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Copper(II) Complexes of Tridentate Schiff Bases of 5-Substituted Salicylaldehydes and Diamines – The Role of the Substituent and the Diamine in the Formation of Mono-, Di- and Trinuclear Species – Crystal Structures and Magnetic Properties

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We describe some copper(II) complexes with tridentate anionic Schiff bases, L^-, derived from the monocondensation of some 5-substituted salicylaldehydes (5-G-salH, G = H, NO_2 and OMe) with ethylenediamine (en) or 1,3-diaminopropane (tn). Mononuclear $[CuL(py)]^+$, dinuclear $[Cu_2L_2]^{2+}$ and trinuclear $[Cu_3L_3(\mu_3\text{-}OH)]^{2+}$ compounds have been obtained, and factors affecting the nuclearity of complexes were investigated and found to depend on reaction conditions, the nature of G and the length of the diamine. The crystal structures of seven representative compounds have been determined. Magnetic studies on a dinuclear and a trinuclear species were also carried out, and the results were interpreted on the basis of the structural data and current superexchange models.

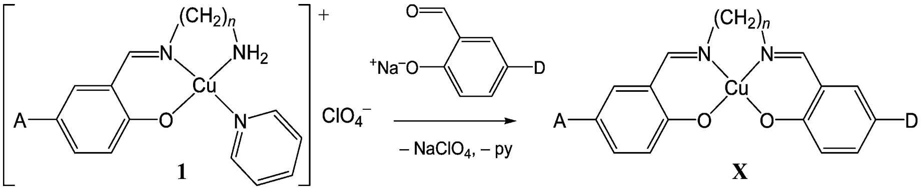
Introduction

With the aim of fine-tuning factors that lead to nonlinear optical response, we have recently described some Cu^{II} complexes of unsymmetrically substituted salen analogues (**X** in Scheme 1), in which the two salicylaldehyde residues carry different substituents at position 5 (hereafter 5-G-salH), namely an electron acceptor, A, and an electron donor, D, group.[1,2]

Attempts at preparing such complexes according to the general procedure shown in Scheme 2 were unsuccessful. The weak point of the outlined synthesis is that the required initial condensation of salicylaldehyde with only one amino group of the diamine, to form the so-called "half unit" ligands, L^- (whose subsequent reaction with a differently substituted salicylaldehyde and copper acetate will give **X**), is not independent on the nature of the diamine.

Reactions of *N*-mono- or *N*,*N*-disubstituted diamines with salH obviously give tridentate half units,[3] but in the case of primary diamines, only few, namely *o*-phenylenediamine, 1,2-diaminocyclohexane and diaminomaleonitrile, have been reported to give such half unit species, provided that the reaction is carried out in a 1:1 ratio.[4] In particular, ethylenediamine (en) or 1,3-diaminopropane (or trimethylenediamine, hereafter tn), which are of direct interest in the present work, gave, at least in our hands, invariably the double condensation products, H_2salen or H_2saltn respectively, even when a fourfold excess of the diamine was used. On the other hand, half units have been synthesised by reaction of primary diamines and ketone groups less reactive than salicylaldehyde, in a 1:1 ratio.[5,6]

According to the literature, the half unit species with en or tn and salH are easily obtained by a template synthesis in the presence of metal ions, giving rise to a rich coordination



Scheme 1.

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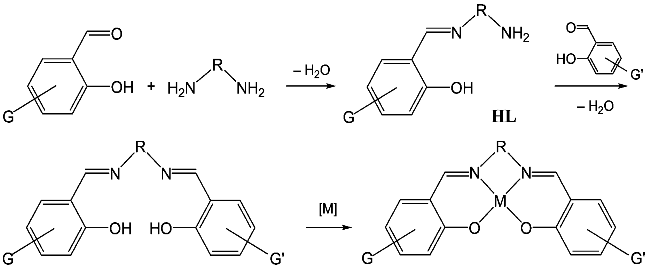
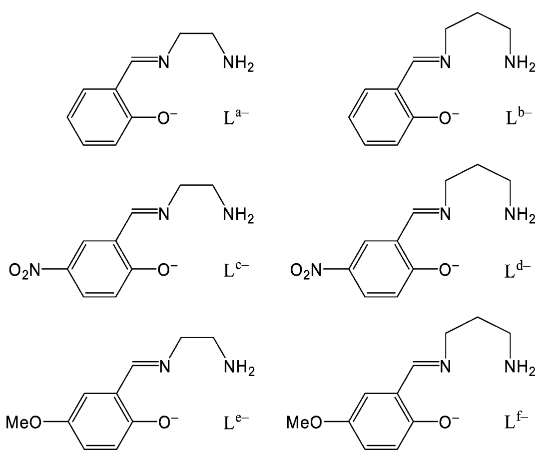


Scheme 2.

chemistry. For example, in the case of Fe^{III}, Cr^{III}, Co^{III} and Ni^{II} the tridentate half units, L^-, form hexacoordinate mononuclear species $[FeL_2]^+$,[7] $[CrL_2]^+$,[8] $[CoL_2]^+$,[9] and $[NiL_2]$,[10] whereas in the presence of Cu^{II}, mononuclear Cu^{II} complexes, $[CuL(py)]^+$ (**1**),[11–13] can be obtained by performing the reaction in the presence of pyridine or other auxiliary ligands. Compounds **X** can then be synthesised by reaction of **1** with another salicylaldehyde (Scheme 1).[1]

In the absence of an auxiliary ligand, the fourth coordination site of copper can be occupied by a bridging phenolato oxygen atom of another "CuL" moiety, giving rise to dinuclear species $[Cu_2L_2]^{2+}$ (**2**)[14] (see Scheme 4). Trinuclear species $[Cu_3L_3(\mu_3\text{-}OH)]^{2+}$ have also been described.[12,15] All these reports are scattered, though. We therefore decided to investigate the chemistry of these Cu^{II} complexes in more detail. Here we report the conditions under which the various species are formed and, in particular, discuss the influence of the salicylaldehyde substituents and the length of the diamine (en and tn). The synthetic work is supported by the X-ray structural analysis of seven selected compounds. Results of magnetic studies on a dinuclear and a trinuclear species are also reported and interpreted on the basis of the structural data and existing superexchange theories.

The tridentate ligands described in this paper and their numbering are summarised in Scheme 3.



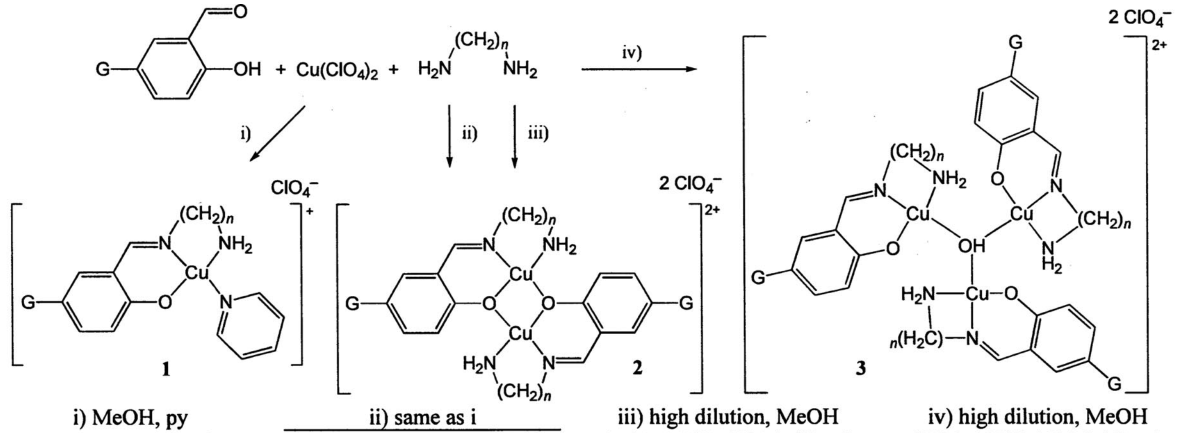
Scheme 3.

Results and Discussion

Reaction of copper perchlorate, a diamine and a salicylaldehyde gives rise to mono-, di- or trinuclear derivatives, depending on reaction conditions, the nature of the substituent G of the salicylaldehyde and the diamine. The results are summarised in Scheme 4.

Mononuclear Complexes 1

These complexes are prepared by a template reaction of salicylaldehyde (5-G-salH), diamine (en or tn) and copper perchlorate in a 1:1:1 molar ratio, in the presence of pyr-



i) MeOH, py
salH/Cu(ClO$_4$)$_2$/diamine = 1:1:1

Compd.	*n*	G	Yield
1a	2	H	75 %
1b	3	H	84 %
1c	2	NO_2	87 %
1d	3	NO_2	86 %
1e	2	OMe	40 %

ii) same as i

Compd.	*n*	G	Yield
2f	3	OMe	34 %

iii) high dilution, MeOH
salH/NaOH/Cu(ClO$_4$)$_2$/diamine = 1:1:1.5:1.5
not obtained with G = NO_2

Compd.	*n*	G	Yield
2a	2	H	45 %
2b	3	H	51 %
2e	2	OMe	57 %
2f	3	OMe	86 %

iv) high dilution, MeOH
salH/NaOH/Cu(ClO$_4$)$_2$/diamine = 1:1.3:1:1
not obtained with G = OMe

Compd.	*n*	G	Yield
3a	2	H	63 %
3b	3	H	50 %
3c	2	NO_2	63 %
3d	3	NO_2	62 %

Scheme 4.

idine (Scheme 4).[11,12] It has been reported that in the first step, Cu^{2+}, salicylaldehyde and pyridine give [Cu(sal)(py)$_2$]$^+$.[11] Moreover, in the case of 5-NO$_2$-salH, we could isolate the intermediate [(5-NO$_2$-sal)$_2$Cu], which gave **1c** or **1d** upon treatment with pyridine and en or tn, respectively. However, compounds **1** were usually synthesised directly without isolation of the intermediate.

Slight modifications of the synthetic procedure were necessary, depending on the substituent G of salicylaldehyde and the diamine. The less acidic 5-MeO-salH needed a solution of KOH in alcohol for deprotonation, whereas with 5-NO$_2$-salH, one mol equivalent excess of pyridine was sufficient, but only in the case of en, since in the case of tn, NaOH was necessary to obtain complex **1d**. With unsubstituted salH, an excess of pyridine must be avoided, because it led to precipitation of [Cu(py)$_4$](ClO$_4$)$_2$.

The hypothetical mononuclear compound **1f** was not obtained: reaction of 5-MeO-salH, Cu^{II} and tn gave, even in the presence of pyridine, the dinuclear species **2f** (see Experimental Section for details).

The composition of all complexes has been confirmed by elemental (C, H, N) analyses. The IR spectra show bands in the 1650–1600 cm^{-1} region ($\nu_{C=N}$) and at 3330–3230 cm^{-1} due to the N–H stretches of the coordinated NH$_2$ groups. The band due to the perchlorate anion appears at around 1100 cm^{-1}. This band is split in compounds **1b** and **1d**, because of the loss of the T_d symmetry that suggests a O$_3$ClO···Cu interaction, as found in the crystal structure of compound **1b** (see below).

Interestingly, we have also obtained a mononuclear compound, **1c′**, in which the fourth coordination position is occupied by a water molecule instead of pyridine. This compound was isolated as a reaction intermediate during the synthesis of the trinuclear complex **3c**. Its structure has been confirmed by X-ray diffraction analysis.

Crystal Structures of 1b and 1c′

The structures of complexes **1b** and **1c′** are shown in Figure 1 and Figure 2, respectively. Relevant interatomic distances are reported in Table 1. Both complexes show the expected square-planar geometry around the Cu atom. In both cases, the asymmetric unit includes one perchlorate ion, interacting with copper through an oxygen atom, O1p, placed approximately in an apical position. Such interaction is stronger in **1c′** [2.563(4) Å]. In the case of **1b**, the copper atom is further involved in a relatively strong interaction with the O1 oxygen atom of a centrosymmetry-related molecule [2.4008(9) Å], forming a head-to-tail dimer, in which copper is practically hexacoordinate. The structure of **1c′** includes two more water molecules, Ow1 and Ow2 (see Figure 2; hydrogen atoms have not been determined), hydrogen-bonded to the water molecule coordinated to the metal.

Both complexes are characterised by very slight tetrahedral distortion of the donor set, as indicated by the values of the O1–N2–N1–N3 (for **1b**) and O1–N2–N1–O2 (for **1c′**) "torsions", which are equal to –5.82(4)° and –5.0(2)°, respectively. Complex **1c′** is essentially planar; only its en carbons, C1 and C2, are significantly outside the least-squares plane through the donor atoms. On the contrary, in complex **1b**, neither the salicylaldehyde moiety nor the pyridine ring is coplanar with the donor set. The least-

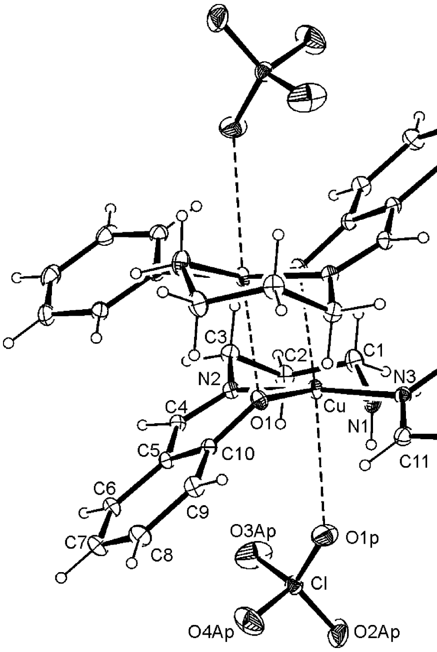


Figure 1. ORTEP plot of a centrosymmetric pair of complex **1b** with the atom-numbering scheme and short intermolecular contacts. Displacement ellipsoids are drawn at the 20% probability level.

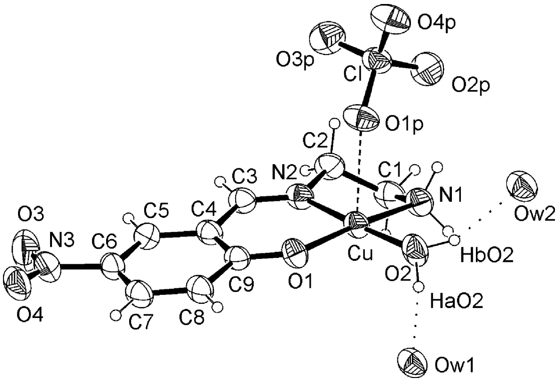


Figure 2. ORTEP plot of complex **1c′** with the atom-numbering scheme and short intermolecular contacts [HaO2···Ow1 1.82(7) Å, and HbO2···Ow2 1.92(7) Å]. Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Selected bond lengths and intermolecular contacts (in Å) for mononuclear compounds **1b** and **1c′**.

	1b	**1c′**
Cu–N1	2.0190(12)	1.988(5)
Cu–N2	1.9854(11)	1.927(5)
Cu–N3/O2[a]	2.0393(12)	1.926(5)
Cu–O1	1.9377(10)	1.899(4)
Cu···O1p	2.8527(12)	2.563(4)
Cu···O1^{i}[b]	2.4008(9)	–

[a] N3 for complex **1b**; O2 for complex **1c′**. [b] i: 1 – *x*, 2 – *y*, –*z*.

squares plane through atoms C4 to C10 and that through the pyridine atoms form dihedral angles equal to 44.09(4) and 41.82(4)°, respectively, with the N1,N2,O1,N3 least-squares plane. The observed deviation from planarity in **1b** could be ascribed to the relatively strong intermolecular interaction within the centrosymmetric pair, as suggested by the fact that the salicylaldehyde moieties are bent out of such dimeric units.[16]

Dinuclear Complexes 2

Complexes **2a**,**b**,**e**,**f** were prepared by a high-dilution method,[14] in the presence of NaOH and by using a 1.5-fold excess of both copper and diamine (see Scheme 4 and Experimental Section). In the case of salH, it was observed that either the presence of a slight excess of base or the lack of excess copper and diamine yielded the trinuclear complexes **3a** and **3b**.

As stated above, compound **2f** was obtained while attempting the preparation of **1f**: reaction of 5-MeO-salH, Cu^{II} and tn, gave, on long standing, **2f** as a crystalline material, suitable for X-ray structure determination. No dinuclear compound with 5-NO_2-salH (i.e., **2c** and **2d**) was ever obtained. Attempted preparations of these compounds always gave the trinuclear derivatives **3c** and **3d**.

Crystal Structures of 2a, 2e and 2f

The structures of complexes **2a**, **2e** and **2f** are shown in Figure 3, Figure 4 and Figure 5, respectively, from different perspectives, and relevant interatomic distances are reported in Table 2. These complexes are characterised by a pair of "long" Cu–O bonds (Cu1–O2 and Cu2–O1, ranging from 1.950 to 1.993 Å), which keep together the two mononuclear half units, as distinguished from the other pair of Cu–O coordination bonds (Cu1–O1 and Cu2–O2, falling in the typical range 1.913–1.943 Å). The asymmetric units include two perchlorate ions partially disordered over two sites (labelled with the letters A and B, respectively) and, in the case of **2a**, also a coordinated methanol molecule. The copper atoms have a distorted square-pyramidal coordination geometry, whose apical position is occupied by either a methanol oxygen O1m (**2a**), or a perchlorate oxygen (**2e**, **2f**), with Cu···O distances between 2.423 and 2.650 Å. In particular, in **2a** the methanol oxygen is coordinated to both copper atoms of the same dinuclear complex, while in **2e** a perchlorate ion bridges two equivalent complex molecules through atoms O1p and O2p. With the exception of Cu2 in **2a** and Cu1 in **2e**, all the other copper atoms interact, although much more weakly, with another perchlorate oxygen atom placed on the opposite side of the square pyramid (Cu···O distances from 2.835 to 2.999 Å).

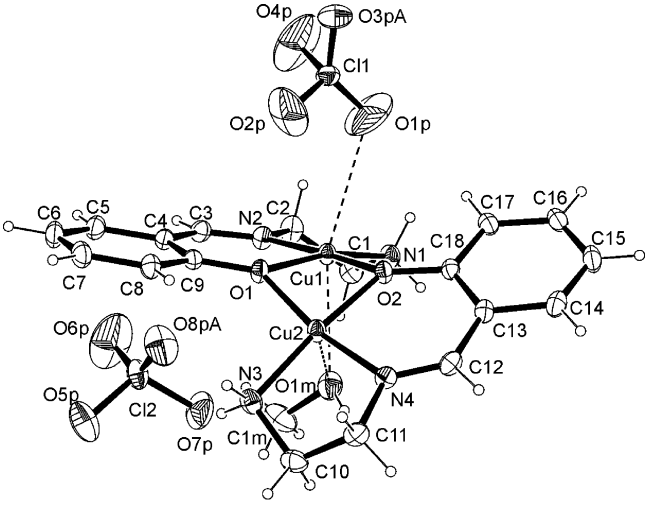


Figure 3. ORTEP plot of compound **2a** showing the complex, the two perchlorate ions and the methanol molecule of the asymmetric unit, with the atom-numbering scheme and short intermolecular contacts. Displacement ellipsoids are drawn at the 20% probability level.

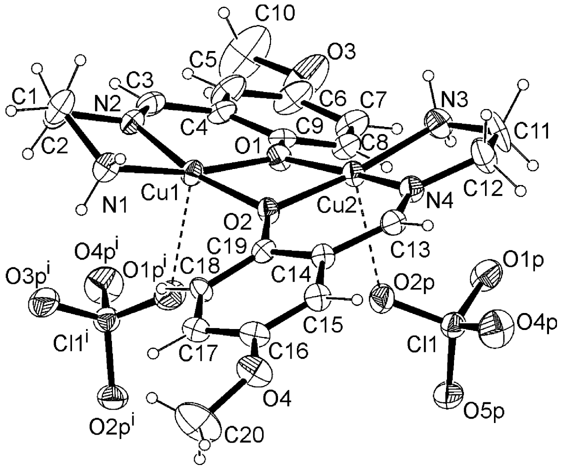


Figure 4. ORTEP plot of compound **2e** showing the complex and two equivalent perchlorate ions, with the atom-numbering scheme and short intermolecular contacts. Displacement ellipsoids are drawn at the 20% probability level.

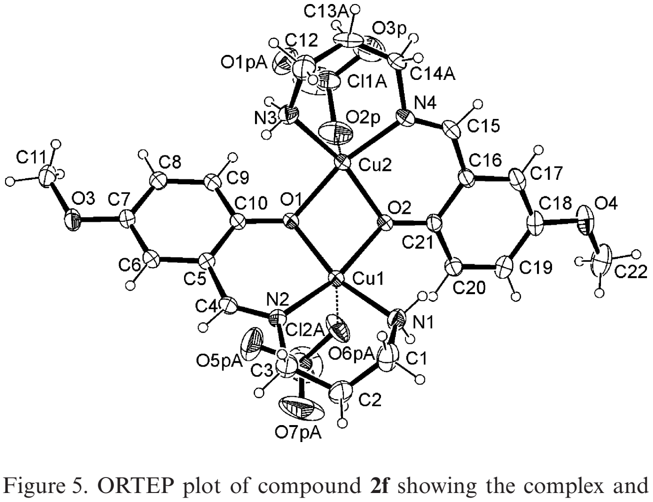


Figure 5. ORTEP plot of compound **2f** showing the complex and the two perchlorate ions of the asymmetric unit, with the atom-numbering scheme and short intermolecular contacts. Displacement ellipsoids are drawn at the 30% probability level.

Table 2. Selected bond lengths, intermolecular contacts (in Å) and bond angles (in °) for dinuclear compounds **2a**, **2e** and **2f**.

	2a	**2e**	**2f**
Cu1–N1	1.987(3)	1.983(3)	1.958(3)
Cu1–N2	1.921(3)	1.928(3)	1.961(3)
Cu1–O1	1.931(2)	1.930(2)	1.924(2)
Cu1–O2	1.968(2)	1.950(2)	1.993(2)
Cu2–N3	1.995(3)	1.971(3)	1.965(3)
Cu2–N4	1.919(3)	1.925(3)	1.955(3)
Cu2–O2	1.943(2)	1.927(2)	1.913(2)
Cu2–O1	1.952(2)	1.975(2)	1.986(2)
Cu1···Cu2	2.8666(6)	2.9888(7)	2.9399(9)
Cu1···O1p^i	2.948(11)[a]	2.459(3)[a]	2.835(6)[a,b]
Cu1···O6p	–	–	2.432(7)[b]
Cu1···O1m	2.650(3)	–	–
Cu2···O2p	–	2.528(2)	2.494(3)
Cu2···O6p	–	2.975(3)	–
Cu2···O1p^i	–	–	2.999(7)[a,b]
Cu2···O1m	2.480(3)	–	–
Cu1–O1–Cu2	95.17(10)	99.86(9)	97.51(9)
Cu1–O2–Cu2	94.28(10)	100.87(9)	97.60(9)

[a] i: *x*, *y*, *z* (**2a**); i: –*x*, 1/2 + *y*, 1/2 – *z* (**2e**); i: *x* – 1, *y*, *z* (**2f**). [b] These values refer to distances with atoms of set A of the disordered perchlorate ions.

In complex **2a**, the N_2O_2 donor sets show a slight (<0.130 Å) tetrahedral distortion from their least-squares planes, and the copper atoms lie within 0.102 Å above these planes. A lower distortion (<0.085 Å) of the N_2O_2 planes is observed in **2e** and **2f**. Interestingly, in the latter structures the copper atoms are pushed away from these planes towards the apical perchlorate oxygen, with concomitant shortening of the Cu···O distances. The Cu···basal plane distances are 0.156(1) and 0.108(1) Å for Cu1 and Cu2, respectively, in **2e**; these distances are 0.187(1) and 0.167(1) Å for Cu1 and Cu2, respectively, in **2f**.

The two half units of these complexes are reciprocally arranged to give an overall conformation deviating from planarity. The different degree of distortion, as given for example by the dihedral angle between the two N_2O_2 basal planes [41.99(8), 42.5(2), 27.88(6) and 50.31(7)° in **2a**, **2b**,[17] **2e** and **2f**, respectively], seems to be imputable to packing forces rather than intramolecular effects.

Magnetic Properties of 2f

The temperature dependence of the $\chi_M T$ product for compound **2f** between 80 and 290 K is shown in Figure 6a. The data clearly reveal the presence of a strong $Cu^{II}\cdots Cu^{II}$ antiferromagnetic coupling within the complex.

Indeed, the room-temperature $\chi_M T$ value (per mol of dimer) is about 0.2 $cm^3 mol^{-1} K$, which is much smaller than ca. 0.8 $cm^3 mol^{-1} K$, the expected value for two noncoupled $S = 1/2$ spins. It decreases continuously when the temperature is lowered. Below $T \approx 125$ K the compound is virtually diamagnetic, and $\chi_M T \neq 0$ only because of the temperature-independent paramagnetism and the presence of a small amount of a paramagnetic impurity which follows the Curie law. The presence of the paramagnetic impurity is revealed, in Figure 6b, by the increase in χ_M with T at low temperatures.

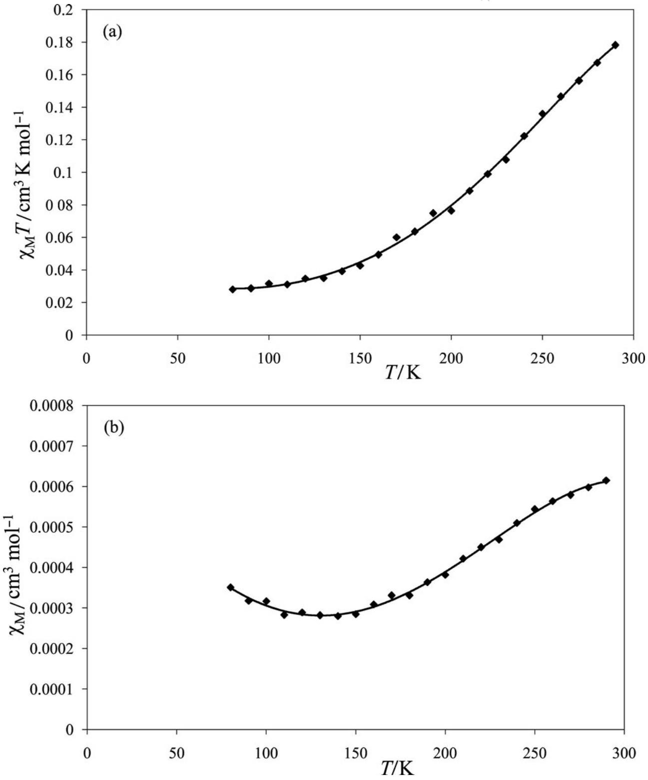


Figure 6. Experimental and theoretical (continuous line) temperature dependences of $\chi_M T$ (a) and of χ_M (b) for compound **2f**.

The experimental data are well described by the dimer HDVV (Heisenberg, Dirac, Van Vleck) model $H_{ex} = -2J\, \mathbf{S_1}\cdot\mathbf{S_2}$ (J is the exchange coupling constant, $J < 0$ refers to antiferromagnetism and $J > 0$ to ferromagnetism) which, with use of the Van Vleck formalism,[18] leads to Equation (1).

$$\chi_M T = (2N\mu_B{}^2 g^2/k)\,[3 + \exp(-2J/kT)]^{-1}\,(1 - P) + (N\mu_B{}^2 g^2/2k)P + 2N\alpha \qquad (1)$$

where P represents the fraction of paramagnetic impurity, $N\alpha$ is the temperature-independent paramagnetism (assumed to be 60×10^{-6} $cm^3 mol^{-1}$ per Cu) and the other symbols have their usual meaning. The best fit to the data obtained by letting J, g and P vary, gave $2J = -620$ cm^{-1}, $g = 2.09$ and P = 0.022. The theoretical curve is shown in Figure 6a.

Owing to the continuing intense interest that is being shown towards magnetostructural correlations in exchange coupled systems,[19] the effect of the structure on the observed magnetic properties for **2f** invites a few comments.

Experimentally, the foundation of magnetostructural correlation in dinuclear systems is based on the systematic studies of Hodgson, Hatfield and co-workers on a series of μ-hydroxido-bis[(diamine)Cu^{II}] complexes.[20] The results have established that the $-2J$ singlet–triplet splitting in this series of largely planar dimers is determined only by the Cu–O–Cu angle, θ, of the bridging Cu_2O_2 moiety, according to the relation given in Equation (2).

$$-2J = -74.53\ (\text{cm}^{-1}\,\text{deg}^{-1})\ \theta + 7270\ (\text{cm}^{-1}) \qquad (2)$$

This seminal study has been the inspiration for several MO theoretical models of magnetic exchange.[21] Subsequent experimental and theoretical efforts have shown that other factors besides θ, can be important in determining J in related Cu_2O_2 systems.[19] For compound **2f** (and **2b**[17]), the effects of two such factors need be considered: the deviation from planarity of the Cu_2O_2 ring and the nature of the substituent linked to the bridging oxygen atoms.

The former effect was first observed and theoretically justified by Charlot et al.[22] In a general manner, when a hydroxido-bridged Cu^{II} dimer is bent in such a way that the dihedral angle (τ) between the two Cu–O_2 planes diminishes from 180°, at a parity of bridging angles, the coupling becomes less antiferromagnetic.

Conversely, the coupling is found to be much more antiferromagnetic in compounds where the hydroxido-bridge hydrogen atom is replaced by the more electronegative phenyl group relative to complexes of the OH-bridged series having the same Cu–O–Cu angle.

Although this latter effect has not been uniformly interpreted theoretically,[23–25] Thompson et al.[25] have found that a series of 11 virtually planar (μ_2-phenoxido)-bridged dinuclear complexes of Cu^{II} with Cu–O(ph)–Cu, α angles in the range 98.8–104.7° exhibit a phenomenological linear correlation between J and α of the form given in Equation (3).

$$-2J = 31.95\ (\text{cm}^{-1}\,\text{deg}^{-1})\ \alpha - 2462\ (\text{cm}^{-1}) \qquad (3)$$

From this correlation, the expected $2J$ value for **2f** [where α(average) = 97.55°] is $-655\ \text{cm}^{-1}$, in excellent agreement (5%) with the observed value of $-620\ \text{cm}^{-1}$. On this basis, it is tempting to conclude that the singlet–triplet splitting in **2f** is little affected by the τ distortion of 143.2(1)°. However, such a conclusion is rendered uncertain by a consideration of the data obtained[17] for the strictly related dinuclear species **2b**: $2J = -362\ \text{cm}^{-1}$, $\alpha = 95.25°$ and $\tau = 141.8°$.

It may be noted that the $2J$ value for **2b** is considerably smaller (38%) than the $-581\ \text{cm}^{-1}$ value expected from Equation (3) in the presence of a τ distortion which differs little (1%) from that in **2f**. Whether or not the nature of the *para* substituents (OMe in **2f** and H in **2b**) in the phenyl rings of the two compounds may play a role in determining their different magnetic behaviour is an interesting problem for future investigation.

Trinuclear Complexes 3

These complexes can be better prepared in high yields with the high-dilution procedure, but with 5-G-salH/Cu/diamine/NaOH in a 1:1:1:1.3 ratio. Although other examples of μ_3-OH trinuclear species have been reported,[3c,12,15] none of them was prepared by a direct template synthesis. As described above, the reaction used for preparing **2c** and **2d** gave, instead, the trinuclear derivatives **3c** and **3d**. No trinuclear compound with G = OMe was obtained; dinuclear species were always formed.

It is likely that formation of trinuclear species occurs via the intermediacy of aqua complexes. In fact, upon diffusion of diisopropyl ether into the methanol solution of the synthetic mixture of **3c**, the mononuclear compound $[CuL^c(H_2O)]ClO_4$ (**1c′**) crystallised out. In this compound, the fourth coordination position of copper is occupied by a water molecule, as described above. This aqua complex can be proposed as the species, present in solution, that, under basic conditions, is deprotonated to a hydroxido derivative, which aggregates to form the trinuclear compounds. In fact, in the absence of base, **3c** and **3d** do not form.

The ν(OH) stretching of the μ_3-OH moiety appears as a broad band under the NH_2 region. Compounds **2a** and **2b** show a strong band at 1280 (en) and 1290 (tn) cm^{-1}, which is shifted and doubled at 1310 and 1340 cm^{-1} in **3a** and **3b**. Although we could not assign these bands, they are diagnostic of di- or trinuclear species.

Crystal Structures of 3a and 3c

These complexes contain a pyramidal μ_3-OH group bridging almost symmetrically three metallacyclic units, which are arranged nearly perpendicular with respect to each other: the dihedral angles between the least-squares planes of the six-membered rings containing the Cu atoms, measure, on average, 76.8(2)° and 80.4(1)° in **3a** and **3c**, respectively. These complexes can then be described as propellers, the Cu–half-unit moieties constituting the propeller blades, tetrahedrally arranged around the OH group. Both right- and left-handed propellers are present, on account of the centrosymmetry of the crystal structure of such complexes.

The asymmetric unit of compound **3a** comprises two independent molecules of the trinuclear complex (molecules a and b, see Figure 7), four perchlorate ions and seven water molecules. Selected bond lengths, bond angles and torsion angles are reported in Table 3. The two molecules are very similar, molecule b being slightly more pyramidal, as denoted by the larger distance of the bridging oxygen atom from the plane of the copper atoms [0.797(3) Å in molecule b vs. 0.768(4) Å in molecule a]. The Cu atoms are in a slightly distorted square-planar geometry. Moreover, the oxygen atoms of each metallacyclic unit coordinate to the copper atoms of an adjacent unit at typical distances corresponding to an apical position for a square-pyramidal coordination around Cu [r(Cu···O) values range from 2.387(4) to 2.465(5) Å]. On the other side, the copper atoms, with exception of Cu1 and Cu5, interact with oxygen atoms of the perchlorate ions or water [r(Cu···O) values range from 2.736(7) to 3.165(8) Å].

The asymmetric unit of compound **3c** comprises one molecule of the trinuclear complex, two perchlorate ions and one acetone molecule (Figure 8). Selected bond lengths and angles are reported in Table 3. The bridging oxygen atom, O4, is placed at 0.798(2) Å from the plane of the copper atoms. Similar to **3a**, the Cu atoms are in a slightly distorted square-planar geometry, and their coordination sphere is completed by two oxygen atoms placed at either side of the basal plane: one oxygen atom of an adjacent

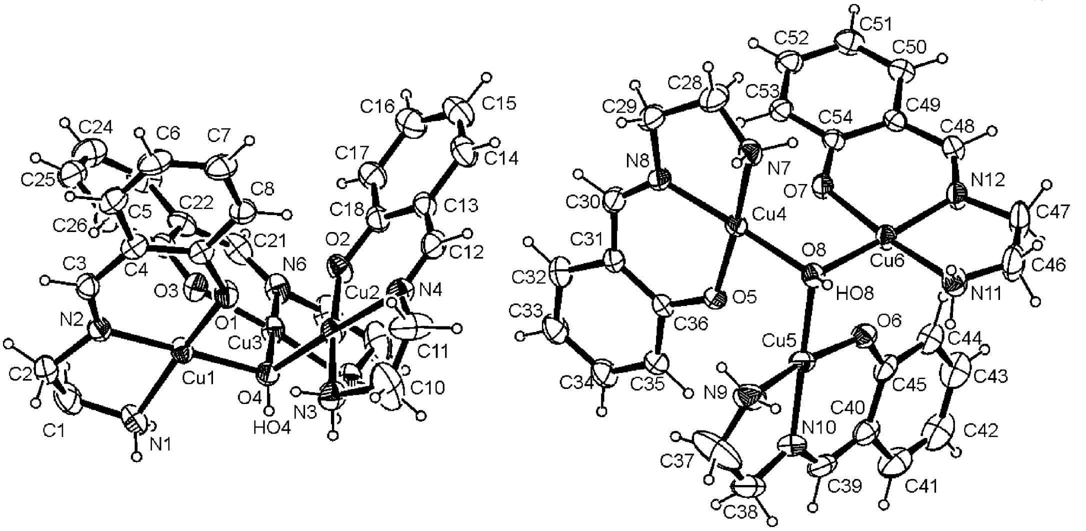


Figure 7. ORTEP plot of the asymmetric unit of **3a** (perchlorate ions and water molecules not shown for clarity) with the atom-numbering scheme. Molecule a is on the left, molecule b is on the right. Displacement ellipsoids are drawn at the 20% probability level.

Table 3. Selected bond lengths (in Å), bond angles and torsion angles (in °) for compounds **3a** and **3c**.

3a				**3c**	
Molecule a		Molecule b			
Cu1–O4	1.976(4)	Cu4–O8	1.991(4)	Cu1–O4	1.9886(19)
Cu2–O4	1.989(4)	Cu5–O8	1.979(4)	Cu2–O4	1.9818(18)
Cu3–O4	1.982(5)	Cu6–O8	1.994(4)	Cu3–O4	2.0176(18)
Cu1–N1	1.994(6)	Cu4–N7	2.004(5)	Cu1–N1	2.009(2)
Cu1–N2	1.925(6)	Cu4–N8	1.927(5)	Cu1–N2	1.940(2)
Cu1–O1	1.898(4)	Cu4–O5	1.910(4)	Cu1–O1	1.9282(18)
Cu2–N3	1.984(6)	Cu5–N9	2.017(7)	Cu2–N3	1.994(2)
Cu2–N4	1.928(6)	Cu5–N10	1.924(7)	Cu2–N4	1.941(2)
Cu2–O2	1.908(5)	Cu5–O6	1.902(5)	Cu2–O2	1.9208(18)
Cu3–N5	1.994(6)	Cu6–N11	2.004(6)	Cu3–N5	2.000(2)
Cu3–N6	1.936(7)	Cu6–N12	1.921(5)	Cu3–N6	1.946(2)
Cu3–O3	1.908(4)	Cu4–O5	1.910(4)	Cu3–O3	1.9227(18)
Cu1···O3	2.387(4)	Cu4···O7	2.398(4)	Cu1···O3	2.3674(18)
Cu2···O1	2.465(5)	Cu5···O5	2.392(4)	Cu2···O1	2.4476(17)
Cu3···O2	2.414(5)	Cu6···O6	2.362(5)	Cu3···O2	2.3091(18)
		Cu4···O1p^{i}	2.736(7)	Cu1···O1ac	2.850(2)
Cu2···Ow1	2.807(9)			Cu2···O1p	2.5685(18)
Cu3···O5p	3.150(18)	Cu6···O9p	3.165(8)	Cu3···O5p	3.190(2)
Cu1···Cu2	3.2012(13)	Cu4···Cu5	3.1647(11)	Cu1···Cu2	3.190(2)
Cu1···Cu3	3.1348(10)	Cu4···Cu6	3.1681(11)	Cu1···Cu3	3.1818(4)
Cu2···Cu3	3.1573(11)	Cu5···Cu6	3.1316(12)	Cu2···Cu3	3.1617(4)
Cu1–O4–Cu2	107.7(2)	Cu4–O8–Cu5	105.7(2)	Cu1–O4–Cu2	106.52(8)
Cu1–O4–Cu3	104.8(2)	Cu4–O8–Cu6	105.3(2)	Cu1–O4–Cu3	104.22(8)
Cu2–O4–Cu3	105.3(2)	Cu5–O8–Cu6	104.0(2)	Cu2–O4–Cu3	104.49(8)
Cu1–O4–Cu3–O3	9.0(2)	Cu4–O8–Cu6–O7	–5.8(2)	Cu1–O4–Cu3–O3	–11.62(8)
Cu2–O4–Cu1–O1	6.6(2)	Cu5–O8–Cu4–O5	–6.3(2)	Cu2–O4–Cu1–O1	–3.65(9)
Cu3–O4–Cu2–O2	10.4(2)	Cu6–O8–Cu5–O6	–7.0(2)	Cu3–O4–Cu2–O2	–9.79(8)

metallacyclic unit [*r*(Cu···O) = 2.375(1) Å on average] on one side, and one oxygen atom of the perchlorate ion or the acetone molecule [*r*(Cu···O) values range from 2.569(2) to 3.190(2) Å] on the other side.

As for the effect of the NO_2 group, in **3c** it may be noted that, while the average Cu–N(H_2) distance remains virtually unchanged in the two complexes, the average Cu–N(C_2) and Cu–O(C) distances both increase on going from **3a** [1.927(6) and 1.906(5) Å, respectively] to **3c** [1.942(2) and 1.924(2) Å, respectively]. The Cu–O(H) distances are marginally affected, increasing from 1.985(4) to 1.996(2) Å, on average, on going from **3a** to **3c**.

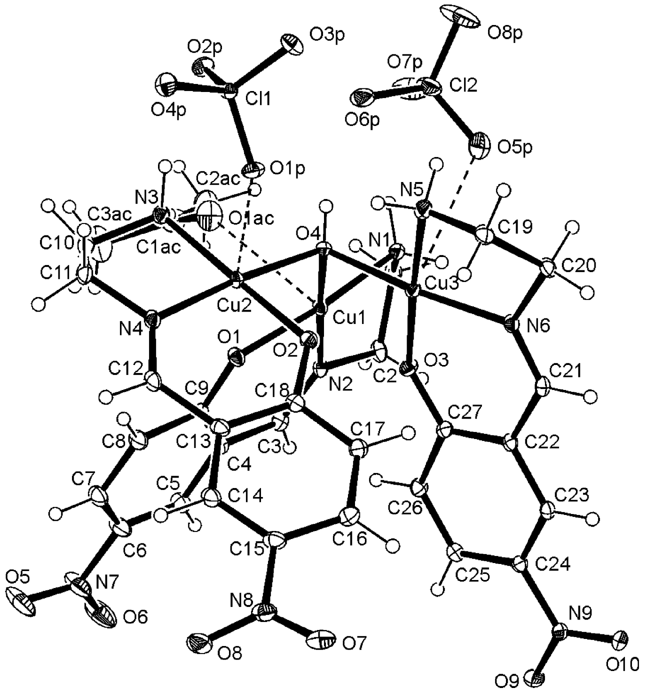


Figure 8. ORTEP plot of the full asymmetric unit of **3c** with short intermolecular contacts. Displacement ellipsoids are drawn at the 30% probability level.

Magnetic Properties of 3c

Exchange coupled triangular Cu^{II} clusters are currently of great interest in research areas as different as the role of polymetallic sites in enzymatic catalysis[26] and the physics of magnetic materials.[27] Compounds like **3a** and **3c** are of particular interest from a magnetic point of view since they comprise isolated equilateral triangle "plaquettes" of $\mathbf{S_1} = \mathbf{S_2} = \mathbf{S_3} = 1/2$ spins with equivalent exchange pathways between any two spin sites. Such a topology is the archetype of spin frustration. In short: if the spins are treated as collinear vectors, only two of the three spins can be antiferromagnetically coupled simultaneously. The remaining spin experiences geometric frustration, because the total exchange energy of the trimer is the same, regardless of whether the third spin is antiferromagnetically coupled with the first or the second spin, i.e., the ground state of the spin arrangements is degenerate.[28]

The simplest description of exchange coupling in such a system is given by the isotropic HDVV (Heisenberg, Dirac, Van Vleck) spin Hamiltonian [Equation (4)], where negative values of the J spin coupling parameter favour antiparallel spin alignment.

$$H = -2J\,(\mathbf{S_1}\cdot\mathbf{S_2} + \mathbf{S_2}\cdot\mathbf{S_3} + \mathbf{S_3}\cdot\mathbf{S_1}) \qquad (4)$$

Hamiltonian (4) can be easily solved by introducing an intermediate two-vector coupling, e.g. $\mathbf{S^*} = \mathbf{S_1} + \mathbf{S_2}$, and then coupling $\mathbf{S^*}$ with $\mathbf{S_3}$. $\mathbf{S^*}$ takes the values 1 or 0 (for $\mathbf{S_1} \pm \mathbf{S_2}$, respectively), and the trimer total spin $\mathbf{S_T} = \mathbf{S^*} \pm \mathbf{S_3}$ is 1/2 for $\mathbf{S^*} = 0$ and 3/2 or 1/2 for $\mathbf{S^*} = 1$. Taking the $3J/2$ energy of the levels with $\mathbf{S_T} = 1/2$ as the energy origin, the relative energies of the $E(S_T,S^*)$ spin levels are: $E(1/2, 1) = 0$, $E(1/2,0) = 0$ and $E(3/2, 1) = -3J$. Therefore, if $J < 0$, one has two degenerate doublet ground states and a quartet excited state with an energy separation of $-3J$.

When the Van Vleck formalism is applied,[21] the $\chi_M T$ product is given by Equation (5).

$$\chi_M T = (N\mu_B{}^2 g^2/4k)\,[1 + 5\exp(3J/kT)]\,/\,[1 + \exp(3J/kT)] \qquad (5)$$

where the symbols have their usual meaning. Figure 9 shows the experimental temperature dependence of the $\chi_M T$ product for the **3c** compound between 4 K and 290 K as well as the excellent theoretical description of the data provided by Equation (5) with best fit parameters $J = -10.1$ cm^{-1} and $g = 2.08$. Previously obtained data for **3a**[12] were interpreted likewise, giving $J = -6.5$ cm^{-1} and $g = 2.08$. The J values for the two compounds are in good qualitative agreement, especially in view of the fact that the **3a** and **3c** structures, although similar, are not identical.

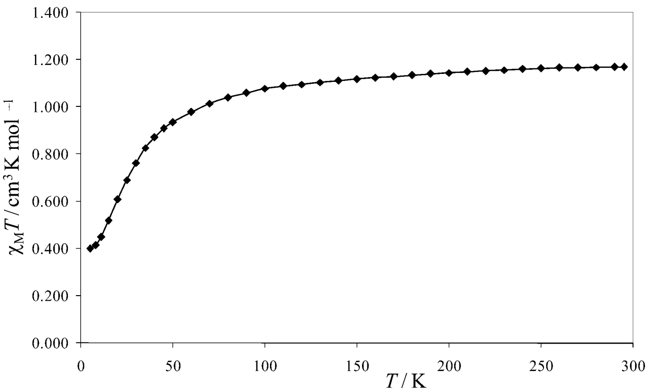


Figure 9. Experimental and theoretical (continuous line) temperature dependence of $\chi_M T$ for compound **3c**.

The reported J values for compounds containing $Cu_3(\mu_3$-X), with X = OH, O, Cl,[29] range from small positive (ferromagnetic) to negative values, which can be of few wavenumbers, as in the present case, but also of about -500 cm^{-1}. Up to now, the relative merit of the several chemical and structural factors which may contribute to determine the sign and magnitude of J for this series is not known with certainty. The combined structural and magnetic properties of **3a** and **3c** are of particular interest, since they allow to directly ascertain the viability of the Cu–(μ_3-OH)–Cu exchange pathway.

The X-ray structural data show that, in both trinuclear compounds, the Cu_3OH grouping is approximately tetrahedral, that the coordination environment of each Cu^{II} is square-planar with one site occupied by the hydroxyl oxygen and that the coordination plane of each Cu^{II} is almost perpendicular to those of the other two.

This indicates that the three Cu^{II} ions have magnetic orbitals of the x^2–y^2 type (in appropriate reference frames) of which two lobes are placed in the O(H)···Cu···N(C_2) axis and the other two lie in mutually orthogonal planes. The orientation of the latter being clearly unfavourable for any significant $Cu^{II}\cdots Cu^{II}$ interaction along the sides of the Cu_3

triangle, the magnetic orbitals can delocalise unpaired electron density only by σ overlap of their Cu→O(H) directed lobes with the filled sp^3 hybrid orbitals of the bridging hydroxyl group. This overlap, in the case of perfectly tetrahedral Cu_3OH grouping (and hence strictly orthogonal sp^3 functions) leads to $Cu_i \cdots Cu_j$ superexchange pathways of the type $(x^2–y^2)_i \parallel (sp^3)_i \perp (sp^3)_j \parallel (x^2–y^2)_j$, where the symbols $\parallel$ and $\perp$ mean overlap and orthogonality, respectively. The evergreen Anderson's theory of superexchange[30] predicts ferromagnetic or weak antiferromagnetic coupling for such a pathway, which is in qualitative agreement with the relatively small negative J values that have been obtained for **3a** and **3c**. Indeed, hybrid orbitals with Cu–O–Cu angles of ≈ 105° require a larger weight of the s orbital than in the case of ideal sp^3 hybrid orbitals, and this is expected to be in favour of antiferromagnetic coupling.

The nice fit of the experimental data obtained with use of the isotropic Hamiltonian [Equation (4)] leads to a consideration of the role of "Antisymmetric Exchange" (AE) in compounds containing triangular Cu^{II} clusters. Several such compounds have been reported,[31] whose dependence of the magnetic susceptibilities at low temperatures cannot be described by an HDVV model. In particular, the $\chi_M T$ value becomes smaller than ≈ 0.4 $cm^3\,mol^{-1}\,K$, the expected value for a ground state with $S = 1/2$.

Interestingly, for Cu^{II} trimers with local $x^2–y^2$ ground states, such effects have been observed when the molecular symmetry is close to C_3 or higher,[32] but not when, as in the present and similar cases,[26,33] the magnetic centres are not related by any symmetry element because of the virtual orthogonality of their coordination planes.

The discrepancies from the HDVV model are commonly accounted for by integrating Hamiltonian (4) with an AE term (also referred to as the Dzyaloshinsky–Moriya interaction) of the form $H' = \mathbf{G_{ij}}\cdot(\mathbf{S_i} \times \mathbf{S_j})$, where $\mathbf{G_{ij}}$ is a constant vector.[32] This "non-Heisenberg" coupling has its minimum energy when the two spins are perpendicular to each other and therefore competes with the isotropic exchange, which tends to orient the spins in either parallel or antiparallel directions.

In order to explain the absence of a discernible AE effect in **3a**, **3c** and similar compounds, it is useful to consider a perturbation theory model originally proposed by Moriya.[34] In this model, the AE interaction between two magnetic centres, not related by an inversion symmetry, is described as a second order perturbation effect produced by a synergistic combination of local spin–orbit coupling and of superexchange interactions involving the ground states as well as the excited states of the two centres.

As the structural data for **3a** and **3c** indicate that the magnetic orbital of each Cu^{II} is $x^2–y^2$ in the ground state and xy in the lowest excited state, only the $\mathbf{G}_z$ component of the AE interaction between e.g. centres 1 and 2 need be considered (vide infra), and it can be represented[35] by Equation (6).

$$\mathbf{G}_{z(1,2)} = 2i\lambda\,[\langle a_1|L_{iz}|b_1\rangle\,(-2J_{a1\to a2,a2\to b1})/\Delta_1 - \langle a_2|L_{jz}|b_2\rangle\,(-2J_{a2\to a1,a1\to b2})/\Delta_2] \qquad (6)$$

where λ is the spin–orbit coupling constant of Cu^{II}, $|a_i\rangle$ and $|b_i\rangle$ (i = 1, 2) represent the ground ($x^2–y^2$) and excited (xy) states of atom i, L_{iz} is the z component of the local orbital angular momentum operator which couples $|a_i\rangle$ and $|b_i\rangle$ ($\langle a_i|L_{iz}|b_i\rangle = -2i$ while $\langle a_i|L_{ix}|b_i\rangle = \langle a_i|L_{iy}|b_i\rangle = 0$), Δ_i is the energy difference between $|b_i\rangle$ and $|a_i\rangle$, and finally, the two integrals in parentheses are given by Equations (7) and (8).

$$J_{a1\to a2,a2\to b1} = \langle a_1(1)a_2(2)\,|H_{ex}|\,b_1(2)a_2(1)\rangle \qquad (7)$$

$$J_{a2\to a1,a1\to b2} = \langle a_1(1)a_2(2)\,|H_{ex}|\,a_1(2)b_2(1)\rangle \qquad (8)$$

where (1) and (2) represent the electrons. Equation (7) represents a superexchange interaction in which electron (1) is transferred from a_1 to a_2 and electron (2) from a_2 to b_1, while in the interaction equation [Equation (8)], electron (2) is transferred from a_2 to a_1 and electron (1) from a_1 to b_2.

Equation (6) clearly shows that, as noted above, AE is determined by a local spin–orbit interaction and by a superexchange interaction between the ground state of one magnetic centre and the excited state of the other centre and vice-versa. Expressions similar to Equation (6) can describe the $\mathbf{G}_{z(2,3)}$ and $\mathbf{G}_{z(3,1)}$ components of $\mathbf{G}_z$. In the absence of any symmetry element for the trimer, one has $\mathbf{G}_z = \mathbf{G}_{z1,2} + \mathbf{G}_{z2,3} + \mathbf{G}_{z3,1}$.

For **3a**, **3c** and similar compounds, the local $x^2–y^2$ ground state of each spin centre can couple with its xy excited state since $L_z|xy\rangle = -2i\,|x^2–y^2\,\rangle$, making the AE interaction possible for each spin pair, but, owing to the near orthogonality of the coordination planes of the three magnetic centres, the interaction between the $x^2–y^2$ ground state of one spin centre and the xy excited state of another spin centre [represented by Equations (7) and (8)] is virtually zero. This prevents the occurrence of AE or makes it very small, as experimentally observed.

Electronic Spectra

All compounds show a broad, unresolved absorption around 16000 cm^{-1} (625 nm) due to the envelopment of d–d transitions of the Cu^{II} d^9 ion. Whenever a comparison between similar compounds can be made, one can note a small but significant and systematic low-energy shift in the NO_2 – H – OMe series and on passing from the en to the tn derivatives. The latter probably results from different tetrahedral distortions of the Cu coordination set. Charge transfer (CT) bands appear at 27300 cm^{-1} (366 nm) for compounds with salH (G = H), at 25200 cm^{-1} (397 nm) for compounds with OMe and at 28100 cm^{-1} (356 nm) for G = NO_2; no relevant difference between en and tn derivatives was observed. There is a concomitant decrease in both energy and extinction coefficient in the NO_2 – H – OMe series, as for the d–d transitions.

Reactivity

A point of interest is the possibility of interconversion between the various mono-, di- and trinuclear species. Some possibilities have been investigated, and the results are presented.

Treatment of either the mono- or the dinuclear compounds with NaOH produces the μ_3-OH trinuclear derivatives according to Equations (9) and (10).

$$3[CuL(py)]ClO_4 + NaOH \rightarrow [Cu_3L_3(\mu_3\text{-}OH)](ClO_4)_2 + 3py + NaClO_4 \quad (9)$$

$$3[Cu_2L_2](ClO_4)_2 + 2NaOH \rightarrow 2[Cu_3L_3(\mu_3\text{-}OH)](ClO_4)_2 + 2NaClO_4 \quad (10)$$

Compound **1c** requires 2 mol equivalents of NaOH to be transformed into **3c**, suggesting a synergic effect of the NO_2 and en bridge that gives special stability to **1c**. This reaction gave **3c** (and **1d** gave **3d**) in very low yields, together with some decomposition products. The conversions of **1a** to **3a** and **1b** to **3b** are almost quantitative, making this an alternative synthetic method for accessing these trinuclear compounds. It is worth noting that it is also possible to obtain the trinuclear compounds **3e** and **3f** only by allowing **2e** and **2f** to react with NaOH, even though in rather low yields; these compounds are not accessible by direct synthesis. For these compounds, a μ_3-OMe bridge is proposed on the grounds of their mass spectra (see Experimental Section) and because of the isolation of the dinuclear species $[(py)_2Cu(\mu_2\text{-}OMe)_2Cu(py)_2](ClO_4)_2$ as intermediate.[36]

Mass spectra of compounds **1** showed only peaks corresponding to $[ML]^+$, suggesting that pyridine is weakly coordinated to copper, consequently it was expected that the reaction of these complexes with aqueous $HClO_4$ would produce the dinuclear derivatives by removal of pyridine and dimerisation of two "naked" $[CuL]^+$ subunits through bridging phenolato oxygen atoms, according to Equation (11).

$$2[CuL(py)]ClO_4 + 2HClO_4 \rightarrow [Cu_2L_2](ClO_4)_2 + 2(pyH)ClO_4 \quad (11)$$

Interestingly, when compound **1a** was treated with $HClO_4$, compound **1a′** precipitated, which had a $Cu/L^a/ClO_4$ = 1:1:1 stoichiometry according to analysis results. The infrared spectrum of this compound shows a red shift of the ν_{NH2} bands with respect to **2a** and a splitting into three bands of the ν_3 band of the ClO_4 species (1149, 1110, 1081 cm^{-1}), which is indicative of the loss of the T_d symmetry, suggesting its coordination to copper. The C=N stretch is at 1641 cm^{-1}, i.e., at the same wavenumber for dinuclear **2a**. We think that this compound is a dinuclear species with a bridging perchlorato moiety (as found in the crystal structure of **2e**). Unfortunately, it proved impossible to obtain crystals of **1a′** suitable for X-ray analysis, because slow concentration of the methanol solution gave **3a**, whereas diffusion of diisopropyl ether yielded **2a**. Compound **1a′** was obtained also by the high dilution method in the absence of NaOH.

Compound **1b** does not react with stoichiometric $HClO_4$, and a slight excess of the acid leads to hydrolysis. This can be ascribed to the stronger coordination of pyridine in **1b**, compensating the weaker interaction of the diamine bridge (see above the bond lengths), again pointing out how the length of the diamine bridge influences the behaviour and stability of these compounds. The NO_2 derivatives **1c** and **1d** hydrolyse under acidic conditions to give $[Cu(5\text{-}O_2N\text{-}sal)_2]$.

Treatment of compound **3a** and **3b** with $HClO_4$ gave the dinuclear species **2a** and **2b**, whereas compounds with the nitro group hydrolysed under acidic conditions.

Conclusions

In an attempt to rationalise the chemistry of copper complexes with the tridentate Schiff bases shown in Scheme 3, the syntheses of new mono-, di- and trinuclear copper(II) species have been presented and rationalised, highlighting, in particular, the effects of substituents G (OMe, H, NO_2) in position 5 of the salicylaldehyde, the length of the aliphatic diamine and the reaction conditions.

In conclusion, the main factor influencing the formation of di- and trinuclear species by direct synthesis is the nature of G. The presence of the electron acceptor NO_2 group renders the hydroxyl group of the salicylaldehyde more acidic, and, conversely, the phenolato oxygen atom less negatively charged, decreasing its bridging ability. Moreover, the increased positive charge on the Cu^{2+} ion makes the coordinated H_2O molecule of intermediate species like **1c′** rather acidic, favouring deprotonation and formation of the μ_3-OH complexes. On the contrary, the presence of the strong electron-donating group OMe makes the phenolato atom more electron-rich, increasing its bridging ability and favouring the formation of dinuclear species. The influence of the length of the diamine is more difficult to rationalise. Hypothetical mononuclear **1f** is not formed, presumably because of combined electronic and geometric factors.

The structure of some representative examples of mono-, di- and trinuclear complexes has been determined by X-ray diffraction. No relevant differences have been observed when comparing the coordination geometries within each half unit of complexes with different nuclearity. In several cases, the perchlorate anion was found to take part in the coordination sphere of the copper atom, with Cu···O distances as short as 2.432 Å, in spite of its scarce tendency to act as a ligand. In particular, three of such contacts were shorter than 2.5 Å. This feature has been found to be independent of the nuclearity of the complexes. In one case (complex **2e**) the perchlorate anion acts as a bidentate ligand bridging two equivalent complex molecules. A survey of the Cambridge Structural Database,[37] which involved searching for copper–perchlorate contacts below the sum of Cu and O van der Waals radii, 2.92 Å, revealed that the Cu···O distance was 2.690 Å on the average, and for just 9.7% of the 1011 retrieved fragments this distance was below 2.5 Å.

Variable-temperature magnetic susceptibility experiments performed on the dinuclear **2f** have revealed a strong antiferromagnetic intradimer exchange coupling that can be only partially rationalised on the basis of the X-ray structure and of the previously reported data for related compounds. The results of similar experiments on the trinuclear **3c** (and **3a**[12]) show the presence of relatively weak $Cu_3(\mu_3\text{-}OH)$ antiferromagnetic coupling. Interestingly, the experimental data do not reveal any antisymmetric exchange effect and can be nicely described by a simple isotropic Heisenberg model. Both the weak antiferromagnetic exchange and the absence of antisymmetric exchange (AE) effects are consistent with the near orthogonality of the three Cu^{II} magnetic orbital planes revealed by the X-ray structures.

Experimental Section

General: All chemicals were reagent grade. Solvents were used as received. Elemental analyses were performed at the Microanalytical Laboratory at our University. FAB-MS spectra were recorded with a VCA Analytical 7070 EQ instrument, while ESI-MS spectra were acquired with an LCQ Advantage Thermofluxional instrument. UV/Vis spectra were recorded with a JASCO V-530 spectrophotometer in methanol solution; λ values are accurate to ±0.5 nm and spectra are reported as wavenumbers (cm^{-1}) [ε ($L\,mol^{-1}\,cm^{-1}$)]. Infrared spectra were recorded by using KBr disks with a JASCO FT-IR 410 spectrophotometer having 2 cm^{-1} resolution.

Magnetic Measurements: Room-temperature magnetic moments, μ_{eff}, were measured with a magnetic susceptibility balance MK1, Sherwood Scientific Ltd. (Cambridge). Variable-temperature susceptibility measurements of the **2f** and **3c** derivatives were performed by using a Faraday type magnetometer equipped with a helium continuous-flow cryostat built by Oxford Instruments. Susceptibilities were corrected for the diamagnetism of the ligand systems, estimated as -3.2×10^{-3} and -4.36×10^{-3} $cm^3\,mol^{-1}$, for **2f** and **3c**, respectively.

X-ray Crystal Structure Determinations

Crystals suitable for X-ray diffraction were obtained by slow evaporation of methanol solutions for compounds **1b** and **2a**, by slow diffusion of diisopropyl ether in methanol for compounds **1c′** and **2a**, and by slow diffusion of diisopropyl ether in acetone for compound **3c**. Crystals of **2e** and **2f** were obtained directly from the reaction mixtures.

Crystal data and details of data collection and refinement for compounds **1b**, **1c′**, **2a**, **2e**, **2f**, **3a** and **3c** are given in Tables 4 and 5. In some cases, crystals were extremely thin, making necessary the use of synchrotron radiation. Data collection for compounds **1c′** and **2e** was performed with the X-ray Diffraction line XRD1 of the Elettra Synchrotron Light Laboratory (Trieste, Italy). The programs MOSFLM,[38] version 6.11c, and SCALA[39] were used for

Table 4. Crystallographic and data collection parameters for compounds **1b**, **1c′**, **2a**, **2e**.

	1b	**1c′**	**2a**	**2e**
Crystal Data				
Empirical formula	$C_{15}H_{18}ClCuN_3O_5$	$C_9H_{12}ClCuN_3O_{10}$	$C_{19}H_{26}Cl_2Cu_2N_4O_{11}$	$C_{20}H_{26}Cl_2Cu_2N_4O_{12}$
Moiety formula	$C_{15}H_{18}CuN_3O\cdot ClO_4$	$C_9H_{12}CuN_3O_4\cdot ClO_4\cdot 2H_2O$	$C_{18}H_{22}Cu_2N_4O_2\cdot 2(ClO_4)\cdot CH_3OH$	$C_{20}H_{26}Cu_2N_4O_4\cdot 2(ClO_4)$
M	419.31	421.21	684.42	712.43
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$Pbca$
a /Å	10.6212(9)	16.446(3)	7.9711(6)	21.515(4)
b /Å	11.2501(9)	12.879(3)	11.6171(9)	9.808(2)
c /Å	14.2743(12)	7.3670(15)	14.7462(12)	25.504(5)
α /°	90	90	76.888(1)	90
β /°	105.104(1)	91.30(3)	85.873(1)	90
γ /°	90	90	74.540(1)	90
V /Å^3, Z	1646.7(2), 4	1560.0(5), 4	1281.70(17), 2	5382.1(19), 8
D_x /Mg m^{-3}	1.691	1.789	1.773	1.758
Reflns for cell determination	6868	132	6580	148
2θ /° for cell determination	4.3–63.6	16.6–52.0	5.1–50.7	5.4–60.0
μ /mm^{-1}	1.521	1.629	1.933	1.848
Temperature /K	253(2)	293(2)	293(2)	293(2)
Colour, habit	dark green, prism	blue, prism	light blue, prism	green, needle
Dimensions /mm	0.43 × 0.35 × 0.15	0.25 × 0.04 × 0.01	0.48 × 0.28 × 0.14	0.21 × 0.01 × 0.01
Data Collection				
Radiation, λ /Å	Mo-K_α, 0.71073	synchrotron, 0.8	Mo-K_α, 0.71073	synchrotron, 0.8
Scan type	ϕ and ω	ϕ	ϕ and ω	ϕ
$2\theta_{max}$ /°	65.1	54.0	50.8	60.0
h range	$-15 \rightarrow 16$	$-18 \rightarrow 18$	$-9 \rightarrow 9$	$-26 \rightarrow 26$
k range	$-16 \rightarrow 16$	$-14 \rightarrow 14$	$-14 \rightarrow 14$	$-12 \rightarrow 12$
l range	$-20 \rightarrow 21$	$-8 \rightarrow 8$	$-17 \rightarrow 17$	$-31 \rightarrow 31$
Intensity decay, %	none	none	none	none
Measured reflections	34637	8980	17434	26261
Independent reflections	5694	2081	4717	5470
Reflns with $I > 2\sigma(I)$	4865	1754	3763	4583
R_{int}	0.027	0.121	0.025	0.064
Refinement on F^2				
$R[F^2>2\sigma(F^2)]$, $wR[F^2>2\sigma(F^2)]$	0.0294, 0.0807	0.0849, 0.2098	0.0389, 0.0977	0.0413, 0.1144
S	1.043	1.097	1.047	1.102
No. of parameters, restraints	253, 0	224, 2	361, 0	380, 0
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e Å^{-3}	0.374, –0.480	0.676, –0.809	0.801, –0.491	0.503, –0.624

Table 5. Crystallographic and data collection parameters for compounds **2f**, **3a**, **3c**.

	2f	**3a**	**3c**
Crystal Data			
Empirical formula	$C_{22}H_{30}Cl_2Cu_2N_4O_{12}$	$C_{54}H_{82}Cl_4Cu_6N_{12}O_{31}$	$C_{30}H_{37}Cl_2Cu_3N_9O_{19}$
Moiety formula	$C_{22}H_{30}Cu_2N_4O_4 \cdot 2(ClO_4)$	$2(C_{27}H_{34}Cu_3N_6O_4) \cdot 4(ClO_4) \cdot 7H_2O$	$C_{27}H_{31}Cu_3N_9O_{10} \cdot 2(ClO_4) \cdot C_3H_6O$
M	740.48	1918.35	1089.21
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a /Å	7.628(3)	11.911(2)	14.809(3)
b /Å	11.311(4)	23.120(5)	16.734(3)
c /Å	17.261(6)	28.425(6)	16.836(3)
a /°	76.190(10)	90	90
β /°	78.671(10)	100.74(3)	91.06(3)
γ /°	78.866(10)	90	90
V /Å^3, Z	1401.3(9), 2	7690(3), 4	4171.5(14), 4
D_x /Mg m^{-3}	1.755	1.645	1.734
Reflns for cell determination	6998	11689	5141
2θ /° for cell determination	4.9–56.0	4.4–42.3	4.4–51.6
μ /mm^{-1}	1.778	1.857	1.732
Temperature /K	293(2)	293(2)	90(2)
Colour, habit	brown-yellow, prism	blue, prism	blue, prism
Dimensions /mm	$0.18 \times 0.15 \times 0.05$	$0.43 \times 0.20 \times 0.13$	$0.22 \times 0.13 \times 0.13$
Data Collection			
Radiation, λ /Å	Mo-K_a, 0.71073	Mo-K_a, 0.71073	Mo-K_a, 0.71073
Scan type	ϕ and ω	ϕ and ω	ϕ and ω
$2\theta_{max}$ /°	56.0	58.0	52.8
h range	$-10 \rightarrow 10$	$-16 \rightarrow 16$	$-18 \rightarrow 18$
k range	$-14 \rightarrow 14$	$-31 \rightarrow 31$	$-20 \rightarrow 20$
l range	$-22 \rightarrow 22$	$-38 \rightarrow 38$	$-21 \rightarrow 21$
Intensity decay, %	none	none	none
Measured reflections	39625	113165	62747
Independent reflections	6752	20449	8545
Reflns with $I > 2\sigma(I)$	6318	8871	6986
R_{int}	0.033	0.086	0.055
Refinement on F^2			
$R[F^2>2\sigma(F^2)]$, $wR[F^2>2\sigma(F^2)]$	0.0476, 0.1108	0.0652, 0.1719	0.0309, 0.0694
S	1.168	1.000	1.015
No. of parameters, restraints	470, 6	970, 2	572, 1
$(\Delta/\sigma)_{max}$	0.001	0.002	0.001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ /e Å^{-3}	0.590, –0.385	0.733, –0.572	0.776, –0.489

data reduction. Intensity data for the other compounds were collected with a Bruker Apex CCD area detector by using graphite-monochromated Mo-K_a radiation. For these compounds, data reduction was performed with SAINT, and absorption corrections based on multiscan were obtained with SADABS.[40] All structures were solved by direct methods with SIR92[41] and refined by SHELXL-97.[42] The program ORTEPIII was used for graphics.[43]

In some cases, the structures are characterised by partial statistical disorder, which has been described by splitting the involved atoms into two positions, labelled by adding the letters A and B to the numbering scheme. This disorder concerns, partially or totally, the perchlorate ions; but in one structure (**2f**), also the atoms C13 and C14, belonging to one aliphatic bridge of tn, had to be split.

CCDC-684254, -684255, -684256, -684257, -684258, -684259, -684260 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.

Synthesis of Mononuclear Complexes 1[1,11,12]

[CuL^a(py)](ClO$_4$) (1a): An aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1500 mg, 4.00 mmol in 5 mL) was added to a stirred solution of salH (490 mg, 4.00 mmol) in methanol (10 mL) followed by the addition of py (0.60 mL, 8.00 mmol). The mixture was stirred at room temperature for 1 h when en (240 mg, 4.00 mmol) was added; after 3 h at room temperature, the dark violet solid **1a** was filtered, washed with methanol and diisopropyl ether and dried in vacuo. Yield: 1260 mg (75%). MS (FAB): m/z (%) = 226 [CuL^a]$^+$ (100). $C_{14}H_{16}ClCuN_3O_5$ (405.30): calcd. C 41.49, H 3.98, N 10.37; found C 41.63, H 4.09, N 10.53. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 16150 (120), 27320 (4900), 37730 (13600), 41500 (23300), 44840 (23300) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3324, 3269, ν(C=N) 1632 cm^{-1}. μ_{eff} = 1.74 μ_B.

[CuL^b(py)](ClO$_4$) (1b): This dark green compound was prepared as above from $Cu(ClO_4)_2 \cdot 6H_2O$ (1500 mg, 4.00 mmol), salH (490 mg, 4.00 mmol), py (0.65 mL, 8.00 mmol) and tn (297 mg, 4.00 mmol). Yield: 1430 mg (84%). MS (FAB): m/z (%) = 240 [CuL^b]$^+$ (100). $C_{15}H_{18}ClCuN_3O_5$ (419.32): calcd. C 42.97, H 4.33, N 10.02; found C 42.60, H 4.02, N 9.87. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15700 (80), 27320 (4960), 37450 (13800), 41500 (22900), 45000 (23600) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3315, 3256, ν(C=N) 1631 cm^{-1}. μ_{eff} = 1.77 μ_B.

[CuL^c(py)](ClO$_4$) (1c): This light brown compound was prepared as above from $Cu(ClO_4)_2 \cdot 6H_2O$ (640 mg, 1.73 mmol), 5-NO$_2$-salH (290 mg, 1.73 mmol), py (420 µL, 5.20 mmol) and en (115 µL, 1.73 mmol). Yield: 780 mg (87%). MS (FAB): m/z (%) = 271 [CuL^c]$^+$ (100). $C_{14}H_{15}ClCuN_4O_7$ (450.29): calcd. C 37.34, H 3.36, N 12.44; found C 37.38, H 3.31, N 12.28. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15960 (130), 28090 (18060), 39920 (23470), 42200

(20850) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3320, 3269, ν(C=N) 1651, 1603, $\nu(NO_2)$ 1325, 1303 cm^{-1}. μ_{eff} = 1.90 μ_B.

[CuL^d(py)](ClO$_4$) (1d): 5-NO$_2$-salH (550 mg, 3.30 mmol) and NaOH (3.3 mL of 1 mol L^{-1} ethanol solution) were mixed in methanol (20 mL) followed by the addition of aqueous $Cu(ClO_4)_2\cdot 6H_2O$ (5 mL, 1215 mg, 3.30 mmol) and py (0.53 mL, 6.60 mmol). The slurry was stirred at room temperature for 1 h, then tn (245 mg, 3.30 mmol) was added. The dark green product was filtered after 3 h, washed with methanol and diisopropyl ether and dried in vacuo. Yield: 1310 mg (86%). MS (FAB): *m/z* (%) = 285 [CuL^d]$^+$ (100). $C_{15}H_{17}ClCuN_4O_7$ (464.32): calcd. C 38.80, H 3.69, N 12.07; found C 38.94, H 3.50, N 12.28. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15500 (100), 28010 (18900), 39840 (27100) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3313, 3253, ν(C=N) 1629, $\nu(NO_2)$ 1318 cm^{-1}. μ_{eff} = 1.80 μ_B.

[CuL^e(py)](ClO$_4$) (1e): 5-MeO-salH (180 µL, 1.45 mmol) and KOH (2.90 mL, 1.45 mmol, 0.5 mol L^{-1} in ethanol) were mixed in methanol (10 mL) followed by the addition of $Cu(ClO_4)_2\cdot 6H_2O$ (535 mg, 1.45 mmol) and py (240 µL, 3.00 mmol). The mixture was stirred at room temperature for 1 h, $KClO_4$ was filtered off, and en (96 µL, 1.45 mmol) was added to the green solution that was left whilst stirring for 3 h. The red brown [Cu(5,5′-OMe-salen)] formed was discharged, and the filtrate was treated with diisopropyl ether to yield **1e** as a dark green solid. Yield: 250 mg (40%). MS (FAB): *m/z* (%) = 256 [CuL^e]$^+$ (60). $C_{15}H_{18}ClCuN_3O_6$ (435.32): calcd. C 41.39, H 4.17, N 9.65; found C 41.68, H 4.07, N 9.41. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 16500 (100), 25250 (3650), 40000 (17500), 44400 (20000) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3328, 3265, ν(C=N) 1636, 1608 cm^{-1}. μ_{eff} = 1.75 μ_B.

[CuL^c(H$_2$O)](ClO$_4$)·2H$_2$O (1c′): This green compound was obtained from crystallisation of the reaction mixture of compound **3c** (see below) with diisopropyl ether, starting from 5-NO$_2$-salH (396 mg, 2.35 mmol), NaOH (95 mg, 2.35 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (1224 mg, 3.30 mmol) and en (200 µL, 3.30 mmol). Yield: 450 mg (45%). MS (ESI): *m/z* (%) = 271 [CuL^c]$^+$ (25), 278 [CuL^c(H$_2$O)]$^+$ (65), 312 [CuL^c(OH) + Na]$^+$ (100). $C_9H_{12}ClCuN_3O_8\cdot 2H_2O$ (425.237): calcd. C 25.42, H 3.79, N 9.88; found C 25.42, H 3.66, N 9.33. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15920 (130), 28170 (19170), 40200 (23060), 42400 (21580) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3292, 3230, ν(C=N) 1658, 1604, $\nu(NO_2)$ 1351, 1332, $\nu(ClO_4)$ 1113, 1086 cm^{-1}. μ_{eff} = 1.85 μ_B.

[CuL^a(ClO$_4$)] (1a′): It was obtained as a dark green compound by the same high-dilution method used for dinuclear compounds (see below), but with no addition of NaOH: salH (220 µL, 3.00 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (1665 mg, 4.50 mmol) and en (315 µL, 4.50 mmol). Yield: 620 mg (63%).

Synthesis of 1a′ from 1a: Aqueous $HClO_4$ (1.33 mL of 0.58 mol L^{-1} solution, 0.77 mmol) was added to a methanol (10 mL) suspension of **1a** (332 mg, 0.77 mmol). The mixture was stirred at room temperature for 2 h and left aside for one day, after whcih **1a′** was filtered, washed with methanol and diisopropyl ether and dried in vacuo. Yield: 55 mg (22%). MS (ESI): *m/z* (%) = 226 [CuL^a]$^+$ (100). $C_9H_{11}ClCuN_2O_5$ (326.195): calcd. C 33.14, H 3.40, N 8.59; found C 33.05, H 3.65, N 8.25. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3300, 3236, ν(C=N) 1641, 1597, $\nu(ClO_4)$ 1149, 1112, 1080 cm^{-1}. μ_{eff} = 1.69 μ_B.

Synthesis of Dinuclear Complexes 2[14]

[Cu$_2$L$^a_2$(μ_2-MeOH)](ClO$_4$)$_2$ (2a): NaOH (137 mg, 3.42 mmol) was added to a solution of salH (260 µL, 3.53 mmol) in methanol (250 mL). The yellow solution was heated to reflux, and a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (1770 mg, 4.79 mmol) and en (320 µL, 4.79 mmol) in methanol (4 mL) and water (4 mL) was added under vigorous stirring. The mixture was heated under reflux for 3 h. The green solution was concentrated to 50 mL, filtered and left aside for 3 days; compound **2a** was recovered as a deep green solid, washed with methanol, diisopropyl ether and dried in vacuo. Yield: 495 mg (45%). MS (ESI): *m/z* (%) = 226 [CuL^a]$^+$ (100), 451 [Cu$_2$L$^a_2$ – H]$^+$ (75). $C_{19}H_{26}Cl_2Cu_2N_4O_{11}$ (684.43): calcd. C 33.34, H 3.83, N 8.19; found C 33.00, H 3.70, N 8.19. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 16090 (220), 27320 (8900), 37380 (23680), 41490 (40200), 44740 (41250) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3325, 3252, ν(Me*OH*) 3277, ν(C=N) 1643, 1601, $\nu(ClO_4)$ 1085 cm^{-1}. μ_{eff} = 1.17 μ_B per Cu atom.

[Cu$_2$L$^b_2$(μ_2-MeOH)](ClO$_4$)$_2$ (2b): This dark green compound was prepared as above from salH (240 µL, 3.26 mmol), NaOH (127 mg, 3.20 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (1700 mg, 4.60 mmol) and tn (385 µL, 4.60 mmol). Yield: 590 mg (51%). MS (ESI): *m/z* (%) = 240 [CuL^b]$^+$ (100), 479 [Cu$_2$L$^b_2$ – H]$^+$ (60). $C_{21}H_{30}Cl_2Cu_2N_4O_{11}$ (712.49): calcd. C 35.40, H 4.24, N 7.86; found C 35.31, H 4.15, N 7.37. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15850 (220), 27320 (9980), 37280 (27210), 41490 (42950), 44940 (45310) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3321, 3256, ν(Me*OH*) 3303, ν(C=N) 1628, 1598, $\nu(ClO_4)$ 1086 cm^{-1}. μ_{eff} = 1.16 μ_B per Cu atom.[17]

[Cu$_2$L$^e_2$](ClO$_4$)$_2$ (2e): This dark green compound was prepared as above from 5-MeO-salH (290 µL, 2.30 mmol), NaOH (92 mg, 2.30 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (1267 mg, 3.40 mmol) and en (230 µL, 3.40 mmol). Yield: 470 mg (57%). MS (ESI): *m/z* (%) = 256 [CuL^e]$^+$ (100), 511 [Cu$_2$L$^e_2$ – H]$^+$ (50). $C_{20}H_{26}Cl_2Cu_2N_4O_{12}$ (712.44): calcd. C 33.72, H 3.68, N 7.86; found C 33.71, H 3.37, N 7.83. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 16170 (240), 25190 (9770), 40240 (39660), 44640 (46180) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3301, 3254, ν(C=N) 1652, ν(C–O) 1271, $\nu(ClO_4)$ 1088 cm^{-1}. μ_{eff} = 0.86 μ_B per Cu atom.

[Cu$_2$L$^f_2$](ClO$_4$)$_2$ (2f): This dark green compound was prepared as above from 5-MeO-salH (275 µL, 2.20 mmol), NaOH (88 mg, 2.20 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (1211 mg, 3.30 mmol) and tn (270 µL, 3.30 mmol). Yield: 700 mg (86%). This compound was also obtained by following the same method used to synthesise **1e**, while trying to obtain the hypothetical mononuclear compound **1f** [CuL^f(py)](ClO$_4$), starting from 5-MeO-salH (375 µL, 3.00 mmol), KOH (6.0 mL of 0.5 mol L^{-1} alcoholic solution, 3.00 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (1105 mg, 3.00 mmol), py (480 µL, 6.00 mmol) and tn (250 µL, 3.00 mmol). Treatment with diisopropyl ether did not yield **1f**, but untreatable mixtures. Leaving the solution aside for one week gave **2f** as deep green crystals. Yield: 380 mg (34%). MS (FAB): *m/z* (%) = 270 [CuL^f]$^+$ (100), 370 [CuL^{f}ClO$_4$ + H]$^+$ (20). $C_{22}H_{30}Cl_2Cu_2N_4O_{12}$ (740.50): calcd. C 35.68, H 4.08, N 7.57; found C 35.73, H 4.19, N 7.61. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15750 (170), 25200 (9450), 37450 (20800), 40490 (38000) cm^{-1}. IR: $\tilde{\nu}$ = $\nu(NH_2)$ 3303, 3254, ν(C=N) 1631, 1611, ν(C–O) 1276, $\nu(ClO_4)$ 1069 cm^{-1}. μ_{eff} = 0.90 μ_B per Cu atom.

Synthesis of Trinuclear Complexes 3

[Cu$_3$L$^a_3$(μ_3-OH)](ClO$_4$)$_2$ (3a): This green compound was prepared directly by the same high-dilution method used for dinuclear complexes, but with different stoichiometric ratios: salH (220 µL, 3.00 mmol), NaOH (160 mg, 4.00 mmol), $Cu(ClO_4)_2\cdot 6H_2O$ (1116 mg, 3.00 mmol) and en (210 µL, 3.00 mmol). Yield: 560 mg (63%).

Alternative synthesis of 3a from 1a: Aqueous NaOH (2.5 mL of 0.1 mol L^{-1} solution) was added to a suspension of **1a** (304 mg, 0.75 mmol) in methanol (10 mL), and the mixture was stirred at room temperature for 1 h. **3a** was filtered, washed with methanol and diisopropyl ether and dried in vacuo. Yield: 125 mg (56%).

Alternative synthesis of 3a from 2a: Aqueous NaOH (160 µL of 1.72 mol L^{-1} solution) was added to a suspension of **2a** (274 mg, 0.40 mmol) in methanol (5 mL), and the mixture was stirred at room temperature for 1 h. The compound was filtered, washed with methanol and diisopropyl ether and dried in vacuo. Yield: 148 mg (62 %). MS (ESI): *m/z* (%) = 226 $[\mathrm{CuL^a}]^+$ (100), 451 $[\mathrm{Cu_2L^a{}_2} - \mathrm{H}]^+$ (40), 794 $[\mathrm{Cu_3L^a{}_3(OH)(ClO_4)}]^+$ (10). $\mathrm{C_{27}H_{34}Cl_2Cu_3N_6O_{12}}$ (896.14): calcd. C 36.19, H 3.82, N 9.38; found C 32.40, H 4.01, N 9.43. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 16140 (310), 27320 (13500), 37380 (36520), 41490 (61980), 44740 (63060) cm^{-1}. IR: $\tilde{\nu}$ = ν($\mathrm{NH_2}$) 3332, 3277, ν(C=N) 1639, 1600, ν($\mathrm{ClO_4}$) 1095 cm^{-1}. μ_eff = 1.69 μ_B per Cu atom.

$[\mathrm{Cu_3L^b{}_3(\mu_3\text{-}OH)](ClO_4)_2}$ (3b): This green compound was prepared as above from salH (220 µL, 3.00 mmol), NaOH (160 mg, 4.00 mmol), $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$ (1116 mg, 3.00 mmol) and tn (250 µL, 3.00 mmol). Yield: 470 mg (50 %).

Alternative Synthesis of 3b from 1b: As above from aqueous NaOH (80 µL of 1.72 mol L^{-1} solution) and **1a** (175 mg, 0.41 mmol). Yield: 100 mg (78 %).

Alternative Synthesis of 3b from 2b: As above from aqueous NaOH (2.5 mL of 0.1 mol L^{-1} solution) and **2b** (262 mg, 0.37 mmol). Yield: 141 mg (61 %). MS (ESI): *m/z* (%) = 240 $[\mathrm{CuL^b}]^+$ (100), 479 $[\mathrm{Cu_2L^b{}_2} - \mathrm{H}]^+$ (80), 497 $[\mathrm{Cu_2L^b{}_2(OH)}]^{2+}$ (50), 737 $[\mathrm{Cu_3L^b{}_3(OH)}]^{2+}$ (10). $\mathrm{C_{30}H_{40}Cl_2Cu_3N_6O_{12}}$ (938.22): calcd. C 38.41, H 4.30, N 8.96; found C 38.36, H 4.31, N 9.06. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15760 (280), 27250 (14780), 37170 (39390), 41410 (62490), 44840 (64410) cm^{-1}. IR: $\tilde{\nu}$ = ν($\mathrm{NH_2}$) 3322, 3277, ν(C=N) 1625, 1598, ν($\mathrm{ClO_4}$) 1094 cm^{-1}. μ_eff = 1.69 μ_B per Cu atom.

$[\mathrm{Cu_3L^c{}_3(\mu_3\text{-}OH)](ClO_4)_2}$ (3c): This emerald-green compound was prepared as above from 5-$\mathrm{NO_2}$-salH (500 mg, 3.00 mmol), NaOH (160 mg, 4.00 mmol), $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$ (1113 mg, 3.00 mmol) and en (210 µL, 3.00 mmol). Yield: 644 mg (63 %). MS (ESI): *m/z* (%) = 271 $[\mathrm{CuL^c}]^+$ (100), 288 $[\mathrm{CuL^c(OH)}]$ (70), 541 $[\mathrm{Cu_2L^c{}_2} - \mathrm{H}]^+$ (80). $\mathrm{C_{27}H_{31}Cl_2Cu_3N_9O_{18}}$ (1031.13): calcd. C 31.45, H 3.03, N 12.23; found C 30.85, H 3.03, N 12.28. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15940 (390), 28130 (56860), 40080 (68390), 42280 (64760) cm^{-1}. IR: $\tilde{\nu}$ = ν($\mathrm{NH_2}$) 3330, 3276, ν(C=N) 1654, 1604, ν($\mathrm{NO_2}$) 1315, ν($\mathrm{ClO_4}$) 1103 cm^{-1}. μ_eff = 1.67 μ_B per Cu atom.

$[\mathrm{Cu_3L^d{}_3(\mu_3\text{-}OH)](ClO_4)_2}$ (3d): This emerald-green solid was prepared as above from 5-$\mathrm{NO_2}$-salH (390 mg, 2.35 mmol), NaOH (125 mg, 3.10 mmol), $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$ (870 mg, 2.35 mmol) and tn (190 µL, 2.35 mmol). Yield: 515 mg (62 %). MS (ESI): *m/z* (%) = 285 $[\mathrm{CuL^d}]^+$ (100). $\mathrm{C_{30}H_{37}Cl_2Cu_3N_9O_{18}}$ (1073.22): calcd. C 33.57, H 3.48, N 11.75; found C 32.86, H 3.35, N 11.75. UV/Vis: $\tilde{\nu}$ (ε, L mol^{-1} cm^{-1}) = 15710 (320), 28090 (53640), 40160 (62940), 42020 (58140) cm^{-1}. IR: $\tilde{\nu}$ = ν($\mathrm{NH_2}$) 3312, 3266, ν(C=N) 1636, 1604, ν($\mathrm{NO_2}$) 1318, ν($\mathrm{ClO_4}$) 1105. μ_eff = 1.67 μ_B per Cu atom.

$[\mathrm{Cu_3L^e{}_3(\mu_3\text{-}OMe)](ClO_4)_2}$ (3e): Aqueous NaOH (35 µL of 1.72 mol L^{-1} solution) was added to a suspension of **2e** (130 mg, 0.18 mmol) in methanol (10 mL), and the mixture was stirred at room temperature for 6 h. The meagre green compound was filtered, washed with methanol and diisopropyl ether and dried in vacuo. Yield: 25 mg (20 %). MS (ESI): *m/z* (%) = 256 $[\mathrm{CuL^e}]^+$ (50), 543 $[\mathrm{Cu_2L^e{}_2(MeO)}]^+$ (100), 798 $[\mathrm{Cu_3L^e{}_3(OMe)} - \mathrm{H}]^+$ (50). $\mathrm{C_{31}H_{42}Cl_2Cu_3N_6O_{15}{\cdot}4H_2O}$ (1072.31): calcd. C 34.72, H 4.70, N 7.84; found C 34.48, H 4.55, N 7.81. IR: $\tilde{\nu}$ = ν($\mathrm{NH_2}$) 3338, 3280, ν(C=N) 1639, ν($\mathrm{ClO_4}$) 1091 cm^{-1}.

$[\mathrm{Cu_3L^f{}_3(\mu_3\text{-}OMe)](ClO_4)_2}$ (3f): Aqueous NaOH (0.5 mL of 0.33 mol L^{-1} solution) was added to a suspension of **2f** (176 mg, 0.24 mmol) in methanol (10 mL), and the mixture was stirred at room temperature for 6 h. The meagre green compound was filtered, washed with methanol and diisopropyl ether and dried in vacuo. Yield: 26 mg (14 %). MS (ESI): *m/z* (%) = 270 $[\mathrm{CuL^f}]^+$ (100), 795 $[\mathrm{Cu_3L^f{}_3} - \mathrm{OMe}]^+$ (70). $\mathrm{C_{34}H_{48}Cl_2Cu_3N_6O_{15}{\cdot}MeOH{\cdot}4.5H_2O}$ (1155.439): calcd. C 36.38, H 5.28, N 7.27; found C 36.37, H 5.02, N 7.19. IR: $\tilde{\nu}$ = ν($\mathrm{NH_2}$) 3318, 3271, ν(C=N) 1631, ν($\mathrm{ClO_4}$) 1093 cm^{-1}.

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variation, 0.058 Å, refers to the Cu–N2 bond. The longer bonds observed in **1b** could be explained by a reduced charge delocalisation within the complex, associated with the lack of planarity in this structure. This hypothesis appears to be confirmed by a comparison of structure of **1b** with that reported for **1a**,[13] where the two independent complex molecules are both much more planar than **1b**. The average Cu–N and Cu–O distances of **1a** on the side of the salicylaldehyde moiety, in fact, measure 1.949(6) and 1.900(4) Å, respectively.

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