Oximato Complexes. Part 2.[1] Dinuclear Dimethylglyoximato Complexes of Copper(II) with a New Co-ordination Mode of the Oximate Ligand†

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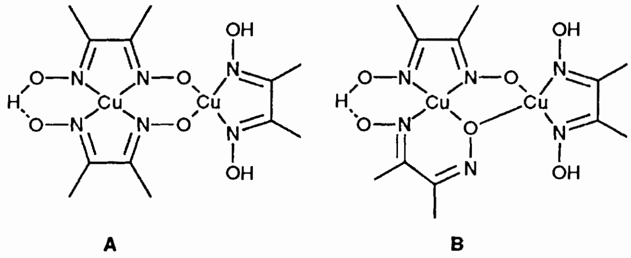
Three new dinuclear copper(II) complexes of formula $[Cu_2(dmg)(Hdmg)(H_2dmg)]Cl \cdot H_2O$ **1**, $[Cu_2(dmg)(Hdmg)(H_2dmg)]ClO_4$ **2** and $[\{Cu_2(dmg)(Hdmg)(H_2dmg)\}_2(SO_4)] \cdot 2.5H_2O$ **3** (H_2dmg = dimethylglyoxime) have been synthesised. The crystal structure of **3** was solved by single-crystal X-ray diffraction methods: monoclinic, space group *C*2/*c*, $a = 22.736(2)$, $b = 21.367(12)$, $c = 11.781(7)$ Å, $\beta = 122.97(5)^\circ$ and $Z = 4$. The structure consists of two cationic binuclear $[Cu_2(dmg)(Hdmg)(H_2dmg)]^+$ units bridged by a sulfate anion, leading to a neutral tetrameric entity, and lattice water. In the dinuclear cation the copper(II) ions are bridged by two oximate groups, one through the nitrogen and oxygen atoms and the other only through the oxygen atom. The intramolecular Cu(1) ··· Cu(2) distance is 3.266(2) Å. The geometry around the copper atoms is a distorted square pyramid: the basal plane for Cu(1) comprises three nitrogen and one oxygen atom of the $Hdmg^-$ and dmg^{2-} groups, whereas that of Cu(2) is formed by two nitrogens of H_2dmg and two oximate oxygens; two oxygen atoms from a sulfate ion occupy the apical position of each copper atom. The temperature dependence of the molar magnetic susceptibility (100–300 K) for **1**–**3** reveals a very strong intramolecular antiferromagnetic coupling between copper(II) ions (*J ca.* -950 cm^{-1}).

In Part 1 [1] we reported the synthesis and characterization of a dinuclear copper(II) complex of formula $[Cu_2(dmg)(Hdmg)(H_2dmg)]ClO_4 \cdot 1.5H_2O$ (H_2dmg = dimethylglyoxime) which was obtained by the reaction of $[Cu(Hdmg)_2]$ with Cu^{2+}. This compound shows a very strong antiferromagnetic coupling between copper(II) ions which are doubly bridged by two oximate groups in *cis* arrangement (Scheme 1, **A**). A different synthetic method, based on the reaction of $[Cu(Hdmg)_2]$ with $[Cu(H_2dmg)]^{2+}$, allowed us to obtain a series of new complexes differing from the former in the co-ordination mode of the oxime group (Scheme 1, **B**). We report here their spectroscopic and magnetic characterization, together with the crystal structure of one of them, namely the sulfate derivative. As far as we are aware, it is the first structurally characterized compound [2] in which an oxime group acts as a bridging ligand only through the oxygen atom. The ability of this particular co-ordination mode to transmit electronic effects between metal ions is investigated.



Scheme 1

Experimental

Materials.—Copper(II) salts and dimethylglyoxime were of reagent grade, obtained from commercial sources and used as received; $[Cu(Hdmg)_2]$ was prepared as described previously.[1]

Synthesis of the Complexes.—$[Cu_2(dmg)(Hdmg)(H_2dmg)]Cl \cdot H_2O$ **1**. A mixture of $[Cu(Hdmg)_2]$ (147 mg, 0.5 mmol) and freshly made $[Cu(H_2dmg)]Cl_2$, prepared by mixing methanolic solutions of copper(II) chloride dihydrate (85 mg, 0.5 mmol) and dimethylglyoxime (58 mg, 0.5 mmol) as reported in ref. 3, in methanol (30 cm^3) was gently refluxed for 1 h with vigorous stirring. The resulting solution was filtered and allowed to stand at room temperature. Slow evaporation of the solvent rendered black-purple prismatic crystals of **1** which were filtered off and air-dried (Found: C, 27.8; H, 4.70; N, 15.70. Calc. for $C_{12}H_{23}ClCu_2N_6O_7$: C, 27.4; H, 4.40; N, 16.00%).

$[Cu_2(dmg)(Hdmg)(H_2dmg)]ClO_4$ **2** *and* $[\{Cu_2(dmg)(Hdmg)(H_2dmg)\}_2(SO_4)] \cdot 2.5H_2O$ **3**. These compounds were obtained following the above procedure but substituting perchlorate (**2**) or sulfate (**3**) for chloride reagents (Found: C, 25.00; H, 3.55; N, 15.20. Calc. for $C_{12}H_{21}ClCu_2N_6O_{10}$ **2**: C, 25.20; H, 3.70; N, 14.70. Found: C, 27.30; H, 4.85; N, 15.25. Calc. for $C_{24}H_{47}Cu_4N_{12}O_{18.5}S$ **3**: C, 26.55; H, 4.35; N, 15.50%).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: emu = S.I. × $10^6/4\pi$.

Physical Techniques.—Elemental analyses (C, H, N) were performed by the Microanalytical Service of the Universidad Autónoma de Madrid (Spain). Infrared spectra were recorded on a Perkin Elmer 882 spectrophotometer as KBr pellets and visible solution spectra on a Cary 1 UV/VIS spectrophotometer. Magnetic susceptibility measurements on complexes **1**–**3** were carried out at 100–300 K with a fully automatized AZTEC DSM8 pendulum-type susceptometer[4] equipped with a TBT continuous-flow cryostat and a Brüker BE15 electromagnet, operating at 1.8 T. The apparatus was calibrated with $Hg[Co(NCS)_4]$. Corrections for the diamagnetism of these compounds were estimated from Pascal's constants.[5] Magnetic susceptibility data were also corrected for magnetization of the sample holder.

X-Ray Structural Determination.—Diffraction data for complex **3** were collected at 291 K with a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Cell data and details of experimental conditions are given in Table 1. The unit-cell parameters were derived from least-squares refinement of 25 well centred reflections ($11 < \theta < 12°$). The intensities of two reference reflections, monitored every 2 h throughout data collection, showed no sign of crystal deterioration. Intensity data were collected in the range $1 < \theta < 20°$ with scan width ($1.3 + 0.34 \tan \theta$). The intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was performed by the use of DIFABS.[6]

The structure was solved by direct methods[7] followed by successive Fourier syntheses and least-squares refinements (CRYSTALS).[8] Full-matrix least-squares refinements were carried out (272 parameters) with anisotropic thermal parameters for all atoms. Hydrogen atoms were neither found in difference maps nor introduced in calculated positions. The final values of the discrepancy indices R and R' were 0.076 and 0.079, respectively. The function minimized was $\Sigma w(||F_o| - F_c||)^2$ and in the last stages of the refinement each reflection was assigned a weight $w = w'[1 - (||F_o| - |F_c||)/6\sigma|F_o|)^2]^2$, where $w' = 1/\Sigma A_r T_r(X)$ with three coefficients A_r (1.31, 0.503, 0.905) for the Chebyshev's polynomial $T_r(X)$ with $X = F_o/F_o(\text{max.})$. Criteria for a satisfactory complete analysis were the ratio of the root mean square shift to standard deviation being less than 0.1 : 1 and no significant features in the final difference map. All calculations were carried out on a Micro Vax II computer. Fractional atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Structure of Complex **3**.—The crystal structure consists of tetranuclear neutral $[\{Cu_2(dmg)(Hdmg)(H_2dmg)\}_2(SO_4)]$ entities and lattice water molecules. In each tetranuclear unit the sulfate anion acts as a bridging ligand between two symmetry-equivalent ($1 - x, y, \frac{1}{2} - z$) dinuclear cations $[Cu_2(dmg)(Hdmg)(H_2dmg)]^+$, with the sulfur atom located on a binary axis [Fig. 1(*b*)]. In these cations, the $Cu(dmg)(Hdmg)^-$ fragment co-ordinates to the $Cu(H_2dmg)^{2+}$ unit through the oximate oxygens to afford a dinuclear skeleton doubly bridged by oximate groups. The two oximato bridges are not equivalent. One has the usual Cu–N–O–Cu two-atom form and the other the unexpected Cu–O–Cu monoatomic form. As far as we know, this is a new co-ordination mode of the oximato group. The sulfate anion establishes a third bridge between the metal ions in the dinuclear cation. A perspective view of this cation, with the atom-numbering scheme, is depicted in Fig. 1(*a*).

Table 1 Summary of crystal data, intensity-data collection and structure refinement for complex **3**

Formula	$C_{24}H_{47}Cu_4N_{12}O_{18.5}S$
M	1086
Crystal symmetry	Monoclinic
Space group	$C2/c$
a/Å	22.736(2)
b/Å	21.367(12)
c/Å	11.781(7)
β/°	122.97(5)
U/Å^3	4801(3)
Z	4
D_c/g cm^{-3}	1.50
μ/(Mo-Kα)/cm^{-1}	18.7
F(000)	2220
Crystal size/mm	0.45 × 0.45 × 0.20
Scan type	ω–2θ
No. of measured reflections	2227
No. of unique reflections [$I \geqslant 3\sigma(I)$]	1433
No. of refined parameters	272
$R\{=[\Sigma(\|\|F_o\| - \|F_c\|\|)/\Sigma\|F_o\|]\}$	0.076
$R'\{=[\Sigma w(\|\|F_o\| - \|F_c\|\|)^2/\Sigma w\|F_o\|^2]^{\frac{1}{2}}\}$	0.079

Table 2 Positional parameters for complex **3** with standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
Cu(1)	0.380 20(9)	0.317 59(8)	0.219 0(2)
Cu(2)	0.328 88(9)	0.202 44(8)	0.002 8(2)
S	0.500 0	0.217 2(2)	0.250 0
N(1)	0.373 3(7)	0.321 5(7)	0.377(1)
N(2)	0.316 4(6)	0.200 7(8)	0.218(2)
N(3)	0.369 6(7)	0.327 6(7)	0.040(1)
N(4)	0.409 2(7)	0.405 7(6)	0.226(1)
N(5)	0.290 2(6)	0.118 4(6)	−0.007(1)
N(6)	0.321 3(7)	0.165 7(7)	−0.161(1)
O(1)	0.395 4(8)	0.374 5(6)	0.451(1)
O(2)	0.322 8(6)	0.243 9(5)	0.145(1)
O(3)	0.350 1(6)	0.282 7(5)	−0.049(1)
O(4)	0.423 1(7)	0.445 9(5)	0.327(1)
O(5)	0.277 8(7)	0.092 8(6)	0.086(1)
O(6)	0.336 1(7)	0.195 9(6)	−0.247(1)
O(7)	0.477 4(4)	0.257 0(4)	0.321 2(9)
O(8)	0.442 0(4)	0.176 1(4)	0.151 1(9)
O(9)	0.467 9(8)	0.242 7(8)	−0.098(1)
O(10)*	0.500 0	0.344(2)	0.750 0
C(1)	0.347 9(9)	0.277 0(9)	0.414(2)
C(2)	0.329 5(8)	0.218 4(8)	0.342(2)
C(3)	0.389 1(8)	0.382 6(7)	0.016(2)
C(4)	0.406 7(9)	0.427 3(8)	0.121(2)
C(5)	0.278 6(8)	0.082 6(8)	−0.103(2)
C(6)	0.293 4(9)	0.113 1(8)	−0.201(2)
C(11)	0.346(1)	0.284(1)	0.538(2)
C(21)	0.314(1)	0.163(1)	0.402(2)
C(31)	0.392(1)	0.390 1(9)	−0.108(2)
C(41)	0.414(1)	0.494 3(7)	0.097(2)
C(51)	0.255(1)	0.135(9)	−0.119(2)
C(61)	0.281(1)	0.079(1)	−0.324(2)

* Assigned an occupancy of 0.25.

The co-ordination geometry around both copper(II) ions is best described as distorted square pyramidal, $Cu(1)N_3O_2$ and $Cu(2)N_2O_3$: three oxime nitrogen and one oximate oxygen atoms at Cu(1) and two oxime nitrogen and two oximate oxygen atoms at Cu(2) comprise the corresponding basal planes; the fifth co-ordination position of both square pyramids is occupied by a weakly bound sulfate oxygen atom [2.262(9) and 2.257(8) Å for Cu(1)–O(7) and Cu(2)–O(8), respectively]. Concerning the basal plane around Cu(1), the Cu–O bond distance (1.92 Å) is shorter than that of average Cu–N (1.98 Å). The four equatorial bonds to Cu(2) lie in the range 1.97–2.01 Å. The four equatorial donor atoms around each copper atom are nearly coplanar [maximum deviations 0.049 Å at N(3) and 0.020 Å at N(6)]. Atoms Cu(1) and Cu(2) lie out of their mean

Table 3 Selected bond distances (Å) and angles (°) for complex **3**

Cu(1)–N(1)	1.96(1)	Cu(2)–O(2)	1.97(1)
Cu(1)–N(3)	2.00(1)	Cu(2)–O(3)	1.97(1)
Cu(1)–N(4)	1.98(1)	Cu(2)–N(5)	1.98(1)
Cu(1)–O(2)	1.92(1)	Cu(2)–N(6)	2.01(1)
Cu(1)–O(7)	2.262(9)	Cu(2)–O(8)	2.257(8)
N(1)–Cu(1)–O(2)	94.6(6)	O(3)–Cu(2)–O(2)	90.9(5)
N(1)–Cu(1)–N(3)	167.0(5)	O(3)–Cu(2)–N(5)	161.9(5)
N(3)–Cu(1)–N(4)	77.7(6)	O(3)–Cu(2)–N(6)	87.0(5)
N(1)–Cu(1)–N(4)	96.8(6)	O(2)–Cu(2)–N(5)	103.1(5)
N(4)–Cu(1)–O(2)	157.5(5)	O(2)–Cu(2)–N(6)	171.6(5)
O(2)–Cu(1)–N(3)	87.0(6)	N(5)–Cu(2)–N(6)	77.5(5)
O(7)–Cu(1)–N(1)	94.5(4)	O(8)–Cu(2)–O(3)	95.1(4)
O(7)–Cu(1)–O(2)	89.9(4)	O(8)–Cu(2)–O(2)	91.8(4)
O(7)–Cu(1)–N(3)	98.4(4)	O(8)–Cu(2)–N(5)	95.9(4)
O(7)–Cu(1)–N(4)	108.4(4)	O(8)–Cu(2)–N(6)	96.5(5)

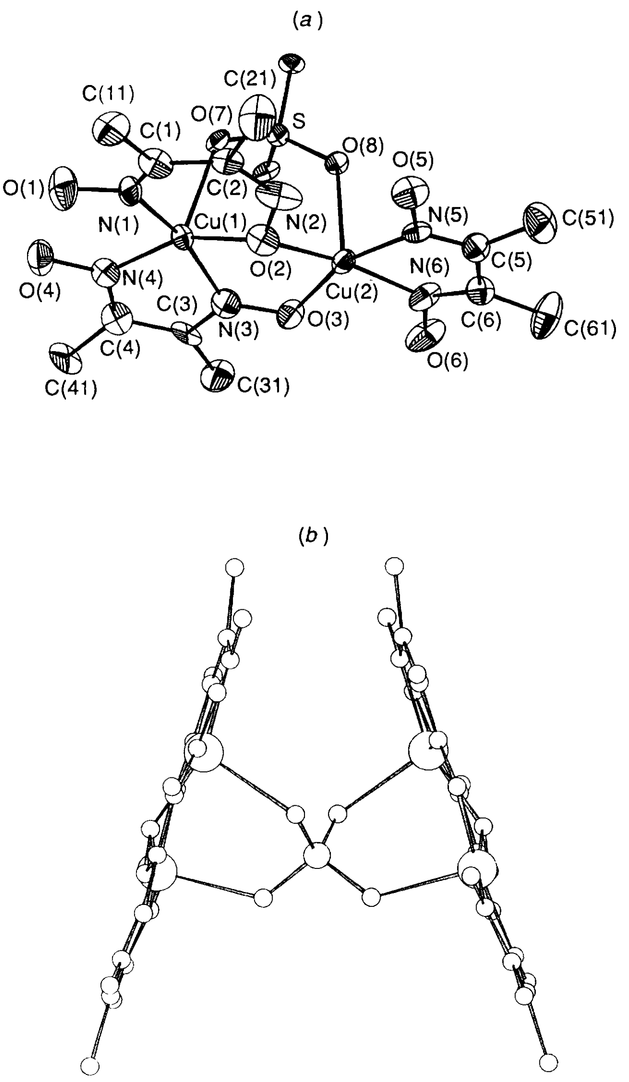

Fig. 1 Perspective view of (*a*) the cationic unit of complex **3** with the numbering system (thermal ellipsoids drawn at the 30% probability level) and (*b*) the resulting tetranuclear neutral unit with the sulfate bridge

least-squares basal planes by 0.259 and 0.161 Å, respectively, in the direction of the axially bound sulfate oxygen atoms. The dihedral angle between the mean basal planes is 13°. The angles subtended at the copper atoms are close to the ideal value of 90° except for the two ligands forming five-membered rings [77.7 and 77.5° for N(3)–Cu(1)–N(4), and N(5)–Cu(2)–N(6), respectively] (see below). The central five-membered Cu(1)O(2)-Cu(2)O(3)N(3) ring is not planar [Cu(1) and Cu(2) are 0.192 and 0.191 Å above the mean plane towards the axially co-ordinated sulfate oxygen atoms and O(2) is 0.245 Å below it].

Charge-balance considerations dictate that there are three oxime protons per dinuclear unit (three dimethylglyoxime ligands). However, no oxime hydrogen atom was found in the X-ray diffraction study. In the light of the reported dimethylglyoxime-containing copper(II) complexes,[1,9,10] it may be anticipated that the O(2) and O(3) oxime protons are ionized and consequently the three oxime hydrogens would be attached to the O(5), O(6) and O(4) or O(1) atoms. The short O(1) ··· O(4) separation (2.42 Å) is consistent with the occurrence of a strong hydrogen bond between these oxygen atoms. This value is even shorter than those observed for hydrogen-bonded oxygen–oxygen oxime distances in the structures of other metal(II)–oxime complexes.[1,11–13] In the light of these considerations, it can be concluded that neutral H_2dmg is co-ordinated to Cu(2), whereas one $Hdmg^-$ and one dmg^{2-} are bound to Cu(1).

The H_2dmg and one of the two dimethylglyoximato ligands co-ordinate to copper(II) ions in a chelating fashion through the oxime nitrogen atoms, each five-membered ring being almost exactly planar [largest deviations 0.041 Å at C(3) for the Cu(1)N(3)C(3)C(4)N(4) ring and 0.042 Å at C(6) for the Cu(2)N(5)C(5)C(6)N(6) ring]. The other dimethylglyoximate ligand is singular because it is co-ordinated to Cu(1) through one nitrogen and one oxygen atom giving a six-membered Cu(1)N(1)C(1)C(2)N(2)O(2) chelate ring. This ring is not planar [Cu(1) and C(2) lie above the mean plane whereas C(1) and O(2) are below it].

The sulfate anion behaves as a μ_4, σ ligand. Each of the four oxygen atoms is bound to one copper ion, bridging the metal ions in the dimeric unit and bridging also both dimers to yield the tetranuclear molecule, as shown in Fig. 1. This co-ordination mode is uncommon for the sulfate anion and only one example of it has been reported for the related SeO_4^{2-}.[14] The sulfate anion has the expected tetrahedral geometry, with the S–O bond lengths and the intra-anion O–S–O bond angles averaging 1.475 Å and 109.2°, respectively.

Two water molecules are also present per dinuclear unit. One [O(9)] occupies a general position and the other [O(10)], with an occupancy of 0.25, is located on a binary axis. The O(7) ··· O(9^{I}) separation [2.80(2) Å] suggests the occurrence of hydrogen bonding between water molecules and sulfate anions (I $1 - x, y, \frac{1}{2} - z$).

The intradimer Cu(1) ··· Cu(2) separation is 3.266(2) Å whereas the shortest interdimer Cu(1) ··· Cu(2^{II}) (II $\frac{1}{2} - x, \frac{1}{2} - y, -z$) distance is 4.011(2) Å.

Infrared Spectra.—The infrared spectra of complexes **1**–**3** are nearly identical, except for the bands corresponding to the anions and lattice water. Complex **2** shows a strong absorption band near 1100 (antisymmetric stretch) and a sharp and split feature at 627, 637 cm^{-1} (antisymmetric bend) of the perchlorate anion, while **3** shows only two strong sulfate bands corresponding to the ν_3 and ν_4 vibrations, located at 1116 and 620 cm^{-1} respectively without splitting, which are consistent with an approximately T_d symmetry for the sulfate anion.[15] The more remarkable feature of the oximato groups is the splitting of the NO stretching (sharp features at 1205 and 1200 cm^{-1}). In the previous paper dealing with the **A** isomer,[1] only a single feature at *ca.* 1200 cm^{-1} was observed for the NO stretching. The presence of two different co-ordination modes of the oxime group in the **B** isomer is consistent with this splitting.

Electronic Spectra.—The electronic absorption spectra in the visible region of methanolic solutions of **1**–**3** are nearly identical

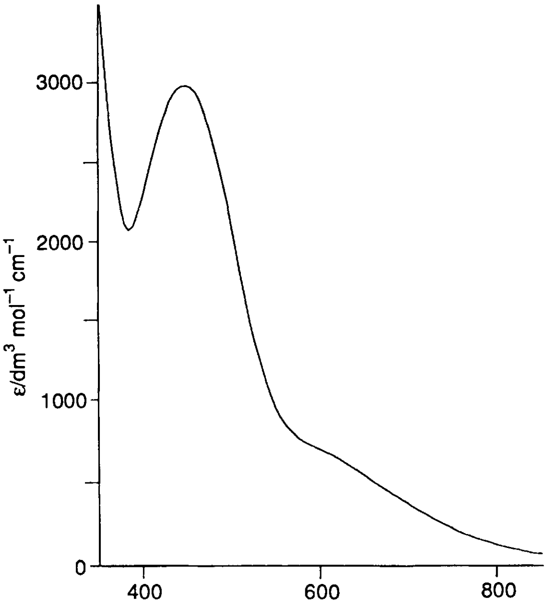

Fig. 2 Visible absorption spectrum of complex **2** in methanol

and were found to obey Beer's law in the concentration range 1×10^{-3}–1×10^{-4} mol dm^{-3}. These solutions contain the dinuclear cation $[Cu_2(dmg)(Hdmg)(H_2dmg)]^+$ and display an intense band near 450 nm with a shoulder at 600 nm (Fig. 2). This spectrum significantly differs from that previously reported for the **A** isomer cation,[1] which only displays a single band centred at 500 nm. These features show that the two structures found in the solid state (Scheme 1) are retained in solution. So, $[Cu_2(dmg)(Hdmg)(H_2dmg)]^+$ can exist in two isomeric forms in solution, **A** and **B**. The formation of the latter is favoured under acidic conditions. For instance, when a methanolic solution of **A** is carefully acidified, the visible spectrum slowly changes: a shift of the intense charge-transfer band from 500 to 450 nm is observed together with the appearance of a shoulder at 600 nm. These changes follow the isomerization of **A** to **B**.

The intense absorption band at 450 nm ($\varepsilon \approx 2 \times 10^3$ dm^3 mol^{-1} cm^{-1}) can be assigned to the ligand-to-metal charge-transfer transition from the bridging oximate oxygen non-bonding orbital to the vacant 3d orbital of the metal ion,[1] by analogy with a detailed study on related dialkoxo-bridged dinuclear copper(II) complexes.[16] The fact that this band is lacking in the visible spectrum of the monomeric $[Cu(Hdmg)_2]$ complex supports this conclusion.

The shoulder near 600 nm in the spectrum of the **B** isomer may originate in a d–d transition. Such an absorption is not seen for the related **A** isomer and therefore it can be tentatively assigned to the CuN_3O chromophore; accordingly, the d–d transition of the CuN_4 chromophore of the **A** isomer would be shifted to lower wavelengths and then masked by the more intense band at 500 nm.

Magnetic Properties.—The room-temperature values of $\chi_M T$ for complexes **1**–**3** (χ_M being the molar magnetic susceptibility for two copper atoms) are very low (*ca.* 0.10 cm^3 mol^{-1} K). Keeping in mind that the expected value for two non-coupled copper(II) ions is about 0.75 cm^3 mol^{-1} K, these data reveal a very strong antiferromagnetic coupling between the copper(II) ions. The temperature dependences of the magnetic susceptibility for all compounds are almost identical. That of **3** is shown in Fig. 3. The magnetic data are adequately described by the Bleaney–Bowers expression[17] with J *ca.* -950 cm^{-1} and $g = 2.05$. The J values of these copper(II) complexes are in the range observed for other dinuclear complexes with a similar bridging network, consisting of one deprotonated oximate and one hydroxo group.[18]

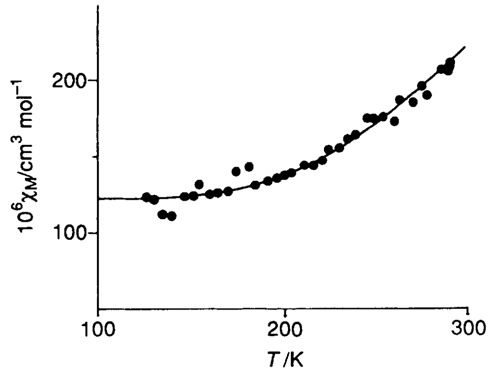

Fig. 3 Temperature dependence of the magnetic susceptibility per two copper atoms for complex **3**

It is worth noting that the $-J$ value reported for $[Cu_2(dmg)(Hdmg)(H_2dmg)]ClO_4{\cdot}1.5H_2O$ (>1000 cm^{-1})[1] is similar or even slightly greater than that obtained for complexes **1**–**3**, in spite of the larger intermetallic distance (3.52 and 3.26 Å for the first compound[1] and **3** respectively). This result shows that the NO group has a remarkable ability to mediate strong antiferromagnetic interactions when it acts as a bridging ligand either through the nitrogen and the oxygen atoms (Scheme 1, **A**) or only through the oxygen atom (Scheme 1, **B**).

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