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FULL PAPER

Synthesis and magnetic properties of a series of bi- and tri-nuclear complexes of copper(II) with the unsymmetrical tetradentate Schiff-base ligand 3-[*N*-2-(pyridylethyl)formimidoyl]salicylic acid, H_2fsaaep, and crystal structures of [{Cu(Hfsaaep)Cl}$_2$] and [{Cu(fsaaep)(H_2O)}$_2$]

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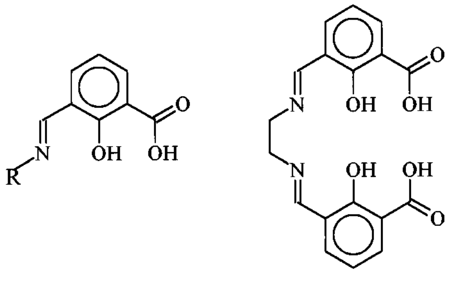
Three oligonuclear complexes of copper(II), [{Cu(Hfsaaep)Cl}$_2$] **1**, [{Cu(fsaaep)(H_2O)}$_2$] **2** and [Cu_3(fsaaep)$_2$][ClO_4]$_2$ **3** have been synthesized, using the unsymmetrical tetradentate Schiff-base ligand 3-[*N*-2-(pyridylethyl)formimidoyl]salicylic acid, H_2fsaaep. The crystal structures of complexes **1** and **2** have been solved. That of **1** consists of discrete binuclear entities with copper atoms bridged by two chloride anions. The copper atoms are related by an inversion center and exhibit a slightly distorted square pyramidal stereochemistry. The Cu · · · Cu separation within the binuclear unit is 3.825(2) Å. The structure of **2** consists of neutral centrosymmetric binuclear entities. The copper(II) ions are bridged by phenolic oxygen atoms, assuming a square-pyramidal geometry. The distance between the copper atoms is 3.0279(4) Å. Variable-temperature magnetic susceptibility measurements indicated a very weak ferromagnetic coupling of the copper(II) ions in compound **1** ($J = 0.15$ cm^{-1}) and an antiferromagnetic coupling in compounds **2** and **3** ($J = -617$ and -228 cm^{-1}, respectively).

Introduction

The search for rational routes leading to multimetallic complexes with low nuclearities has been stimulated by the potential relevance of these compounds to bioinorganic chemistry.[1] Furthermore, intensive magneto-structural investigations of discrete homo- and hetero-polynuclear complexes have contributed to the understanding of the factors governing the sign and the magnitude of the exchange interactions between paramagnetic centers, either identical or different.[2] A synthetic strategy for discrete polynuclear complexes must fulfill the following conditions: (i) control the nuclearity, that is the number of metallic ions within the molecular entity; (ii) control the topology of the metallic centers, which are usually paramagnetic ions.

Several synthetic approaches have been proposed to design discrete polynuclear complexes. One of them consists in the ingenious use of compartmental ligands, which are organic molecules able to hold together two or more metal ions. The Schiff bases derived from 2,6-diformyl-4-methylphenol (Robson-type ligands) and from 3-formylsalicylic acid are among the most popular ligands belonging to this family.[3,4] These ligands are especially appropriate to generate either homobinuclear complexes, symmetrical or dissymmetrical, or heterobinuclear complexes. Two main types of ligands **I** and **II** have been obtained starting from 3-formylsalicylic acid.[4] Both of them generate binuclear complexes. It is worth mentioning that the Schiff base **II**, a compartmental, acyclic side-off ligand, has dissimilar compartments. Consequently, it is an excellent ligand for the stepwise synthesis of heterobinuclear complexes.[5]

Recently[6,7] we have reported on a new type of unsymmetrical tetradentate Schiff base derived from 3-formylsalicylic acid



I **II**

(H_2fsa), which is very suitable for the design of homo- and hetero-trinuclear systems. In this paper we focus on two binuclear and one trinuclear complex, which are derived from the tetradentate Schiff base 3-[*N*-2-(pyridylethyl)formimidoyl]salicylic acid, H_2fsaaep, namely [{Cu(Hfsaaep)Cl}$_2$] **1**, [{Cu(fsaaep)(H_2O)}$_2$] **2** and [Cu_3(fsaaep)$_2$][ClO_4]$_2$ **3**.

Experimental

Syntheses

The chemicals were purchased from Aldrich and all manipulations performed using the materials as received. 3-Formylsalicylic acid has been synthesized according to Duff and Bills.[8] The Schiff base 3-[*N*-2-(pyridylethyl)formimidoyl]salicylic acid, H_2fsaaep, and the copper(II) binuclear complexes, [{Cu(Hfsaaep)Cl}$_2$] **1** and [{Cu(fsaaep)(H_2O)}$_2$] **2**, were prepared as reported.[6] The homotrinuclear complex, [Cu_3(fsaaep)$_2$][ClO_4]$_2$ **3**, can be obtained by one of the following routes: (i) treating the ligand itself, H_2fsaaep, in Na_2CO_3 or

LiOH aqueous solutions with copper(II) perchlorate; (ii) treating the copper(II) dimer **2** with the corresponding amount of copper(II) perchlorate; (iii) by a template procedure. The latter method is most direct and, consequently, the most suitable. To an aqueous solution (50 mL) containing 2 mmol of H_2fsa and 0.252 g $LiOH \cdot H_2O$ or 0.319 g Na_2CO_3 were added 2 mmol of 2-(2-aminoethyl)pyridine with stirring at room temperature. After 20 min an aqueous solution (50 mL) containing 3.2 mmol copper(II) perchlorate was added very slowly with stirring. The resulting mixture was stirred for 3 h, then the green precipitate of **3** was filtered off, washed with water and dried under vacuum (Found: C, 38.9; H, 2.7; Cl, 7.8; Cu, 20.2; N, 5.7. Calc.: C, 38.83; H, 2.58; Cl, 7.66; Cu, 20.58; N, 6.04%). IR data (KBr, cm^{-1}): 3400m, 2927w, 1633vs, 1600vs, 1569vs, 1549 (sh), 1485m, 1446s, 1414m, 1364m, 1281w, 1240m, 1144w, 1112s, 1094s, 1040w, 963w, 876w, 765m, 706w, 675w, 622w and 434w.

Single crystals of complex **1** were obtained by slow evaporation from methanol–acetonitrile (1:1), those of **2** by slow evaporation from a dimethylformamide solution.

CAUTION: no problems were encountered during the preparation of the perchlorate derivative described above. However, suitable care must be taken when handling such potentially explosive materials.

Crystallographic data collection and structure determination

A parallelepiped (0.25 × 0.16 × 0.13 mm) crystal of complex **1** was mounted on a CAD4 Enraf-Nonius X-ray diffractometer. Orientation matrices and accurate unit-cell constants were derived from a least-squares refinement of the setting angles of 25 reflections with θ between 7.17 and 17.92°. The data were corrected for Lorentz-polarization effects and secondary extinction. Structure determination was carried out using Patterson and Fourier techniques. The refinement was done by full-matrix least-squares analysis.[9] The H atoms located from Fourier-difference maps were introduced in the last cycles of refinement as fixed contributors. The crystallographic data for compound **2** were collected using a Siemens-SMART-CCD diffractometer. The data were corrected for Lorentz-polarization effects and an empirical correction was applied using the intensities of equivalent reflections at different φ and ω angles (minimum/maximum transmission 0.3446/0.8013).[10] The structure was solved by direct methods and subsequent least squares refinement against F^2.[11] All hydrogen atoms were located from the Fourier-difference map and refined.

The crystal data for compounds **1** and **2** and conditions of intensity measurements are gathered in Table 1.

CCDC reference number 186/1297.

Other measurements

The IR spectra (KBr pellets) were recorded on a Bio-Rad FTS 135 spectrophotometer, diffuse reflectance UV–VIS spectra with a VSU-2P (Carl Zeiss) spectrophotometer and solution spectra on a UV-4 (Unicam) spectrophotometer. Magnetic measurements were carried out on a MPMS-5 Quantum Design SQUID magnetometer working down to 1.8 K. X-Band powder EPR spectra were recorded at room temperature on an ER 200D Bruker spectrometer.

Results and discussion

Our synthetic approach is based on the observation that dianionic unsymmetrical tetradentate ligands of the type **III** should generate either binuclear (**IV**) or trinuclear (**V**) complexes (Scheme 1). The chemistry developed in this work is summarized in Scheme 2. The metal-to-ligand molar ratio as well as the presence of a base (Na_2CO_3 or LiOH) or, alternatively, of an acid (HCl) clearly influence the nature of the polynuclear complexes which are formed. In a basic medium, with metal-to-ligand molar ratios of 1:1 and 3:2, respectively the dianionic ligand can generate either binuclear neutral, **2**, or trinuclear, **3**, species. Conversely, in HCl solution, a chloro-bridged dimer **1** is obtained. It is interesting that the formation of two chelate rings with the copper(II) ion favors most probably the deprotonation of the phenolic group instead of the carboxyl one.

The chloro-bridged dimer **1** can be converted into complex **2** by treating it with a Na_2CO_3 or LiOH aqueous solution. The reaction of **2** with copper(II) perchlorate yields the trinuclear complex **3**. We recall here that, by using compound **2** as a precursor, hexanuclear clusters $[\{LnCu_2(fsaaep)_2(NO_3)_3\}_2]$ have been synthesized and the crystal structure of the praseodymium(III) derivative has been solved.[6] The structure was found to consist of $[Pr_2Cu_4]$ units exhibiting the **IVa** $\{Cu_2\}$ moiety. Consequently, we have postulated for compound **2** the structure **IVa**. The crystallographic investigation of **2**, which we report in this paper, shows a rather unexpected structure, namely of type **IVb**, with non-co-ordinating pyridyl groups. We were not able to obtain single crystals for compound **3**. However, the crystal structure of the above mentioned $\{Pr_2Cu_4\}$ derivative supports the formation of the homotrinuclear complex represented in Scheme 1. The magnetic properties are also in line with this structure (see below).

Structure of $[\{Cu(Hfsaaep)Cl\}_2]$

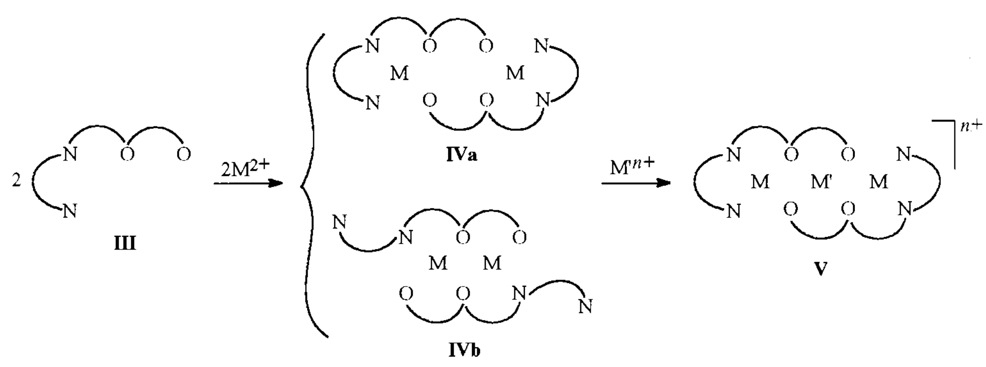
The structure consists of dimeric neutral entities formed by $CuClO_3N_2C_{15}H_{13}$ units related by inversion through (0, 0, 0) (Fig. 1). One copper atom is bonded unsymmetrically by two chloride anions, thus forming a double bridge. The Cu ··· Cu(a) distance in the dimeric entity is 3.825(1) Å and the angle Cu–Cl–Cu(a) is 95.27(4) Å (Table 2). Almost orthogonal to the plane [Cu, Cl, Cu(a), Cl(a)] occur two ligands centered around the copper atom, the ligating atom set being nearly planar. One intramolecular hydrogen bond relates O(2) to O(1).

The copper atom is co-ordinated by two chloride atoms, two nitrogen atoms and one oxygen atom. The oxygen and nitrogen distances from the copper atom vary between 1.908(4) and 2.019(4) Å (Table 2), while the Cu–Cl distances range from 2.308(1) to 2.846(1) Å. The co-ordination polyhedron of the copper atom may be described as a distorted square pyramid, with N(1), N(2), O(1) and Cl forming the equatorial bonds and Cl(a) forming the axial one. The atoms N(1), N(2), O(1) and Cl deviate from planarity, with atom to mean plane distances ranging from 0.026(1) Å, Cl, to 0.290(4) Å, N(2). The copper atom displacement from the basal plane is 0.0967(6) Å towards the apical ligand. The percentage of trigonal distortion from square pyramidal geometry is described by the parameter τ, defined as $[(\theta - \varphi)/60] \times 100$,[12] where θ and φ are angles between the donor atoms forming the plane in a square pyramidal geometry ($\tau = 0$ for an ideal square-pyramidal geometry, while $\tau = 100\%$ for the ideal trigonal bipyramidal geometry). The τ parameter for complex **1** (22%) indicates, indeed, that the co-ordination geometry at the copper atoms is best described as distorted square pyramidal.

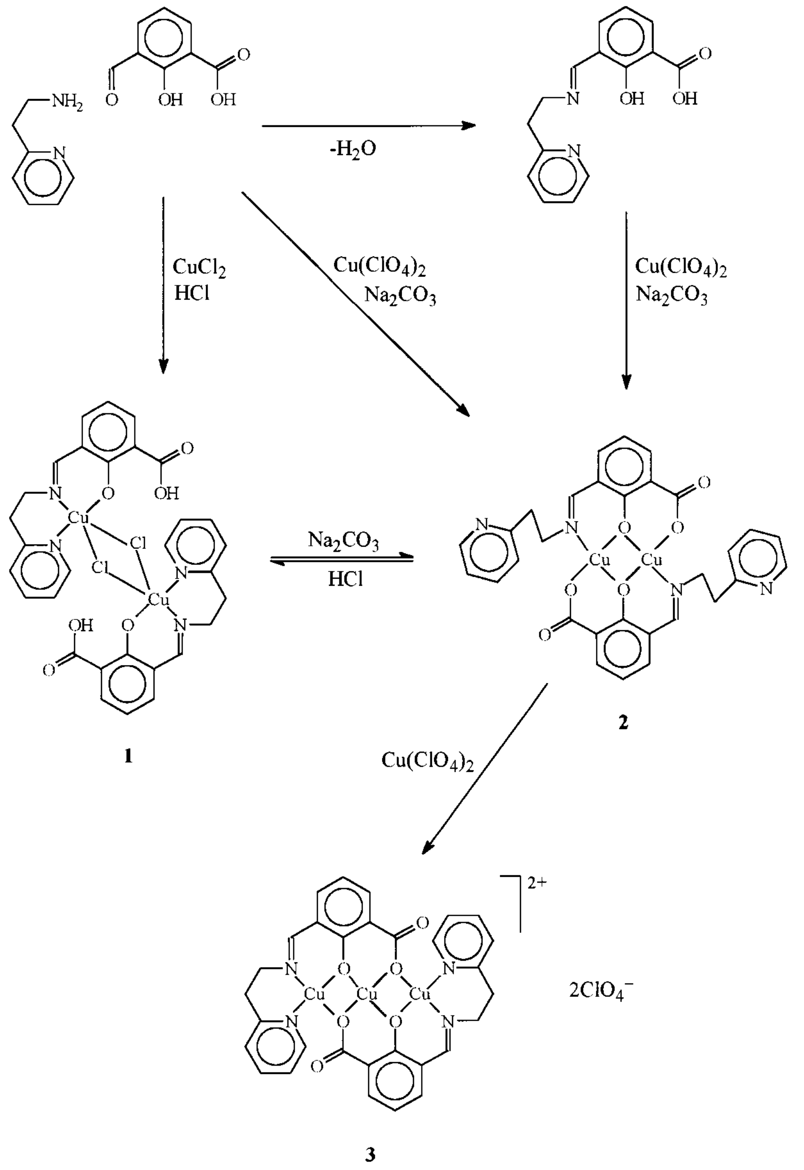
The angles within the ligands are in the normal range. Concerning the two rings, N(1) to C(5) and C(9) to C(14), their bond distances present only slight deviations, which are significant. The two rings are almost planar, atom to mean plane distances not exceeding 0.018(6) and 0.012(6) Å, respectively. The crystal structure arises from the stacking of these two rings in the sequence N(1) to C(5), C(9) to C(14), C(9) to C(14) and N(1) to C(5) through the stacking axis [111].

Structure of $[\{Cu(fsaaep)(H_2O)\}_2]$

The crystal structure of compound **2** is shown in Fig. 2, along with the atom numbering scheme. Selected bond distances and angles are collected in Table 2. The structure consists of neutral centrosymmetric binuclear entities. The copper(II) ions are bridged by phenolic oxygen atoms. The pyridyl groups are not



Scheme 1



Scheme 2

co-ordinated. The co-ordination geometry around the copper atoms is square pyramidal ($\tau = 4\%$). The basal positions are occupied by one nitrogen atom arising from the azomethine group, and by three oxygen atoms, two bridging phenolic oxygens and one from the carboxylato group, while the apical position is occupied by the aqua ligand. The distances Cu–N (1.964 Å) and Cu–O (average 1.937 Å) are comparable to those found in similar compounds. The elongated fifth bond [2.350(2) Å] involves the oxygen atom arising from the aqua ligand. The Cu · · · Cu distance within the binuclear unit is 3.0279(4) Å. The Cu–O(Ph)–Cu bridging angles are 101.81(5)°.

Spectroscopic and magnetic properties

The diffuse reflectance spectra of the two structurally characterized binuclear complexes, **1** and **2**, show, indeed, the characteristic features of five-co-ordinated copper(II) ions, with a more or less distorted square-pyramidal stereochemistry. Both spectra consist of a large unsymmetrical band with maximum around 690 ($\approx$14500) and 700 nm ($\approx$14280 cm^{-1}), respectively, and a tail/shoulder on its low-energy side. Owing to the small deviation from the square-pyramidal stereochemistry, the solid state spectrum of **2** can easily be interpreted

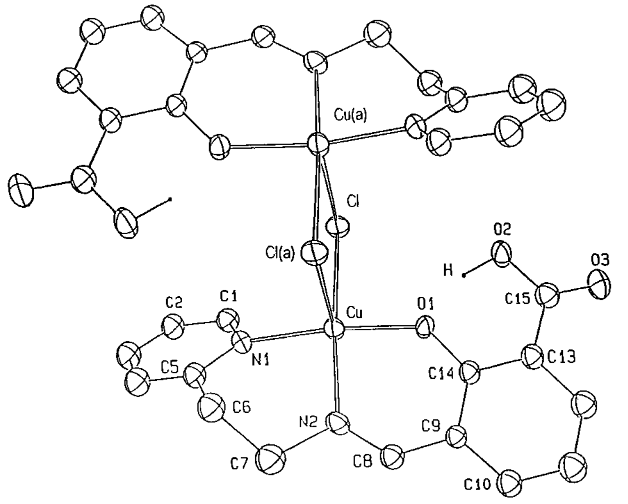


Fig. 1 Molecular structure of [{Cu(Hfsaaep)Cl}$_2$] **1** with the atom numbering scheme.

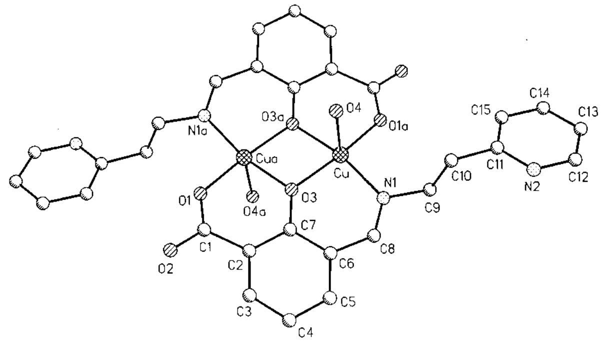


Fig. 2 Molecular structure of [{Cu(fsaaep)(H$_2$O)}$_2$] **2** with the atom numbering scheme.

Table 1 Crystal data for complexes **1** and **2** and details of refinement

	1	**2**
Molecular formula	$C_{30}H_{26}Cl_2Cu_2N_4O_6$	$C_{30}H_{28}Cu_2N_4O_8$
M	736.65	699.64
T/K	294(2)	183(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	9.765(2)	6.9370(4)
b/Å	8.628(1)	21.5069(12)
c/Å	17.957(4)	9.6788(6)
β/°	104.94(2)	103.0720(10)
U/Å^3	1461.8(2)	1406.59(14)
Z	4	2
D_c/g cm^{-3}	1.670	1.652
F(000)	748	716
μ/cm^{-1}	16.9	15.73
Crystal size/mm	0.25 × 0.16 × 0.13	0.40 × 0.20 × 0.10
$2\theta_{max}$/°	50	54
Total data measured	2162	7706
No. observed reflections	1449 [$I > 3\sigma(I)$]	2605 [$I > 2\sigma(I)$]
No. parameters	125	255
Final R indices	$R = 0.038$	$R1 = 0.027$
	$R' = 0.057$	$wR2 = 0.068$

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2** with estimated standard deviations (e.s.d.s) in parentheses

Complex **1**			
Cu–O(1)	1.908(4)	Cu–Cl	2.308(1)
Cu–N(1)	2.019(4)	Cu–Cl(a)	2.846(1)
Cu–N(2)	1.997(4)	Cu···Cu(a)	3.825(1)
O(1)–Cu–N(1)	161.1(1)	N(1)–Cu–Cl(a)	102.1(1)
O(1)–Cu–N(2)	90.4(2)	N(2)–Cu–Cl	174.3(1)
O(1)–Cu–Cl	86.0(1)	N(2)–Cu–Cl(a)	91.3(1)
O(1)–Cu–Cl(a)	96.4(1)	Cl–Cu–Cl(a)	84.73(4)
N(1)–Cu–N(2)	92.7(2)	Cu–Cl–Cu(a)	95.27(4)
N(1)–Cu–Cl	92.1(1)		
Complex **2**			
Cu–O(1a)	1.9110(12)	Cu–O(3a)	1.9480(12)
Cu–O(3)	1.9535(11)	Cu–N(1)	1.9645(14)
Cu–O(4)	2.350(2)	Cu···Cu(a)	3.0279(4)
O(1a)–Cu–O(3a)	93.33(5)	O(1a)–Cu–O(3)	169.99(5)
O(3a)–Cu–O(3)	78.19(5)	O(1a)–Cu–N(1)	94.75(5)
O(3a)–Cu–N(1)	167.59(6)	O(3)–Cu–N(1)	92.79(5)
O(1a)–Cu–O(4)	96.62(6)	O(3a)–Cu–O(4)	89.78(5)
N(1)–Cu–O(4)	98.62(6)	O(1a)–Cu–Cu(a)	132.28(4)
O(3a)–Cu–Cu(a)	39.16(3)	O(3)–Cu–Cu(a)	39.03(3)
N(1)–Cu–Cu(a)	131.27(4)	O(4)–Cu–Cu(a)	89.04(4)
C(1)–O(1)–Cu(a)	129.21(11)	C(7)–O(3)–Cu(a)	126.74(10)
C(7)–O(3)–Cu	130.64(11)	Cu(a)–O(3)–Cu	101.81(5)
C(8)–N(1)–Cu	120.00(11)	C(8)–N(1)–Cu	123.39(13)

assuming the following sequence of d orbitals: $d_{x^2-y^2} \gg d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$. The high energy absorption ($\approx$14280 cm^{-1}) can be assigned as a d_{xz}, $d_{yz} \longrightarrow d_{x^2-y^2}$ transition and the low energy shoulder ($\approx$8000 cm^{-1}) as a $d_{xy} \longrightarrow d_{x^2-y^2}$ transition.[13]

The electronic spectrum of complex **2**, measured in methanol, differs from the spectrum recorded by diffuse reflectance technique. The solution spectrum consists also of a broad band, but its maximum is blue-shifted (515 nm) with respect to the one recorded in the solid state (700 nm). That means that the structural motif **IVb**, which is observed in the crystals, is not preserved in solution. The alteration of the structure of **2** in solution is a necessary step for the formation of homo- and hetero-trinuclear complexes, as illustrated in Scheme 1. The trinuclear complex, **3**, exhibits a very large band centered at 730 nm ($\approx$13700 cm^{-1}). The assignment of this spectrum is difficult, due to the presence of two different copper(II) chromophores. In the infrared spectrum the ClO_4^- mode at $\approx$1100 cm^{-1} is somewhat split (1112 and 1094 cm^{-1}), probably indicating the (semi)co-ordination of the two perchlorate anions to one or two copper(II) ions.

Magnetic measurements of compounds **1**, **2** and **3** were made between 1.8 and 300 K. Let us briefly review some magneto-structural correlations concerning di-chloro-bridged copper(II) dimers. Hatfield and co-workers[14a] have shown that the singlet–triplet gap in such compounds varies in a regular way with the quotient φ/R_0, where φ is the angle at the bridging ligand, Cu^{II}–Cl–Cu^{II}, and R_0 is the long, out-of-plane Cu^{II}–Cl bond distance. It was found that for values of this quotient which are lower than 32.6 and higher than 34.8° Å^{-1} the exchange interaction is antiferromagnetic. For values falling between these limits the exchange interaction was found to be ferromagnetic (only few experimental data are available).[14] In the case of our chloro-bridged dimer, [{Cu(Hfsaaep)Cl}$_2$] **1**, the value of the quotient φ/R_0 (33.6° Å^{-1}) suggests a ferromagnetic interaction between the two copper(II) ions. Indeed, the results of the cryomagnetic investigation, shown in the form of a $\chi_m T$ *versus* T plot (Fig. 3), indicate a very weak but unquestionably ferromagnetic coupling of the copper(II) ions. The results are well interpreted on the basis of the Bleaney–Bowers equation. The best fit leads to the parameters $g = 2.07$ and $J = 0.15$ cm^{-1}. The reliability factor, defined as $R(\chi_m T) = \Sigma(\chi_m T^{obs} - \chi_m T^{calc})^2/\Sigma(\chi_m T^{obs})^2$, is equal to 4.8×10^{-6}. Compound **1** presents a rhombic EPR spectrum centered around $g = 2.12$ (2.20, 2.12 and 2.05) and a half field transition. This spectrum is easily interpreted as that of a triplet state with no fine structure.

The $\chi_m T$ *vs.* T plot for the phenolato-bridged dimer **2** is given in Fig. 4. The $\chi_m T$ value at 250 K is low (0.1 cm^3 K mol^{-1}) and decreases upon cooling. This behavior is characteristic of a large singlet–triplet energy gap. The plateau of $\chi_m T$ (or the increase of the magnetic susceptibility, χ_m) below 70 K is due to the proportion, ρ, of a paramagnetic, uncoupled, copper(II) impurity. Consequently, the experimental data were fitted using

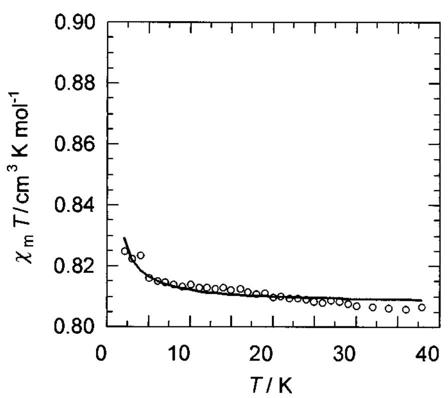


Fig. 3 Plot of χT *vs.* T for [{Cu(Hfsaaep)Cl}$_2$] **1**.

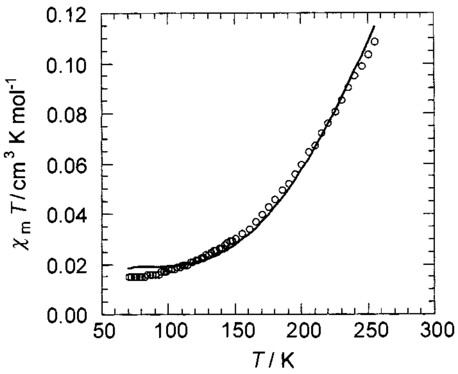


Fig. 4 Plot of χT *vs.* T for [{Cu(fsaaep)(H$_2$O)}$_2$] **2**.

the Bleaney–Bowers equation (1), modified to take into account

$$\chi_m T = (2Ng^2\beta^2/k)[3 + \exp(-J/kT)]^{-1}(1 - \rho) + \rho(Ng^2\beta^2/2k) + N_\alpha T \quad (1)$$

the paramagnetic impurities. By least-squares fitting: $g = 2.15$, $J = -617$ cm^{-1}, $\rho = 0.022$, and the temperature independent paramagnetism, $N_\alpha = 120 \times 10^{-6}$ cm^3 mol^{-1}. The reliability factor $R(\chi_m T)$ is then 3.1×10^{-3}. The value of the coupling constant has the same order of magnitude as those found by Okawa and co-workers[4a] for a series of very similar compounds (their crystal structures are, however, unknown and the magnetic measurements were carried out only down to liquid nitrogen temperature). Compound **2** is EPR silent.

Recently,[15] magneto-structural correlations in bis(phenoxide)-bridged macrocyclic binuclear copper(II) complexes have shown that, as in the case of bis(hydroxide) and bis(alkoxide) bridged binuclear copper(II) complexes, the leading factor in determining the exchange interaction is the Cu–O(Ph)–Cu angle. It has been shown that, for Cu–O(Ph)–Cu angles ranging from 98.8 to 104.7°, the values of the coupling constant, $-J$, encompass the domain 689–902 cm^{-1}. Assuming a linear dependence between $-J$ and the Cu–O(Ph)–Cu bridging angle, a, Thompson *et al.*[15] derived the relationship (2). The Cu–O(Ph)–Cu angle in compound **2** is 101.8°. The value of J, predicted by equation (2), is then -790 cm^{-1}, higher than the experimental one (-617 cm^{-1}). This difference is most probably an effect of the electron-withdrawing substituents bound to the phenolic groups.[15,16]

$$-J = 31.95a - 2462\ \text{cm}^{-1} \quad (2)$$

The magnetic behavior of compound **3** is typical for a {Cu$^{\text{II}}_3$} complex with antiferromagnetically coupled copper(II) ions (Fig. 5). From room temperature down to 100 K the $\chi_m T$ product decreases continuously and then reaches a plateau close to 0.456 cm^3 K mol^{-1}, which corresponds to the $S = \frac{1}{2}$ ground state. Below 10 K $\chi_m T$ decreases abruptly, indicating the onset of intermolecular interactions.

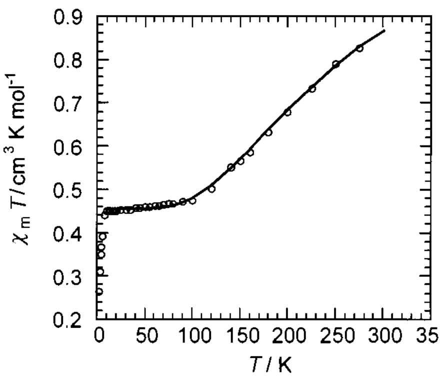


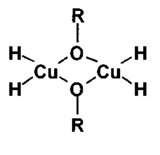
Fig. 5 Plot of χT *vs.* T for the trinuclear complex [Cu$_3$(fsaaep)$_2$][ClO$_4$]$_2$ **3**.

For a linear Cu1–Cu2–Cu3 system the energies of the low-lying states are obtained using the isotropic spin Hamiltonian (3). By applying the Van Vleck equation and assuming identical average g factors, the theoretical expression of the magnetic susceptibility is (4). The quality of the fit does not depend on j and hence cannot be determined from the magnetic data. The least-squares fitting leads to $J = -228$ cm^{-1}, $g = 2.20$ with $R(\chi_m T) = 1.5 \times 10^{-4}$. The antiferromagnetic interaction between adjacent copper(II) ions is moderately strong. The EPR spectrum presents a quasi isotropic signal centered at $g = 2.104$ and is typical of a $S = \frac{1}{2}$ state.

$$\mathcal{H} = -J(S_{Cu1}S_{Cu2} + S_{Cu2}S_{Cu3}) - jS_{Cu1}S_{Cu3} + g_{Cu1}\beta H(S_{Cu1} + S_{Cu3}) + g_{Cu2}\beta H S_{Cu2} \quad (3)$$

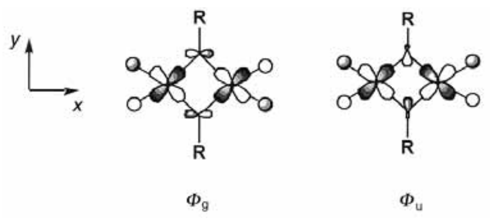
$$\chi_m T = (Ng^2\beta^2/4k)\{1 + \exp[(j/kT) - (J/kT)] + 10\exp[(j/kT) + (J/2kT)]\}/\{1 + \exp[(j/kT) - (J/kT)] + 2\exp[(j/kT) + (J/2kT)]\} \quad (4)$$

Much theoretical work has been devoted to the study of magneto-structural correlations in di-μ-hydroxo and di-μ-alkoxo bridged complexes using semiempirical methods,[17–19] *ab initio* calculation[20] and recently DFT methods.[21] The large variation of the coupling constant, J, *versus* the bridging angle, $-J = 74.53a - 7270$ for di-μ-hydroxo and $-J = 82.1a - 7857$ for the di-μ-alkoxo compounds, is now well understood.[22] In order to explain both the strong value of the antiferromagnetic interaction and the weak influence of the Cu–O(Ph)–Cu bridging angle ($-J = 31.95a - 2462$) on the magnetic properties in diphenoxide-bridged copper(II) complexes, when compared to the J values and the angular dependence of the interaction observed for bis(hydroxide) and bis(alkoxide) bridged binuclear copper(II) complexes, we carried out extended Hückel calculations with fragment orbitals analysis on the model structure shown, with R = H, Me or Ph.



Several models have been proposed to relate the magnetic coupling constant to a theoretical expression.[17] We have used the well known relationship given by Hay *et al.*[18] For a copper(II) binuclear system with two unpaired electrons the singlet–triplet splitting is given by eqn. (5) where ε_g and ε_u are the energies of the singly occupied molecular orbitals (SOMOs) Φ_g and Φ_u depicted in Scheme 3 and K_{ab}, J_{aa} and J_{ab} are two electron integrals. We assumed that the two electron

$$J = 2K_{ab} - (\varepsilon_g - \varepsilon_u)^2/(J_{aa} - J_{ab}) \quad (5)$$



Scheme 3

orbitals are weakly sensitive to structural changes and only the one electron term $(\varepsilon_g - \varepsilon_u)^2$ was taken into account. Two fragments A and B are considered, the first one is formed with the two copper ions and the four terminal hydrogen atoms, and the second is constituted of the two oxygen atoms of the R groups. Without the oxygen bridges the u combination of the A fragment (mainly $d_{x^2-y^2}$ orbitals) is slightly lower in energy than the g combination owing to its bonding character. The energies of the g and u MOs are modified by the interaction with the second fragment. Two main factors influence the energies of these orbitals, first the overlap S_{ij} between the MO of the two fragments A and B, and secondly, the energy difference between the MO fragments in the interaction. The energy correction for a MO i centered on the A fragment is approximately given by formula (6). Unfortunately, the energy difference

$$e_i - e_i^0 \propto \Sigma_{j\in B} S_{ij}^2/(e_i^0 - e_j^0) \qquad (6)$$

between the MO of the fragments and the overlap between them very often have antagonistic effects and it is difficult to infer which factor will dominate.† The change from hydroxo to alkoxo and phenoxo bridges leads precisely to these contradictory effects as is depicted in Fig. 6. Clearly, there is at least one orbital of the bridge with the right symmetry close in energy to the g and u combination of the $d_{x^2-y^2}$ orbitals. For the phenoxo bridge, one orbital of g symmetry for the bridge is almost degenerate with the d orbitals. However, this better energy matching between the orbitals of the two fragments arises from an extensive mixing between the p_x and the sp_y orbitals of the oxygen atoms together with the orbitals of the R groups. This mixing leads mechanically to a decrease of the weight of the atomic orbitals of oxygen in the MO of the fragment and, consequently, to a decrease of the overlap between the MO of the bridge and the g and u combination of the $d_{x^2-y^2}$ orbitals. The outcome of the calculation, in the case of the phenolato bridge, shows that this effect is dramatically larger for the u orbital than for the g one. This is illustrated by the local charge on the p_x and sp_y orbitals of the oxygen atom in the orbital of fragment B. The charge is reduced to 0.06 for the sp_y (u symmetry) orbital and has to be compared to 0.18 for the p_x orbital. The low electron density on the oxygen atoms for the u symmetry orbital of fragment B reduces considerably the overlap with the d orbitals, no matter what the value of the bridging angle is. Thus, contrary to the hydroxo and alkoxo bridges, the Φ_u molecular orbital has a lower energy than the Φ_g even for small bridging angles. The crossing angle for the two orbitals leading to a ferromagnetic coupling is foreseen for really small angles. This is verified experimentally with the empirical law established by Thompson *et al.* By extrapolating the straight line given by eqn. (2) to $J = 0$ cm^{-1}, the accidental orthogonality would be reached at ≈77°, a value of the Cu–O(Ph)–Cu bridging angle which is well below the one found for bis(hydroxide) and bis(alkoxide) bridged binuclear copper(II) complexes (≈97°). As already mentioned, copper complexes with small phenoxo bridge angles (<97°) are not known.

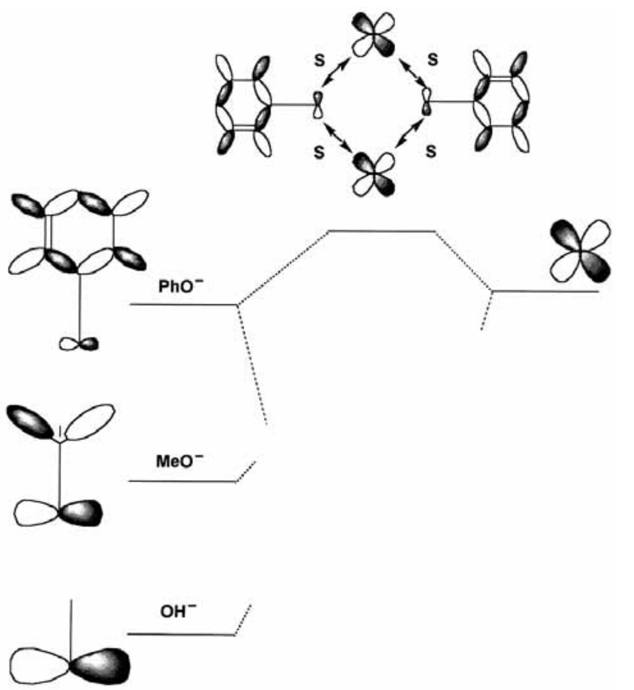


Fig. 6 Schematic representation of the antagonistic effects of the energy difference between the MOs of the fragments and their overlap (see text).

The effect of the Cu–O–Cu bridge angle on the exchange interaction has been studied extensively for μ-hydroxo and μ-alkoxo binuclear complexes.[20–22] For both series of compounds a correlation between the bridging angle θ and the out of plane displacement of the hydrogen or C atoms (angle τ) has been established. Experimentally, a large value of τ is associated with a small θ. When this correlation is taken into account in the theoretical calculation, it is possible to interpret both the ferromagnetic behavior observed in μ-hydroxo compounds for the small value of θ and also the important variation of coupling constant J with the bridging angle θ.

It is worth noting that for all μ-phenoxo compounds we have a τ angle equal to zero owing to the nature of the ligands which are generally binucleating. We carried out calculations on μ-phenoxo compounds by varying the θ angle while maintaining the ring of the phenoxo bridge in the molecular plane. The results confirm a moderate influence of θ on the value of the coupling constant as is found experimentally.

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† For instance, with the hydroxo bridged compound both g and u combinations of the d orbitals are destabilized by the interaction with the pure oxygen p_x orbital (g symmetry) and the MO of symmetry u. The latter orbital is a bonding orbital between the oxygen and hydrogen atoms, so its energy is lower than that of the pure p_x orbital. This means that the denominator in formula (6) is greater for the u symmetry than for the g one. Besides, for a small bridging angle (less than ≈100°) the overlap between the fragment orbital is greater for the u symmetry than for the g one, which implies a greater numerator in formula (6) for the u symmetry. The calculation shows that this effect dominates and hence for a small angle the Φ_u orbital is higher in energy than the Φ_g orbital.

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