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Supramolecular Dimers of Copper(II) Complexes Resulting from Designed Host–Guest Interactions

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Syntheses, characterization and crystal structures of four designed host–guest compounds of the compositions $[\{Cu^{II}L^1\}_2 \subset (H_3N(\text{ethylene})NH_3)](NO_3)_2$ (**1**), $[\{Cu^{II}L^1\}_2 \subset (H_3N(\text{propylene})NH_3)](NO_3)_2$ (**2**), $[\{Cu^{II}L^1\}_2 \subset (H_3N(\text{butylene})NH_3)](NO_3)_2$ (**3**) and $[\{Cu^{II}L^2\}_2 \subset (H_3N(\text{ethylene})NH_3)](NO_3)_2$ (**4**) are described in this investigation [H_2L^1 = *N*,*N*′-ethylenebis(3-methoxysalicylaldimine); H_2L^2 = *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine); ethylene = $(CH_2)_2$; propylene = $(CH_2)_3$; butylene = $(CH_2)_4$]. Compounds **2** and **3** crystallize in the orthorhombic *Pcab* and monoclinic *C*2/*c* systems, respectively, while the space group of compounds **1** and **4** is triclinic $P\bar{1}$. In all of these four compounds **1**–**4**, the two $^+NH_3$ sites of the $[H_3N(CH_2)_nNH_3]^{2+}$ dication (n = 2–4) behave as guests in the O_4 compartment of two $[Cu^{II}L^1/L^2]$ moieties through bifurcated N–H···O(phenoxo) and N–H···O(methoxy/ethoxy) hydrogen-bonding interactions. Evidently, two mononuclear copper(II) moieties are interlinked by bridging supramolecular synthons, resulting in the formation of a supramolecular dimer in the title compounds. From the extent of displacement of the N atoms of $[H_3N(CH_2)_nNH_3]^{2+}$ from the least-squares $O(\text{phenoxo})_2O(\text{methoxy/ethoxy})_2$ plane, it is clear that $[Cu^{II}L^1]$ is a better host than $[Cu^{II}L^2]$ for the diprotonated diamine guests. Comparison of the inclusion of water and diprotonated diamines in $[Cu^{II}L^1/L^2]$ is also described in the present investigation. Interestingly, of the two guest species, water and diprotonated diamines, $[Cu^{II}L^2]$ prefers the former and $[Cu^{II}L^1]$ prefers the latter.

Introduction

Studies on supramolecular interactions and the self-assemblies resulting from them have attracted much attention in recent years.[1–10] Aesthetic beauty, development of new topologies and utilization as functional materials of the supramolecular aggregates are the major aspects in this research area. It may be noted that noncovalent interactions, namely, strong and weak hydrogen-bonding, C–H···π, π···π stacking, halogen–halogen, sulfur–sulfur and gold–gold interactions are being increasingly utilized to generate self-assembled structures.[1–10]

Inclusion compounds are those in which a molecule (host) is the container of another compound (guest) and the nature of attraction between the host and guest molecules are weak interactions like ion–dipole interactions, hydrogen-bonding and π···π stacking.[1,2,11–19] Much research has been carried out into the design and synthesis of inclusion compounds because of their potential for molecular recognition, separation and catalysis.[1]

A number of mono-, di- and oligonuclear compounds have been derived previously from the compartmental Schiff base ligands obtained on condensation of 3-methoxy/ethoxysalicylaldehyde with diamines.[11–38] The mononuclear compounds of copper(II), nickel(II) and oxovanadium(IV) derived from these ligands are either nonhydrated[14,16,20–23] or contain coordinated,[12,21,24–26] solvated[27] or encapsulated[18–19] water molecule. However, while mononuclear copper(II), nickel(II) and oxovanadium(IV) compounds derived from 3-ethoxysalicylaldehyde–diamine ligands are dominated by inclusion products, the inclusion of water takes place only rarely in compounds derived from 3-methoxysalicylaldehyde–diamine ligands.

Only one mononuclear copper(II) compound $[Cu^{II}L^1(H_2O)]$ has been isolated so far derived from *N*,*N*′-ethylenebis(3-methoxysalicylaldimine) (H_2L^1; Scheme 1),[24] while three types of mononuclear copper(II) compounds $[Cu^{II}L^2]$, $[Cu^{II}L^2 \subset (H_2O)]$ and $[Cu^{II}L^2(H_2O)]$ derived from *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine) (H_2L^2; Scheme 1) are known.[11,12] It has also been established that the inclusion compound $[Cu^{II}L^2 \subset (H_2O)]$ is most stable among these three.[12] Again, as in the mononuclear compound $[Cu^{II}L^2 \subset (H_2O)]$, water encapsulation takes place in the Cu^{II}-3d and Cu^{II}-alkali metal systems derived from H_2L^2

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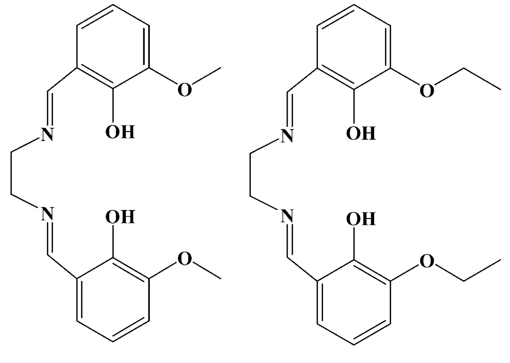
resulting in the formation of interesting examples of tetrametal self-assemblies consisting of cocrystallized dinuclear and mononuclear units.[11,32] Regarding the Cu^{II}-3d and Cu^{II}-alkali metal complexes derived from H_2L^1, a number of dinuclear,[34] trinuclear,[35] tetranuclear[36] and polymeric[37] compounds have been reported. The second metal ion in these complexes resides either in the O_4 cavity or in between the two O_4 cavities. However, water encapsulation does not take place in any of these complexes. In fact, the central metal ions in these complexes are not even coordinated to water molecule. With the anticipation that existence of coordinated water molecule may result in water inclusion and cocrystallization, we have recently derived systems containing coordinated water molecules.[35b] But water inclusion does not take place even in these compounds. All in all, it seems on the basis of reported results that copper(II)–H_2L^2 system is more potential than copper(II)–H_2L^1 system to interact with water molecule as the guest. The remarkable different behaviour of the two closely similar systems is surprising and therefore it will be interesting to explore the host–guest interaction of these two hosts with other guests. In this study, we are particularly interested in the nature of the inclusion products formed by the two hosts, $[Cu^{II}L^1]$ and $[Cu^{II}L^2]$, with diprotonated diamines as the guests. Moreover, if such organic moieties behave as guests in the $[Cu^{II}L^1]$ and $[Cu^{II}L^2]$ hosts, the products should contain two copper(II) moieties that will be interlinked by the guest synthons to generate supramolecular dimers resulting from designed host–guest interaction. It is relevant also to mention that one such dimer of oxovanadium(IV) has been reported during the course of exploring the relative donor properties of vanadyl oxygen atom.[38] However, as the types of compounds and host–guest combination are dependent on several subtle effects, it will be interesting to explore the possibility of interaction of diprotonated diamines with the O_4 cavities of $[Cu^{II}L^1]$ and $[Cu^{II}L^2]$. With the twofold aims, namely, to study the comparative inclusion phenomenon of diprotonated diamines in $[Cu^{II}L^1]$ and $[Cu^{II}L^2]$ and to derive dimers of mononuclear complexes interlinked by supramolecular synthon, we describe here the syntheses, characterization and crystal structures of four compounds of composition $[\{Cu^{II}L^1\}_2\subset(H_3N(ethylene)NH_3)](NO_3)_2$ (**1**), $[\{Cu^{II}L^1\}_2\subset(H_3N(propylene)NH_3)](NO_3)_2$ (**2**), $[\{Cu^{II}L^1\}_2\subset(H_3N(butylene)NH_3)](NO_3)_2$ (**3**) and $[\{Cu^{II}L^2\}_2\subset(H_3N(ethylene)NH_3)](NO_3)_2$ (**4**) are described in this investigation (ethylene = $(CH_2)_2$; propylene = $(CH_2)_3$; butylene = $(CH_2)_4$).



H_2L^1 **H_2L^2**

Scheme 1. Chemical structures of H_2L^1 and H_2L^2.

Results and Discussion

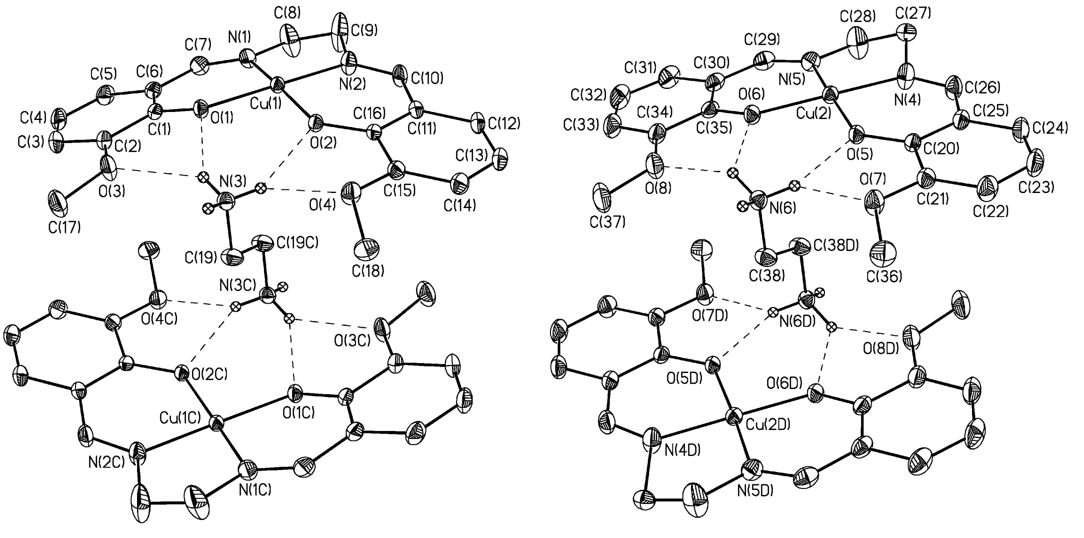
Syntheses and Characterization

Reactions of $[H_3N(ethylene)NH_3](NO_3)_2$ with $[Cu^{II}L^1(H_2O)]$ and $[Cu^{II}L^2\subset(H_2O)]$ produce the green-coloured compound $[\{Cu^{II}L^1\}_2\subset(H_3N(ethylene)NH_3)](NO_3)_2$ (**1**) and the red-coloured compound $[\{Cu^{II}L^2\}_2\subset(H_3N(ethylene)NH_3)](NO_3)_2$ (**4**), respectively. Similarly, reactions of $[Cu^{II}L^1(H_2O)]$ with $[H_3N(propylene)NH_3](NO_3)_2$ and $[H_3N(butylene)NH_3](NO_3)_2$ produce the brown-coloured compound $[\{Cu^{II}L^1\}_2\subset(H_3N(propylene)NH_3)](NO_3)_2$ (**2**) and the green-coloured compound $[\{Cu^{II}L^1\}_2\subset(H_3N(butylene)H_3N)](NO_3)_2$ (**3**), respectively. In contrast, it has yet not been possible by us to isolate the analogous compounds $[\{Cu^{II}L^2\}_2\subset(H_3N(CH_2)_nNH_3)](NO_3)_2$ (n = 3 and 4) in spite of our many efforts; the starting compound $[Cu^{II}L^2\subset(H_2O)]$ is deposited from the filtrate of the reaction mixture of $[Cu^{II}L^2\subset(H_2O)]$ and $[H_3N(CH_2)_nNH_3](NO_3)_2$ (n = 3 and 4) on standing.

The characteristic imine stretches for compounds **1**–**4** appear as a strong signal in the region 1632–1638 cm^{-1}. The presence of nitrates in the title compounds is evidenced by the appearance of three bands in the range 1443–1450, 1381–1394 and 1302–1311 cm^{-1}. For the mononuclear compound $[Cu^{II}L^2\subset(H_2O)]$, four weak intensity bands appear in the region 2900–3055 cm^{-1} assigned to C–H vibrations. The IR spectrum of compound **4** is characterized by three bands in this region (3064, 2974 and 2927 cm^{-1}). However, in comparison to the mononuclear compound, significant enhancement in the intensity of these three bands in **4** indicates the superposition of C–H and N–H vibrations. The C–H vibrations of $[Cu^{II}L^1(H_2O)]$ appear as four weak intensity bands in the region 2825–3050 cm^{-1}. As in **4**, C–H and N–H vibrations are merged and observed as two or three medium intensity bands in **1**–**3**.

Description of Crystal Structures of 1–4

The crystal structures of $[\{Cu^{II}L^1\}_2\subset(H_3N(ethylene)NH_3)](NO_3)_2$ (**1**), $[\{Cu^{II}L^1\}_2\subset(H_3N(propylene)NH_3)](NO_3)_2$ (**2**), $[\{Cu^{II}L^1\}_2\subset(H_3N(butylene)NH_3)](NO_3)_2$ (**3**) and $[\{Cu^{II}L^2\}_2\subset(H_3N(ethylene)NH_3)](NO_3)_2$ (**4**) are shown in Figures 1, 2, 3, and 4, respectively. One half of the molecules **1**, **3** and **4** is symmetry related to the other half due to the presence of an inversion centre at (0, 0, 0), (1/2, 1/2, 0) and (0, 1/2, 1/2), respectively, whereas the asymmetric unit of **2** represents the whole molecule. In the structure of **1**, there are two independent units (Unit I and Unit II). Otherwise, the structures of the four compounds are of similar type consisting of two mononuclear copper(II) moieties,



Unit I **Unit II**

Figure 1. Crystal structure of $[\{Cu^{II}L^1\}_2\subset(H_3N(ethylene)NH_3)](NO_3)_2$ (**1**). The nitrate ions and the hydrogen atoms (except for $^+NH_3$ moieties) are omitted for clarity. Symmetry: C, 1 – *x*, 1 – *y*, 1 – *z*; D, –*x*, 1 – *y*, 2 – *z*.

one diprotonated diamine and two nitrate ions. The copper(II) centre occupies the salen type N_2O_2 cavity, while the larger O(phenoxo)$_2$O(methoxy/ethoxy)$_2$ compartment is partially occupied by one $^+NH_3$ site of the diprotonated diamine. Of the three hydrogen atoms of the $^+NH_3$ groups, two of the hydrogen atoms form bifurcated hydrogen bonds with one phenoxo and one methoxy/ethoxy oxygen resulting in the inclusion of the $[H_3N(CH_2)_nNH_3]^{2+}$ dication in the O_4 compartment of two mononuclear copper(II) species. The third hydrogen atom of the $^+NH_3$ sites does not interact with the O_4 compartment. Evidently, two $[Cu^{II}L^1/L^2]$ moieties act as host for the guest $[H_3N(CH_2)_nNH_3]^{2+}$ and this host–guest combination results in the interlinking of the two mononuclear copper(II) moieties and therefore the aggregates $[\{Cu^{II}L^1/L^2\}_2\subset([H_3N(CH_2)_nNH_3]^{2+}$ in **1**–**4** may be considered as supramolecular dimers.

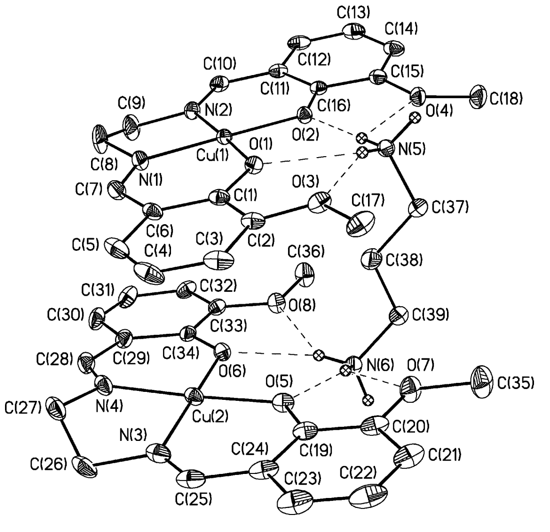


Figure 2. Crystal structure of $[\{Cu^{II}L^1\}_2\subset(H_3N(propylene)NH_3)](NO_3)_2$ (**2**). The nitrate ions and the hydrogen atoms (except for $^+NH_3$ moieties) are omitted for clarity.

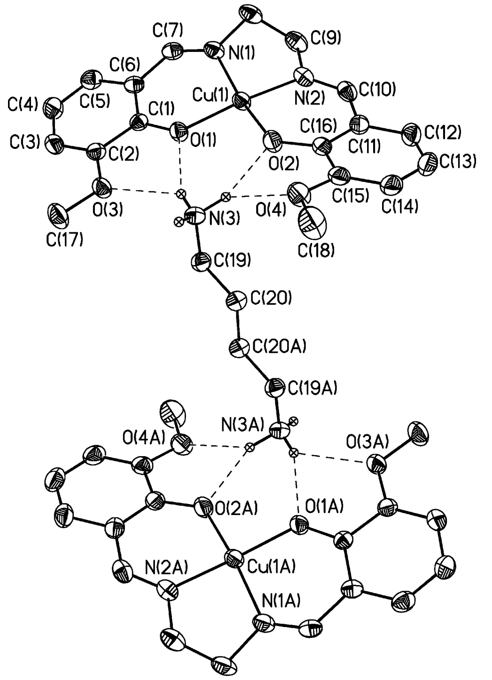


Figure 3. Crystal structure of $[\{Cu^{II}L^1\}_2\subset(H_3N(butylene)NH_3)](NO_3)_2$ (**3**). The nitrate ions and the hydrogen atoms (except for $^+NH_3$ moieties) are omitted for clarity. Symmetry: A, 0.5 – *x*, 0.5 – *y*, 1 – *z*.

The bond lengths and angles for the copper(II) centres in **1**–**4** are listed in Table 1. The coordination geometry of the copper(II) centres in **1**–**4** is slightly distorted square planar. The Cu–N/O bond lengths, *cisoid* angles and

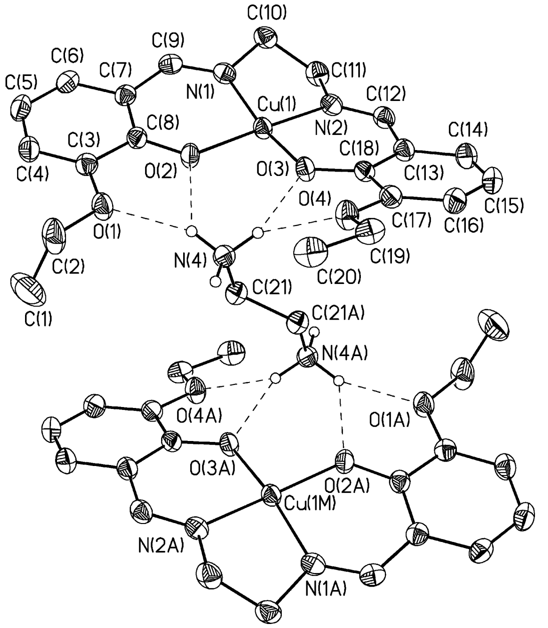


Figure 4. Crystal structure of [{$Cu^{II}L^2$}$_2$⊂(H_3N(ethylene)NH_3)](NO_3)$_2$ (**4**). The nitrate ions and the hydrogen atoms (except for $^+NH_3$ moieties) are omitted for clarity. Symmetry: A, –*x*, 1 – *y*, 1 – *z*.

Table 1. Bond lengths [Å] and bond angles [°] in the coordination environments of the copper(II) centres in **1**–**4**.

	Bond lengths		Bond angles	
1	Cu(1)–O(1)	1.9467(19)	O(1)–Cu(1)–N(2)	175.08(10)
	Cu(1)–O(2)	1.9209(19)	O(2)–Cu(1)–N(1)	170.81(10)
	Cu(1)–N(1)	1.946(2)	O(1)–Cu(1)–O(2)	90.98(8)
	Cu(1)–N(2)	1.936(2)	O(1)–Cu(1)–N(1)	92.65(9)
	Cu(2)–O(5)	1.922(2)	O(2)–Cu(1)–N(2)	92.85(9)
	Cu(2)–O(6)	1.9303(19)	N(1)–Cu(1)–N(2)	83.11(11)
	Cu(2)–N(4)	1.931(3)	O(5)–Cu(2)–N(5)	175.00(9)
	Cu(2)–N(5)	1.942(3)	O(6)–Cu(2)–N(4)	175.91(10)
			O(5)–Cu(2)–O(6)	90.32(8)
			O(5)–Cu(2)–N(4)	92.97(10)
			O(6)–Cu(2)–N(5)	92.82(10)
			N(4)–Cu(2)–N(5)	83.75(11)
2	Cu(1)–O(1)	1.911(3)	O(1)–Cu(1)–N(2)	176.79(16)
	Cu(1)–O(2)	1.922(3)	O(2)–Cu(1)–N(1)	175.59(17)
	Cu(1)–N(1)	1.933(4)	O(1)–Cu(1)–O(2)	90.35(13)
	Cu(1)–N(2)	1.937(4)	O(1)–Cu(1)–N(1)	93.48(18)
	Cu(2)–O(5)	1.928(4)	O(2)–Cu(1)–N(2)	92.75(15)
	Cu(2)–O(6)	1.907(3)	N(1)–Cu(1)–N(2)	83.5(2)
	Cu(2)–N(3)	1.936(5)	O(5)–Cu(2)–N(4)	173.87(15)
	Cu(2)–N(4)	1.966(5)	O(6)–Cu(2)–N(3)	173.34(18)
			O(5)–Cu(2)–O(6)	90.55(13)
			O(5)–Cu(2)–N(3)	93.1(2)
			O(6)–Cu(2)–N(4)	92.58(17)
			N(3)–Cu(2)–N(4)	84.4(2)
3	Cu(1)–O(1)	1.8966(16)	O(1)–Cu(1)–N(2)	167.90(7)
	Cu(1)–O(2)	1.9054(17)	O(2)–Cu(1)–N(1)	167.59(7)
	Cu(1)–N(1)	1.938(2)	O(1)–Cu(1)–O(2)	91.45(7)
	Cu(1)–N(2)	1.938(2)	O(1)–Cu(1)–N(1)	93.28(8)
			O(2)–Cu(1)–N(2)	93.62(8)
			N(1)–Cu(1)–N(2)	84.02(9)
4	Cu(1)–N(1)	1.9446(13)	N(1)–Cu(1)–O(3)	167.06(5)
	Cu(1)–N(2)	1.9308(13)	O(2)–Cu(1)–N(2)	174.35(5)
	Cu(1)–O(2)	1.9066(11)	N(1)–Cu(1)–O(2)	93.10(5)
	Cu(1)–O(3)	1.9048(11)	N(1)–Cu(1)–N(2)	84.86(6)
			N(2)–Cu(1)–O(3)	94.09(5)
			O(2)–Cu(1)–O(3)	89.07(5)

transoid angles in these four complexes vary between 1.8966(16) and 1.966(5) Å, 83.11(11) and 94.09(5)° and 167.06(5) and 176.79(16)°, respectively, while the range of deviation of the donor atoms and displacement of the metal centres from the respective least-squares N_2O_2 planes are 0.0126–0.1951 Å and 0.0013–0.0938 Å, respectively.

The geometries of the hydrogen bonds in compounds **1**–**4** are listed in Table 2, and compared in Table 3. The range of donor···acceptor contacts is 2.769–3.070 Å indicating that hydrogen bonds may be considered as moderately strong. However, as some of the N–H···O angles are small (111.7° for example), the hydrogen bonds responsible for host–guest interaction in the title compounds should be considered as ranging from weak to moderately strong. It may be relevant to compare the geometries of N–H···O hydrogen bonds in **1**–**4** with that of the O–H···O hydrogen bonds responsible for water inclusion in [$Cu^{II}L^2$⊂(H_2O)] and 3d–3d cocrystals, [{$Cu^{II}L^2M^{II}(H_2O)_3$}{$Cu^{II}L^2$}$_2$](ClO_4)$_2$ (M = Cu, Co, or Mn).[11] In these cases, the donor···acceptor contacts (2.740–3.099 Å) and the O–H···O angles (114.0–156.5°) are indicative that the inclusion of water molecules in these systems is also due to hydrogen-bonding interactions.

The relative extent of the inclusion of $^+NH_3$ sites in **1**–**4** may be understood from the displacement of the cationic nitrogen from the least-squares O(phenoxo)$_2$O(methoxy/ethoxy)$_2$ plane. These displacement values in **1**–**4** along with the related values regarding the water inclusion in [$Cu^{II}L^2$⊂(H_2O)] and [{$Cu^{II}L^2M^{II}(H_2O)_3$}{$Cu^{II}L^2$}$_2$](ClO_4)$_2$ are compared in Table 3.[11] For the inclusion of N(5) in the O(1)O(2)O(3)O(4) compartment in **2**, the displacement is only 0.03 Å indicating almost perfect inclusion. Similar perfect inclusion of water molecule is known in [$Cu^{II}L^2$⊂(H_2O)].[11] For other sites in compounds **1**–**3**, which are derived from *N*,*N*′-ethylenebis(3-methoxysalicylaldimine), the displacement values are in the range 0.27–0.64 Å indicating partial inclusion. In contrast, the protonated amine nitrogen in compound **4**, which is derived from *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine), is only weakly encapsulated as evidenced by the displacement value of 1.14 Å, which is in the range (0.92–1.23 Å) of the displacement of the water oxygen atom in the dinuclear–mononuclear cocrystals.[11]

Although compounds **1** and **4** are derived from the same diprotonated diamine, the displacement of the cationic nitrogen atom in **1** (0.39 Å for Unit I and 0.27 Å for Unit II) is much less than that (1.14 Å) in compound **4**. This indicates that between the O_4 compartments of *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine) and *N*,*N*′-ethylenebis(3-methoxysalicylaldimine), the latter has more potential for the inclusion of diprotonated diamines. As already mentioned, it has not been yet possible to derive host–guest aggregate containing [$Cu^{II}L^2$] and [$H_3N(CH_2)_nNH_3$]$^{2+}$ (*n* = 3, 4) in spite of many efforts. This also indicates that the O_4 compartment of H_2L^2 is less preferable for diprotonated

Table 2. Geometries (distances in Å and angles in °) of the hydrogen bonds in **1**–**4**.

	D–H···A	D···A	H···A	D–H···A
1	N(3)–H(3A)···O(1)	2.840	2.162	142.5
	N(3)–H(3A)···O(3)	2.877	2.212	140.7
	N(3)–H(3C)···O(2)	2.805	2.201	131.1
	N(3)–H(3C)···O(4)	2.855	2.105	152.9
	N(6)–H(6A)···O(6)	2.825	2.080	131.6
	N(6)–H(6A)···O(8)	2.867	2.021	143.6
	N(6)–H(6C)···O(5)	2.773	2.092	132.0
	N(6)–H(6C)···O(7)	2.836	2.054	145.2
2	N(5)–H(5B)···O(1)	2.818	2.338	113.8
	N(5)–H(5B)···O(3)	2.894	2.058	156.0
	N(5)–H(5C)···O(2)	2.785	1.902	172.5
	N(5)–H(5C)···O(4)	2.823	2.370	111.7
	N(6)–H(6B)···O(6)	2.853	2.174	132.7
	N(6)–H(6B)···O(8)	2.914	2.116	148.8
	N(6)–H(6C)···O(5)	2.823	2.028	148.1
	N(6)–H(6C)···O(7)	2.970	2.280	134.3
3	N(3)–H(3A)···O(1)	2.930	2.274	149.3
	N(3)–H(3A)···O(3)	2.906	2.359	132.4
	N(3)–H(3C)···O(2)	2.916	2.142	137.8
	N(3)–H(3C)···O(4)	3.009	2.170	146.6
4	N(4)–H(4B)···O(1)	2.886	2.028	156.7
	N(4)–H(4B)···O(2)	2.811	2.169	127.0
	N(4)–H(4C)···O(3)	2.769	2.054	134.5
	N(4)–H(4C)···O(4)	3.070	2.246	150.3

Table 3. Comparison of the strength of the hydrogen bonds and extent of inclusion in **1**–**4**, $[Cu^{II}L^2\subset(H_2O)]$[11] and $[\{Cu^{II}L^2M^{II}(H_2O)_3\}\{Cu^{II}L^2\}_2](ClO_4)_2$ (M = Cu, Co, or Mn).[11]

	D···A [Å]	D–H···A [°]	d_N[a] or d_O[b] [Å]
1 Unit I	2.805–2.877	131.1–152.9	0.39
1 Unit II	2.773–2.867	131.6–145.2	0.27
2 O(1)O(2)O(3)O(4) Compartment	2.785–2.894	111.7–172.5	0.03
2 O(5)O(6)O(7)O(8) Compartment	2.823–2.970	132.7–148.8	0.64
3	2.906–3.009	132.4–149.3	0.44
4	2.769–3.070	127.0–156.7	1.14
$[Cu^{II}L^2\subset(H_2O)]$	2.903–3.048	144.5–147.3	0.00
3d–3d cocrystals[b]	2.740–3.099	114.0–156.5	0.92–1.23

[a] Displacement of nitrogen of $^+NH_3$ site of diprotonated diamine from the least-squares $O(phenoxo)_2O(methoxy/ethoxy)_2$ plane in **1**–**4**. [b] Displacement of oxygen of H_2O from the least-squares $O(phenoxo)_2O(ethoxy)_2$ plane in $[Cu^{II}L^2\subset(H_2O)]$ and 3d–3d cocrystals of composition $[\{Cu^{II}L^2M^{II}(H_2O)_3\}\{Cu^{II}L^2\}_2](ClO_4)_2$ (M = Cu, Co, or Mn).

diamine. On the other hand, as already discussed, while the Cu^{II}-H_2L^2 system is a better suited to the water encapsulation, no example of water encapsulation in the Cu^{II}-H_2L^1 system is known.

Electronic Spectroscopy

Compounds **1**–**4** are practically insoluble in common organic solvents, except in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Electronic spectra of 0.5×10^{-3} (M) solutions in DMF of these compounds were recorded in 450–900 nm wavelength range. All the four compounds exhibit a broad band, due to d–d transition of copper(II) centre, at 578 nm having ε values of 360, 380, 370 and 380 $M^{-1}cm^{-1}$ (in terms of per mol of copper(II)), respectively. The d–d band of copper(II) of the mononuclear compounds $[Cu^{II}L^1(H_2O)]$ and $[Cu^{II}L^2\subset(H_2O)]$ in DMF appears at 577 nm (ε = 395 $M^{-1}cm^{-1}$) and 574 nm (ε = 405 $M^{-1}cm^{-1}$), respectively. As the position and intensity of the d–d band of the mononuclear compounds are very close to those of the dimers **1**–**4**, it seems that the dimers dissociate in DMF to monomers. For better understanding of the solution behaviour of these systems, spectrophotometric titration of the mononuclear complexes with diammonium salts, $[H_3N(CH_2)_nNH_3](NO_3)_2$ (n = 2, 3 and 4) were carried out in DMF, in which the dimers are soluble, and also in MeOH, in which preparation of dimers were performed.

Spectrophotometric titrations of 10^{-3} M solution of $[Cu^{II}L^1(H_2O)]$ with $[H_3N(propylene)NH_3](NO_3)_2$, $[H_3N(ethylene)NH_3](NO_3)_2$ and $[H_3N(butylene)NH_3](NO_3)_2$ in MeOH are shown in Figure 5 and Figures S1 and S2 (Supporting Information), respectively. In all these three cases, the d–d band of $[Cu^{II}L^1(H_2O)]$ at 571 nm (ε = 380 $M^{-1}cm^{-1}$) in MeOH is gradually redshifted with decrease of intensity and the saturation takes place at $[Cu^{II}L^1(H_2O)]$: $[H_3N(CH_2)_nNH_3](NO_3)_2$ ration of 1:2, 1:0.5 and 1:1, respectively, for n = 2, 3 and 4. While λ_{max} from 571 nm for $[Cu^{II}L^1(H_2O)]$ increases to the same value of 583 nm at saturation in these three cases, the ε values at saturation decrease to 270, 253 and 301 $M^{-1}cm^{-1}$, respectively. The shifting of the band by *ca.* 12 nm and the decrease of its intensity indicate that the dimer exists in MeOH and the formation of **1**, **2** and **3** is completed at $[Cu^{II}L^1(H_2O)]$: $[H_3N(CH_2)_nNH_3](NO_3)_2$ ration of 1:2, 1:0.5 and 1:1, respectively. Due to less solubility of $[Cu^{II}L^2\subset(H_2O)]$ in MeOH, a slightly dilute solution (0.7×10^{-3} [M]) of this mononuclear complex had to use for spectrophotometric titration with $[H_3N(ethylene)NH_3]$-

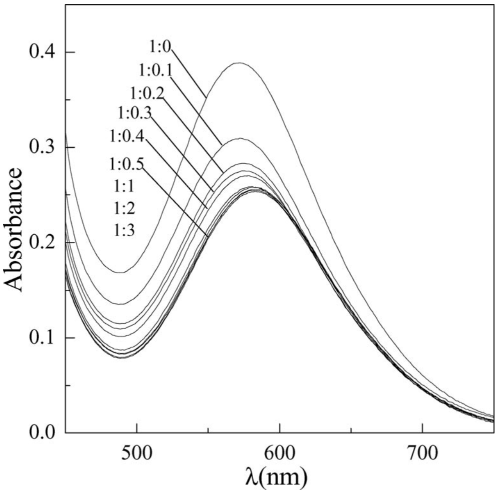


Figure 5. Spectrophotometric titration of $[Cu^{II}L^1(H_2O)]$ (10^{-3} M) with $[H_3N(propylene)NH_3](NO_3)_2$ (10^{-3} M) in MeOH. Equivalent ratio of the copper(II) complex and diammonium salt has been indicated in the Figure.

$(NO_3)_2$. As shown in Figure S3, the d–d band at 570 nm (ε = 320 $\text{M}^{-1}\,\text{cm}^{-1}$) is redshifted to 589 nm (ε = 230 $\text{M}^{-1}\,\text{cm}^{-1}$) with diminution of intensity. The saturation takes place in this case at 1:3.

While formation of **2** is completed at required stoichiometric ration 1:0.5, the saturation for **3**, **1** and **4** takes place at 1:1, 1:2 and 1:3, respectively. It is difficult to rationalize these differences. The relative extent of inclusion of $^{+}NH_3$ sites in **1**–**4** has been already discussed in terms of displacement (d_N) of the cationic nitrogen from the least-squares O(phenoxo)$_2$O(methoxy/ethoxy)$_2$ plane. The requirement of more excess (1:3) of diammonium salt for **4** may be related to weakest inclusion (d_N = 1.14 Å). Similarly, the completion of reaction at required stoichiometric ration (1:0.5) for **2** is probably due to strong inclusion (d_N = 0.03 Å), at least at one end. However, d_N values being 0.44 Å for **3** and 0.27 and 0.39 Å for **1**, the completion of dimer formation at 1:1 and 1:2 ratio, respectively, can not be rationalized in terms of extent of inclusion.

The spectrophotometric titrations of 10^{-3} M solution of $[Cu^{II}L^1(H_2O)]$ with $[H_3N(\text{ethylene})NH_3](NO_3)_2$, $[H_3N(\text{propylene})NH_3](NO_3)_2$ and $[H_3N(\text{butylene})NH_3](NO_3)_2$ in DMF are shown in Figure 6 and Figures S4 and S5 (Supporting Information), respectively. In all these three cases the d–d band of $[Cu^{II}L^1(H_2O)]$ at 577 nm (ε = 395 $\text{M}^{-1}\,\text{cm}^{-1}$) is slightly redshifted with decrease of intensity and the saturation with λ_{max} = 581 nm takes place at $[Cu^{II}L^1(H_2O)]$:$[H_3N(CH_2)_nNH_3](NO_3)_2$ ration of 1:2. Although, in comparison to the mononuclear complex, the λ_{max} changes by only 4 nm, the decrease of the ε values at saturation (251, 239 and 271 $\text{M}^{-1}\,\text{cm}^{-1}$, respectively) as well as gradual change to reach a saturation are indicative that dimer formation also takes place in DMF. However, in comparison to 1:0.5 or 1:1 ration in MeOH to reach the saturation for two systems, the dimer formation in DMF takes place at 1:2, indicating that formation is easier in MeOH. The spectrophotometric titration of 10^{-3} M solution of $[Cu^{II}L^2\subset(H_2O)]$ with $[H_3N(\text{ethylene})NH_3](NO_3)_2$ in DMF is shown in Figure S6. In this case, the d–d band of $[Cu^{II}L^2\subset(H_2O)]$ at 574 nm (ε = 405 $\text{M}^{-1}\,\text{cm}^{-1}$) in DMF is also slightly redshifted with decrease of intensity and the saturation with λ_{max} = 581 nm takes place at $[Cu^{II}L^1\subset(H_2O)]$:$[H_3N(\text{ethylene})NH_3](NO_3)_2$ ration of 1:3; the ε value at saturation being 278 $\text{M}^{-1}\,\text{cm}^{-1}$.

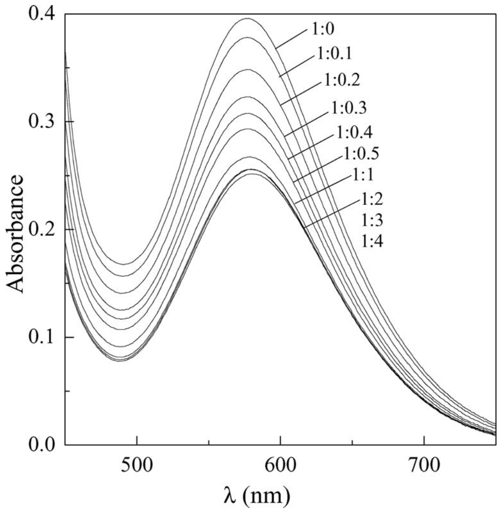


Figure 6. Spectrophotometric titration of $[Cu^{II}L^1(H_2O)]$ (10^{-3} M) with $[H_3N(\text{ethylene})NH_3](NO_3)_2$ (10^{-3} M) in DMF. Equivalent ratio of the copper(II) complex and diammonium salt has been indicated in the Figure.

Conclusions

The formation of self-assembled dimers of mononuclear copper(II) compounds, $[Cu^{II}L^1]$ and $[Cu^{II}L^2]$, resulting from the inclusion of diprotonated diamines into the O_4 cavities is a major outcome of the present investigation [H_2L^1 = *N*,*N′*-ethylenebis(3-methoxysalicylaldimine); H_2L^2 = *N*,*N′*-ethylenebis(3-ethoxysalicylaldimine)]. We have already mentioned that there is only one example of such dimerization of two mononuclear units; two oxovanadium(IV) units are self-assembled by diprotonated ethylenediamine synthons in that case.[38] However, the perspective of that work was to understand the relative donor properties of vanadyl oxygen and was not focused on supramolecular dimers. To the best of our awareness, there is no example containing a monoprotonated amine encapsulated in the O_4 cavity of the related ligands. However, one compound of oxovanadium(IV) in which a monoprotonated diamine interacts with the O_4 cavity is known.[38] In terms of the supramolecular interaction and the aggregate resulting from it, this latter compound is a host–guest system but is not a supramolecular dimer. The title compounds are therefore among only a few examples containing a protonated amine functionality encapsulated in O(phenoxo)$_2$O(methoxy/ethoxy)$_2$ cavity and only the second examples of such supramolecular dimers. As the utilization of crystal engineering principles to derive designed self-assemblies resulting from noncovalent interactions is a major target,[1–10] the present investigation is important.

As two $[Cu^{II}L^1]$ or $[Cu^{II}L^2]$ complex units and one diprotonated diamine are present in a single crystal of **1**–**4**, these compounds are also examples of cocrystals of inorganic and organic moieties. It may be mentioned that, in contrast to a large number of organic cocrystals,[39–41] multicomponent crystals containing a metal complex as a component are much fewer,[11,12,32] and therefore the title compounds have an additional importance in structural chemistry.

Spectral studies indicate that dimers dissociate in DMF, but complex formation is possible in this solvent in the presence of an excess amount of diammonium salts. Again, complex formation is easier in MeOH in comparison to that in DMF. Spectrophotometric titrations of the mononuclear copper(II) complexes with diammonium salts in both the solvents indicate that the d-d band is redshifted with diminution of intensity.

Although it is not possible to conclude that water encapsulation is not possible in the $[Cu^{II}L^1]$ system, it is true that yet no such inclusion of water takes place in this system. In contrast, another guest, namely diprotonated diamine, does interact with the O_4 cavity of [$Cu^{II}L^1$]. In fact, diprotonated diamines can interact with the O_4 cavities of both of the [$Cu^{II}L^1$] and [$Cu^{II}L^2$] systems. However, [$Cu^{II}L^1$] has more potential and is a more efficient host for diprotonated diamines. In contrast, while water inclusion does not take place so far into [$Cu^{II}L^1$], potential encapsulation of water into [$Cu^{II}L^2$] gives rise to an inclusion product and further interesting examples of cocrystals. It is interesting to note that, while inclusion of both water and diprotonated diamines takes place through bifurcated hydrogen bonds, the opposite tendency of [$Cu^{II}L^1$] and [$Cu^{II}L^2$] in interacting with these two guests is surprising. It should be mentioned that the reason for such behaviour is difficult to predict at this stage.

Experimental Section

Materials and Physical Methods: All of the reagents and solvents were purchased from commercial sources and used as received. The mononuclear complexes [$Cu^{II}L^1(H_2O)$][24] and [$Cu^{II}L^2 \subset (H_2O)$][11] were synthesized by the reported methods. The diprotonated nitrate salts [H_3N(ethylene)NH_3]$(NO_3)_2$, [H_3N(propylene)NH_3]$(NO_3)_2$ and [H_3N(butylene)NH_3]$(NO_3)_2$ were prepared on evaporating solutions of ethylenediamine, 1,3-diaminopropane and 1,4-diaminobutane, respectively, in dilute nitric acid. Elemental (C, H, N) analyses were performed on a Perkin–Elmer 2400 II analyzer. IR spectra were recorded from KBr disks of the samples over the range 400–4000 cm^{-1} on a Perkin–Elmer RXIFT spectrophotometer.

[{$Cu^{II}L^1$}$_2$$\subset$($H_3N$(ethylene)$NH_3$)]$(NO_3)_2$ (1), [{$Cu^{II}L^1$}$_2$$\subset$($H_3N$(propylene)$NH_3$)]$(NO_3)_2$ (2) and [{$Cu^{II}L^1$}$_2$$\subset$($H_3N$(butylene)$NH_3$)]$(NO_3)_2$ (3): All these four compounds were prepared following a similar procedure to that described below for **1**, by using the appropriate diprotonated diammonium nitrates.

A suspension of [$Cu^{II}L^1(H_2O)$] (0.204 g, 0.5 mmol) and [H_3N(ethylene)NH_3]$(NO_3)_2$ (0.186 mg, 1 mmol) in 40 mL of methanol was stirred for a few hours. The resulting mixture was then filtered to remove the suspended particles and the resultant clear green filtrate slowly evaporated. After a few days, a green crystalline compound containing single crystals suitable for X-ray diffraction precipitated and was collected by filtration and dried in vacuo; yield 0.164 g (68 %). $C_{38}H_{46}Cu_2N_8O_{14}$ (965.91): calcd. C 47.25, H 4.80, N 11.60; found C 47.14, H 4.87, N 11.68. IR (KBr): $\tilde{\nu}$ = 3034, 2925 [m, ν(NH/CH)], 1638 [s, ν(C=N)], 1448 (m), 1394 (m), 1302 [s, ν(nitrate)] cm^{-1}.

Data for 2: Brown crystalline compound; yield 0.142 g (58 %). $C_{39}H_{48}Cu_2N_8O_{14}$ (979.93): calcd. C 47.80, H 4.94, N 11.43; found C 47.91, H 4.85, N 11.35. IR (KBr): $\tilde{\nu}$ = 3050, 2932 [m, ν(NH/CH)], 1636 [s, ν(C=N)], 1449 (m), 1383 (s), 1309 [s, ν(nitrate)] cm^{-1}.

Data for 3: Green crystalline compound; yield 0.134 g (54 %). $C_{40}H_{50}Cu_2N_8O_{14}$ (993.96): calcd. C 48.33, H 5.07, N 11.27; found C 48.44, H 4.96, N 11.38. IR (KBr): $\tilde{\nu}$ = 3098, 2931, 2843 [m, ν(NH/CH)], 1632 [s, ν(C=N)], 1443 (m), 1381 (s), 1311 [s, ν(nitrate)] cm^{-1}.

[{$Cu^{II}L^2$}$_2$$\subset$($H_3N$(ethylene)$NH_3$)]$(NO_3)_2$ (4): A suspension of [$Cu^{II}L^2 \subset (H_2O)$] (0.218 g, 0.5 mmol) and [H_3N(ethylene)NH_3]$(NO_3)_2$ (0.186 mg, 1 mmol) in 20 mL of methanol was stirred for a few hours. The resulting mixture was then filtered to remove the suspended particles and the resultant clear green filtrate slowly evaporated. After a few days, a red crystalline compound containing single crystals suitable for X-ray diffraction, precipitated and was collected by filtration and dried in vacuo; yield 0.156 g (61 %). $C_{42}H_{54}Cu_2N_8O_{14}$ (1022.02): calcd. C 49.36, H 5.33, N 10.96; found C 49.45, H 5.25, N 10.84. IR (KBr): $\tilde{\nu}$ = 3064, 2974, 2927 [m, ν(NH/CH)], 1635 [s, ν(C=N)], 1450, 1385, 1304 [s, ν(nitrate)] cm^{-1}.

Table 4. Crystallographic data for **1**–**4**.

	1	**2**	**3**	**4**
Formula	$C_{38}H_{46}Cu_2N_8O_{14}$	$C_{39}H_{48}Cu_2N_8O_{14}$	$C_{20}H_{25}CuN_4O_7$	$C_{21}H_{27}CuN_4O_7$
Formula weight	965.91	979.93	496.98	511.01
Crystal system	triclinic	orthorhombic	monoclinic	triclinic
Space group	$P\bar{1}$	*Pcab*	*C*2/*c*	$P\bar{1}$
a [Å]	9.135(3)	17.270(3)	25.488(5)	9.0986(5)
b [Å]	10.270(3)	22.622(5)	7.291(2)	11.2419(7)
c [Å]	22.456(4)	22.341(5)	23.507(4)	11.6282(7)
α [°]	99.11(2)	90.00	90.00	107.587(1)
β [°]	90.00	90.00	100.73(2)	95.941(1)
γ [°]	100.99(4)	90.00	90.00	96.652(1)
V [Å^3]	2039.9(10)	8728(3)	4292.0(16)	1114.06(11)
Z	2	8	8	2
Temperature [K]	293(2)	293(2)	293(2)	120(2)
2*θ*	4.20–59.92	4.06–58.00	4.34–59.94	3.72–60.16
μ [mm^{-1}]	1.121	1.049	1.068	1.031
$D_{calcd.}$ [g cm^{-3}]	1.573	1.491	1.538	1.523
F(000)	1000	4064	2064	532
Absorption correction	none	none	none	multi-scan
Index ranges	$-12 \le h \le 12$ $0 \le k \le 14$ $-31 \le l \le 31$	$-23 \le h \le 23$ $0 \le k \le 30$ $-30 \le l \le 30$	$-35 \le h \le 35$ $-10 \le k \le 0$ $-33 \le l \le 33$	$-12 \le h \le 12$ $-15 \le k \le 15$ $-16 \le l \le 16$
Reflections collected	12461	45116	12462	11675
Independent refl. / R_{int}	11849 / 0.0330	11609 / 0.1263	6236 / 0.0811	6022 / 0.0225
R_1[a] / wR_2[b] [$I > 2\sigma(I)$]	0.0433 / 0.1198	0.0502 / 0.1321	0.0343 / 0.0769	0.0309 / 0.0754
R_1[a] / wR_2[b] (for all F_o^2)	0.1179 / 0.1410	0.1865 / 0.1955	0.1240 / 0.0979	0.0388 / 0.0790

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

Crystal Structure Determination of 1–4: The crystallographic data of **1**–**4** are summarized in Table 4. Diffraction data of **4** were collected at 120 K with a Bruker Smart 1 K CCD diffractometer, while those of compounds **1**–**3** were collected with an Enraf–Nonius CAD4 diffractometer at 293 K. Data of **4** were processed using SAINT[42] and the structure was solved by direct methods in SHELXS[43] and refined by full-matrix least-squares on F^2 in SHELXL-97.[44] Hydrogen atoms were positioned geometrically (aromatic C–H 0.95 Å, ethyl C–H 0.99 Å, methyl C–H 0.98 Å and amine N–H 0.91 Å) and refined using a riding model with the isotropic displacement parameters fixed at $U_{\mathrm{iso}}(\mathrm{H}) = 1.2$ times U_{eq} of the parent carbon atom for the aromatic and ethyl hydrogen atoms, $U_{\mathrm{iso}}(\mathrm{H}) = 1.5$ times U_{eq} of the parent carbon atom for the methyl hydrogen atoms and $U_{\mathrm{iso}}(\mathrm{H}) = 1.5 \times U_{\mathrm{eq}}$ of the parent nitrogen atom for the amine hydrogen atoms. In the case of **1**–**3**, data collection and reduction were done by CAD4 Express Enraf–Nonius programs package and XCAD4. All data were corrected for Lorentz polarization effects. The three structures were solved by direct methods using SIR92[45] and refined by full-matrix least-squares on F^2 using SHELXL-97.[44] In **1** and **2**, hydrogen atoms were positioned geometrically and refined using a riding model, the isotropic displacement parameters were constrained to be 1.2 times the U_{eq} of the carrier atoms (1.5 times for hydrogen atoms of methyl groups) and refined except for amines hydrogen atoms in **2** which were located from a difference Fourier map and then refined. In **3**, all hydrogen atoms were located from a difference Fourier map and refined with isotropic thermal parameters. The final least-squares refinements (R_1) based on $I > 2\sigma(I)$ converged to 0.0433, 0.0502, 0.0343 and 0.0309 for **1**–**4**, respectively.

CCDC-734837 (for **1**), -734838 (for **2**), -734839 (for **3**) and -734836 (for **4**) contain the supplementary crystallographic data for this article. 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 also the footnote on the first page of this article): Six figures showing the results of spectrophotometric titrations.

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