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]$ consists of the $[(Cu^{II}L^1)_2K^I]^+$ cation and a nitrate anion. In the cation, one potassium(I) ion (K(1)) is coordinated to the two phenoxo and two ethoxy oxygen atoms of each of the two $[Cu^{II}L^1]$ moieties, $[Cu(1)L^1]$ and $[Cu(2)L^1]$, and thus the potassium(I) is sandwiched in between two mononuclear copper(II) species. Evidently, potassium(I) ion in this double-decker cation is octacoordinated, by four bridging phenoxo oxygen atoms (O(2), O(3), O(6), and O(7)) and four ethoxy oxygen atoms (O(1), O(4), O(5), and O(8)), while the pairs of metal ions Cu(1)···K(1) and Cu(2)···K(1) in the Cu(1)···K(1)···Cu(2) trinuclear core are diphenoxo-bridged. The bond distances in the coordination environment of the K(I) ions lie in two distinct ranges; the bond lengths involving the four bridging phenoxo oxygen atoms (2.652(2)−2.699(2) Å) are significantly shorter than those involving the four ethoxy oxygen atoms (3.003(2)−3.166(2) Å). The range of the bond angles in the coordination environment of K(1) is 51.48(6)−174.40(7)°.

The structure of $[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]$ unit consists of the triple-decker cation $[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}]^+$ and a nitrate anion. In the $[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}]^+$ cation, the two potassium(I) ions are sandwiched between a pair of $[Cu^{II}L^1]$ moieties resulting in the formation of the triple-decker system. Each of the two potassium(I) ions, K(2) and K(3A), are coordinated to the two phenoxo (O(10) and O(11) for K(2); O(18) and O(19) for K(3A)) and two ethoxy oxygen atoms (O(9) and O(12A) for K(2); O(17) and O(20) for K(3A)) of each of the two terminal mononuclear moieties ($[Cu(3)L^1]$ for K(1); $[Cu(5)L^1]$ for K(3A)) and to one phenoxo (O(15) for K(2); O(14) for K(3A)) and one ethoxy (O(16) for K(2); O(13) for K(3A)) oxygen atom of the central mononuclear moiety ($[Cu(4)L^1]$). Evidently, the two terminal Cu···K pairs, Cu(3)···K(2) and Cu(5)···K(3A), are diphenoxo-bridged, while the two central Cu···K pairs, Cu(4)···K(2) and Cu(4)···K(3A), are monophenoxo-bridged. The two potassium(I) ions, K(2) and K(3A), are bridged to each other by a nitrate ion. In contrast to the octacoordinated potassium(I) ion (K(1)) in the double-decker cation $[(Cu^{II}L^1)_2K^I]^+$, the two potassium(I) centers (K(2) and K(3A)) in the triple-decker cation $[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}]^+$ is heptacoordinated by three bridging phenoxo oxygen atoms, three ethoxy oxygen atoms and one oxygen of bridging nitrate. In the coordination environment of K(2), as in the case of K(1), the bond lengths involving the ethoxy oxygen atoms (2.857(2)−2.968(2) Å) are longer than those involving the phenoxo oxygen atoms (2.729(2)−2.804(2) Å). Because of disorder, it is not possible to compare the molecular geometry of the coordination environment of K(3A) or K(3B). The bond distance involving K(2) and nitrate oxygen should also not be compared with other bond distances due to the disorder in the bridging nitrate atoms.

In the double-decker system, the Cu−O(phenoxo)−K bridge angles (ca. 100°) are slightly smaller than the Cu−O−Na bridge angle (ca. 103°) in compound **1**. The Cu−O(phenoxo)−K(2) bond angles in the triple-decker system lie in two distinct ranges: those (ca. 103°) involving the terminal copper(II) centers are much smaller than that (ca. 110°) involving the central copper(II) center. The Cu···K distances (3.52−3.90 Å) involving K(1) and K(2) in **2** are significantly longer than the Cu···Na distance (3.35 Å) in **1**.

The molecular geometry (Tables S3 and S4, Supporting Information) of the square planar coordination environment of the five copper(II) centers in **2** are similar to that in compounds **1** and **4**−**6**.[7a] In this case also, the Cu−N bond lengths are

slightly longer than its respective *trans* Cu−O distance. The ranges of the *cisoid* angles, *transoid* angles and the average deviation of the donor centers, and the displacement of the metal ion from the corresponding least-squares N_2O_2 plane are, respectively, 84.11(11)−94.58(10)°, 174.36(10)−178.80(10)°, 0.003−0.082 Å, and 0.004−0.020 Å.

Cocrystallization in 1 and 2. As already mentioned, the 3d-3d bimetallic systems $[\{Cu^{II}L^1M^{II}(H_2O)_3\}\{Cu^{II}L^1\}_2](ClO_4)_2$ (**4**−**6**) are [2×1+1×2] self-assembled cocrystals of dinuclear $[Cu^{II}L^1M^{II}(H_2O)_3]^{2+}$ cation and two mononuclear $[Cu^{II}L^1]$ moieties.[7a] Encapsulation of two of the three coordinated water molecules in the two O_4 compartments of two mononuclear species is the reason for the formation of the 3d-3d cocrystals. In $[\{Cu^{II}L^1Na^I(H_2O)_2\}\{Cu^{II}L^1\}_2](NO_3)$ (**1**), there are two coordinated water molecules and each of these are encapsulated in the O_4 compartment of two mononuclear species. Evidently, compound **1**, similar to **4**−**6**, is a [2×1+1×2] cocrystal of dinuclear $[Cu^{II}L^1Na^I(H_2O)_2]^+$ cation and two mononuclear $[Cu^{II}L^1]$ moieties. In the case of $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**2**), one trinuclear double-decker cation $[(Cu^{II}L^1)_2K^I]^+$ and one pentanuclear triple-decker cation $[(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)]^+$ coexist in a single crystal. Evidently, compound **2** is a [3×1+5×1] cocrystal of a double-decker and a triple-decker system.

Conclusions

The composition of 3d-4f and 3d-3d compounds derived from *N,N′*-ethylenebis(3-ethoxysalicylaldimine) (H_2L^1) are dinuclear and tetrametallic dinuclear−mononuclear cocrystals, respectively. We started this investigation to explore the composition of the products obtained on reaction of the inclusion compound $[Cu^{II}L^1\subset(H_2O)]$ and the alkali metal salts. As discussed, the compound $[\{Cu^{II}L^1Na^I(H_2O)_2\}\{Cu^{II}L^1\}_2](NO_3)$ (**1**) containing copper(II) and sodium(I) is a [2×1+1×2] cocrystal, similar to the 3d-3d complexes. The reason of the cocrystallization in **1** is similar to that of the 3d-3d cocrystals. It is interesting to note that tendency of potential encapsulation of a water molecule in the vacant O_4 cavity of the mononuclear $[Cu^{II}L^1]$ species enforces sodium(I) to behave similarly like 3d metal ions. Evidently, this unprecedented structural resemblance of an alkali metal ion with 3d metal ions possesses importance in structural chemistry. It may be mentioned at this point that the $Cu^{II}Na^I$ compounds derived from 3-methoxysalicylaldehyde-diamine ligands are dinuclear. The second title compound $[\{(Cu^{II}L^1)_2K^I\}(NO_3)]\cdot[\{(Cu^{II}L^1)_3K^I_2(\mu\text{-}NO_3)\}(NO_3)]\cdot 0.2H_2O$ (**2**) is a cocrystal of a double-decker and a triple decker moiety. As, to the best of our knowledge, there is only one reported example of double-decker−triple-decker cocrystal, the composition of the compound **2** is also an important aspect. The composition of compound **2** is different than those of the compounds **1** and previously reported tetrametallic assemblies $[\{Cu^{II}L^1M^{II}(H_2O)_3\}\{Cu^{II}L^1\}_2](ClO_4)_2$ (M = Cu (**4**), Co (**5**) or Mn (**6**)).[7a] However, the similarity of all the 3d-3d or 3d-alkali metal compounds **1**, **2**, and **4**−**6** is that these are cocrystals. It seems therefore that the ligand system H_2L^1 has a potential tendency to stabilize cocrystals of different combinations of metal ions and of different compositions. It should however be noted that, while the coexistence of different moieties in **1** and **4**−**6** can be explained on the basis of the hydrogen bonding interactions of the O_4 cavity of $[Cu^{II}L^1]$ with the water hydrogens, the reason for cocrystallization of a double-decker and a triple-decker unit in **2** cannot be rationalized. To summarize, the structural resemblance of sodium(I) with 3d metal ions and a second example of a double-decker−triple-decker cocrystal (the first example containing an alkali metal ion) are the major outcomes of the present investigation.

Acknowledgment. Financial support from the Department of Science and Technology, the Government of India (SR/S1/IC-12/2008), is gratefully acknowledged. S.H. thanks CSIR, Government of India, and R.K. thanks Centre for Research in Nanoscience and Nanotechnology, University of Calcutta, for providing fellowships. J.A.K.H. and H.A.S. would like to thank the EPSRC EP/E048994/1 for financial assistance.

Supporting Information Available: Figures S1−S2, Tables S1−S5, and crystallographic data in CIF format for compounds **1** and **2**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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