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Pseudohalide-Controlled Assemblies of Copper–Schiff Base Complexes with an Encapsulated Sodium Ion: Synthesis, Crystal Structure, and Computational Studies

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Three new hetero-bimetallic coordination complexes [Na(Cu^{II}L¹)₂](ClO₄)·0.5H₂O (**1**), [Na(Cu^{II}L²)₂][Cu^I₂(μ_{1,3}-NCS)₃]_n (**2**), and {[Na(Cu^{II}L³)₂](μ_{1,5}-dca)}_n (**3**; dca = dicyanamide) have been synthesized by using different Schiff base ligands [e.g., L¹H₂ = *N,N'*-bis(3-methoxysalicylideneimino)-1,3-diaminopentane, L²H₂ = *N,N'*-bis(3-ethoxysalicylideneimino)-1,3-diaminopropane, and L³H₂ = *N,N'*-bis(5-bromo-3-methoxysalicylideneimino)-1,3-diaminopropane] in the presence of pseudohalide coligands N₃⁻, SCN⁻, and N(CN)₂⁻ (dca), respectively. The ligands and the complexes have been characterized by microanalytical and spectroscopic techniques. The structures of the complexes, determined by single-crystal X-ray diffraction studies, show that in all cases a trinuclear

Na(Cu^{II}L)₂ unit is formed, but of different configurations. **1** does not include N₃⁻ anions. In contrast, in **2**, SCN⁻ extrudes partial in situ reduction of Cu^{II} to lead to the formation of an infinite [Cu^I₂(μ_{1,3}-NCS)₃]_n anionic chain; and in **3**, N(CN)₂⁻ bridges the metal–ligand assemblies to form a 1D polymeric chain. ESI-MS, UV/Vis spectroscopy, and cyclic voltammetry were performed to investigate the solution-state behavior of the complexes. Theoretical calculations of the optimized geometries of the complexes were carried out at the BLYP/DNP level to determine their relative stabilities from the HOMO–LUMO gap and chemical softness values.

Introduction

Compartmental Schiff bases with multiple N/O-donor sites are useful for easy and successful synthesis of multinuclear homo- and/or heterometallic complexes with interesting stereochemistry.^[1–3] Polydentate phenol-based Schiff base ligands are usually bicompartamental (i.e., they provide two adjacent coordination sites with dissimilar environment and are binucleating agents).^[3b,4] Our group^[5–10] and others^[11–17] have reported many such phenol-based N₂O₂- or N₂O₄-donor compartmental Schiff base ligands, which contain a tetradentate inner core formed of two imino nitrogen atoms and two μ-phenoxo oxygen atoms, and an outer compartment that provides two μ-O_(phenoxo) (for N₂O₂ species) or an O₄-donor set that chelates through two μ-phenoxo and two alkoxo oxygen atoms (for N₂O₄ species).

Such compartmental ligands encompass a metal ion in the inner compartment, but the bridging nature of the phenoxo oxygen atoms hunts for another metal ion to be accommodated in the outer compartment. Such a metal–ligand assembly represents a fascinating group of systems known as “ligand complexes”,^[16,17] which are effective complexing agents not only for p-, d-, and f-block elements but also for alkali-metal ions. In fact, the phenoxo and alkoxo oxygen atoms that form the outer compartment act as a host and coordinate a guest metal ion to develop bi- or trinuclear homo-/heterometallic complexes.^[18]

In continuation of our earlier studies, we have synthesized three new N₂O₄-donor compartmental Schiff bases L¹H₂ (Scheme 1) by the condensation of one equivalent of 1,3-diamines and two equivalents of 3-alkoxysalicylaldehyde derivatives: *N,N'*-bis(3-methoxysalicylideneimino)-1,3-diaminopentane (L¹H₂), *N,N'*-bis(3-ethoxysalicylideneimino)-1,3-diaminopropane (L²H₂), and *N,N'*-bis(5-bromo-3-methoxysalicylideneimino)-1,3-diaminopropane (L³H₂). Copper complexes of these ligands have been synthesized in the presence of NaN₃, NaSCN, and NaN(CN)₂, with the aim of accessing the influence of the pseudohalide anions. Pseudohalide ions organize discrete metal–salicylaldehyde units into multidimensional extended architectures. At the same time, it is clear that the counter cation (Na⁺ here) fits well in the outer compartment of the “ligand com-

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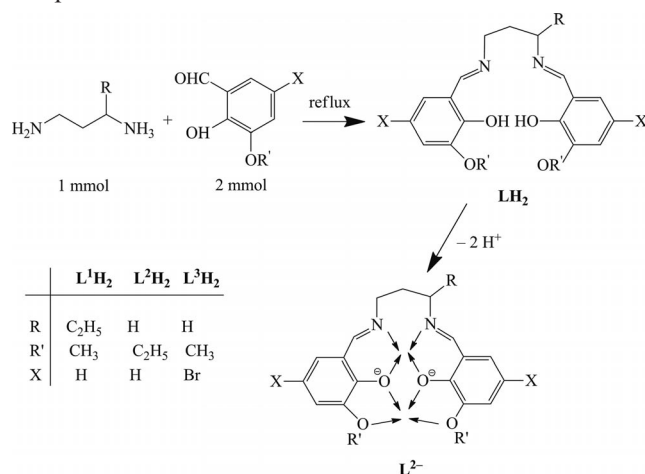
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plexes” to form hetero-bimetallic molecules. In the literature, there are many reports of discrete di/trinuclear 3d/alkali metal/salicylaldehyde complexes,^[16,19,20] but very few of their extended architectures,^[20–22] which motivated us to explore this area of research. All complexes, which are of the formula $[\text{Na}(\text{Cu}^{\text{II}}\text{L}^1)_2](\text{ClO}_4) \cdot 0.5\text{H}_2\text{O}$ (**1**), $[\text{Na}(\text{Cu}^{\text{II}}\text{L}^2)_2][\text{Cu}^{\text{I}}_2(\mu_{1,3}\text{-NCS})_3]_n$ (**2**), and $\{\text{Na}(\text{Cu}^{\text{II}}\text{L}^3)_2(\mu_{1,5}\text{-dca})\}_n$ (**3**), consist of a $\text{Cu}^{\text{II}}\text{L}-\text{Na}^{\text{I}}-\text{Cu}^{\text{II}}\text{L}$ interconnected trinuclear sandwich-type moiety of different configurations. In fact, the Schiff base ligand encompasses a Cu^{II} ion into the tetradentate N_2O_2 -donor inner compartment, and two of these “ligand complexes” provide an octadentate crown ether type coordination set (through the outer compartments) to encapsulate the Na^{I} ion.



Scheme 1. The synthetic routes and the mode of coordination of the Schiff base ligands.

Whereas in the first case compound NaN_3 has no role in extending the molecule but rather provides the Na atom only, in the second complex, NaSCN , in addition to being a source of Na, acts as a reducing agent^[23] for the in situ partial reduction of $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ to form infinite anionic $[\text{Cu}^{\text{I}}_2(\mu_{1,3}\text{-NCS})_3]_n$ chains, thereby intervening in the discrete cationic $\text{Cu}^{\text{II}}-\text{Na}^{\text{I}}-\text{Cu}^{\text{II}}$ metal–ligand assembly. To the best of our knowledge, the X-ray crystal structure of this kind of $\text{Cu}^{\text{I}}-\text{SCN}$ anionic chain electrostatically connected to the cationic units has been reported only once, by Paul et al.^[23] (although with a different topology). $\text{NaN}(\text{CN})_2$ is also a source of Na, whereas the anion bridges the trinuclear $\text{Cu}^{\text{II}}\text{L}-\text{Na}^{\text{I}}-\text{Cu}^{\text{II}}\text{L}$ entities into an infinite one-dimensional array in the third complex. We have also theoretically investigated the relative stability of the complexes by applying the Becke–Lee–Yang–Parr correlation exchange function and double numerical with polarization (BLYP/DNP)-level calculations to their optimized geometries.

Results and Discussion

Crystal Structure Descriptions

$[\text{Na}(\text{CuL}^1)_2](\text{ClO}_4) \cdot 0.5\text{H}_2\text{O}$ (**1**)

A perspective view of complex **1** is presented in Figure 1 and a selection of bond lengths and angles are listed in Table 1.

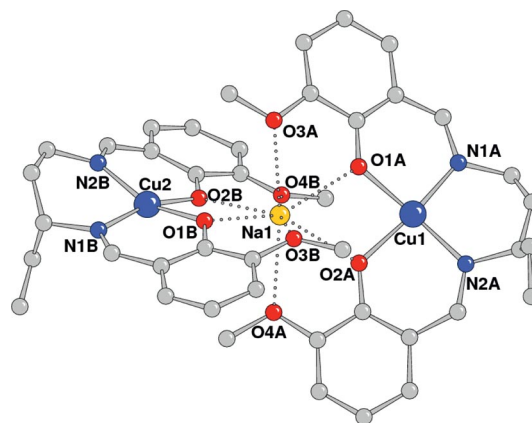


Figure 1. Perspective view of the complex cation $[\text{Na}(\text{L}^1\text{Cu}^{\text{II}})_2]^+$ (**1**) with atom-numbering scheme of coordinating atoms.

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**.

Bond lengths [Å]			
Cu1–O1A	1.9042(17)	Na1–O1B	2.4120(19)
Cu1–O2A	1.9191(17)	Na1–O2B	2.422(2)
Cu1–N2A	1.948(2)	Na1–O1A	2.4355(19)
Cu1–N1A	1.960(2)	Na1–O2A	2.445(2)
Cu2–O2B	1.9130(19)	Na1–O3B	2.5311(18)
Cu2–O1B	1.9169(18)	Na1–O3A	2.532(2)
Cu2–N1B	1.950(3)	Na1–O4B	2.5443(19)
Cu2–N2B	1.970(3)	Na1–O4A	2.570(2)
Bond angles [°]			
O1A–Cu1–O2A	83.42(7)	O1B–Cu2–O2B	82.58(8)
O1A–Cu1–N1A	92.59(9)	O1B–Cu2–N1B	92.68(9)
O1A–Cu1–N2A	162.22(9)	O1B–Cu2–N2B	159.32(11)
O2A–Cu1–N1A	159.58(9)	O2B–Cu2–N1B	164.60(11)
O2A–Cu1–N2A	93.29(9)	O2B–Cu2–N2B	93.36(11)
N1A–Cu1–N2A	96.27(10)	N1B–Cu2–N2B	96.03(12)

The molecular complex is built by two CuL^1 units that embrace a central Na ion to form a distorted propeller-like arrangement. Each copper ion is located at the inner N_2O_2 cavity of the bicompartamental ligand; they are square planar, coordinated by two phenoxo oxygen and two imino nitrogen atoms of the doubly deprotonated ligand $[\text{L}^1]^{2-}$. The coordination bond angles of copper ions show small deviations from 90° (Table 1), which suggests that both of the terminal metals present an almost ideal square-planar geometry. The copper atoms Cu1 and Cu2 are slightly displaced from their corresponding mean planes by 0.022 and 0.051 Å, respectively. Each CuL^1 unit is twisted with respect to the other so that the coordination N_2O_2 mean planes (O1AN1AN2AO2A around Cu1 and O1BN1BN2BO2B around Cu2) form a dihedral angle of 49.76° . The sodium ion is encapsulated within the external O_8 compartment formed by four methoxo oxygen atoms and four bridging phenoxo oxygen atoms of two CuL^1 entities. The $\text{Cu}^{\text{II}}-\text{Na}^{\text{I}}-\text{Cu}^{\text{II}}$ trimetallic core is almost linear, being held at an angle of 174.64° . The Cu1–Na1 and Cu2–Na1 distances are 3.5097(10) and 3.4987(11) Å, respectively. The Cu–O bond lengths vary from 1.9042(17) to 1.9191(17) Å, slightly shorter than the Cu–N ones in the range 1.948(2)–

1.970(3) Å, and these values are comparable with previous reports.^[24]

The central sodium ion has an octacoordination formed by the trapezoids of the μ -bridging phenoxo oxygen atoms O1A, O2A, and methoxo oxygen atoms O3A, O4A of one ligand, and those of the counterpart O1B, O2B, O3B, and O4B, thus resulting in a distorted dodecahedral geometry. The four Na–O_{methoxo} bonds (mean 2.544 Å) are longer than the four Na–O_{phenoxo} bonds (mean 2.429 Å; Table 1).

Finally, the perchlorate anion, present in the lattice for the charge neutralization, shows a non-conventional hydrogen bond with the proton of the azomethine carbon atom C14A, as well as the lattice water molecule that weakly interacts with methylene proton H11B of the ethyl side chain of the ligand (Table S1 and Figure S1 in the Supporting Information). It is worth noting that the water molecule resides almost at the apical position of Cu2 at a distance of 3.70 Å from it, which suggests a possible square-pyramidal coordination geometry for the copper ions in solution.

[Na(Cu^{II}L²)₂][Cu^I₂($\mu_{1,3}$ -NCS)₃]_n (2**)**

The asymmetric unit of **2** contains a heterotrimeric [Na(Cu^{II}L²)₂]⁺ cationic moiety and a [Cu^I₂($\mu_{1,3}$ -NCS)₃][−] counteranion, a perspective view of which is shown in Figure 2 (a and b), respectively. A selection of bond lengths and angles are listed in Table 2.

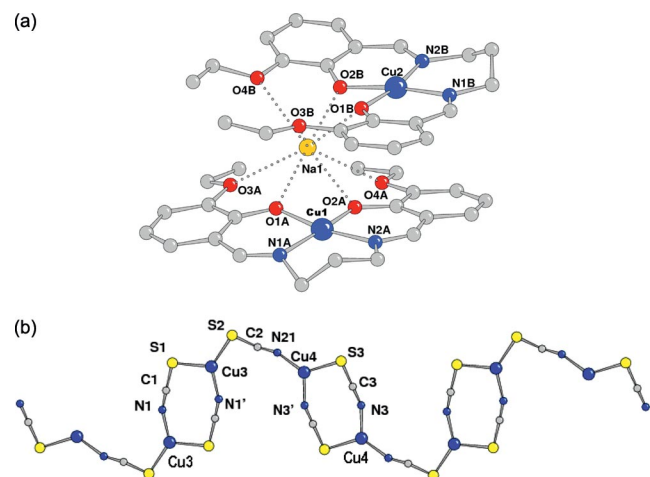


Figure 2. (a) Molecular structure of the complex cation [Na(Cu^{II}L²)₂]⁺ of **2**. (b) View of the polymeric [Cu^I₂($\mu_{1,3}$ -NCS)₃]_n[−] arrangement in **2** running along the *c* axis.

Similar to complex **1**, Cu1 and Cu2 are tetracoordinated by the N₂O₂-donor set of the inner cavity of [L²]^{2−}, with the Cu–O and Cu–N bond lengths following a similar trend as in **1** and in reported complexes.^[24] However, the two copper coordination mean planes are almost parallel, with a dihedral angle of 8.79°. The Na ion, coordinated by four ethoxo oxygen atoms (O3A, O3B, O4A, and O4B) and four μ -phenoxo oxygen atoms (O1A, O2A, O1B, and O2B) is sandwiched between two CuL² moieties, as shown in Figure 2a. The Na–O_{ethoxo} bond lengths (mean 3.002 Å) are significantly larger than the μ -bridging Na–O_{phenoxo} linkages (mean 2.417 Å; Table 2). The Na–O_{ethoxo} bonds in **2**

Table 2. Selected bond lengths [Å] and angles [°] for complex **2**.

Bond lengths [Å]			
Cu1–O1A	1.921(7)	Na1–O4A	3.092(8)
Cu1–O2A	1.910(5)	Na1–O2A	2.465(7)
Cu1–N1A	1.997(8)	Na1–O2B	2.370(6)
Cu1–N2A	1.977(9)	Na1–O3B	3.064(7)
Cu2–O1B	1.918(5)	Na1–O4B	2.978(6)
Cu2–O2B	1.922(5)	Cu3–S1	2.275(4)
Cu2–N1B	1.975(7)	Cu3–S2	2.201(3)
Cu2–N2B	1.993(7)	Cu3–N1	1.933(9)
Na1–O1A	2.369(6)	Cu4–S3	2.273(5)
Na1–O2A	2.465(7)	Cu4–N3	1.929(11)
Na1–O3A	2.876(7)	Cu4–N21	1.929(17)
Bond angles [°]			
O1A–Cu1–O2A	80.5(3)	O1B–Cu2–O2B	80.0(2)
O1A–Cu1–N1A	90.4(3)	O1B–Cu2–N1B	92.0(2)
O1A–Cu1–N2A	170.0(3)	O1B–Cu2–N2B	169.8(2)
O2A–Cu1–N1A	169.1(3)	O2B–Cu2–N1B	171.0(2)
O2A–Cu1–N2A	91.3(3)	O2B–Cu2–N2B	90.8(2)
N1A–Cu1–N2A	98.4(3)	N1B–Cu2–N2B	97.6(3)
S1–Cu3–S2	118.57(12)	S3–Cu4–N3	107.0(3)
S1–Cu3–N1	107.7(3)	S3–Cu4–N21	126.8(6)
S2–Cu3–N1	133.7(3)	N3–Cu4–N21	126.2(6)

are considerably longer than Na–O_{methoxo} bonds of **1** on account of the bulky ethoxy groups. Unlike **1**, the cationic heterotrimeric entity is nonlinear with Cu1–Na1–Cu2 ions forming an angle of 110.8(1)°, and Cu1–Na1 and Cu2–Na1 distances of 3.345(3) and 3.332(3) Å, respectively.

The Cu^INCS-based 1D chain is formed from the self-assembly of monoanionic [Cu^I₂($\mu_{1,3}$ -NCS)₃][−] units. The array of trimeric cationic units serve as templates for the formation of the Cu^INCS-based anionic chain and are trapped within the layers of this 1D chain. Two Cu^I ions bridged by double SCN[−] chains in a cooperative manner result in an eight-membered metallacyclic loop. Adjacent centrosymmetric loops alternately composed of two Cu³ and two Cu⁴ atoms linked by double μ -SCN[−] bridges are connected through a single SCN[−] bridge, thus propagating in 1D along the *c* axis through the intervening space of the array of cationic units as shown in Figure 3.

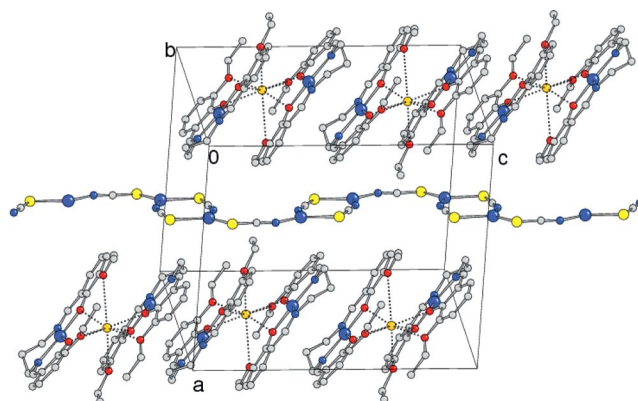


Figure 3. Crystal-packing diagram of **2** with the 1D anionic polymers [Cu^I₂($\mu_{1,3}$ -NCS)₃]_n[−] inserted among the [Na(L²Cu^{II})₂]⁺ entities.

Both Cu3 and Cu4 atoms show a distorted trigonal-planar geometry, with Cu3 being coordinated by two S atoms [Cu3–S1 2.275(4) and Cu3–S2 2.201(3) Å] and one N atom [Cu3–N1 1.933(9) Å] from three different $\mu_{1,3}$ -SCN[−] ligands, whereas Cu4 is coordinated by two N atoms [Cu4–N3 1.929(11) and Cu4–N21 1.929(17) Å] and one S atom [Cu4–S3 2.273(5) Å]. The Cu–S distances in our system are slightly shorter than those reported in the polymeric compound $\{[C_5H_6N][Cu_2(NCS)_3]\}_n$, in which they fall in the 2.319(3)–2.493(4) Å range.^[25] The distance between Cu3 and Cu4 is 5.379 Å along the single SCN[−] connection.

$\{[Na(Cu^II L^3)_2](\mu_{1,5}\text{-dca})\}_n$ (3**)**

A perspective view of the centrosymmetric trinuclear entity of **3** with the atom-numbering scheme is presented in Figure 4, whereas bond lengths and angles are listed in Table 3.

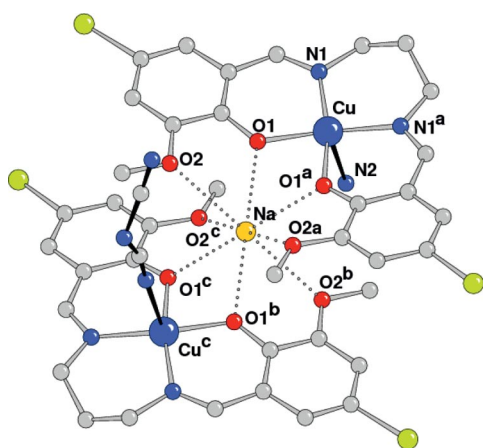


Figure 4. Perspective view of complex $\{[Na(Cu^II L^3)_2](\mu_{1,5}\text{-dca})\}_n$ (**3**) with C_{2h} symmetry.

Table 3. Crystallographically independent bond lengths [Å] and angles [°] for complex **3**.

Bond lengths [Å]			
Cu–O1	1.919(3)	Na–O1	2.504(3)
Cu–N1	1.980(3)	Na–O2	2.768(3)
Cu–N2	2.644(13)		
Bond angles [°]			
O1–Cu–O1a ^[a]	78.52(18)	N1–Cu–N1a	97.9(2)
O1–Cu–N1	91.42(14)	O1–Cu–N2	99.0(3)
O1–Cu–N1a	168.41(15)	N1–Cu–N2	88.1(3)

[a] Symmetry transformations used to generate equivalent atoms: $x, -y + 1, z$.

Here two $[CuL^3]$ units are bonded to the central sodium ion to form a heterotrimeric $CuL^3\text{--}Na\text{--}CuL^3$ metallic core, which, unlike **1** and **2**, possesses a C_{2h} symmetry. The heterotrimeric metals are perfectly collinear and have a Cu–Na distance of 3.5432(8) Å. In the present case, the copper centers are coordinated by a dca ligand, thus the geometry of the Cu^{II} center, located at the inner N₂O₂ cavity of $[L^3]^{2-}$, can be best described as a distorted square-

pyramidal with Addison parameter $\tau = 0.026$, ($\tau = |\beta - a|/60^\circ$, for which β and a are the two largest angles around the central atom; these are 0 and 1 for the perfect square-pyramidal and trigonal-bipyramidal geometries, respectively).^[26] The four basal sites are occupied by two symmetry-related imine nitrogen (N1, N1^a) and two phenoxo oxygen (O1, O1^a) atoms of $[L^3]^{2-}$. The apical position of each Cu^{II} center is occupied by the N2 end of a $\mu_{1,5}$ -bridging dca ligand, and the Cu^{II} atoms are displaced by 0.107 Å from the square base towards the apical nitrogen atom N2. The sodium ion, positioned on a $2/m$ symmetry site, connects the complexes in pairs through Na–O interactions.

The Na atom is coordinated by four symmetry-equivalent methoxo oxygen atoms O2, O2^a, O2^b, and O2^c, and the four μ_2 -bridging phenoxo oxygen atoms O1, O1^a, O1^b, and O1^c, thereby resulting in a distorted dodecahedral geometry. The four longer Na–O bonds that involve the methoxo oxygen atoms [Na–O1 ($\times 4$) 2.504(3) Å] are shorter than those that involve the phenoxo oxygen atoms [Na–O2 ($\times 4$) 2.768(3) Å]. The dicyanamide N(CN)₂[−] anion, which guarantees the electroneutrality, is disordered over two positions around a center of symmetry, so that the dicyanamide connects one copper ion at 2.644(13) Å; the other terminal dca N donor is at 3.10 Å from the symmetry-related Cu (likely for steric reasons or packing requirements). In any case, a 1D zigzag polymeric chain along the crystallographic c axis can be outlined (Figure 5).

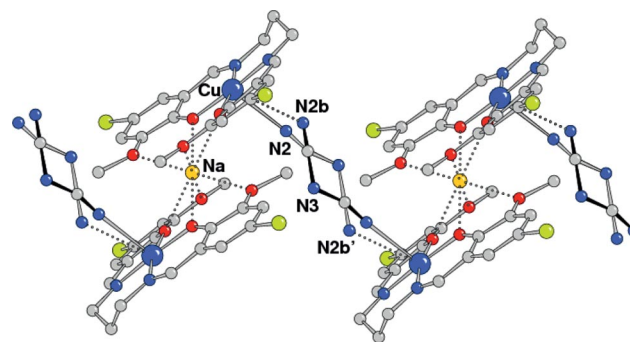


Figure 5. Detail of the crystal-packing of **3**.

Structural Correlation

The different configurations of the $Cu^II L^3\text{--}Na^I\text{--}Cu^II L^3$ units in complexes **1–3** deserve a more detailed discussion, although at first sight the Cu–Na distances are comparable as they are in the range 3.332(3)–3.5432(8) Å. In fact, in **1** the two CuL units interact in a propeller-like fashion as defined by the dihedral angle of 63.99°, formed by the almost coplanar O₄-donor sets that coordinate the sodium in a crown ether type environment, whereas the N₂O₂ mean planes define an angle of 49.76°. On the other hand, in **2** and **3** the two copper coordination mean planes, separated by approximately 2.88 and 1.90 Å, respectively, are almost parallel in **2** (dihedral angle of 8.79°) and, for the crystallo-

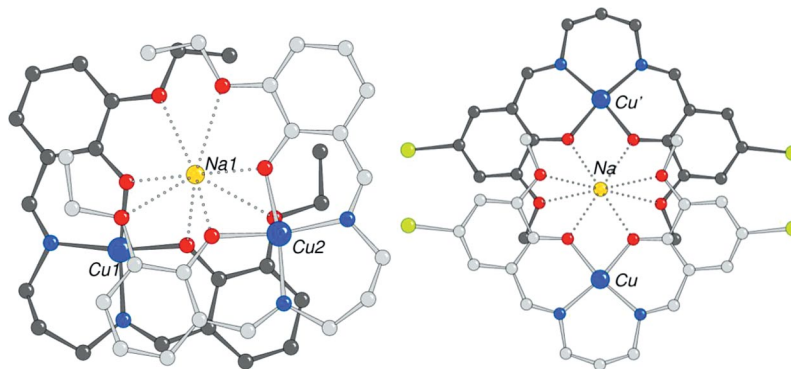


Figure 6. View of complexes **2** and **3** showing the tilted arrangement of the CuL moieties in **2**, which requires a rotation of approximately 82° to attain the configurational arrangement observed in **3**.

graphically imposed symmetry, parallel in the latter. However whereas complex **3** is centrosymmetric (Cu–Na–Cu angle of 180°), in **2** the CuL units are tilted toward each other so that the intermetallic angle is reduced to 110.8(1)°. The different configurations observed in these complexes (a perspective view is provided in Figure 6) were addressed by the different pseudohalides used, by packing requirements, and by orientational restrictions in the ligands caused by bulky substituents.

Our group had previously reported a homo-trinuclear Cu^{II} complex with two independent crystallographic units [i.e., [Cu₃(μ-L')₂(ClO₄)₂] and [Cu₃(μ-L')₂(H₂O)(ClO₄)₂]^[9] with a salen-type ligand system [L'H₂ = OHC₆H₄-CH=NCH₂CH₂CH(CH₂CH₃)N=CHC₆H₄OH]. As an extension of our previous work, we have increased the denticity in the present ligands with an additional –OMe group in the aromatic rings of L¹H₂ and L³H₂ and with a –OEt in the case of L²H₂. In all three compounds a trinuclear metal cluster was obtained, but the increased denticity of the ligand required a larger metal ion (than Cu^{II}) that was able to be accommodated within the large outer compartment formed by the two O₄-donor sets of the ligand fragments. Thus in complexes **1**, **2**, and **3**, an Na⁺ ion enters into the central core to form a hetero-trinuclear Cu^{II}–Na^I–Cu^{II} metal cluster rather than the homo-trinuclear Cu₃ previously obtained.^[9]

Fourier-Transform Infrared Spectra

Fourier-transform infrared spectra of all the complexes were analyzed and compared with those of the corresponding free ligands. The stretching vibrations are listed in

Table 4. Strong, sharp absorption bands at 1629, 1640, and 1635 cm⁻¹ in the spectra of L¹H₂, L²H₂, and L³H₂, respectively, on account of the C=N stretching indicate the formation of the Schiff base ligands. Condensation of all the primary amine groups was confirmed by the absence of the N–H stretching bands in the 3150–3450 cm⁻¹ region. In the complexes, the ν_{C=N} stretching vibrations at 1609, 1610, and 1615 cm⁻¹ in **1**, **2**, and **3**, respectively, were shifted considerably towards lower frequencies relative to that of the free ligands, which indicated the coordination of the imine nitrogen atom to the metal center.^[27] Well-defined bands observed at 3449, 3448, and 3465 cm⁻¹ in the spectra of L¹H₂, L²H₂, and L³H₂, respectively, are due to O–H stretching, which disappeared in the spectra of **2** and **3** upon deprotonation of the O–H group during complexation, whereas a band at 3448 cm⁻¹ in the spectrum of **1** might be attributed to the presence of lattice water molecules. The phenolic C–O stretching bands at 1254, 1255, and 1260 cm⁻¹ in the spectra of L¹H₂, L²H₂, and L³H₂, respectively, were shifted to 1223, 1226, and 1234 cm⁻¹ in **1–3**, respectively, thereby supporting the deprotonation and coordination of the phenolic oxygen donors to the metal center. The ligand coordination to the metal centers was indicated by a band that appeared at 439 cm⁻¹ for **1** and at 454 cm⁻¹ for both **2** and **3**, which are mainly assigned to ν_(Cu–N) in each case. The characteristic bifurcated absorption band for perchlorate anion appeared at 1081–1110 cm⁻¹ in the spectrum of **1**. The presence of bridging SCN⁻ in **2** was indicated by a sharp bifurcated band within the 2127–2109 cm⁻¹ range.^[28] In the spectrum of **3**, several observed ν_{C≡N} bands at 2244, 2189, and 2134 cm⁻¹ were attributed to the ν_{sym} + ν_{asym}(C≡N), ν_{asym}(C≡N), and ν_{sym}(C≡N) modes of the bridging dicyanamide ligand, respectively.^[29–33]

Table 4. IR spectroscopic data [cm⁻¹] of ligands L¹H₂, L²H₂, L³H₂, and complexes **1–3**.

	ν(C=N)	ν(C–O _{Phenolic})	ν(O–H/H ₂ O)	ν(M–N)	ν(ClO ₄ ⁻)	ν(SCN ⁻)	ν(C≡N)
L ¹ H ₂	1629	1254	3449	–	–	–	–
L ² H ₂	1640	1255	3448	–	–	–	–
L ³ H ₂	1635	1260	3465	–	–	–	–
1	1609	1223	3448	439	1081–1110	–	–
2	1610	1226	–	454	–	2127–2109	–
3	1615	1234	–	454	–	–	2244–2134

ESI Mass Spectra of 1–3

Positive-ion electrospray mass spectra of solutions of the complexes in acetonitrile gave molecular ion peaks at m/z 454 for **1** and **2**, and at m/z 583 for **3**. The signals for **1** and **2** correspond to the species $[L^nCuNa - 2H]^+$ ($n = 1, 2$), whereas the signal for **3** at m/z 583 can be attributed to the species $[L^3CuNa - 3H]^+$. The structural assignments for such ions are also supported by their characteristic isotopic distributions, which are particularly affected by the presence of copper ($^{63}Cu/^{65}Cu$ of 1:0.44). Thus it is evident from the mass spectroscopic study of **1–3** that the discrete CuL assemblies associated with a sodium ion exist in solution.

Electronic Spectra

The UV/Vis spectra of the Schiff base ligands and of the complexes were recorded at 300 K in DMF. The observed UV/Vis bands are listed in Table 5, and the spectra of the complexes in DMF are shown in Figure 7. The spectra of the free ligands exhibit two intraligand charge-transfer (CT) bands in the 260–290 nm range, which can be attributed to $\pi \rightarrow \pi^*$ transitions, and at 330, 342, and 339 nm for L^1H_2 ,

Table 5. UV/Vis absorption bands of the ligands and complexes (**1–3**) in DMF at room temperature $\{\lambda_{ab}$ [nm] (ϵ [$M^{-1}cm^{-1}$]) $\}$.

	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	LMCT	d–d
L^1H_2	264 (11350)	330 (2380)	–	–
L^2H_2	260 (8460)	342 (4670)	–	–
L^3H_2	290 (7310)	339 (4350)	–	–
1	242 (44780)	–	365 (9430)	570 (560)
2	283 (31788)	–	374 (10050)	606 (433)
3	280 (43670)	–	377 (13720)	606 (535)

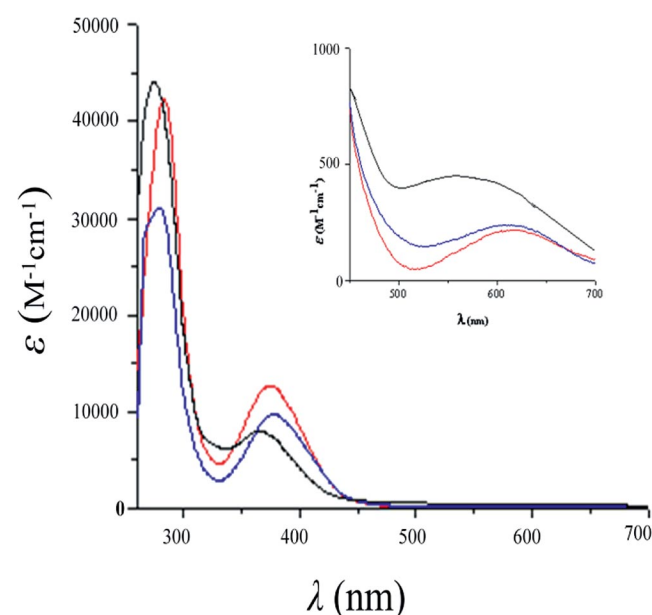


Figure 7. UV/Vis absorption spectra of complexes **1** (in black), **2** (in blue), and **3** (in red) in DMF at room temperature. The inset shows d–d transition bands.

L^2H_2 , and L^3H_2 , respectively, which can be attributed to $n \rightarrow \pi^*$ transitions. Two distinct absorption bands appeared in the spectra of the complexes at 242, 365 nm for **1**, 283, 374 nm for **2**, and 280, 377 nm for **3**. The high-energy bands at 242, 283, and 280 nm in **1**, **2**, and **3**, respectively, originate from $\pi \rightarrow \pi^*$ transitions of the aromatic rings.^[34] Ligand-to-metal charge-transfer transition bands (LMCT) appeared at 365, 374, and 377 nm in complexes **1**, **2**, and **3** respectively, at the expense of the $n \rightarrow \pi^*$ transition bands of the respective free ligands.^[34] Much weaker and less well-defined broad bands are found in the spectra of the complexes in the 550–650 nm range; these are assigned to the d–d transition, which is typical for a Cu^{II} Schiff base complex.^[34,35]

Cyclic Voltammetry

Redox properties of **1–3** were investigated by cyclic voltammetry in DMF medium with tetrabutylammonium perchlorate as the supporting electrolyte at a scan rate of

Table 6. Redox potential of complexes **1–3** in DMF at a scan rate of 100 mV s^{-1} .

	E_{pc1} [V]	E_{pc2} [V]	E_{pa1} [V]	E_{pa2} [V]
1	0.617	–1.073	0.688	–
2	0.018	–1.050	0.245	0.482
3	0.633	–1.028	0.611	1.115

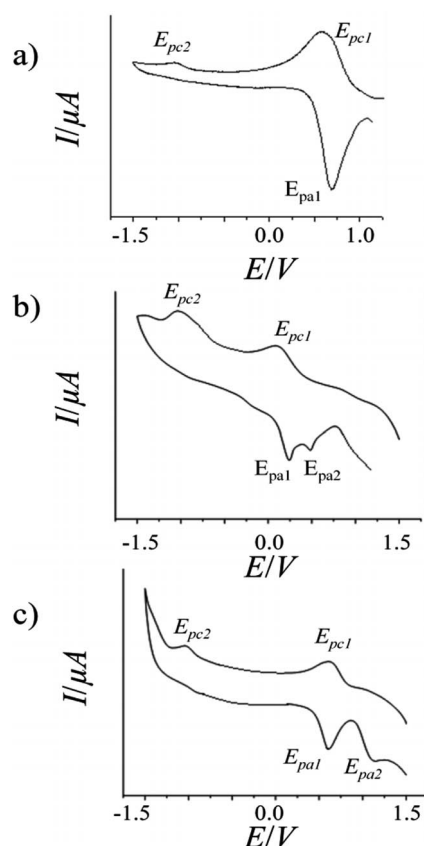


Figure 8. Cyclic voltammogram of (a) **1**, (b) **2**, and (c) **3**.

100 mV s⁻¹. The redox potential data of **1–3** are listed in Table 6, and the cyclic voltammograms are depicted in Figure 8. It is evident from mass spectroscopy that in solution the trinuclear LCu–Na–CuL clusters are disrupted, with the LCu moieties being separated by solvent molecules. Hence the electrochemistry of the complexes is characteristic of individual Cu^{II} centers. The cyclic voltammograms of the three complexes show two reduction peaks, E_{pc1} and E_{pc2} , during the cathodic scan. E_{pc1} corresponds to the Cu^{II}→Cu^I reduction of the CuL species. Some Cu^I ions generated in this process are adsorbed onto the electrode surface and are further reduced to metallic copper at E_{pc2} .^[36,37] On the reverse sweep, the complexes show a sharp oxidation peak E_{pa1} that corresponds to the composite processes of Cu⁰→Cu^{II} and Cu^I→Cu^{II} oxidation. Complexes **2** and **3** show additional E_{pa2} oxidation peaks for the irreversible oxidation of Cu^{II}→Cu^{III}.^[38]

Computational Studies

The geometry of complexes **1**, **2**, and **3**, as derived from their X-ray crystallographic data, was fully optimized by using the Vosko–Wilk–Nusair (VWN) functional and double-numerical (DN) basis sets as implemented in the program DMol³.^[39] Then single-point calculations were

performed on the optimized geometries at the BLYP/DNP level. The relative stability and reactivity of the complexes were compared by calculating their HOMO–LUMO gap and chemical softness values. The calculated geometric parameters of some selected bonds of the complexes (Table 7), which preserve their conformation, are in very good agreement with the experimental data. To gain some insight into the stability of the complexes, we calculated chemical hardness and HOMO–LUMO gaps of all the complexes. The optimized structures along with HOMO and LUMO plots are shown in Figure 9. The HOMO–LUMO gaps of **1**, **2**, and **3** are 0.936, 0.896, and 0.170 eV, respectively. The

Table 7. Copper coordination bond lengths of complexes **1**, **2**, and **3** calculated at the VWN/BN level compared with experimental X-ray values.

	Complex 1		Complex 2		Complex 3	
	DFT	Exp.	DFT	Exp.	DFT	Exp.
Cu1–N1	1.919	1.960	1.961	1.997	2.006	1.980
Cu1–N10	1.924	1.948	1.949	1.977	1.895	1.980
Cu1–O1	1.936	1.904	1.975	1.921	1.940	1.919
Cu1–O7	1.943	1.919	1.946	1.910	1.909	1.919
Cu2–N5	1.928	1.950	1.957	1.975	2.012	1.980
Cu2–N9	1.942	1.970	1.956	1.993	1.894	1.980
Cu2–O3	1.958	1.917	1.950	1.918	1.941	1.919
Cu2–O5	1.941	1.913	2.005	1.922	1.906	1.919

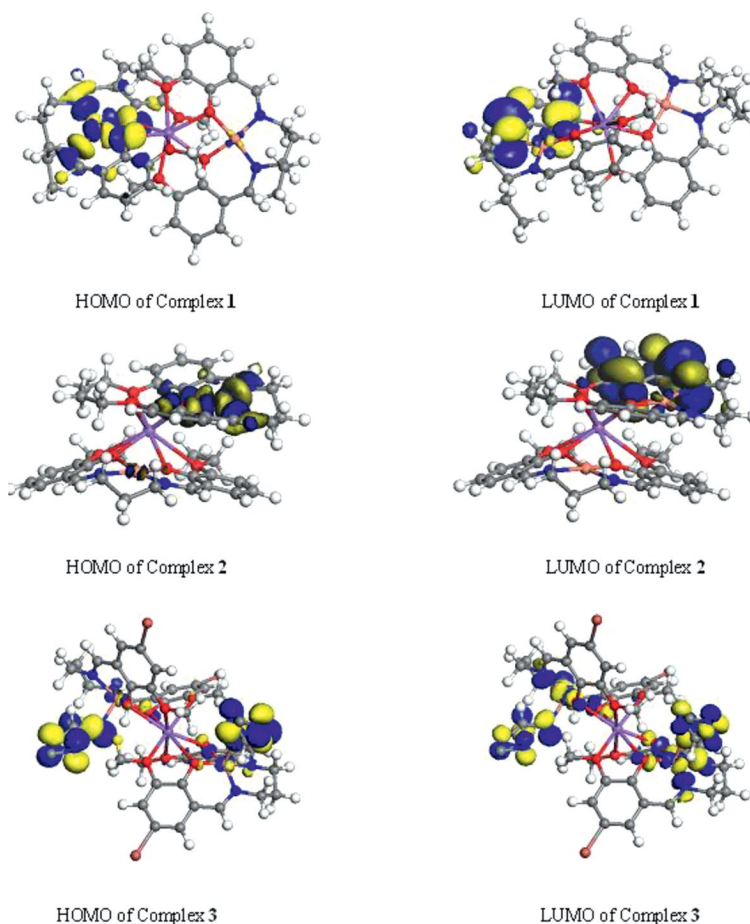


Figure 9. Optimized structures of **1**, **2**, and **3**, along with HOMO and LUMO orbitals.

chemical softness values of the complexes were also calculated by using Koopman's theorem, and they were found to be 2.14, 2.23, and 11.76 eV⁻¹ for **1**, **2**, and **3**, respectively. Calculated HOMO–LUMO gaps and chemical softness values (Table 8) show that complex **3** is the most reactive one among the three, and the stability of the complexes increases in the order **1** > **2** > **3**.

Table 8. Energy of HOMO and LUMO, their gaps [eV], and chemical softness values of the complexes calculated at the BLYP/DNP level of the optimized geometries obtained from VWN/DN-level calculations.

	E_{HOMO}	E_{LUMO}	HOMO–LUMO gap	Softness
1	-2.944	-2.008	0.936	2.14
2	-2.893	-1.997	0.896	2.23
3	-4.433	-4.263	0.170	11.76

Conclusion

In this study we report three complexes **1–3** synthesized from different Schiff base ligands LH₂ that comprise the same bicompartamental N₂O₂- and O₄-donor sets. Hence two molecules of each ligand accommodate two small Cu²⁺ ions in the N₂O₂ inner compartment with tetradentate chelation, and a large Na⁺ ion is accommodated in between with a crown ether type coordination that results from two O₄-donor sets. A Cu^{II}–Na^I–Cu^{II} hetero-trinuclear metal complex of different configuration is formed in each case. The CuL units interact to encapsulate the sodium ion in a propeller-like fashion in **1**, and to sandwich the sodium in **2** and **3**. Structural variation in complexes and different behaviors occur for the pseudohalide anions. In the case of **1**, by using NaN₃, the N₃⁻ ions are left behind by the system. In **2**, NaSCN was used, and SCN⁻ ions, likely too small to aggregate the large trinuclear units, started a side in situ reaction to partially reduce Cu^{II} to Cu^I ions to form an anionic 1D chain consisting of [Cu^I₂(μ_{1,3}-NCS)₃]⁻ units. The use of NaN(CN)₂ in complex **3** helps to connect the large complex cations by the μ_{1,5}-bridging mode of long dicyanamide (dca) spacers to form a zigzag 1D chain. Calculation of orbital energy and chemical softness revealed that **3** is the most reactive one among the three complexes.

Experimental Section

General Remarks: The FTIR spectra of the compounds were recorded with a Perkin–Elmer RX I FTIR spectrometer with KBr pellets in the range 4000–400 cm⁻¹. The electronic spectra were recorded with a Perkin–Elmer Lambda 40 (UV/Vis) spectrometer using DMF in the range 800–200 nm. Elemental analyses were carried out with a Perkin–Elmer 2400 II Elemental Analyzer. Electrochemical studies were performed with a VersaStat-Potentiostat II cyclic voltammeter using DMF as solvent, whereas tetrabutylammonium perchlorate was used as the supporting electrolyte at different scan rates. Platinum and saturated calomel electrode (SCE) were the working and the reference electrodes in the process, respectively. Mass spectra of **1–3** were analyzed with a Qtof Micro YA263 mass spectrometer.

Chemicals: All the chemicals and solvents were of analytical grade and used as received. *O*-Vanillin (i.e., 2-hydroxy-3-methoxybenzaldehyde), 5-bromo-*o*-vanillin (i.e., 5-bromo-2-hydroxy-3-methoxybenzaldehyde), 2-hydroxy-3-ethoxybenzaldehyde, 1,3-propylenediamine (i.e., 1,3-diaminopropane), ethylpropyldiamine (i.e., 1,3-diaminopentane), sodium dicyanamide, sodium thiocyanate, and sodium azide were purchased from Aldrich Chemical Company. Copper acetate monohydrate was purchased from Loba. Copper perchlorate hexahydrate was prepared by the standard procedure.^[9]

Caution! Azides and perchlorates are potentially explosive and should be handled with much care and in small amounts, though no problem was encountered.

Syntheses of the Schiff Base Ligands L¹H₂, L²H₂, and L³H₂

[N,N'-Bis(3-methoxysalicylideneimino)-1,3-diaminopentane] (L¹H₂): L¹H₂ was obtained by the reflux condensation of 1,3-diaminopentane (10 mmol, 1.195 mL) with *o*-vanillin (20 mmol, 3.04 g) in methanol (100 mL). The ligand was heated to reflux for 3 h, thereby resulting in a yellow solution. Vacuum evaporation of this solution gave the desired ligand in semisolid form, yield 0.289 g (78%). C₂₁H₂₆N₂O₄ (370.44): calcd. C 68.07, H 7.08, N 7.56; found C 68.00, H 7.02, N 7.54. FTIR (KBr): $\tilde{\nu}$ = 1629 ν (C=N), 1254 ν (C–O_{Phenolic}), 3449 ν (O–H) cm⁻¹. UV/Vis: λ = 264 ($\pi \rightarrow \pi^*$), 330 ($n \rightarrow \pi^*$) nm.

[N,N'-Bis(3-ethoxysalicylideneimino)-1,3-diaminopropane] (L²H₂): L²H₂ was obtained by the reflux condensation of 1,3-diaminopropane with 3-ethoxy-2-hydroxybenzaldehyde in a 2:1 molar ratio in methanol for 1 h.^[40] Upon cooling the solution, the ligand was precipitated as an orange solid, yield 0.322 g (87%). C₂₁H₂₆N₂O₄ (370.44): calcd. C 68.09, H 7.08, N 7.56; found C 68.01, H 7.12, N 7.51. FTIR (KBr): $\tilde{\nu}$ = 1640 ν (C=N), 1255 ν (C–O_{Phenolic}), 3448 ν (O–H) cm⁻¹. UV/Vis: λ = 260 ($\pi \rightarrow \pi^*$), 342 ($n \rightarrow \pi^*$) nm.

[N,N'-Bis(5-bromo-3-methoxysalicylideneimino)-1,3-diaminopropane] (L³H₂): L³H₂ was prepared by following the same procedure as for L¹H₂ but using 5-bromo-*o*-vanillin (20 mmol, 4.62 g) and 1,3-diaminopropane (10 mmol, 0.833 mL). The crystalline ligand, which had a deep yellow color, separated out upon cooling the solution and was collected by filtration and dried, yield 0.45 g (90%). C₁₉H₂₀Br₂N₂O₄ (500.18): calcd. C 45.62, H 4.03, N 5.60; found C 45.72, H 3.98, N 5.70. FTIR (KBr): $\tilde{\nu}$ = 1635 ν (C=N), 1260 ν (C–O_{Phenolic}), 3465 ν (O–H) cm⁻¹. UV/Vis: λ = 290 ($\pi \rightarrow \pi^*$), 339 ($n \rightarrow \pi^*$) nm.

Syntheses of the Complexes

[Na(CuL¹)₂](ClO₄)·0.5H₂O (1**):** Cu(ClO₄)₂·6H₂O (0.372 g, 1 mmol) was dissolved in 2-propanol (20 mL) by stirring and slight warming. A solution of the Schiff base (L¹H₂) in methanol (10 mL, 1 mmol) was added to it, followed by dropwise addition of an aqueous solution of NaN₃ (0.065 g, 1 mmol). The mixture was allowed to stir for 40 min with gentle heating. The dark green solution was filtered and kept at 16 °C for crystallization by slow evaporation. The very next day, a dark green crystalline product was obtained and recrystallized from a mixture of 2-propanol (10 mL), acetone (10 mL), and *n*-hexane (5 mL). After two days, dark green, block-shaped crystals suitable for X-ray crystallography were obtained, yield 0.8461 g (85%). C₄₂H₄₉ClCu₂N₄NaO_{12.50} (995.37): calcd. C 50.63, H 4.96, N 5.63; found C 50.66, H 4.98, N 5.66. FTIR (KBr): $\tilde{\nu}$ = 1609 ν (C=N), 1223 ν (C–O_{Phenolic}), 3448 ν (O–H), 439 ν (Cu–N) cm⁻¹. UV/Vis: λ = 242 ($\pi \rightarrow \pi^*$), 365 (LMCT) nm. ESI-MS: m/z [L¹CuNa – 2H]⁺ = 454.

[Na(Cu^{II}L²)₂][Cu^I₂(μ_{1,3}-NCS)₃]_{*n*} (2**):** A solution (10 mL) of the solid orange Schiff base, L²H₂ (0.741 g, 2 mmol), in methanol was added

Table 9. Crystal-structure parameters of complexes 1–3.

	1	2	3
Empirical formula	C ₄₂ H ₄₉ ClCu ₂ N ₄ NaO _{12.50}	C ₄₅ H ₄₈ Cu ₄ N ₇ NaO ₈ S ₃	C ₄₀ H ₃₆ Br ₄ Cu ₂ N ₇ NaO ₈
<i>M_r</i>	995.37	1188.23	1212.47
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/a</i>	<i>C2/m</i>
<i>a</i> [Å]	17.323(2)	13.3715(7)	10.9221(9)
<i>b</i> [Å]	17.819(2)	22.0209(13)	20.908(2)
<i>c</i> [Å]	16.295(2)	16.5055(8)	9.2262(7)
β [°]	92.998(2)	93.184(5)	94.199(5)
<i>V</i> [Å ³]	5023.1(11)	4852.6(4)	2101.2(3)
<i>Z</i>	2	4	2
λ [Å]	0.71073	0.71073	0.71073
<i>D</i> _{calcd.} [Mg m ⁻³]	1.316	1.627	1.916
μ [mm ⁻¹]	0.968	1.927	4.888
<i>F</i> (000)	2060	2424	1196
θ range [°]	1.64–19.63	5.03–26.37	1.95–27.48
Total data	14101	31557	2446
Unique data	4379	9796	2446
<i>R</i> _{int}	0.0303	0.0487	0.0000
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	3431	6539	1682
Parameters	602	634	150
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0808	0.1018	0.0543
<i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.2365	0.2542	0.1223
GoF	1.057	1.111	1.042
Residuals [e Å ⁻³]	0.850, -0.669	2.107, -0.546	1.01, -1.11

dropwise to a solution of Cu(OOCCH₃)₂·H₂O (0.597 g, 3 mmol) in methanol with constant stirring followed by dropwise addition of an aqueous solution of NaSCN (0.16, 2 mmol). The solution was further stirred for 30 min at 40 °C. The resulting dark green filtrate was kept undisturbed at 30 °C. The dark green crystalline product obtained after a week was recrystallized from a mixture of dichloromethane (10 mL) and acetone (10 mL). After two days, black needle-shaped crystals suitable for X-ray diffraction appeared, yield 0.9743 g (82%). C₄₅H₄₈Cu₄N₇NaO₈S₃ (1188.23): calcd. C 45.45, H 4.04, N 8.25; found C 45.48, H 4.09, N 8.19. FTIR (KBr): $\tilde{\nu}$ = 1610 ν (C=N), 1226 ν (C–O_{phenolic}), 454 ν (Cu–N) cm⁻¹. UV/Vis: λ = 283 ($\pi \rightarrow \pi^*$). 374 (LMCT) nm. ESI-MS: *m/z* [L²CuNa – 2H]⁺ = 454.

{[Na(Cu^{II}L³)₂]($\mu_{1,5}$ -dca)}_n (3): Cu(OOCCH₃)₂·H₂O (0.597 g, 3 mmol) was dissolved in a mixture of methanol/acetonitrile (20 mL, 1:1) by stirring. A solution of the solid yellow Schiff base ligand, L³H₂ (1.0 g, 2 mmol), in methanol was added to it followed by dropwise addition of aqueous solution of NaN(CN)₂ (0.178 g, 2 mmol). The mixture was stirred for an additional 30 min at 65 °C. The resulting deep green filtrate was kept undisturbed at 30 °C. After five days, green plate-shaped single crystals suitable for X-ray diffraction appeared, yield 0.8730 g (72%). C₄₀H₃₆Br₄Cu₂N₇NaO₈ (1212.47): calcd. C 39.59, H 2.97, N 8.08; found C 39.69, H 2.87, N 8.12. FTIR (KBr): $\tilde{\nu}$ = 1615 ν (C=N), 1234 ν (C–O_{phenolic}), 454 ν (Cu–N) cm⁻¹. UV/Vis: λ = 280 ($\pi \rightarrow \pi^*$), 377 (LMCT) nm. ESI-MS: *m/z* [L³CuNa – 3H]⁺ = 583.

Crystallographic Data Collection and Structure Refinements: Good-quality, air-stable single crystals of 1–3 (of dimensions 0.20 × 0.10 × 0.09, 0.51 × 0.12 × 0.08, and 0.09 × 0.12 × 0.55 mm³, respectively) were mounted on a Bruker CCD area diffractometer equipped with a graphite monochromator (Mo-K α , λ = 0.71073 Å). Intensity data for 1 and 2 were collected at 295(2) K and for 3 at 293(2) K. The structures were solved by direct methods^[41] and subsequent Fourier analyses. In compound 1, one ethyl chain and the perchlorate anion were found disordered over two positions: the respective occupancies in the two cases were refined at 0.714(6)/

0.286(6) and 0.556(2)/0.444(2). In 2, a disorder was found for the nitrogen atom of an SCN group as well as for one propylene bridge of the two independent [L²]²⁻ ligands: these were satisfactorily solved with refined occupancies of 0.80(4)/0.20(4) and 0.514(13)/0.486(13), respectively. In 3, the N(CN)₂⁻ anion, as it is close to a center of symmetry, results in being split over two positions with a 50:50 ratio. All hydrogen atoms at geometrical positions were treated as riding on the atom to which they are attached. All the calculations were performed using the WinGX system, version 1.80.5.^[42] The crystallographic data for complexes 1–3 are summarized in Table 9.

CCDC-888503 (for 1), -888504 (for 2), and -888505 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Hydrogen-bond dimensions for 1 (Table S1), coordination bond angles of sodium ions in 1–3, and a picture of the unit cell of 1 (Figure S1).

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