Novel square-planar cyclic tetranuclear copper(II) complex containing oximate bridges. Synthesis, crystal structure and magnetic properties of tetrakis[diaqua(μ-1,3-dimethylviolurato)-copper(II)] tetraperchlorate dihydrate

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The tetranuclear complex $[Cu_4(L)_4(H_2O)_8][ClO_4]_4 \cdot 2H_2O$ (HL = 1,3-dimethylvioluric acid, *i.e.* 1,3-dimethyl-5-(hydroxyimino)-2,4,6(1H,3H,5H)-pyrimidinetrione) has been prepared and its crystal structure determined by X-ray diffraction methods. The structure consists of a tetranuclear cation $[Cu_4(L)_4(H_2O)_8]^{4+}$, four non-co-ordinated perchlorate anions and two water molecules located on a 4-fold rotation-inversion axis. Within each cation the four copper(II) ions, linked through four bis(bidentate) L^- ligands, are arranged at the vertices of a strict square-planar parallelogram with edge and diagonal Cu···Cu distances of 4.764(3) and 6.738(4) Å, respectively. Each oxime group acts as a bridge between adjacent copper ions with an *anti* conformation and each copper is co-ordinated by two L^- ligands. The copper atoms exhibit a CuO_5N elongated distorted octahedral co-ordination environment, with three oxygen atoms and one nitrogen atom of the L^- ligands at equatorial positions and the water oxygens at axial positions. From variable-temperature magnetic susceptibility measurements the compound was found to exhibit a very strong antiferromagnetic exchange interaction through the oximate bridges with $J = -349$ cm^{-1} $[-J(S_{Cu} \cdot S_{CuA} + S_{CuA} \cdot S_{CuC} + S_{CuC} \cdot S_{CuB} + S_{CuB} \cdot S_{Cu})]$, leading to complete spin coupling at 70 K.

Tetranuclear d-block metal complexes are of current interest in bioinorganic modelling, multielectron transfer, catalytic and new extended materials, as well as in magnetochemical investigations.[1] Owing to their relative ease of synthesis, and of the design of many tetranucleating chelating ligands for use in bioinorganic model and magnetochemical studies, there are many examples of Cu_4 clusters, which exhibit a large diversity of structural types.[1] Among them, structurally and magnetically characterized planar cyclic structures with no diagonal bridging groups are rather scarce[2–5] and, as far as we know, those adopting a strict square-planar structure have not been reported up to now.

Polydentate ligands containing oxime groups are known to form a variety of hetero- and homo-polynuclear complexes, in which the oximate bridging group generally mediates very strong magnetic exchange interactions between metal ions.[6–14] Most of them are dinuclear and trinuclear species and, with the exception of two recently reported linear tetranuclear[11,12] and one cubic octanuclear especies,[13] to the best of our knowledge no other examples of structurally and magnetically characterized genuine higher nuclearity oximate-bridged complexes exist. In this paper we report the synthesis, crystal structure and magnetic properties of $[Cu_4(L)_4(H_2O)_8][ClO_4]_4 \cdot 2H_2O$ (HL = 1,3-dimethylvioluric acid, *i.e.* 1,3-dimethyl-5-(hydroxyimino)-2,4,6(1H,3H,5H)-pyrimidinetrione), a tetranuclear copper(II) complex with a square planar ring of copper(II) atoms and bis-(bidentate) bridging 1,3-dimethylviolurate ligands, which can be considered as a new example of metallacrowns.

Experimental

Physical measurements

Elemental analyses were carried out at the Technical Services of the University of Granada on a Fisons-Carlo Erba model EA 1108 analyzer. The IR spectra were recorded on a Perkin-Elmer 983 G spectrometer using KBr pellets. Variable-temperature magnetic susceptibility data were collected on powdered samples of the compounds with use of a SQUID-based sample magnetometer on a Quantum Design Model MPMS instrument. Data were corrected for the diamagnetism of the ligands using Pascal's constants. Variable-temperature EPR spectra were measured with a Bruker ER 200D spectrometer equipped with a nitrogen cryostat.

CAUTION: perchlorate salts are potentially explosive and should only be handled in small quantities. All reagents were of analytical grade and used without further purification.

Preparation of compounds

$[Cu_4(L)_4(H_2O)_8][ClO_4]_4 \cdot 2H_2O$. 6-Chloro-1,3-dimethyluracil (1 g, 5.70 mmol) was added to a stirred solution of 1,5-diamino-3-hydroxypentane (0.33 g, 2.85 mmol) in 20 ml of ethanol containing 8.6 mmol of triethylamine and the resulting solution refluxed for two hours. A white precipitate formed, which was filtered off, washed with ethanol and air dried. To a stirred suspension of this white precipitate (0.5 g, 1.27 mmol) in 50 ml of water were added $NaNO_2$ (0.175 g, 2.54 mmol), $CuCl_2$ (0.34 g, 2.54 mmol) and 3 mmol of glacial acetic acid. After stirring overnight a brown solid precipitated, which was filtered off, washed with water (3 × 5 ml), 3 ml of ethanol and air dried. Its elemental analysis does not match for any formulae of a pure compound. All attempts to obtain a pure compound were unsuccessful. The brown solid (0.5 g) was added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.11 g, 3 mmol) in 50 ml of ethanol–acetonitrile–water (1:1:0.25) and the resulting suspension refluxed. After 1 h the suspension had all dissolved and after 2 h of reflux the hot solution was filtered. The deep brown solution, kept at room temperature, provided brown crystals of the tetranuclear compound (0.67 g, yield 30% based on 6-chloro-1,3-

dimethyluracil). Calc. for $C_6H_{11}ClCuN_3O_{10.5}$: C, 18.36; H, 2.80; N, 10.70. Found: C, 18.42; H, 2.75; N, 10.80%. IR (KBr, cm^{-1}): ν(OH) 3438, 3426; ν(C=O) 1601, ν(Cl–O) 1084, 1116, 1144.

X-Ray data collection and structure determination

Crystal data. [Cu(L)(H$_2$O)$_2$]$_4$[ClO$_4$]$_4$·2H$_2$O, C$_{48}$H$_{88}$Cl$_8$Cu$_8$N$_{24}$-O$_{84}$, brown-yellow block, dimensions $0.88 \times 0.78 \times 0.40$ mm, tetragonal, space group $I\bar{4}$, $a = 18.761(4)$, $c = 7.524(4)$ Å, $U = 2648(2)$ Å^3, $Z = 2$, $\mu = 1.913$ mm^{-1} $F(000) = 1584$. Data were collected at 150(2) K using a Siemens P4 diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). A total of 1641 reflections was collected ($2\theta_{max} = 25.0°$) and corrected for Lorentz-polarization and absorption effects. The structure was solved by direct methods and refined by full matrix least squares on F^2, using all 1540 independent reflections ($R_{int} = 0.0239$). Similar refinements were obtained in space groups $I4$ and $I\bar{4}$; the latter was selected as $I4$ required a disorder in the perchlorate counter ion which is not present in $I\bar{4}$. The oxime section of the ligand is disordered and was modelled with equal occupancy of two equivalent positions. All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters except for the disordered section. Hydrogen atoms bonded to carbon atoms were inserted at calculated positions but those of the water molecules were not located. The structure was refined as a racemic twin and refinement, on 191 parameters, converged with $R1 = 0.0912$, $wR2 = 0.1721$, goodness-of-fit = 1.095 (all data) and conventional $R1 = 0.0784$ (2σ data). There were no significant residual peaks in the electron density map. All programs used in the structure solution and refinement are contained in the SHELX 97 package.[15] Selected bond lengths and angles are listed in Table 1.

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See http//www.rsc.org/suppdata/dt/1999/2923/ for crystallographic files in .cif format.

Results and discussion

The synthesis of [Cu$_4$(L)$_4$(H$_2$O)$_8$][ClO$_4$]$_4$·2H$_2$O **1** can be achieved *via* the sequence of reactions indicated in Scheme 1: (i) condensation between the diamine and 6-chloro-1,3-dimethyl-uracil in a basic medium; (ii) nitrosation of the condensation product leading to a pentadentate pseudomacrocyclic ligand and subsequent formation with CuCl$_2$ of an intermediate complex or mixture of complexes, in which the copper(II) ions should be co-ordinated in a chelate fashion by the nitrogen atom of the amino group and either the nitrogen or oxygen atom of the oximato group, and (iii) hydrolysis of the C6–N amine bonds with an excess of Cu(ClO$_4$)$_2$·6H$_2$O and formation of the tetranuclear compound **1**. It should be noted that the hydrolysis of 6-amino-5-nitrosouracil derivatives to produce violuric acid derivatives is a rather common process. In fact, a suitable method of obtaining the HL ligand is the hydrolysis, in a strong acid medium, of 6-amino-1,3-dimethyl-5-nitroso-uracil.[16] It seems that substitution on the amino group facilitates this process. In this regard, when either the complex [Cu(HL^1)Cl] (HL^1 is an N$_4$ tetradentate pseudomacrocyclic ligand analogous to that formed in step (ii) but having a butanediyl chain linking the amino groups in position 6 or the ligand 6-methylamino-1,3-dimethyl-5-nitrosouracil is treated with an excess of [Cu(bipy)$_2$][ClO$_4$]$_2$ the mononuclear complex [Cu(L)(bipy)(EtOH)ClO$_4$] is formed.[8,17] It should be pointed out that the direct reaction between HL and Cu(ClO$_4$)$_2$ in an aqueous medium does not produce the tetranuclear compound but the octahedral mononuclear complex [Cu(L)$_2$(H$_2$O)$_2$].[16]

The HL ligand contains one ionizable proton that is involved in a ketone oxime ⇌ hydroxynitroso tautomeric equilibrium (Fig. 1), so that the L$^-$ anion might potentially exhibit three different co-ordination modes: (i) N,O-bidentate through the the oxime-N atom and the O atom of a neighbouring carbonyl
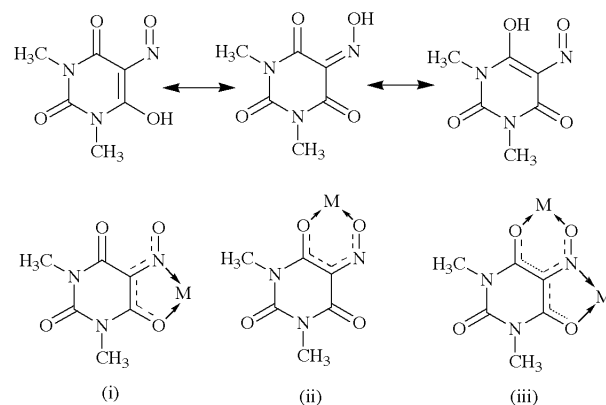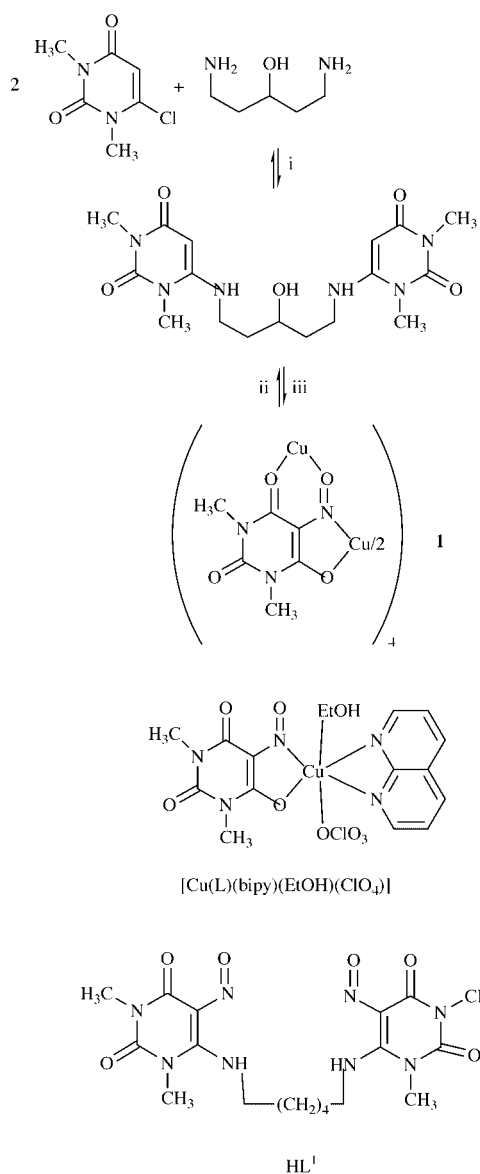

Fig. 1 Tautomeric equilibrium and co-ordination modes of the 1,3-dimethylviolurate ligand.

Scheme 1 Sequence of reactions for the synthesis of complex **1**. (i) NEt$_3$ in ethanol, (ii) NaNO$_2$–CuCl$_2$–AcH in water, (iii) Cu(ClO$_4$)$_2$·6H$_2$O in ethanol–acetonitrile–water.

group to form a five-membered chelate ring, (ii) O,O-bidentate through the oxime-O atom and the oxygen atom of a neighbouring carbonyl to form a six-membered chelate ring and (iii) bis(bidentate) bridging, a combination of the first two. Complexes adopt the first mode or a mixture of the first and the second[16,17] (the NO group is usually disordered between two
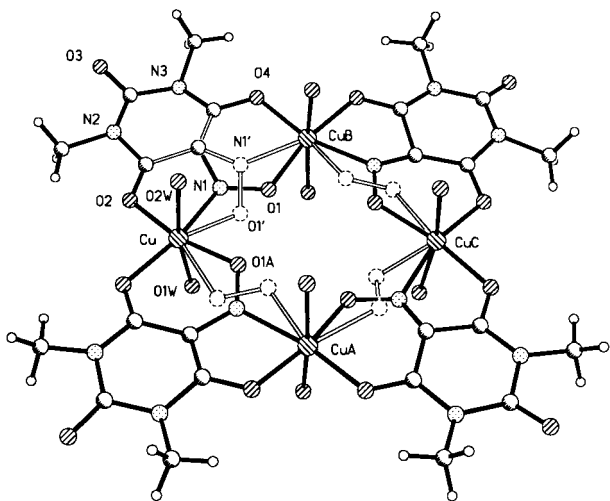
Fig. 2 Molecular structure of complex **1**. Perchlorate anions are omitted for clarity.
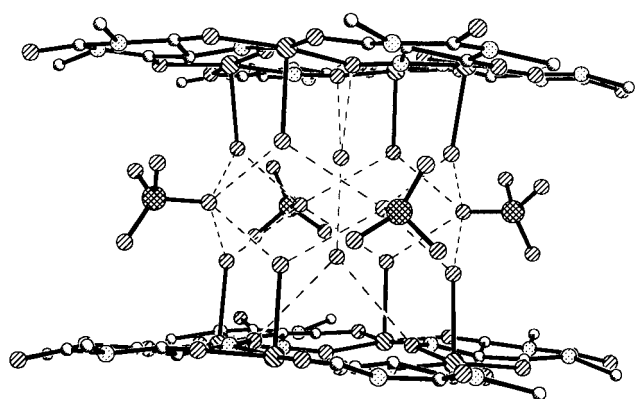

Fig. 3 Hydrogen-bonding network involving two neighbouring planar cations, water molecules and perchlorate anions.

positions) but the bis(bidentate) mode has not been found up to now. In fact, the compound $[Cu_4(L)_4(H_2O)_8][ClO_4]_4 \cdot 2H_2O$ represents the first example of polynuclear complex containing the L⁻ ligand. Nevertheless, very recently, an octanuclear nickel-complex with the violurate ligand exhibiting this co-ordination mode has been characterized.[13]

The IR spectrum of complex **1** lacks C=O stretching vibrations in the 1640–1750 cm⁻¹ range, in contrast to what is observed for the HL ligand and previously structurally characterized copper(II) complexes containing the L⁻ anion in the bidentate co-ordination mode (i) or (ii).[16] This is consistent with delocalized C4=O and C6=O bonds and a bis(bidentate) bridging mode for the ligand.

Crystal structure

The structure of this complex consists of a tetranuclear cation $[Cu_4(L)_4(H_2O)_8]^{4+}$, four nonco-ordinated perchlorate anions and two water molecules located on a 4-fold inversion axis. The molecular geometry and the atom-labelling scheme of the cation are shown in Fig. 2. Within each cation, with S_4 molecular symmetry, the four copper(II) ions, linked through four bis-(bidentate) L⁻ ligands, are arranged at the vertices of a strictly square-planar parallelogram with edge and diagonal Cu · · · Cu distances of 4.764(3) and 6.738(4) Å, respectively. The copper(II) ion exhibits a (4+2) elongated distorted octahedral CuO_5N chromophore. The basal plane is made up from a carbonyl oxygen and an oxime oxygen from one L⁻ ligand and a carbonyl oxygen and the oxime nitrogen from a second L⁻ ligand, whereas the axial positions are occupied by two water molecules. Each oxime group therefore acts as a bridge between

adjacent copper ions with an *anti* conformation and each copper is co-ordinated by two L⁻ ligands. The oxime bridge is disordered on two sets of crystallographic positions, N1–O1 and N1′–O1′ with equal occupancy. It should be noted that this is rather common in polynuclear complexes of 5-oximate pyrimidine bridging ligands with donor atoms in vicinal positions to the oxime groups.[6,7,17] The edge Cu · · · Cu distance is similar to the metal–metal distances found for other polynuclear complexes also having *anti* oximato bridges.[6,13] The dihedral angles between the pyrimidine and the five- and six-membered chelate ring mean planes are less than 10.2°, thus indicating that, without taking into consideration the co-ordinated water molecules, the whole cation is essentially planar (Fig. 3).

Finally, there is an extensive hydrogen-bonding network above and below the plane of the cation, involving all the water molecules and the perchlorate anions (Fig. 3). This serves to link the structure into columns running parallel to the *c* axis. Relevant hydrogen-bonding distances are also given in Table 1.

Magnetic properties

The temperature dependences of molar magnetic susceptibility χ_m(4Cu) and effective magnetic moment μ_{eff} (4Cu) for a polycrystalline sample of the tetranuclear complex **1** in the range 2–300 K are displayed in Fig. 4. As the temperature is lowered χ_m decreases from 1.8×10^{-3} cm³ mol⁻¹ at room temperature, reaches a minimum of 1.6×10^{-4} cm³ mol⁻¹ at 65 K and below this temperature increases to 4.4×10^{-3} cm³ mol⁻¹ at 2 K. The effective magnetic moment at room temperature of 2.10 μ_B, which is very low compared to that expected for four independent copper ions, decreases with decreasing temperature and reaches a plateau (0.27 μ_B) between 70 and 2 K. The shapes of both curves are characteristic of strong antiferromagnetic coupling among the copper(II) ions leading to a singlet ground state. The residual moment of 0.27 μ_B at 2 K and the corresponding rise of the χ_m values below 65 K are due to the presence of a monomeric impurity ($S = 1/2$) in the sample.

In keeping with the structure of the complex, the magnetic data have been analysed with a spin Hamiltonian for the exchange interaction of four spins $S = 1/2$, eqn. (1) where J and

$$H = g\beta S_T - J(S_{Cu} \cdot S_{CuA} + S_{CuA} \cdot S_{CuC} + S_{CuC} \cdot S_{CuB} + S_{CuB} \cdot S_{Cu}) - j(S_{Cu} \cdot S_{CuC} + S_{CuA} \cdot S_{CuB}) \quad (1)$$

j describe the exchange interactions sketched in Fig. 4. For a large isotropic interaction the total spin $S_T = S_{Cu} + S_{CuA} + S_{CuB} + S_{CuC}$ is a good quantum number and so are the intermediates $S_1 = S_{Cu} + S_{CuC}$ and $S_2 = S_{CuA} + S_{CuB}$. The energies $E(S_T,S_1,S_2)$ of the low-lying states deduced from the above Hamiltonian and labelled using S_T, S_1 and S_2 are as in eqns. (2)–(6).

$$E(0,0,0) = 0 \quad (2)$$

$$E(1,1,0) = E(1,0,1) = -j \quad (3)$$

$$E(0,1,1) = 2J - 2j \quad (4)$$

$$E(1,1,1) = J - 2j \quad (5)$$

$$E(2,1,1) = -J - 2j \quad (6)$$

Therefore there are two spin singlets, three triplets and one quintet. In the case of antiferromagnetic coupling the singlet (0,1,1) is the ground state. The theoretical expression for the magnetic susceptibility per mol of tetranuclear complex obtained from the above energy levels, taking into consideration that the *g* values for the multiplets are equal to the local *g* values of the copper(II) ions, is as in eqn. (7) where ρ is the portion of paramagnetic impurity that follows the Curie law. The quality of the fitting does not depend on j, so that J can be obtained with a reasonable accuracy from susceptibility data

$$\chi_m = (2N\beta^2 g^2/kT)\frac{\exp[(2j - J)kT] + 2\exp(j/kT) + 5\exp[(J + 2j)/kT]}{1 + \exp[(2j - 2J)/kT] + 3\exp[(2j - J)/kT] + 5\exp[(J + 2j)/kT] + 6\exp(j/kT)}(1 - \rho) + (N\beta^2 g^2/kT)\rho \quad (7)$$

Table 1 Selected bond lengths [Å] and angles [°] for complex **1**

Cu–O(1′)[a]	1.891(14)	Cu–N(1)[a]	2.069(17)
Cu–O(1)[a]	1.911(13)	Cu–N(1′)[a]	2.094(19)
Cu–O(2)	1.929(8)	Cu–O(1W)	2.25(2)
Cu–O(4)	1.947(8)	Cu–O(2W)	2.268(19)
O(1′)[a]–Cu–O(2)	101.4(5)	O(1)[a]–Cu–O(1W)	93.5(8)
O(1)[a]–Cu–O(2)	167.2(5)	O(2)–Cu–O(1W)	89.2(7)
O(1′)[a]–Cu–O(4)	163.2(6)	O(4)–Cu–O(1W)	92.8(7)
O(1)[a]–Cu–O(4)	101.2(5)	N(1)–Cu–O(1W)	82.1(9)
O(2)–Cu–O(4)	91.1(3)	N(1′)[a]–Cu–O(1W)	84.8(9)
O(2)–Cu–N(1)[a]	74.4(5)	O(1′)[a]–Cu–O(2W)	93.9(7)
O(4)–Cu–N(1)[a]	164.6(6)	O(1)[a]–Cu–O(2W)	80.8(7)
O(1′)[a]–Cu–N(1′)[a]	91.6(7)	O(2)–Cu–O(2W)	94.7(6)
O(2)–Cu–N(1′)[a]	164.1(6)	O(4)–Cu–O(2W)	96.3(6)
O(4)–Cu–N(1′)[a]	74.5(5)	N(1)[a]–Cu–O(2W)	90.2(8)
N(1)[a]–Cu–N(1′)[a]	119.2(6)	N(1′)[a]–Cu–O(2W)	93.7(8)
O(1′)[a]–Cu–O(1W)	76.4(7)	O(1W)–Cu–O(2W)	170.1(5)

Hydrogen bond distances (Å)

O1W–O11[1]	2.91(3)	O3W–O1	3.06(2)
O1W–O11[2]	2.95(3)	O3W–O3W[6]	2.58(5)
O2W–O11[3]	2.99(2)	O3W–O1′	3.00(2)
O2W–O11[4]	3.07(2)	O3W–O2W[5]	3.29(2)
		O3W–O1W	3.10(2)

Symmetry equivalents: 1 $0.5 - x, 1.5 - y, -0.5 + z$; 2 $1.5 - y, 0.5 + x, 1.5 - z$; 3 $0.5 - x, 1.5 - y, 0.5 + z$; 4 $1.5 - y, 0.5 + x, 2.5 - z$; 5 $y, 1 - x, 2 - z$; 6 $y, 1 - x, 1 - z$. [a] 50% Occupancy.
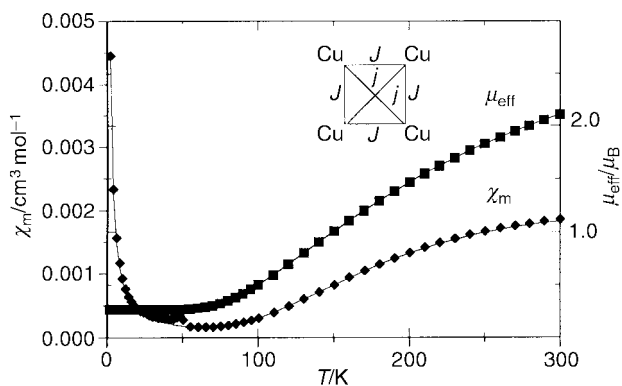

Fig. 4 Thermal dependence of the molar magnetic susceptibility χ_m and effective magnetic moment μ_{eff} for the tetramer **1**. The solid lines are generated from the best-fit parameters.

while j is determined with a high degree of uncertainty. In view of this the experimental data were fitted by holding $j = 0$ and allowing J, g and ρ to vary. The parameters resulting from the best fitting of the magnetic data are $J = -349(5)$ cm^{-1}, $g = 2.15(3)$ and $\rho = 0.0051(1)$ ($R = 1.1 \times 10^{-7}$). The polycrystalline X-band EPR spectrum of the tetramer at room temperature exhibits an almost isotropic featureless resonance at $g = 2.17$. Its linewidth and position appear to be temperature independent down to 150 K. At 100 K the resonance becomes less symmetric and exhibits hyperfine structure with $A_{\parallel} = 150 \times 10^{-4}$ cm^{-1}. This together with the increase of the signal intensity as the temperature is lowered mean that the signal is more likely to be due to the small $S = 1/2$ impurity found also in the magnetic susceptibility measurement. Since the first excited state, a triplet largely separated from the singlet ground state (349 cm^{-1}), must be almost depopulated at 100 K, monomeric molecules (0.5%) are well isolated in a diamagnetic matrix, thus allowing the appearance of hyperfine structure.

The strong antiferromagnetic coupling observed for the tetramer is not unexpected, since bridging oximato groups, either in *syn* or *anti* conformation, are known to exhibit a remarkable efficiency in mediating very strong magnetic exchange interactions, which are provided by an orbital exchange pathway essentially of σ nature. The magnitude of the exchange interaction, however, is rather lower than the values reported for bi- and tri-nuclear complexes with *syn-syn* double oximato bridges,[7] which usually exhibit J values between -600 and -1000 cm^{-1}. This may be primarily due to the inability of the extended pathway involving the ketonic oxygens to mediate any appreciable interaction, so that the exchange interaction must be mainly supported by the oximato-bridging group. In good accordance with this, Cu–Cu and Cu–Ni oximato-bridged binuclear complexes show a strong decrease of the magnetic exchange interaction on passing from two to one oximate bridging group.[6,14]

Finally, it should be pointed out that the copper(II) ions and nitrogen and oxygen bridging atoms in complex **1** form a 12-membered ring analogous to those observed in crown ethers by substituting a copper(II) ion and a nitrogen atom for the methylene carbons and thus **1** can be considered as a metalla-crown, a new class of molecular recognition agents.[18] The cavity size and the bite distance for **1** are similar to those found in other metallacrowns.[18] Therefore, **1** can potentially accommodate different metal ions into its central cavity. Studies along this line with this and other violuric derivatives are planned.

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