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Role of Coordinated Water and Hydrogen-Bonding Interactions in Stabilizing Monophenoxido-Bridged Triangular $Cu^{II}M^{II}Cu^{II}$ Compounds (M = Cu, Co, Ni, or Fe) Derived from *N*,*N*′-Ethylenebis(3-methoxysalicylaldimine): Syntheses, Structures, and Magnetic Properties

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The syntheses, structures, and magnetic properties of the trinuclear triangular compounds $[\{Cu^{II}L^1\}_2Cu^{II}(H_2O)_2](ClO_4)_2\cdot H_2O$ (**1**) and $[\{Cu^{II}L^1\}_2M^{II}(H_2O)_2](ClO_4)_2$ {M = Ni (**2**), Co (**3**), Fe (**4**)} derived from *N*,*N*′-ethylenebis(3-methoxysalicylaldimine) (H_2L^1) are described. Compound **1** crystallizes in the monoclinic $P2_1/n$ space group, while the crystal system for the isomorphous compounds **2**–**4** is monoclinic $P2_1/c$. In the cations of these compounds, two copper(II) ions occupy the salen type N_2O_2 cavity of two $[L^1]^{2-}$ ligands, while one phenoxido and one methoxy oxygen atom of each of these two $[Cu^{II}L^1]$ moieties coordinate to a central metal ion, which results in the formation of the trinuclear $Cu^{II}{}_2M^{II}$ systems in which the two pairs of central···terminal metal ions are monophenoxido-bridged. In addition, to the two phenoxido bridges, the central metal ion is coordinated to two methoxy and two water oxygen atoms. The coordinated water molecules are strongly hydrogen bonded to the phenoxido and methoxy oxygen atoms. The presence of the coordinated water molecules and the interaction of these water molecules with the phenoxido and methoxy oxygen atoms are proposed to be the governing factors for the stabilization of the rare example of the monophenoxido-bridged $Cu^{II}{}_3$ compound **1** and of the first examples of the monophenoxido-bridged $Cu^{II}{}_2M^{II}$ compounds **2**–**4**. The three metal ions define an isosceles triangle. The phenoxido bridge angles in these compounds are significantly obtuse and vary between 121.10(12)° and 129.84(13)°. On the other hand, the trinuclear cores are highly twisted as evidenced from the range of the dihedral angles (58.5–143.7°) between the basal planes of the terminal and the central metal ions. The variable-temperature (2–300 K) magnetic susceptibilities of compounds **1**–**4** have been measured. The magnetic data for **1** have been analyzed by using a model of two exchange integrals for the two pairs of adjacent metal ions, while one *J* value is considered for the other three complexes. The exchange integrals obtained are: $Cu^{II}{}_3$ compound **1**: $J_1 = -97.6\ cm^{-1}$, $J_2 = -89.5\ cm^{-1}$; $Cu^{II}{}_2Ni^{II}$ compound **2**: $J = -25.4\ cm^{-1}$; $Cu^{II}{}_2Co^{II}$ compound **3**: $J = -9.0\ cm^{-1}$; $Cu^{II}{}_2Fe^{II}$ compound **4**: $J = -6.5\ cm^{-1}$. These moderate to weak antiferromagnetic interactions in **1**–**4** are related to the twisting of the trinuclear cores. The relative order of the exchange integrals can been understood from the nature of the magnetic orbitals. The structural and magnetic results have been compared with previously reported related compounds.

Introduction

The magnetic properties of exchange-coupled discrete compounds have been well investigated,[1–12] and the recent interest focuses mainly on the understanding of the intimate relationship of the spin coupling to develop magnetic materials.[13] Nonetheless, studies of exchange-coupled discrete compounds composed of new or less-investigated bridging moieties remain important in developing and understanding magneto-structural correlations. Trinuclear complexes, in particular, deserve attention because of the possibility of spin frustration in such systems.[14]

A number of 3d, 3d–3d, and 3d–4f complexes derived from 3-methoxy/ethoxysalicylaldehyde–diamine Schiff base ligands have been reported in the literature.[3,15–21] The mononuclear complexes derived from 3-ethoxysalicylaldehyde–diamine ligands (H_2L–OEt) are inclusion products where one water molecule is encapsulated in the O_4 compartment.[19,20] In contrast, the only structurally characterized mononuclear copper(II) compound, $[Cu^{II}(L^1)(H_2O)]$ {H_2L^1 = *N*,*N*′-ethylenebis(3-methoxysalicylaldimine); Scheme 1},

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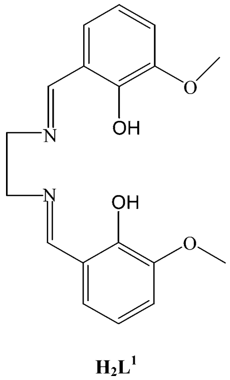
derived from 3-methoxysalicylaldehyde–diamine ligands (H_2L–OMe) contains a coordinated water.[21] Again, as in the mononuclear compounds, water encapsulation also takes place in the 3d–3d systems derived from H_2L–OEt to result in the formation of interesting examples of tetrametal and heptametal self-assemblies consisting of cocrystallized dinuclear and mononuclear units.[19] In the dinuclear unit of these cocrystals, the second metal ion is not linked with the ethoxy oxygen atoms but occupies the O_4 cavity and is coordinated to water molecules, which, in turn, interact with the O_4 cavities of the mononuclear units to form the self-assemblies. With regard to the 3d–3d complexes derived from H_2L–OMe, a number of dinuclear,[15] trinuclear,[16] tetranuclear,[17] and polymeric[12b,18] 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 3d–3d systems. It is surprising to note that in fact no 3d–3d compounds derived from H_2L–OMe contains coordinated water molecule. All in all, it seems that the formation of inclusion products and dinuclear/mononuclear cocrystals, the coordination of the metal ions in the O_4 cavity by water molecules, and the interaction of those water molecules with the O_4 cavity of the mononuclear fragments are possible in complexes derived from H_2L–OEt but not in those derived from H_2L–OMe. This remarkably different behavior of the two similar ligands is interesting and has provoked us to explore this point. We have been particularly interested in the possibility of obtaining a compound derived from H_2L–OMe where the metal ion in the O_4 cavity or in between the O_4 cavities contains coordinating water molecule(s), which, in turn, interacts with the O_4 cavity of the mononuclear fragments. With these aims, we report here the syntheses, structures, and magnetic properties of the 3d–3d complexes obtained on reaction of $[Cu^{II}L^1(H_2O)]$ with the perchlorate salts of copper(II), nickel(II), cobalt(II), and iron(II).



H_2L^1

Scheme 1.

Results and Discussion

Syntheses and Characterization

Reaction of $[Cu^{II}L^1(H_2O)]$ with copper(II) perchlorate produced the trinuclear copper(II) complex with the composition $[\{Cu^{II}L^1\}_2Cu^{II}(H_2O)_2](ClO_4)_2·H_2O$ (**1**). Similarly, $[Cu^{II}L^1(H_2O)]$ smoothly reacted with the perchlorate salts of nickel(II), cobalt(II), and iron(II) to produce the heterotrinuclear complexes with the composition $[\{Cu^{II}L^1\}_2M^{II}(H_2O)_2](ClO_4)_2$ {M^{II} = Ni (**2**), Co (**3**), Fe (**4**)}. The variation in the ratio of the reactants $[Cu^{II}L^1(H_2O)]$ and $M(ClO_4)_2·6H_2O$ (M = Cu, Ni, Co, or Fe) had no effect on the composition of the products.

The characteristic $\nu_{C=N}$ stretching in **1**–**4** appears in the range 1636–1643 cm^{-1} as a strong signal. Additionally, two bands are in the region 1084–1112 cm^{-1} and at ca. 623 cm^{-1} assigned to the ionic perchlorate groups. The vibrations of the water molecules are observed as a weak intensity band in the region 3401–3442 cm^{-1}. It should be mentioned that, for the mononuclear compound $[Cu^{II}L^1(H_2O)]$, the water stretching band appears as a medium intensity band at 3457 cm^{-1}, which indicates that the water molecule is not encapsulated in the O_4 cavity.[19,20]

Description of the Structure of $[\{Cu^{II}L^1\}_2Cu^{II}(H_2O)_2](ClO_4)_2·H_2O$ (1)

The crystal structure of $[\{Cu^{II}L^1\}_2Cu^{II}(H_2O)_2](ClO_4)_2·H_2O$ (**1**) is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The structure of **1** consists of the trinuclear $[\{Cu^{II}L^1\}_2Cu^{II}(H_2O)_2]^{2+}$ cation, two perchlorate anions, and one solvated water molecule. In the cation, two copper(II) ions occupy the salen-type N_2O_2 cavity of two $[L^1]^{2-}$ ligands, and one phenoxido and one methoxy oxygen atoms of each of these two $[Cu^{II}L^1]$ moieties {$[Cu^{II}(1)L^1]$ and $[Cu^{II}(3)L^1]$} coordinate to a third copper(II) center [Cu(2)] to result in the formation of a trinuclear Cu^{II}_3 system in which two pairs of metal ions, Cu(1)···Cu(2) and Cu(2)···Cu(3), are monophenoxido bridged. In addition to the two monodentate methoxy oxygen atoms [O(4) and O(7)] and the two bridging phenoxido oxygen atoms [O(2) and O(5)], two water molecules [H_2OW(1) and H_2OW(2)] coordinate to the central metal ion [Cu(2)]. The Cu(1)···Cu(2), Cu(2)···Cu(3), and Cu(1)···Cu(3) distances are 3.60, 3.48, and 6.06 Å, respectively, while the Cu(1)···Cu(2)···Cu(3), Cu(2)···Cu(3)···Cu(1), and Cu(3)···Cu(1)···Cu(2) angles are 117.4, 31.9, and 30.7°, respectively, which indicates that the three copper(II) centers define an isosceles triangle.

The copper(II) centers [Cu(1) and Cu(3)] in the salen-type N_2O_2 cavity have a slightly distorted square-planar coordination environment. The two Cu–N bond lengths [Cu(1)–N(1) 1.935(3) Å, Cu(1)–N(2) 1.952(3) Å; Cu(3)–N(3) 1.934(3) Å, Cu(3)–N(4) 1.944(4) Å] for both copper(II) centers are almost identical. However, the bond lengths involving the bridging phenoxido oxygen atom [Cu(1)–O(2) 1.975(3) Å; Cu(3)–O(5) 1.981(2) Å] are longer than the bond lengths involving the monodentate phenoxido oxygen atom [Cu(1)–O(1) 1.887(3) Å; Cu(3)–O(6) 1.890(3) Å]. The mean deviation of the respective donor centers from the least-squares planes N(1)–N(2)–O(1)–O(2) and N(3)–N(4)–O(5)–O(6) are 0.11 and 0.06 Å, respectively,

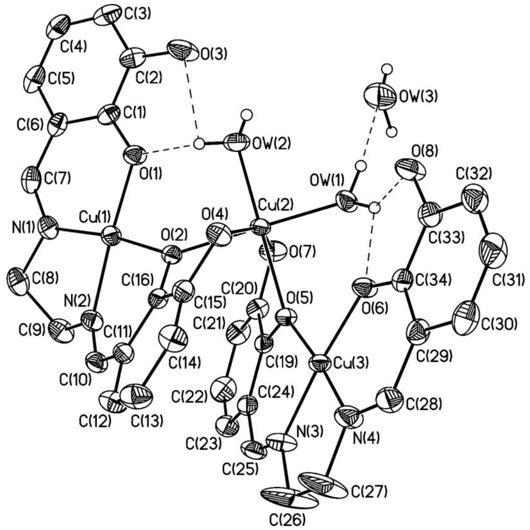


Figure 1. Crystal structure of $[\{Cu^{II}L^{1}\}_2Cu^{II}(H_2O)_2]\cdot(ClO_4)_2\cdot H_2O$ (**1**). Methoxy carbon atoms and the hydrogen atoms, except those of the water molecules, are omitted for clarity.

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

Cu(1)–N(1)	1.935(3)	O(5)–Cu(3)–N(3)	92.22(13)
Cu(1)–N(2)	1.952(3)	O(5)–Cu(3)–O(6)	90.93(10)
Cu(1)–O(1)	1.887(3)	N(3)–Cu(3)–N(4)	83.87(16)
Cu(1)–O(2)	1.975(3)	O(6)–Cu(3)–N(4)	93.16(13)
Cu(3)–N(3)	1.934(3)	O(7)–Cu(2)–O(4)	158.27(10)
Cu(3)–N(4)	1.944(4)	O(5)–Cu(2)–OW(2)	172.06(13)
Cu(3)–O(5)	1.981(2)	O(2)–Cu(2)–OW(1)	179.10(11)
Cu(3)–O(6)	1.890(3)	O(7)–Cu(2)–O(5)	74.33(10)
Cu(2)–O(2)	2.005(2)	O(7)–Cu(2)–O(2)	91.32(11)
Cu(2)–O(5)	2.017(2)	O(7)–Cu(2)–OW(1)	88.84(13)
Cu(2)–O(4)	2.415(3)	O(7)–Cu(2)–OW(2)	97.73(13)
Cu(2)–O(7)	2.282(3)	O(4)–Cu(2)–O(2)	71.00(10)
Cu(2)–OW(1)	1.941(3)	O(4)–Cu(2)–O(5)	92.19(10)
Cu(2)–OW(2)	1.925(3)	O(4)–Cu(2)–OW(1)	108.65(11)
O(1)–Cu(1)–N(2)	171.18(14)	O(4)–Cu(2)–OW(2)	95.32(14)
O(2)–Cu(1)–N(1)	171.37(13)	O(2)–Cu(2)–O(5)	88.50(10)
O(1)–Cu(1)–N(1)	93.76(14)	O(2)–Cu(2)–OW(2)	91.50(12)
O(1)–Cu(1)–O(2)	93.80(11)	O(5)–Cu(2)–OW(1)	90.69(11)
N(1)–Cu(1)–N(2)	83.57(15)	OW(1)–Cu(2)–OW(2)	89.36(13)
O(2)–Cu(1)–N(2)	89.54(12)	Cu(1)–O(2)–Cu(2)	129.84(13)
O(5)–Cu(3)–N(4)	175.09(13)	Cu(2)–O(5)–Cu(3)	121.10(12)
O(6)–Cu(3)–N(3)	175.31(15)		

while the displacement of Cu(1) from N(1)–N(2)–O(1)–O(2) and Cu(3) from N(3)–N(4)–O(5)–O(6) planes are 0.03 and 0.00 Å, respectively, which indicates that the coordination environment of Cu(1) is slightly more distorted. The ranges of the *cisoid* angles [83.57(15)–93.80(11)° for Cu(1); 83.87(16)–93.16(13)° for Cu(3)] for the two metal environments are almost same. However, the *transoid* angles in the Cu(1) environment deviate slightly more from the ideal values [171.18(14) and 171.37(13)° for Cu(1); 175.09(13) and 175.31(15)° for Cu(3)], which again indicate that the coordination environment of the Cu(3) center is slightly less distorted.

The central metal ion [Cu(2)] in the Cu^{II}_3 triangle is hexacoordinate and has a distorted octahedral environment in which two methoxy oxygen atoms [O(4) and O(7)] occupy the axial positions and the basal plane is defined by the two bridging phenoxido oxygen atoms [O(2) and O(5)] and two water oxygen atoms [OW(1) and OW(2)]. The average deviation of the constituent atoms and the displacement of the metal center from the least-squares plane O(2)–O(5)–OW(1)–OW(2) are 0.07 Å and 0.06 Å, respectively. In the basal plane there are two types of bond lengths; those [2.005(2) and 2.017(2) Å] involving bridging phenoxido oxygen atoms are longer than those [1.925(3) and 1.941(3) Å] involving the water oxygen atoms. As expected, as a result of Jahn–Teller distortion, the axial bond lengths are significantly longer. However, although both the donor centers in the axial positions are methoxy oxygen atoms, the two axial bond lengths are significantly different [Cu(2)–O(4) 2.415(3) Å, Cu(2)–O(7) 2.282(3) Å]. Of the two *transoid* angles in the basal plane, O(2)–Cu(2)–OW(1) [179.10(11)°] is very close to the ideal value, while O(5)–Cu(2)–OW(2) [172.06(13)°] deviates slightly. In contrast, the *transoid* angle [O(7)–Cu(2)–O(4) 158.27(10)°] involving the axial ligand atoms deviates appreciably. The *cisoid* angles are in the range 71.00(10)–108.65(11)°. All in all, Cu(2) has a significantly distorted octahedral geometry.

As already mentioned, the metal···metal separations [Cu(1)···Cu(2) 3.48 Å and Cu(2)···Cu(3) 3.60 Å] for the two pairs of monophenoxido-bridged metal centers are different. The two bridge angles [Cu(1)–O(2)–Cu(2) 129.84(13)° and Cu(2)–O(5)–Cu(3) 121.10(12)°] are also different. The dihedral angle between the basal plane of the central metal ion Cu(2) and the square planes of the terminal metal ions Cu(1) and Cu(3) are 143.7 and 121.5°, respectively, which indicates that the trinuclear core is significantly twisted.

As shown in Figure 1, one hydrogen atom of each of the two coordinated water molecules [HW(1B) of OW(1) and HW(2B) of OW(2)] forms bifurcated hydrogen bonds with one phenoxido and one methoxy oxygen atom. The geometries of these hydrogen bonds are summarized in Table 2. The hydrogen bonds can be considered as strong as the donor···acceptor contacts are in the range 2.65–2.78 Å. The second hydrogen atom [HW(1A)] of OW(1) interacts with the oxygen atom of the noncoordinated water molecule [$H_2OW(3)$] in **1**, which results in a water dimer. As summarized in Table 2, the donor···acceptor contact for this hydrogen bond is 2.73 Å and therefore this interaction can also be considered as strong.

Table 2. Distances in [Å] and angles in [°] of the hydrogen bonds in **1**.

D–H···A	D···A	H···A	D–H···A
OW(1)–HW(1B)···O(6)	2.758	2.201	122.1
OW(1)–HW(1B)···O(8)	2.778	2.390	141.8
OW(1)–HW(1A)···OW(3)	2.732	1.826	174.1
OW(2)–HW(2B)···O(1)	2.653	1.807	164.0
OW(2)–HW(2B)···O(3)	2.760	2.390	106.0

Description of the Structures of $[\{Cu^{II}L^1\}_2M^{II}(H_2O)_2](ClO_4)_2$ {M = Ni (2), Co (3), Fe (4)}

Complexes **2**–**4** have similar structures. Their crystal structures are shown in Figures 2, 3, and 4, and selected bond lengths and angles are listed in Table 3. The structures reveal that **2**–**4** are trinuclear $Cu^{II}_2M^{II}$ complexes containing two symmetry-related terminal copper(II) ions [Cu(1) and Cu(1A)], in the salen-type N_2O_2 cavities of two $[L^1]^{2-}$ ligands, and a central metal ion [M(1) = Ni(1), Co(1), and Fe(1) for **2**, **3**, and **4**, respectively], which is bridged to each of the two terminal copper(II) centers by one phenoxido oxygen atom. As will be discussed, the central metal ion of **2**, **3**, and **4** is disordered and occupies two symmetry-related sites [Ni(1) and Ni(1A) for **2**, Co(1) and Co(1A) for **3**, and Fe(1) and Fe(1A) for **4**]. Each of the two phenoxido oxygen atoms of each of the two symmetry-related $[Cu^{II}L^1]$ fragments acts as a bridging center to one of the two symmetry-related sites of the central metal ion, and therefore it is evident that the two pairs of metal ions Cu(1)···M(1) and Cu(1A)···M(1) in the trinuclear core are monophenoxido bridged. The remaining four coordination positions of the central metal ion are occupied by two methoxy oxygen atoms, one from each $[Cu^{II}L^1]$ moiety, and two water oxygen atoms. Three metal ions define an isosceles triangle, with two sides equal to the intramolecular nearest-neighbor distances [Cu(1)···M(1) 3.63, 3.62, and 3.66 Å and Cu(1A)···M(1) 3.61, 3.65, and 3.61 Å for **2**, **3**, and **4**, respectively]. The third side of the triangle corresponds to the distance between the terminal centers [Cu(1)···Cu(1A) 6.78, 6.83, and 6.86 Å for **2**, **3**, and **4** respectively]. The Cu(1)···M(1)···Cu(1A) angle for **2**, **3**, and **4** is 138.7, 140.0, and 141.6°, respectively.

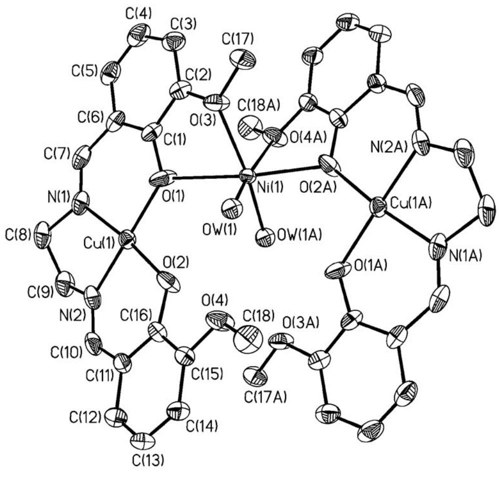


Figure 2. Crystal structure of $[\{Cu^{II}L^1\}_2Ni^{II}(H_2O)_2]\cdot(ClO_4)_2$ (**2**). Hydrogen atoms are omitted for clarity. Symmetry: A, 2 – *x*, –*y*, 2 – *z*. The nickel(II) ion in this molecule occupies two disordered general positions with an occupancy factor of 0.5, close to the center of symmetry of the $P2_1/c$ space group. Of the two disordered sites [Ni(1) and Ni(1A)], one [Ni(1)] is shown here for the sake of simplicity.

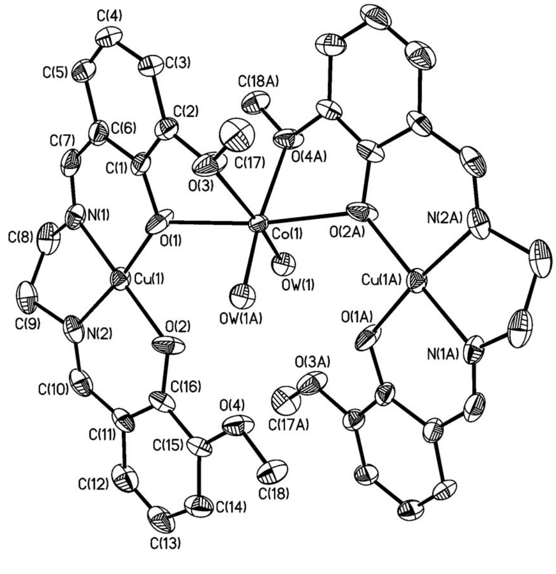


Figure 3. Crystal structure of $[\{Cu^{II}L^1\}_2Co^{II}(H_2O)_2]\cdot(ClO_4)_2$ (**3**). Hydrogen atoms are omitted for clarity. Symmetry: A, 1 – *x*, 1 – *y*, 1 – *z*. The cobalt(II) ion in this molecule occupies two disordered general positions with an occupancy factor of 0.5, close to the center of symmetry of the $P2_1/c$ space group. Of the two disordered sites [Co(1) and Co(1A)], one [Co(1)] is shown here for the sake of simplicity.

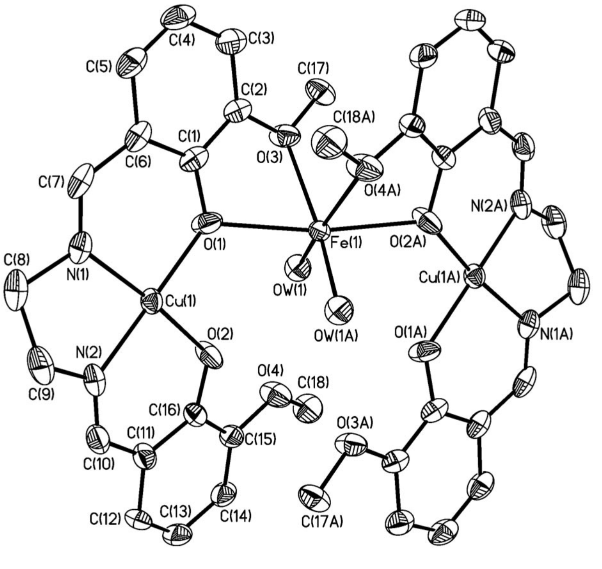


Figure 4. Crystal structure of $[\{Cu^{II}L^1\}_2Fe^{II}(H_2O)_2]\cdot(ClO_4)_2$ (**4**). Hydrogen atoms are omitted for clarity. Symmetry: A, 2 – *x*, 1 – *y*, 1 – *z*. The iron(II) ion in this molecule occupies two disordered general positions with an occupancy factor of 0.5, close to the center of symmetry of the $P2_1/c$ space group. Of the two disordered sites [Fe(1) and Fe(1A)], one [Fe(1)] is shown here for the sake of simplicity.

The coordination environment of the copper(II) ion in **2**–**4** are very similar; the Cu–N(imine) bond lengths (ca. 1.95 Å) are slightly shorter than the Cu–O(phenoxido) bond length (ca. 1.92 Å), the *cisoid* (ca. 83–93°) and *transoid* (ca. 172–175°) angles deviate only a little from the

Table 3. Selected bond lengths [Å] and angles [°] for complexes **2**, **3**, and **4**.

	$Cu^{II}{}_2Ni^{II}$ (**2**)	$Cu^{II}{}_2Fe^{II}$ (**4**)	$Cu^{II}{}_2Co^{II}$ (**3**)	
Cu(1)–N(1)	1.940(3)	1.940(4)	Cu(1)–N(1)	1.951(4)
Cu(1)–N(2)	1.950(3)	1.947(4)	Cu(1)–N(2)	1.942(4)
Cu(1)–O(1)	1.921(3)	1.931(3)	Cu(1)–O(1)	1.918(3)
Cu(1)–O(2)	1.921(2)	1.919(3)	Cu(1)–O(2)	1.931(3)
M(1)–O(1)	2.209(3)	2.263(4)	Co(1)–O(1)	2.171(3)
M(1)–O(2A)	2.129(3)	2.193(4)	Co(1)–O(2A)	2.243(3)
M(1)–O(3)	2.163(3)	2.243(4)	Co(1)–O(3)	2.287(4)
M(1)–O(4A)	2.229(3)	2.348(4)	Co(1)–O(4A)	2.195(3)
M(1)–OW(1)	1.943(2)	1.979(3)	Co(1)–OW(1)	1.949(3)
M(1)–OW(1A)	1.965(2)	1.975(3)	Co(1)–OW(1A)	1.959(3)
O(1)–Cu(1)–N(2)	175.30(13)	174.55(17)	O(1)–Cu(1)–N(2)	172.68(16)
O(2)–Cu(1)–N(1)	172.67(13)	172.98(16)	O(2)–Cu(1)–N(1)	174.73(16)
O(1)–Cu(1)–N(1)	93.29(13)	93.38(16)	O(1)–Cu(1)–N(1)	92.07(16)
O(1)–Cu(1)–O(2)	91.47(10)	91.14(14)	O(1)–Cu(1)–O(2)	91.62(13)
N(1)–Cu(1)–N(2)	83.68(14)	83.55(18)	N(1)–Cu(1)–N(2)	83.84(18)
O(2)–Cu(1)–N(2)	91.91(12)	92.35(16)	O(2)–Cu(1)–N(2)	92.88(16)
O(3)–M(1)–OW(1A)	169.34(9)	165.02(14)	O(3)–Co(1)–OW(1)	168.84(13)
O(1)–M(1)–O(2A)	174.44(10)	170.72(13)	O(1)–Co(1)–O(2A)	172.73(13)
OW(1)–M(1)–O(4A)	170.69(10)	167.85(14)	OW(1A)–Co(1)–O(4A)	166.82(13)
O(3)–M(1)–O(1)	72.63(10)	70.32(13)	O(3)–Co(1)–O(1)	70.97(12)
O(3)–M(1)–O(2A)	102.15(11)	101.77(14)	O(3)–Co(1)–O(2A)	104.96(13)
O(3)–M(1)–O(4A)	90.92(11)	88.43(14)	O(3)–Co(1)–O(4A)	89.62(14)
O(3)–M(1)–OW(1)	87.58(10)	85.83(14)	O(3)–Co(1)–OW(1A)	84.00(13)
OW(1A)–M(1)–O(1)	99.20(10)	100.76(14)	OW(1)–Co(1)–O(1)	99.21(13)
OW(1A)–M(1)–O(2A)	85.74(11)	85.88(15)	OW(1)–Co(1)–O(2A)	84.21(13)
OW(1A)–M(1)–O(4A)	84.57(10)	82.14(14)	OW(1)–Co(1)–O(4A)	87.34(13)
OW(1A)–M(1)–OW(1)	98.40(9)	105.51(13)	OW(1)–Co(1)–OW(1A)	101.02(12)
O(1)–M(1)–O(4A)	105.16(11)	104.63(14)	O(1)–Co(1)–O(4A)	102.37(13)
O(1)–M(1)–OW(1)	83.16(11)	83.49(15)	O(1)–Co(1)–OW(1A)	86.47(14)
O(2A)–M(1)–O(4A)	72.61(10)	69.63(13)	O(2A)–Co(1)–O(4A)	71.25(12)
O(2A)–M(1)–OW(1)	98.72(10)	101.09(15)	O(2A)–Co(1)–OW(1A)	99.23(12)
Cu(1)–O(1)–M(1)	123.18(12)	121.15(16)	Cu(1)–O(1)–Co(1)	124.20(16)
Cu(1A)–O(2A)–M(1)	125.72(12)	122.76(16)	Cu(1A)–O(2A)–Co(1)	122.02(16)

ideal values, and the deviation of the donor atoms (ca. 0.08 Å) and the displacement of the metal ion (ca. 0.015 Å) from the least-squares plane N_2O_2 are very small.

As mentioned, the central metal ion [M(1)] is coordinated to two bridging phenoxido oxygen atoms [O(1) and O(2A)], two methoxy oxygen atoms [O(3) and O(4A)], and two water oxygen atoms [OW(1) and OW(1A)]. The bond lengths involving the two methoxy oxygen atoms are different [2.163(3) and 2.229(3) Å for **2**; 2.195(3) and 2.287(4) Å for **3**; 2.243(4) and 2.348(4) Å for **4**]. Similarly, the two metal–phenoxido bond lengths are also different [2.129(3) and 2.209(3) Å for **2**; 2.171(3) and 2.243(3) Å for **3**; 2.193(4) and 2.263(4) Å for **4**]. In contrast, the two bond lengths involving the water oxygen atoms are almost identical (ca. 1.95 Å for **2** and **3** and ca. 1.97 Å for **4**). The *transoid* angles range between 169.34(9) and 174.44(10)° for **2**, 166.82(13) and 172.73(13)° for **3**, and 165.02(14) and 170.72(13)° for **4**, while the ranges for the *cisoid* angles are 72.61(10)–105.16(11)° for **2**, 70.97(12)–104.96(13)° for **3**, and 69.63(13)–105.51(13)° for **4**. The wide ranges of the bond lengths and angles are indicative that the central metal ion in these three complexes has a highly distorted octahedral coordination environment. However, as the average deviation of the constituent atoms and the displacement of the metal center from the three possible least-squares planes are closely similar, it is not possible to define the basal plane and the axial atoms. By considering the three possible basal planes for the three complexes, the dihedral angle between the square plane of the terminal metal ions and the basal plane of the central metal ion range between 58.5 and 132.4° for **2**, 58.8 and 131.6° for **3**, and 49.7 and 104.9° for **4**, which indicates significant twisting of the trinuclear core. The two bridge angles for a particular complex are almost identical [123.18(12) and 125.72(12)° for **2**; 122.02(16) and 124.20(16)° for **3**; 121.15(16) and 122.76(16)° for **4**].

As the central metal ion in **2**–**4** occupies two sites, it is not possible to know the geometries of the hydrogen bonds. However, the ranges of the O(water)···O(phenoxido/methoxy) contacts (2.76–2.85 Å for **2**; 2.82–2.87 Å for **3**; 2.83–2.88 Å for **4**) indicate that, as in **1**, strong hydrogen bonding also takes place in these complexes.

Comparison of the Structures of 1–4 with the Related Compounds

In the self-assembled dinuclear–mononuclear cocrystals $[\{Cu^{II}L^2M^{II}(H_2O)_3\}\{Cu^{II}L^2\}_2](ClO_4)_2$ {M = Cu (**5**), Co (**6**), Mn (**7**)} derived from *N*,*N*′-ethylenebis(3-ethoxysalicylaldimine) (H_2L^2), each of the two water hydrogen atoms of two coordinated water molecules forms bifurcated hydrogen bonds with the two phenoxido and two ethoxy oxygen atoms of the mononuclear [$Cu^{II}L^2$] moieties, which results in the encapsulation of a water molecule in the O_4 cavity.[19a] As already mentioned, the second metal center in a number of dinuclear, trinuclear, tetranuclear, and polymeric compounds derived from H_2L^1 or other 3-methoxysalicylaldehyde–diamine ligands (H_2L-OMe) resides either in the O_4 cavity or in between the two O_4 cavities.[15–18] In any case, the second metal center is not coordinated to a water molecule. Moreover, the reported 3d–3d compounds derived from H_2L-OMe are diphenoxido bridged. In contrast, the central metal ions in **1**–**4** are coordinated to two water molecules, and the trinuclear core is monophenoxido bridged. Therefore, it seems that the presence of two coordinated water molecules and the involvement of these water molecules in hydrogen-bonding interactions with the phenoxido and methoxy oxygen atoms are the governing factors that stabilize the monophenoxido-bridged trinuclear core in **1**–**4**.

It is relevant to compare the composition of the title compounds with reported related trinuclear compounds. We are aware of a number of phenoxido-bridged trinuclear Cu^{II}_3 compounds in the literature; in most, the two pairs of adjacent metal ions are diphenoxido bridged.[6–8] To the best of our knowledge, only three monophenoxido-bridged Cu^{II}_3 compounds have been reported previously.[9,23] Clearly, compound **1** is an addition in the family of only a few monophenoxido-bridged Cu^{II}_3 compounds. With regard to phenoxido- or any other oxido-bridged trinuclear $Cu^{II}_2M^{II}$ compounds (M = Ni, Co, or Fe), only one Cu^{II}_2-Ni^{II},[10] only one $Cu^{II}_2Fe^{II}$,[24a] and only two $Cu^{II}_2Co^{II}$ compounds are known.[10,24b] The two $Cu^{II}\cdots M^{II}$ pairs in all of these trinuclear compounds are diphenoxido bridged. The monophenoxido-bridged $Cu^{II}_2M^{II}$ compounds **2**–**4** reported herein are at present the only examples of this type of system.

Magnetic Properties

The cryomagnetic behavior ($\chi_M T$ vs. T plots) of the Cu^{II}_3 compound **1** is shown in Figure 5. The $\chi_M T$ value (0.90 $cm^3 mol^{-1} K$) at 300 K of **1** is very close to the theoretical value (1.13 $cm^3 mol^{-1} K$) for three isolated copper(II) ions with $g = 2$. On lowering the temperature, $\chi_M T$ decreases gradually to reach a plateau, 0.4 $cm^3 mol^{-1} K$, in the temperature range 50–2 K. The $\chi_M T$ vs. T plots for the $Cu^{II}_2Ni^{II}$ compound **2** is presented in Figure 6. The $\chi_M T$ value (1.81 $cm^3 mol^{-1} K$) at 300 K in this case is slightly greater than the theoretical value (1.75 $cm^3 mol^{-1} K$; $g = 2$) expected for noninteracting copper(II) (two) and nickel(II) (one) ions. The $\chi_M T$ value of **2** gradually decreases on lowering the temperature to reach a plateau (0.01 $cm^3 mol^{-1} K$) in the temperature range 10–2 K. As shown in Figure 7, the $\chi_M T$ value (3.14 $cm^3 mol^{-1} K$) at 300 K of the $Cu^{II}_2Co^{II}$ compound **3** is greater than the theoretical value (2.63 $cm^3 mol^{-1} K$) for the isolated Co^{II} (one atom, $s = 3/2$) and Cu^{II} (two atoms, $s = 1/2$) ions with $g = 2$. On cooling, the $\chi_M T$ value in this case steadily decreases to 0.24 $cm^3 mol^{-1} K$ at 2 K. The cryomagnetic behavior of the $Cu^{II}_2Fe^{II}$ compound **4** is shown in Figure 8. The $\chi_M T$ value at 300 K for this compound is 4.15 $cm^3 mol^{-1} K$, which is slightly greater than the theoretical value of 3.75 $cm^3 mol^{-1} K$ expected for one high-spin iron(II) and two copper(II) ions with $g = 2$. On lowering the temperature from 300 K to 80 K, the $\chi_M T$ value decreases slowly to 3.5 $cm^3 mol^{-1} K$. On further cooling, it decreases rapidly to 0.79 $cm^3 mol^{-1} K$ at 2 K. The $\chi_M T$ vs. T profiles of **1**–**4** are indicative of the existence of moderate to weak antiferromagnetic interactions in these molecules.

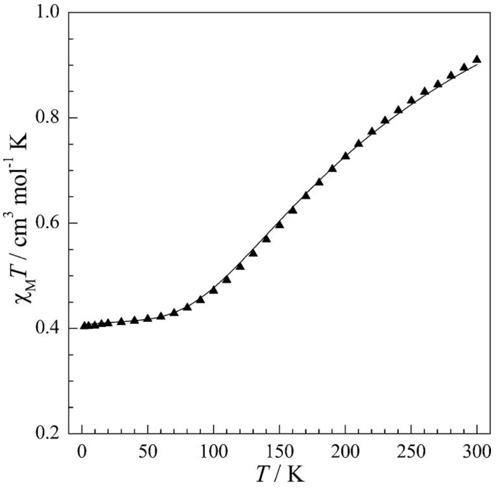


Figure 5. $\chi_M T$ vs. T plots for [$\{Cu^{II}L^1\}_2Cu^{II}(H_2O)_2$]·$(ClO_4)_2$·$H_2O$ (**1**). The solid line represents the simulated curves.

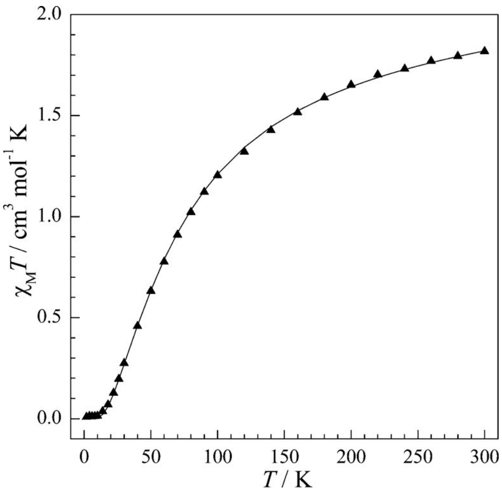


Figure 6. $\chi_M T$ vs. T plots for [$\{Cu^{II}L^1\}_2Ni^{II}(H_2O)_2$]·$(ClO_4)_2$ (**2**). The solid line represents the simulated curves.

Among three possible exchange pathways in **1**–**4**, the interaction between the terminal metal ions [Cu(1) and Cu(3) in **1**, Cu(1) and Cu(1A) in **2**–**4**] should be negligible because of the long distance (>6 Å), and therefore the superexchange between the two pairs of monophenoxido-bridged

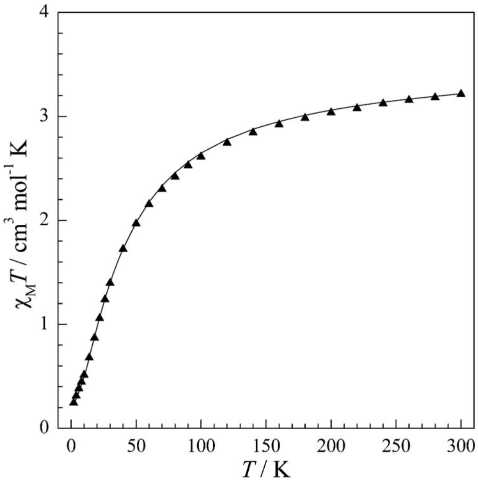


Figure 7. $\chi_M T$ vs. T plots for $[\{Cu^{II}L^1\}_2Co^{II}(H_2O)_2]\cdot(ClO_4)_2$ (**3**). The solid line represents the simulated curves.

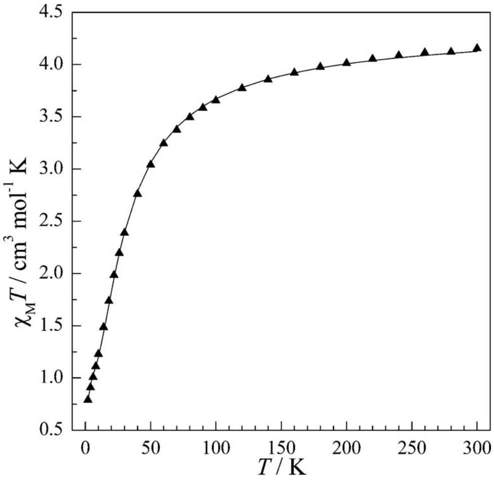


Figure 8. $\chi_M T$ vs. T plots for $[\{Cu^{II}L^1\}_2Fe^{II}(H_2O)_2]\cdot(ClO_4)_2$ (**4**). The solid line represents the simulated curves.

adjacent metal ions govern the magnetic properties. The two terminal···central metal ion distances in compounds **2**–**4** are almost identical, as are the two phenoxido bridge angles. Therefore, by taking the single-ion zero-field splitting of the central metal ion (Ni^{II}, Co^{II}, and Fe^{II}) into consideration, the magnetic behavior of **2**–**4** can be modeled with the following Hamiltonian [Equation (1).

$$H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3) + D[S_{Z,2}{}^2 - {}^1/_3 S_2(S_2+1)] \quad (1)$$

In contrast to those in the $Cu^{II}{}_2M^{II}$ compounds **2**–**4**, the two interactions Cu(1)···Cu(2) and Cu(3)···Cu(2) in the $Cu^{II}{}_3$ compound **1** should be different because of the differences in the metal···metal distances (3.48 Å vs. 3.60 Å), the dihedral angles (143.7° vs. 121.5°) between the basal planes, and the bridge angles [129.84(13)° vs. 121.10(12)°]. Again, these parameters indicate that the Cu(1)···Cu(2) interaction should be relatively more antiferromagnetic than the Cu(3)···Cu(2) interaction. Therefore, the magnetic behavior of **1** can logically be modeled by the following Hamiltonian [Equation (2).

$$H = -2J_1 S_1 \cdot S_2 - 2J_2 S_2 \cdot S_3 \quad (2)$$

With these models, the susceptibility data were fitted by using the program JULX.[25] A fixed value of the temperature-independent paramagnetism (*TIP*) for a particular complex was used in the simulations.

As shown by the solid lines in Figure 5, the susceptibility data of **1** are well simulated with $J_1 = -97.6\ cm^{-1}$, $J_2 = -89.5\ cm^{-1}$, $g = 2.085$, $TIP = 1.8 \times 10^{-4}\ cm^3 mol^{-1}$. In the cases of complexes **2**–**4**, the converging parameter values in the least-squares fittings (Figures 6–8) are: $Cu^{II}Ni^{II}Cu^{II}$ (**2**), $J = -25.4\ cm^{-1}$, $g = 2.142$, $|D| = 0.037\ cm^{-1}$, $TIP = 2.2 \times 10^{-4}\ cm^3 mol^{-1}$; $Cu^{II}Co^{II}Cu^{II}$ (**3**), $J = -9.0\ cm^{-1}$, $g = 2.257$, $|D| = 50.0\ cm^{-1}$, $TIP = 2.2 \times 10^{-4}\ cm^3 mol^{-1}$; $Cu^{II}Fe^{II}Cu^{II}$ (**4**), $J = -6.5\ cm^{-1}$, $g = 2.142$, $|D| = 3.3\ cm^{-1}$, $TIP = 1.2 \times 10^{-4}\ cm^3 mol^{-1}$. It may be noted that significant deviation between the calculated and observed data takes place in the low-temperature region for **3** and **4** if D is fixed at zero (Figures S1 and S2, Supporting Information), which indicates that zero-field splitting has a profound role in these two complexes in governing the magnetic behavior. In the context of the observation of a large D value of 50 cm^{-1} in compound **3**, we would like to mention the role of this parameter in the simulation of the magnetic data of the reported cobalt(II) compounds. Although simulations of magnetic susceptibility data in some cobalt(II) compounds have been performed without considering D,[26a] the zero-field effect is known to govern the magnetic behavior of many cobalt(II) compounds,[2d,12b,26b,26c] and the range of D values in the reported compounds is much wider; a small value of ca. 0.1 cm^{-1} and a large value of ca. 10.5 cm^{-1}, and even ca. 145 cm^{-1}, are known. Large θ values (ca. 30 K or 70 K) used in the simulation process, in some cases, might be replaced by large D values.[26d] It may also be mentioned that the magnetic behavior of the cobalt(II) containing compounds may be so complicated that even by considering the zero-field effect, a poor-quality simulation is obtained.[26e]

It may be relevant to compare the magnetic properties of the title compounds with those of the reported related compounds. Strong antiferromagnetic interactions are usually observed in most $Cu^{II}{}_3$ compounds having a diphenoxido-bridging core between the two pairs of adjacent metal ions.[6] However, there are a few examples exhibiting moderate or weak antiferromagnetic interaction, which arises as a result of either the axial–equatorial arrangement of the phenoxido bridges or the larger value of the dihedral angles between the basal planes.[7,8] Relative to the diphenoxido-bridged systems, the extent of interaction in the monophenoxido-bridged compounds should be reduced because of the participation of one bridge in the latter case.[19] Of the three reported monophenoxido-bridged $Cu^{II}{}_3$ compounds,[9,23] magnetic studies have been carried out for two.[9] In one of these cases, the interaction is weakly ferromagnetic ($J = +5.8\ \mathrm{cm}^{-1}$) despite the obtuse bridge angle of 113.3°. This apparent anomaly has been explained on the basis of the out-of-plane position of the phenyl ring with respect to the Cu_2O plane.[9a] In the second example, despite the larger bridge angle of 124°, the adjacent metal centers are coupled by moderate antiferromagnetic interaction ($J = –135\ \mathrm{cm}^{-1}$), which could be related to the tetrahedral distortion of the metal environments.[9b] In **1**, the two J values of $–97.6\ \mathrm{cm}^{-1}$ and $–89.5\ \mathrm{cm}^{-1}$ correspond to the bridge angles of 129.84(13)° and 121.10(12)°, respectively. As the dihedral angles between the basal planes of the interacting metal centers are 143.7° and 121.5°, the moderate antiferromagnetic interactions in **1** are related to these bent bridges.[1a,11a,19a] It should also be noted that as compound **1** is monophenoxido-bridged and the bridging moieties are significantly twisted, the exchange integral vs. bridge angle correlations of Thompson and Hatfield–Hodgson cannot be applied in this case.[1a,2a,2b]

As already mentioned, the two pairs of adjacent metal ions in the structurally characterized phenoxido-bridged $Cu^{II}_2M^{II}$ compounds are diphenoxido-bridged.[10,24] The interaction between copper(II) and nickel(II) in the only structurally characterized diphenoxido-bridged $Cu^{II}_2Ni^{II}$ compound is strongly antiferromagnetic with $J = –50.6\ \mathrm{cm}^{-1}$.[10] Again, in one of the two structurally characterized $Cu^{II}_2Co^{II}$ compounds, an antiferromagnetic interaction with $J = –26.2\ \mathrm{cm}^{-1}$ has been observed.[10] These two compounds, $Cu^{II}_2Ni^{II}$ and $Cu^{II}_2Co^{II}$, have been derived from the same ligand and have similar types of structures. The phenoxido bridge angles in these two compounds vary between 97.2 and 102.4°. However, the dihedral angles between the basal plane of the central metal ion (Ni^{II} or Co^{II}) with the basal planes of two terminal copper(II) centers are significantly different: 8.3° and 101.8° for the $Cu^{II}_2Ni^{II}$ compound and 5.9° and 82.9° for the $Cu^{II}_2Co^{II}$ compound. Evidently, although the interaction through the bent bridges should be weak, the planar bridges propagate stronger interactions, which results in average J values of –50.6 and $–26.2\ \mathrm{cm}^{-1}$ for the two compounds. In comparison, the $Cu^{II}_2Ni^{II}$ compound **2** ($J = –25.4\ \mathrm{cm}^{-1}$) and the $Cu^{II}_2Co^{II}$ compound **3** ($J = –9.0\ \mathrm{cm}^{-1}$) exhibit weaker interaction despite the more obtuse bridge angles [123.18(12) and 125.72(12)° for **2**; 122.02(16) and 124.20(16)° for **3**]. Although the participation of one phenoxido bridge in the superexchange has an influence,[19] the major factor for the reduced antiferromagnetic interaction in **2** and **3** is the significant twisting of the trinuclear core. It should be mentioned that a similar dependency of the magnetic properties on the bridge angle and planarity of the bridging core has been observed in diphenoxido-bridged discrete dinuclear or dinuclear-based polymeric $Cu^{II}M^{II}$ compounds; the J values range between –11.8 and $–67\ \mathrm{cm}^{-1}$,[11] –8 and $–53\ \mathrm{cm}^{-1}$,[11d,11e,12] and –6 and $–23\ \mathrm{cm}^{-1}$[11d,12a] for the $Cu^{II}Ni^{II}$, $Cu^{II}Co^{II}$, and $Cu^{II}Fe^{II}$ systems, respectively.

The magnitude of the antiferromagnetic interactions in the compounds follows the order, Cu^{II}_3 (**1**; $J_1 = –97.6\ \mathrm{cm}^{-1}$, $J_2 = –89.5\ \mathrm{cm}^{-1}$) > $Cu^{II}_2Ni^{II}$ (**2**; $J = –25.4\ \mathrm{cm}^{-1}$) > $Cu^{II}_2Co^{II}$ (**3**; $J = –9.0\ \mathrm{cm}^{-1}$) > $Cu^{II}_2Fe^{II}$ (**4**; $J = –6.5\ \mathrm{cm}^{-1}$), and can be explained on the basis of magnetic orbitals.[1a,2d,2e,11e] While $d_{x^2-y^2}$ is the only magnetic orbital for copper(II), the number of magnetic orbitals increases on going from copper(II) to iron(II). Of the different types of orbital combinations, only $d_{x^2-y^2} \leftrightarrow d_{x^2-y^2}$ is antiferromagnetic, whereas other combinations are ferromagnetic. Clearly, the ferromagnetic contributions in the compounds increases as $Cu^{II}_2Fe^{II} > Cu^{II}_2Co^{II} > Cu^{II}_2Ni^{II} > Cu^{II}_3$, which results in the Cu^{II}_3 compound (**1**) as the most antiferromagnetic and the $Cu^{II}_2Fe^{II}$ compound (**4**) as the least antiferromagnetic.

Conclusions

The main objective of the present investigation has been to explore the 3d–3d bimetallic compounds derived from 3-methoxysalicylaldehyde–diamine Schiff base ligands, with the aim to explore whether, similarly to the those in the complexes derived from 3-ethoxysalicylaldehyde–diamine ligands, the second metal ion could be coordinated to a water molecule, which, in turn, may interact with the phenoxido and methoxy oxygen atoms to result in the formation of dinuclear–mononuclear cocrystals. As discussed, the second metal center in the title trinuclear compounds is coordinated to two water molecules, which interact with phenoxido and methoxy oxygen atoms. Although water encapsulation and formation of cocrystals does not occur because the central metal ion is located in between the two O_4 cavities, the presence of two coordinated water molecules and the interaction of these water molecules with the phenoxido and methoxy oxygen atom stabilize this rare example of a monophenoxido-bridged Cu^{II}_3 compound, **1**, and the first examples of monophenoxido-bridged $Cu^{II}_2M^{II}$ compounds, **2**–**4**. The pair of monophenoxido-bridged metal centers in these compounds is coupled by moderate to weak antiferromagnetic interactions. Comparison of the results with the exchange behavior of reported, related compounds reveals that moderate or weak antiferromagnetic interactions in **1**–**4** are related to the participation of one phenoxido bridge in superexchange as well as to the large twisting of the trinuclear cores.

Experimental Section

Materials and Physical Measurements: All the reagents and solvents were purchased from commercial sources and used as received. H_2L^1 was obtained by a 2:1 condensation of 3-methoxysalicylaldehyde and ethylenediamine in methanol. 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. Variable-temperature (2–300 K) magnetic susceptibility measurements under a fixed field strength of 1 T were carried out with a Quantum Design MPMS SQUID magnetometer. Diamagnetic corrections were estimated from the Pascal constants.

[$Cu^{II}L^1(H_2O)$]:[21] To a stirred suspension of the ligand H_2L^1 (1.65 g, 5 mmol) in methanol (15 mL) was added dropwise an aqueous solution (5 mL) of $Cu(OAc)_2\cdot H_2O$ (1.0 g, 5 mmol). During the addition, a green product began to deposit. After stirring the mixture for 0.5 h, the green solid was collected by filtration. Recrystallization of the product from dimethylformamide yielded diffraction-quality crystals. Yield: 1.794 g (88 %). $C_{18}H_{20}CuN_2O_5$ (407.915): calcd. C 53.00, H 4.94, N 6.87; found: C 53.20, H 4.88, N 6.96. IR (cm^{-1}, KBr): ν_{O-H}(water) = 3457 (m), $\nu_{C=N}$ = 1644 (s).

$[\{Cu^{II}L^1\}_2Cu^{II}(H_2O)_2]\cdot(ClO_4)_2\cdot H_2O$ (1): To a suspension of $[Cu^{II}L^1(H_2O)]$ (0.204 g, 0.5 mmol) in acetone (10 mL) was added dropwise with stirring a acetone solution (5 mL) of copper(II) perchlorate hexahydrate (0.186 g, 0.5 mmol). Immediately, a red solution formed, which was filtered after 0.5 h to remove any suspended particles. The filtrate was then kept at room temperature for slow evaporation. After a few days, a red crystalline compound that deposited was collected and washed with cold methanol. Recrystallization from an acetone/hexane mixture yielded red single crystals. Yield: 0.22 g (80 %). $C_{36}H_{42}Cl_2Cu_3N_4O_{19}$: calcd. C 39.44, H 3.86, N 5.11; found: C 39.52, H 3.79, N 5.16. IR (cm^{-1}, KBr): ν_{O-H} (water) = 3401 (w), $\nu_{C=N}$ = 1636 (s), ν_{ClO4} = 1084 (vs), 624 (w).

$[\{Cu^{II}L^1\}_2M^{II}(H_2O)_2](ClO_4)_2$ {M = Ni (2), Co (3), Fe (4)}: These three compounds were prepared in the same way as that described for **2** by using the appropriate $M(ClO_4)_2\cdot 6H_2O$. To a stirred suspension of $[Cu^{II}L^1(H_2O)]$ (0.204 g, 0.5 mmol) in acetone (70 mL) was added an acetone solution (10 mL) of $Ni(ClO_4)_2\cdot 6H_2O$ (0.183 g, 0.5 mmol). The color of the solution changed to green. After 0.5 h of stirring, the solution was filtered, and the filtrate was kept for slow evaporation. The diffraction-quality green crystals that deposited over a period of 2 d were collected by filtration and washed with cold acetone. Yield: 0.228 g (85 %). $C_{36}H_{40}Cl_2Cu_2N_4NiO_{18}$: calcd. C 40.28, H 3.76, N 5.22; found: C 40.23, H 3.69, N 5.25. IR (cm^{-1}, KBr): ν_{O-H} (water) = 3442 (w), $\nu_{C=N}$ = 1643 (s), ν_{ClO4} = 1111 (vs), 622 (w). **3:** Brown. Yield: 75 %. $C_{36}H_{40}Cl_2CoCu_2N_4O_{18}$: calcd. C 40.27, H 3.76, N 5.22; found: C 40.32, H 3.72, N 5.19. IR (cm^{-1}, KBr): ν_{O-H} (water) = 3439 (w), $\nu_{C=N}$ = 1642 (s), ν_{ClO4} = 1112 (vs), 624 (w). **4:** Brown. Yield: 82 %. $C_{36}H_{40}Cl_2Cu_2FeN_4O_{18}$: calcd. C 40.39, H 3.77, N 5.23; found: C 40.45, H 3.85, N 5.30. IR (cm^{-1}, KBr): ν_{O-H} (water) = 3429 (w), $\nu_{C=N}$ = 1641 (s), ν_{ClO4} = 1112 (vs), 623 (w).

Crystal Structure Determination of 1–4: The crystallographic data of these four compounds are summarized in Table 4. Diffraction data were collected on an Enraf–Nonius CAD4 diffractometer at 293 K with data collection and reduction by using a CAD4 Express Enraf–Nonius programs package and XCAD4. All data were corrected for Lorentz-polarization effects. The four structures were solved by direct methods by using SIR92 and refined by least-squares methods on F^2 by using SHELXL-97.[22] Hydrogen atoms were inserted at calculated positions with isotropic thermal parameters constrained to be 1.2 times the Ueq of the carrier atoms (1.5 times for hydrogen atoms of the methyl groups) and refined. The hydrogen atoms of the water molecules were first located from a difference Fourier map and then refined with constraints. In compounds **2**–**4**, oxygen atoms of the perchlorate counteranions were statically or dynamically disordered and partially solved. The final least-squares refinements (R_1) based on $I > 2\sigma(I)$ converged to 0.0510, 0.0408, 0.0473, and 0.0507 for **1**–**4**, respectively. Nickel(II), cobalt(II), and iron(II) in compounds **2**, **3**, and **4**, respectively, occupy two disordered general positions with an occupancy factor of 0.5, close to the center of symmetry. This disordered model was compared to an ordered model with Ni^{II}, Co^{II}, and Fe^{II} in **2**, **3**, and **4**, respectively, on the center of symmetry of the $P2_1/c$ space group. This hypothesis of comparing with the ordered model was not, however, refined correctly and thus should not be considered. These structural analyses were corroborated by the determination of the structures of **2** and **4** at 100 K. CCDC-724300 (**1**), 724301 (**2**), 724302 (**3**), 724303 (**4**) [structures at 293 K] and CCDC-729865 (**2**), 729866 (**4**) [structures at 100 K] contain the supplementary crystallographic data for this paper. These data can be obtained

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

	1	**2**	**3**	**4**
Formula	$C_{36}H_{42}Cl_2Cu_3N_4O_{19}$	$C_{36}H_{40}Cl_2Cu_2N_4NiO_{18}$	$C_{36}H_{40}Cl_2CoCu_2N_4O_{18}$	$C_{36}H_{40}Cl_2Cu_2FeN_4O_{18}$
Molecular weight	1096.26	1073.41	1073.63	1070.55
Crystal color	brown	brown	brown	brown
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	13.438(1)	8.389(1)	8.414(1)	8.428(5)
b / Å	25.402(2)	13.892(2)	13.903(2)	13.903(2)
c / Å	14.095(1)	17.515(2)	17.524(2)	17.599(8)
β / °	117.17(1)	100.54(1)	100.49(1)	100.60(5)
V / Å^3	4280.4(6)	2006.8(4)	2015.7(4)	2027.0(15)
Z	4	2	2	2
$D_{calcd.}$ / g cm^{-3}	1.701	1.776	1.769	1.754
F(000)	2236	1096	1094	1092
μ / mm^{-1}	1.685	1.733	1.670	1.609
Temperature / K	293(2)	293(2)	293(2)	293(2)
Crystal size / mm	0.23 × 0.20 × 0.15	0.25 × 0.20 × 0.16	0.25 × 0.20 × 0.175	0.275 × 0.20 × 0.19
2θ / °	4.56–60.14	4.74–59.96	4.72–59.00	4.70–59.96
Reflections collected	25425	11666	11214	11765
Independent reflections	12476	5842	5612	5890
R(int)	0.0730	0.0847	0.1866	0.1131
Absorption/correction	empirical	empirical	empirical	none
T_{min}	0.690	0.593	0.7642	
T_{max}	0.776	0.688	0.8276	
Final R indices [$I > 2\sigma(I)$]				
R_1[a], wR_2[b]	0.0510, 0.1365	0.0408, 0.0969	0.0473, 0.0895	0.0507, 0.1194
R indices (all data)				
R_1[a], wR_2[b]	0.1305, 0.1683	0.1468, 0.1239	0.2349, 0.1252	0.1952, 0.1579

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

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): $\chi_M T$ (observed and calculated with $D = 0$) vs. T plots for compounds **3** and **4**.

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