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Novel copper(II) complexes of "short" salen homologues. Structure and magnetic properties of the tetranuclear complex $[Cu_2(L^2)_2]_2$ $[H_2L^2$ = phenyl-*N*,*N′*-bis(salicylidene)methanediamine] †

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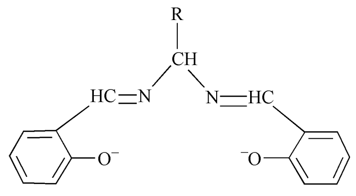
Copper(II) complexes of Schiff bases derived from the condensation of two molecules of salicylaldehyde and methanediamine (L^1) or some phenyl substituted methanediamines (L^2–L^5) have been synthesized and characterised. The crystal structure of the phenylmethanediamine (L^2) derivative has been determined. The ligand acts as bis-bidentate, bridging two copper atoms which are co-ordinated to two phenolato and two imino groups of two ligands. Two binuclear moieties $[Cu_2(L^2)_2]$ are held together through Cu–O(phenolato) interactions between adjacent units forming a pseudo-linear $[Cu_2L^2{}_2]_2$ cluster. Variable temperature magnetic susceptibility data for this derivative reveal the presence of weak antiferromagnetic interactions ($-J \approx 2$–$3\ cm^{-1}$) between nearest neighbour spin centres. The structural factors that may be responsible for the sign and magnitude of the exchange interactions are discussed.

Metal complexes of quadridentate ligands of the salen type $HOC_6H_4CH{=}N(CH_2)_nN{=}CHC_6H_4OH$, $n = 2$, have been investigated extensively because of their properties as catalysts and as models of biological systems. Another reason is the possibility of varying the co-ordination geometries. These ligands usually give rise to mononuclear complexes with a nearly planar co-ordination geometry,[1,2] but analogues with diamines different from ethylenediamine may induce various degrees of distortion. Thus slight to substantial tetrahedral distortions have been found in the case of chiral[3–6] or longer ($n = 3$ or 4) and bulky diamines.[7–11] There are also a few instances in which salen acts as a binucleating ligand.[1,2,12–15]

Despite the extensive investigations carried out on various salen analogues, studies on metal complexes of "short" ($n = 1$) salen homologues, *i.e.* with only one carbon atom between the two imine nitrogen atoms are rare. To our knowledge, with the exception of a brief preliminary account from some of us,[16] there are only two reports of complexes with the ligands described in this paper, namely $[(MoO_2)_2(\mu\text{-}L^1)(\mu\text{-}O)(\mu\text{-}OCH_3)]^-$, with a Mo : ligand ratio 2 : 1 (obtained from salicylaldehyde, urotropine and a polymolybdate anion),[17] and $[VO(L^1)]$ of unknown structure.[18] These ligands are of potential interest because they are expected to form either mononuclear complexes with highly strained four member chelate rings or, alternatively, to avoid such a strain, bi- or poly-nuclear complexes. Models suggest that distorted co-ordination geometries originate in either case. This is particularly relevant in the case of copper, in view of the fact that the properties of copper proteins depend on both the distortion of co-ordination geometries and/or the presence of polynuclear moieties.[19]

This paper describes the synthesis and characterisation of some copper(II) complexes with the ligand *N*,*N′*-bis(salicylidene)methanediamine (H_2L^1) and some arylmethane analogues, H_2L^2–H_2L^5, as well as the crystal structure and magnetic properties of the tetranuclear L^2 derivative.



	R
L^1	H
L^2	C_6H_5
L^3	*p*-ClC_6H_4
L^4	*p*-$CH_3C_6H_4$
L^5	*p*-$NO_2C_6H_4$

Experimental

Elemental analyses were from the microanalytical laboratory, the Milano University. Molecular weights were determined by osmometry at the Microanalytisches Lab Pascher (Germany).

The H_2L ligands were prepared according to literature procedures.[18,20] H_2L^5 does not appear to have been described previously. Proton NMR data for the ligands are collected in Table 1. The melting point of H_2L^4, from different preparations, has been found to be 122 °C, instead of the reported[20] value of 101 °C, however its elemental analysis is correct and its ^1H NMR spectrum (Table 1) in accordance with its structure.

Preparation of the complexes

The copper complexes were all obtained in 80–95% yields by the same procedure, which is described here only for $[Cu_2L^1{}_2]$. Equimolar amounts of copper acetate and H_2L^1 were dissolved in ethanol (15 cm^3 for one mmol), together with 1 cm^3 of tri-

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† Electronic supplementary information (ESI) available: elemental analyses and selected bond lengths and angles. See http://www.rsc.org/suppdata/dt/b0/b003825n/

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Table 1 Relevant ^{1}H NMR data and melting points of the ligands[a]

Compound	OH	N=CH	NCHRN	Other	Melting point/°C
H_2L^1	12.95 (2 H)	8.54 (2 H)	5.46 (2 H, R = H)		140
H_2L^2	12.97 (2 H)	8.48 (2 H)	6.01 (1 H)		126
H_2L^3	12.82 (2 H)	8.58 (2 H)	5.98 (1 H)		145
H_2L^4	13.00 (2 H)	8.57 (2 H)	5.87 (1 H)	2.36 (3 H, CH_3)	122[b]
H_2L^5	12.60 (2 H)	8.62 (2 H)	6.06 (1 H)		123

[a] $CDCl_3$ solutions, δ values in ppm from Me_4Si. All these resonances are singlets. relative intensities in parentheses. [b] Lit. 100–101 °C.[20]

ethylamine. The mixture was stirred at room temperature for three hours, the dark green green precipitate filtered off, washed with ethanol, diisopropyl ether and dried *in vacuo*.

Alternatively, hexamethylenetetramine (urotropine, 1.764 g, 9 mmol) and salicylaldehyde (1.465 g, 12 mmol) were added to a boiling methanol solution of 0.399 g (2.0 mmol) of $Cu(CH_3CO_2)_2 \cdot H_2O$. The mixture was refluxed for two hours, cooled and the precipitate filtered off, washed with methanol and dried *in vacuo*. Yield 85%.

All the complexes have satisfactory elemental analyses. Molecular weight measurements (osmometry, $CHCl_3$ solutions) are in accordance with the dimeric structure Cu_2L_2. Crystals of $[Cu_2L^2{}_2]_2$ suitable for X-ray investigation were obtained by slow diffusion of diisopropyl ether into a concentrated chloroform solution. Bis(salicylideneaminato)copper(II), [Cu(salim)$_2$], was prepared as described in the literature.[21]

Crystal structure determination of $[Cu_2L^2{}_2]_2$

Crystal data. $C_{84}H_{64}Cu_4N_8O_8 \cdot C_6H_{14}O$, *M* 1669.84, triclinic, space group $P\bar{1}$ (no. 2), $a = 16.404(2)$, $b = 16.410(2)$, $c = 17.384(2)$ Å, $\alpha = 100.73(2)$, $\beta = 107.28(2)$, $\gamma = 109.40(2)°$, $T = 293(2)$ K, $Z = 2$, $\mu = 11.13$ cm^{-1}.

35602 Intensity data were collected on a Siemens SMART CCD diffractometer of which 13193 were independent ($R_{int} = 0.040$). An absorption correction was applied using the SADABS routine.[22] The structure was solved by direct methods (SIR 97)[23] and refined with full matrix least squares (SHELX 93)[24] on the basis of 7578 independent reflections with $I > 2\sigma(I)$; $R = 0.043$, $R_{all} = 0.081$.

CCDC reference number 186/2087.

See http://www.rsc.org/suppdata/dt/b0/b003825n/ for crystallographic files in .cif format.

Magnetic susceptibility measurements

Variable temperature susceptibility measurements of the L^1 and L^2 derivatives were performed on samples of different preparations, in the range 4.0–290 K, with use of a Faraday type magnetometer equipped with a helium continuous-flow cryostat built by Oxford Instruments. Susceptibilities (4 Cu) were corrected for the diamagnetism of the ligand system, estimated as -722×10^{-6} and -640×10^{-6} cm^3 K mol^{-1}, for the L^2 and L^1 derivatives, respectively. Our analyses used a temperature-independent paramagnetic term, N_α, of 60×10^{-6} cm^3 per Cu atom and did not include any zero-field splitting.

Results and discussion

The H_2L ligands used in this work were prepared according to published procedures.[18,20] All the new complexes have the CuL stoichiometry, and were prepared by reaction of H_2L with copper acetate in ethanol in the presence of triethylamine. In the absence of the amine the ligands are hydrolysed to formaldehyde or benzaldehyde (as shown by mass spectrometry) and [Cu(salim)$_2$], identified by comparison with an authentic sample[21] (ν_{NH} 3300 and $\nu_{C=N}$ 1626 cm^{-1}). The L^1 complex was prepared also by a one pot synthesis from hexamethylenetetramine (urotropine), salicylaldehyde and copper acetate in boiling methanol.

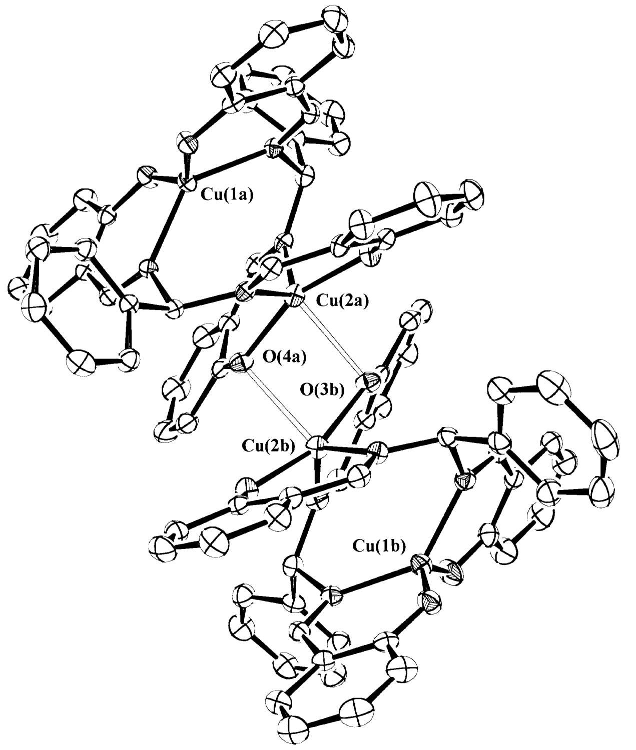

Fig. 1 An ORTEP[25] view of the $[Cu_2L^2{}_2]_2$ complex. Thermal ellipsoids are drawn at 30% probability.

The complexes are green-brown and their infrared spectra show bands due to the C=N stretch in the range 1610–1615 cm^{-1}, about 10 cm^{-1} lower than that of the "free" ligand. All the compounds display effective magnetic moments at room temperature around 1.8 μ_B per Cu atom. They were found to be dimeric in $CHCl_3$ solutions (osmometric measurements).

Structure of $[Cu_2L^2{}_2]_2$

A perspective view of the complex is shown in Fig. 1. The ligand acts as bis-bidentate, bridging two copper atoms to form binuclear units $[Cu_2L^2{}_2]$. Each copper atom is co-ordinated to two phenolato oxygen and two imine nitrogen atoms of two different L^2 ligands. Couples of these binuclear species are arranged to form pseudo-linear $[Cu_2L^2{}_2]_2$ tetranuclear moieties through two short contacts of Cu(2a) and Cu(2b) with the phenolic O(3b) and O(4a) atoms of the adjacent binuclear species [Cu(2a)–O(3b) 2.520(4), Cu(2b)–O(4a) 2.452(4) Å; Cu(2a)–O(3b)–Cu(2b), 91.0(1) and Cu(2a)–O(4a)–Cu(2b), 93.0(1)°]. Crystals derive from the packing of these tetranuclear $[Cu_2L^2{}_2]_2$ entities and clathrated diisopropyl ether solvent molecules in an approximate molar ratio 1 : 1. The solvent molecule shows quite high displacement parameters which either derive from the absence of strong intermolecular interactions with its neighbours or may be indicative of partial occupation of the crystallographic site.

The four copper atoms are almost coplanar, the Cu(1a)–Cu(2a)–Cu(2b)–Cu(1b) torsion angle being 171.9(1)°. The shortest Cu···Cu separation between different tetranuclear

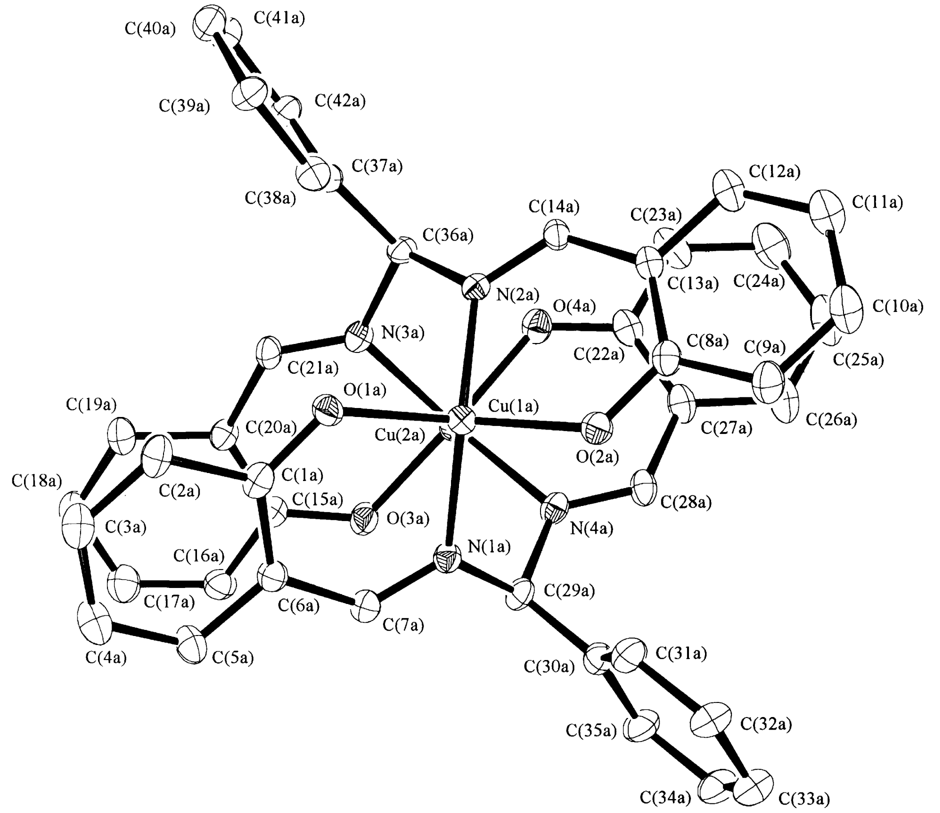

Fig. 2 An ORTEP view of one of the $[Cu_2L^2_2]$ moieties seen along the Cu(1a)–Cu(2a) vector.

units is 5.81 Å. The Cu···Cu distances, within these units, 3.215(1) and 3.242(1) (intradimer) and 3.181(1) Å (interdimer), are typical of very weak or non-bonding interactions, but can be considered as short metal–metal separations (<3.6 Å), similar to those occurring in a number of metalloenzymes containing polymetallic active sites.[19,26] The interesting feature of this structure is that the two Schiff bases form a cage in which two metal atoms are firmly held at a fixed and relatively short distance, without the aid of any directly bridging group, such as the μ-OH species in the binuclear molybdenum compound of L^1 cited above.[17] A comparison can be made with the binuclear $[Cu_2(\text{sal-}m\text{-phen})_2]$[27] and $[Co_2(\text{sal-}m\text{-phen})_2]$,[28] where sal-*m*-phen is the salen analogue with *m*-phenylenediamine. The presence of this diamine precludes formation of mononuclear co-ordination compounds and cage structures similar to that of our compound are formed, but the two metal atoms are held at a longer distance (≈7.4 Å, computed from the data of ref. 28), because of the size of the ligand.

The distorted co-ordination geometries around the metal atoms are of two types: intermediate between square planar and tetrahedral for Cu(1a) and Cu(1b) and between square pyramidal and trigonal bipyramidal for Cu(2a) and Cu(2b), which are involved in additional intradimer interactions (see Fig. 1). These distorted geometries arise from the conformation of the N–C–N bridge between the two metal atoms in a binuclear unit together with the obliged bite angle of the salicylimine moieties (about 94°). Fig. 2 shows one of the binuclear units seen almost along the Cu(1a)–Cu(2a) vector. Except for minor differences due to packing effects, the two binuclear moieties are essentially very similar and display idealised C_2 symmetry. The conformation of the N and O atoms about the Cu–Cu vector is staggered (*syn-anti*) with a rotation of about 45 °.

No unusual features are displayed by the L^2 ligand: the mean values of the C–O and C=N(imine) distances correspond to a predominant double bond character and are in line with those observed in other complexes with Schiff bases.[1]

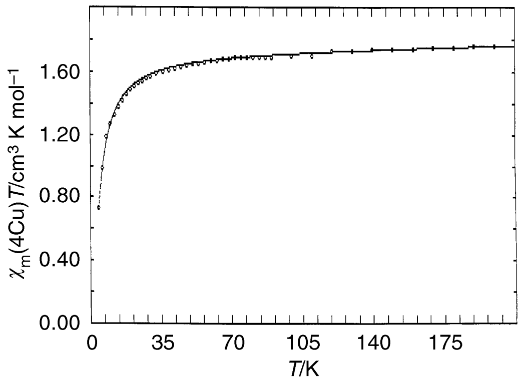

Fig. 3 Experimental and theoretical temperature dependence of χ_m(4 Cu)T for $[Cu_2L^2_2]_2$ between 4 and 200 K.

Magnetic properties

These were studied in detail for two representative complexes, namely of L^1 and L^2. The results of magnetic susceptibility measurements for $[Cu_2L^2_2]_2$ are given in Fig. 3, in the form of a χ_mT *versus* T plot. Upon lowering the temperature χ_mT remains practically constant between 290 and ≈70 K, at a value of about 1.74 cm^3 K mol^{-1}, appropriate for four independent $S = 1/2$ spins with $g = 2.15$, and then tends to zero revealing the presence of dominant antiferromagnetic interactions.

A schematic view of the bridging framework in the tetramer is presented in Fig. 4, where a simplified numbering scheme, useful for the following discussion, is used. Since the six Cu···Cu separations within the cluster are all unequal, a rigorous description of its magnetic structure would require the evaluation of six exchange-coupling constants,[29] which is beyond what can reasonably be expected from fitting procedures. We have, therefore considered an approximate model. This assumes that the differences between the Cu···Cu distances between the outer pairs of copper atoms (0.027(1) Å) and between the Cu(1)···Cu(2)···Cu(3) and Cu(2)···

Table 2 Best fit parameters[a] (cm^{-1}) and agreement factors for $[CuL^2{}_2]_2$

Fit	J_1	J_2	J_3	J_4	$10^4\ F^b$
(1)	−2.43	−2.69	*c*	*c*	1.9
(2)	−2.45	−1.99	−0.56	*c*	1.7
(3)	−2.41	−2.03	−0.51	−0.17	1.7
(4)	−2.44	−2.00	−0.54	−0.04	1.7

[a] *J* values denoted by *c* were arbitrarily held constant to zero. [b] Calculated as described in the text for 46 observations.

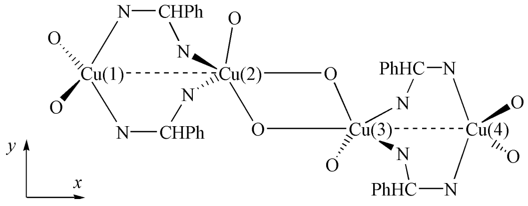

Fig. 4 Schematic view of the bridging framework in $[Cu_2L^2{}_2]_2$, with the simplified numbering scheme (Cu(1) = Cu(1a), *etc.*) utilised in the discussion of the magnetic properties. The origin of the *z* axis is halfway between Cu(2) and Cu(3) and perpendicular to the plane of the figure.

Cu(3)···Cu(4) angles (2°) have a minor influence on superexchange and can therefore be ignored. Consequently the tetranuclear cluster closely approximates C_2 symmetry with the twofold axis, perpendicular to the best plane containing the four Cu atoms and passing halfway between the central copper atoms. In this approximation, the Heisenberg Hamiltonian for the system has the form shown in eqn. (1) where J_1 describes the

$$H = -2J_1\,(S_1{\cdot}S_2 + S_3{\cdot}S_4) - 2J_2\,(S_2{\cdot}S_3) - 2J_3\,(S_1{\cdot}S_3 + S_4{\cdot}S_2) - 2J_4\,(S_1{\cdot}S_4) \quad (1)$$

intradimer interactions, J_2 is the central coupling constant, *etc.* This model has been solved exactly and provides the molar susceptibility expression,[30] eqn. (2), where E_1 and E_6 are the

$$\chi_m\,(4Cu) = (N\mu_\beta{}^2g^2/kT)\,[10\exp(-E_1/kT) + 2\exp(-E_2/kT) + 2\exp(-E_3/\mathrm{kT}) + 2\exp(-E_4/kT)]/[5\exp(-E_1/kT) + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kt)] + 4N_\alpha \quad (2)$$

energies (expressed as functions of the *J* values) of the various spin states (one quintet, three triplets and two singlets), where *N*, μ_β, *g* and *k* have their usual meanings. Although not strictly correct theoretically,[31] eqn. (2) also assumes equal *g* values for all the multiplets, in order to avoid the presence of too many adjustable parameters.

The experimental susceptibility data for the tetramer were fit by eqn. (2) by holding $g = 2.15$ (the value deduced from the Curie–Weiss plot of the high temperature data) and letting two to four coupling constants vary (the remaining ones being held equal to zero). The function minimised in curve fitting was $F = (\chi_1{}^{obs} - \chi_1{}^{calc})^2\ (\chi_1{}^{obs})^{-1}$. Best fit parameters and *F* values are collected in Table 2, Fit (1) is shown in Fig. 3.

All the fitting calculations produce a closely spaced sequence of energy levels with E_1 $(S = 2) > E_3(1) > E_5\ (0) > E_2\ (1) > E_4\ (1) > E_6\ (0)$ and $E_1 - E_6 = 11.4 \pm 0.2\ cm^{-1}$. Addition of J_3 and J_4 to J_1 and J_2 as adjustable parameters neither significantly improves the value of the fit nor produces radical changes of the J_1 and J_2 best values. This strongly suggests that the magnetic structure of the compound is fundamentally determined by the nearest neighbour interactions.

The novel structural features of $[Cu_2L^2{}_2]_2$ invite one to consider the factors that may be responsible for the observed sign and magnitude of J_1 and J_2. Current orbital models[32] for superexchange are useful for this purpose. Such models represent the singlet–triplet splitting for a copper(II) pair as the sum, eqn. (3), of two terms, $2J_F$ (always > 0, ferromagnetic) favouring

$$E_{ST} = 2J = 2J_F + 2J_{AF} \quad (3)$$

a triplet ground state and $2J_{AF}$ (<0, antiferromagnetic) favouring a singlet ground state. The J_F term is generally considered to be small and slowly varying with structural changes, J_{AF} is instead governed by the energy gap between the two MOs formed from the two magnetic orbitals originally describing the unpaired electrons. Accordingly, ferromagnetic coupling can be observed only when the energy gap is zero or nearly zero, due to either strict orthogonality of the magnetic orbitals, imposed by the symmetry of the system, or, less frequently, accidental degeneracy of the MOs.[33]

In order to examine the exchange processes in the tetramer it is useful to define local co-ordinates with the *z* axis parallel to the tetramer twofold axis and *x* axes along the Cu(1)–Cu(2) (and Cu(3)–Cu(4)) vectors. In light of the observed local geometries, the magnetic orbitals centred on Cu(1) and Cu(4) are derived[34a] from the $y^2 - z^2$ metal orbital and those of Cu(2) and Cu(3) from[34b] a mixture of x^2, y^2 and z^2 (with reference to the axis of Fig. 4), delocalised onto both the apical and equatorial ligands, although certainly less to the latter. Since both types of magnetic orbitals transform as the A in C_2 symmetry, J_1 and J_2 may be expected to be antiferromagnetic in nature, as observed.

The small magnitude of J_1 and J_2 invites the following comments. Let us first consider the intradimer interaction, J_1. This, since the oxygen donor atoms are pointing away from the interacting metal centres, primarily involves the $Cu(N–C–N)_2Cu$ bimetallacycle. Weak exchange by this pathway is attributable as follows. (i) The reduced unpaired electron density at the nitrogen atoms due, for those bound to Cu(1), to the relevant reduction of the N–Cu(1)–N *trans* angle (≈130°) from 180° (since such a distortion obviously reduces the overlap between $y^2 - z^2$ and the nitrogen sp^2 orbitals) and for those bound to Cu(2) to their equatorial positions in the pseudo trigonal bipyramid around Cu(2). (ii) The non-symmetric conformation, of a *syn-anti* type, adopted by the Cu–N–C–N–Cu frameworks (Fig. 2, the Cu–N···N–Cu torsional angle is about 70°). Through-space and through-bond orbital interactions in such a conformation are not appropriate[35] effectively to propagate exchange. This concept is best exemplified by the very strong[36] or very weak[37,38] coupling (typically $-J > 100$ and $<3\ cm^{-1}$ respectively) observed in carboxylato bridged copper(II) complexes, according to whether the bridge conformation is *syn-syn* or *syn-anti*. More related, although less evident, support for the above concept is provided by the structural[27] and magnetic[39] properties of the binuclear $[Cu_2(\text{sal-}m\text{-phen})_2]$, where superexchange is propagated by Cu–N–C–C–C–N–Cu pathways of *syn-syn* type. In this latter compound, despite an unfavourable interaction[28] between the magnetic orbitals and the bridge, an interaction of $-J = 0.5\ cm^{-1}$ is propagated over a Cu···Cu distance of 7.4 Å. A comparison of these values with those observed here (≈2 cm^{-1} and 3.23 Å, average, respectively), when it is considered that, other things being equal, *J* is expected[40] to show an R^{-n} dependence (*R* is the distance of the interacting orbitals and *n* is typically >10), strongly suggests that the sal-*m*-phen bridge is much more effective than the L^2 bridge in propagating exchange.

As for the central J_2 coupling constant, its value is in the range observed[41] for previously reported oxygen-bridged dimers having parallel-planar structures in which the bridging oxygen ligands are basal to one copper atom and apical to the other. Such complexes are characterised by feeble magnetic interactions that are mainly dependent on the magnitude of the angle at the bridge as well as the basal to apical Cu–O bond

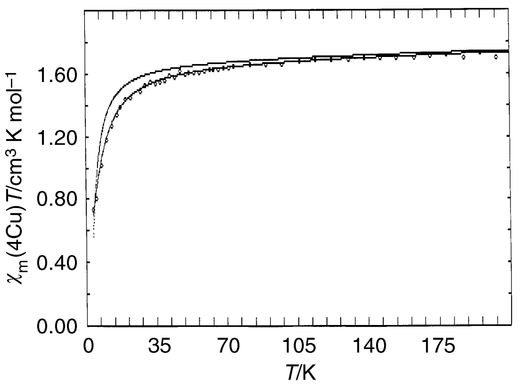

Fig. 5 Experimental and computed $\chi_m(4\text{ Cu})T$ *versus* T plot for the L^1 complex. Upper curve, $[Cu_2L^1_2]$ model with $g = 2.13$ and $J_1 = -3.07$; lower curve, tetranuclear model.

length. Although the differences in structures between the present compound and the above mentioned dimers prevent detailed magneto-structural correlations, the present bridging angles at oxygen of 91 and 93° point out a situation where the antiferromagnetic contribution to J is expected to be small (it should be 0 for an angle of 90°, due to the σ–π symmetry, if pure 2p orbitals were used by oxygen). Additional complicating features in the present case are[42] the deviation from planarity of the Cu_2O_2 fragment (the dihedral angle between the CuO_2 planes is 120°) and the fact that the interacting magnetic orbitals are not parallel.

A last comment concerns the magnetic properties of $[Cu_2L^1_2]$. These were investigated in order to answer the relevant question of whether the formation of the tetranuclear $[Cu_2L^2_2]_2$ cluster is specific to the L^2 ligand or might be a general feature of the related complexes. The χ_mT *vs.* T plot for the L^1 derivative is shown in Fig. 5, where it can also be seen that a poor fit to the data is obtained with a dimer model (*i.e.* eqn. (3), with $J_2 = J_3 = J_4 = 0$) in contrast to the nice fit ($F = 3.0 \times 10^{-4}$ for 46 observations) produced by the use of a tetranuclear nearest neighbours model with $J_1 = -2.60$ cm^{-1} and $J_2 = -5.08$ cm^{-1} (with $g = 2.13$). This seems to indicate that the dimer units found in solution associate in the crystalline state.

Conclusion

This work was undertaken to explore the properties of metal complexes of the "short" salen homologues L^1–L^5, therefore a comparison with the co-ordination modes displayed by salen may be interesting. This ligand forms preferentially complexes of formula [M(salen)] or [{M(salen)}X] (X = Cl, O *etc.*) with metal ions such as Cu^{II} and Co^{II}, and Fe^{III} or Cr^{III} respectively. These complexes sometimes dimerise in the solid state through O(phenolato)–M contacts,[1,2] similar to those found here for $[Cu_2L^2_2]_2$. Co-ordination of salen is nearly planar or displays some tetrahedral distortion, but examples where it is arranged in a bent (*cis*-β) conformation, as in $[MoO_2(\text{salen})]$, are also known.[43] Only in a few instances has salen been found to act as bis-bidentate giving rise to binuclear complexes, examples are [{Co(salen)}$_2$(μ-salen)],[1] [{Rh(CO)$_2$}$_2$(μ-salen)],[12] [{W(CO)$_4$}$_2$(μ-salen)],[15] $[(ReOCl_3)_2(\mu\text{-salen})]^{2-}$ and [{B(OR)$_2$}$_2$(μ-salen)].[13,14] In these molecules only one salen moiety bridges the two metal atoms and formation of such a bridge may be due to a lack of co-ordination sites at the metal centres, which are occupied by other firmly bound ligands. On the contrary, in the present case binucleation occurs because the four membered chelate rings (Cu–N–C–N), in the hypothetical inner complex, would be strongly disfavoured because of severe strain. If the metal to ligand ratio is 1 : 1, structures in which two L form a cage, with the two metal atoms kept at a fixed and relatively short distance, are formed.‡ The conformation of the resulting eight membered bimetallacycle $[Cu(N–C–N)_2Cu]$, together with the fixed bite angle of the salicylimine moiety, originates distorted geometries around the metal atoms. The consequences on the physical properties and the reactivity of these structural features are under thorough investigation.

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‡ It can be anticipated that similar binuclear cage structures have been found also in the case of L^1 and L^2 complexes of other metals.[44]

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