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Oximato Complexes. Part 1. Solution Study, Synthesis, Structure, Spectroscopic and Magnetic Properties of Polynuclear Copper(II) Complexes containing Dimethylglyoxime†

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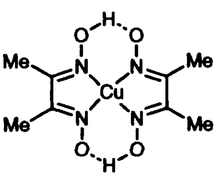
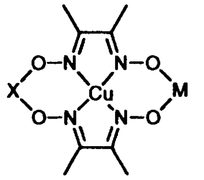
Copper(II) complexes of composition $[Cu_2(Hdmg)_2(H_2dmg)(H_2O)_2][ClO_4]_2{\cdot}H_2O$ **1**, $[Cu_2(dmg)(Hdmg)(H_2dmg)]ClO_4{\cdot}1.5H_2O$ **2** and $[Cu_3(dmg)_2(H_2dmg)_2][ClO_4]_2{\cdot}2H_2O$ **3** (H_2dmg = dimethylglyoxime) were obtained. The crystal structure of complex **1** was solved by single-crystal X-ray diffraction. It crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 15.991(3)$, $b = 11.682(1)$, $c = 14.363(4)$ Å, $\beta = 90.82(5)^\circ$ and $Z = 4$. The structure consists of cationic dinuclear $[Cu_2(Hdmg)_2(H_2dmg)(H_2O)_2]^{2+}$ units, unco-ordinated perchlorate anions and lattice water. The $Cu(H_2dmg)^{2+}$ fragment co-ordinates to the second copper(II) ion through the depronated oximate oxygens of $Cu(Hdmg)_2$ to afford a dinuclear structure doubly bridged by the oximate groups in a *cis* arrangement. The intramolecular $Cu(1) \cdots Cu(2)$ separation is 3.526(4) Å. The configuration about the copper atoms is a distorted square pyramid: the basal plane for Cu(1) comprises two nitrogens of H_2dmg and two oximate oxygens whereas that of Cu(2) is formed by four nitrogens of two $Hdmg^-$ groups; a water molecule occupies the apical position in both cases. Variable-temperature magnetic susceptibility measurements (50–300 K) on complexes **1**–**3** revealed the occurrence of a very strong intramolecular antiferromagnetic interaction through the oximate bridges. The formation of mononuclear, dinuclear and trinuclear copper(II) dimethylglyoxime complexes have been observed by spectrophotometry in ethanolic solutions of copper(II) perchlorate and $[Cu(Hdmg)_2]$. A rational scheme accounting for the nature of the existing species has been proposed in the light of the coupled solution–solid state studies.

One of the best strategies to design and synthesize polynuclear species is the use of mononuclear complexes as ligands, *i.e.* metal complexes which contain potential donor groups for another metal ion.[1] A good example of this is represented by the copper(II)oxamidato complexes.[2] This family of complexes has played a relevant role in molecular magnetism because of the remarkable efficiency of the oxamidate bridge to transmit electronic effects between the metal ions. The bis(oximato) copper(II) complexes, such as bis(dimethylglyoximato)copper(II), $[Cu(Hdmg)_2]$, would be suitable candidates because they can co-ordinate to another metal ion through the deprotonated oximate oxygens to afford polynuclear species and the oximate bridge is able to mediate stronger magnetic interactions than the oxamidate bridge. Although these features were known some years ago, the monomeric copper(II) oximato complexes have been used as precursors of homo- and hetero-polynuclear species only very recently.[3–5] In general, $[Cu(Hdmg)_2]$ can act as a chelating or bis(chelating) ligand after the loss of either one or two protons, respectively. Taking into account the versatility and interest of glyoximes in co-ordination chemistry and molecular magnetism, we have undertaken an investigation of their co-ordinating ability towards transition-metal ions both in solution and in the solid state.

In this paper, we present our first results concerning the investigation into complex formation between $[Cu(Hdmg)_2]$ and copper(II) perchlorate in ethanolic solution. Spectrophotometric data analysis has allowed us to determine the number and nature of the existing species in solution. The synthesis of these species as their perchlorate salts and their spectroscopic and magnetic characterization are reported together with the structure of one of them, namely the dinuclear complex $[Cu_2(Hdmg)_2(H_2dmg)(H_2O)_2][ClO_4]_2{\cdot}H_2O$. As far as we are aware, it is the first example in which the monomeric $[Cu(Hdmg)_2]$ complex acts as a chelating ligand without deprotonation.



$[Cu(Hdmg)_2]$



X = H or M

Experimental

Materials.—Copper(II) perchlorate hexahydrate, sodium perchlorate and dimethylglyoxime (H_2dmg) were of reagent grade purchased from commercial sources and were used as received. Bis(dimethylglyoximato)copper(II) was prepared in good yield by reaction of freshly made copper(II) hydroxide with dimethylglyoxime (1 : 2 molar ratio) in methanol under reflux continuous stirring for 0.5 h. The reagent $Cu(H_2dmg)Cl_2$ was obtained by literature methods.[6]

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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 = SI × $10^6/4\pi$.

Synthesis of the Complexes.—$[Cu_2(Hdmg)_2(H_2dmg)(H_2O)_2][ClO_4]_2{\cdot}H_2O$ **1**. Black purple prisms of complex **1** suitable for X-ray measurements were obtained by slow evaporation of concentrated ethanolic solutions of copper(II) perchlorate hexahydrate and dimethylglyoxime (Cu^{II}: H_2dmg 5:1 molar ratio). The crystals were collected and air-dried (Found: C, 19.50; H, 3.60; N, 10.70. Calc. for $C_{12}H_{28}Cl_2Cu_2N_6O_{17}$: C, 19.85; H, 3.90; N, 11.55%).

$[Cu_2(dmg)(Hdmg)(H_2dmg)]ClO_4{\cdot}1.5H_2O$ **2**. Complex **2** was obtained by slow evaporation of methanolic solutions containing $[Cu(Hdmg)_2]$ and copper(II) perchlorate hexahydrate in a 3:1 molar ratio with continuous stirring under gentle reflux for 1 h. Black-purple prisms thus formed were collected and recrystallized from methanol (Found: C, 24.05; H, 3.80; N, 14.00. Calc. for $C_{12}H_{26}ClCu_2N_6O_{11.5}$: C, 24.05; H, 4.05; N, 14.05%).

$[Cu_3(dmg)_2(H_2dmg)_2][ClO_4]_2{\cdot}2H_2O$ **3**. Complex **3** was obtained by slow evaporation of ethanolic solutions of $[Cu(Hdmg)_2]$ and copper(II) perchlorate hexahydrate (2:1 molar ratio) which were saturated in sodium perchlorate. The yield is improved when a slight excess of Cu^{II} is used. The black-purple microcrystalline product was filtered off, washed with a small portion of cold absolute ethanol and diethyl ether, and air-dried (Found: C, 22.05; H, 3.30; N, 11.85. Calc. for $C_{16}H_{28}Cl_2Cu_3N_8O_{16}$: C, 21.70; H, 3.65; N, 12.65%).

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 1750 FTIR spectrophotometer as KBr pellets and UV/VIS solution spectra on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic susceptibility measurements on complexes **1**–**3** were carried out at 50–300 K with a fully-automatized AZTEC DSM8 pendulum-type susceptometer[7] 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[8] as -275×10^{-6}, -221×10^{-6} and -313×10^{-6} emu mol^{-1}, respectively. Magnetic susceptibility data were also corrected for temperature-independent paramagnetism (60×10^{-6} emu per Cu^{II}) and magnetization of the sample holder.

Crystal Structure Determination.—Diffraction data for complex **1** were collected at 291 K with a Philips PW 1100 four-circle diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Cell data and details of the experimental conditions are given in Table 1. The unit-cell parameters were derived from the least-squares refinement of 25 well centred reflections ($11 < \theta < 12°$). The intensities of two reference reflections, monitored every 2 h throughout the data collection, showed no sign of crystal deterioration. The data collection showed systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) which uniquely define the monoclinic space group $P2_1/n$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was performed using DIFABS.[9]

The structure was solved by direct methods[10] followed by successive Fourier syntheses and least-squares refinements (CRYSTALS)[11] carried out in four blocks (159 parameters). All non-hydrogen atoms were given isotropic thermal parameters due to the low number of data collected (crystals are very small). All hydrogen atoms, except three of the four oxime hydrogens and one from the water of crystallization, were either found on a Fourier difference map or geometrically located and their positions were not refined. They were given an overall isotropic thermal parameter. Atomic scattering factors and corrections for anomalous dispersion were taken from ref. 11. The final values of the discrepancy indices R and R' were 0.073 and 0.083, respectively; $\Sigma w(\|F_o| - |F_c\|)^2$ was minimized using unit weights. In the final difference map the residual maxima and minima were 0.85 and -0.60 e Å^{-3}, respectively. The goodness of fit is 0.2. All calculations were carried out on a VAX 725 computer. Fractional atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively.

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

Formula	$C_{12}H_{28}Cl_2Cu_2N_6O_{17}$
M	726.4
Crystal size/mm	$0.40 \times 0.35 \times 0.20$
Space group	$P2_1/n$
a/Å	15.991(3)
b/Å	11.682(1)
c/Å	14.363(4)
β/°	90.82(5)
U/Å^3	2683(2)
Z	4
D_c/g cm^{-3}	1.80
μ(Mo-Kα)/cm^{-1}	18.1
$F(000)$	1480
Scan type	ω–2θ
Scan width	$1.20 + 0.34 \tan\theta$
θ range/°	1–20
No. of measured reflections	2462
No. of unique reflections[a]	1130
No. of refined parameters	159
$R\{= [\Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|]\}$	0.073
$R'\{= [\Sigma w(\|F_o| - |F_c\|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$[b]	0.083

[a] $I \geq 3\sigma(I)$. [b] Unit weights.

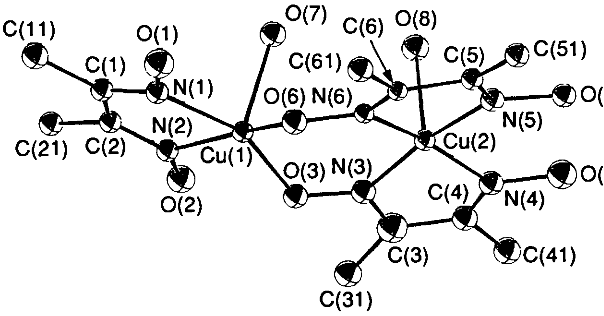


Fig. 1 ORTEP[12] view of the cationic unit of complex **1** with the numbering system. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Description of the Structure of Complex **1**.—The complex consists of a dinuclear cation $[Cu_2(Hdmg)_2(H_2dmg)(H_2O)_2]^{2+}$, two unco-ordinated perchlorate anions and a crystallization water molecule. The $Cu(Hdmg)_2$ fragment co-ordinates to the $Cu(H_2dmg)^{2+}$ unit through the oximate oxygens to afford a dinuclear skeleton doubly bridged by oximate groups in a *cis* arrangement. A perspective view of the dinuclear entity with the atom-numbering scheme is depicted in Fig. 1.

The co-ordination geometry around both copper(II) ions is best described as distorted square pyramidal. Two oxime nitrogen atoms and two oximate oxygen atoms at Cu(1), $Cu(1)N_2O_3$, and four oxime nitrogen atoms at Cu(2), $Cu(2)N_4O$, build the corresponding basal planes; the fifth co-ordination position of the square pyramids about the coppers is occupied by weakly-bound water molecules [2.26(2) and 2.32(2) Å for Cu(1)–O(7) and Cu(2)–O(8), respectively]. For the basal plane of Cu(1), the average Cu–O bond distance (1.93 Å) is considerably shorter than that of Cu–N (2.01 Å) as expected from electronegativity considerations. The four

Table 2 Positional parameters for complex **1** with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.9285(2)	0.1120(3)	0.9123(2)	C(5)	1.040(1)	0.464(2)	0.741(2)
Cu(2)	0.9587(2)	0.2572(3)	0.7003(2)	C(6)	1.047(1)	0.393(2)	0.825(1)
N(1)	0.932(1)	0.120(2)	1.054(1)	C(11)	0.879(2)	0.054(2)	1.205(2)
N(2)	0.867(1)	−0.026(2)	0.955(1)	C(21)	0.788(2)	−0.126(2)	1.077(2)
N(3)	0.929(1)	0.097(2)	0.713(1)	C(31)	0.888(2)	−0.091(3)	0.637(2)
N(4)	0.935(1)	0.213(2)	0.569(1)	C(41)	0.880(2)	0.063(2)	0.462(2)
N(5)	0.998(1)	0.411(2)	0.675(1)	C(51)	1.085(2)	0.573(2)	0.732(2)
N(6)	1.008(1)	0.297(2)	0.823(1)	C(61)	1.091(2)	0.438(2)	0.912(2)
O(1)	0.976(1)	0.208(2)	1.101(1)	Cl(1)	0.6719(4)	0.0772(7)	0.6576(5)
O(2)	0.828(1)	−0.096(2)	0.892(1)	O(9)	0.709(1)	0.047(2)	0.744(1)
O(3)	0.928(1)	0.036(1)	0.791(1)	O(10)	0.726(1)	0.147(2)	0.603(1)
O(4)	0.938(1)	0.283(2)	0.492(1)	O(11)	0.661(2)	−0.029(3)	0.607(2)
O(5)	0.993(1)	0.466(1)	0.589(1)	O(12)	0.597(2)	0.124(3)	0.664(2)
O(6)	1.009(1)	0.230(1)	0.901(1)	Cl(2)	0.1964(4)	0.2449(7)	0.6358(5)
O(7)	0.809(1)	0.216(1)	0.898(1)	O(13)	0.120(1)	0.197(2)	0.636(2)
O(8)	0.819(1)	0.306(2)	0.719(1)	O(14)	0.197(1)	0.360(2)	0.601(2)
C(1)	0.889(2)	0.050(2)	1.099(2)	O(15)	0.223(2)	0.257(3)	0.725(2)
C(2)	0.847(1)	−0.033(2)	1.039(2)	O(16)	0.255(2)	0.180(2)	0.585(2)
C(3)	0.909(2)	0.040(3)	0.635(2)	O(17)	0.368(2)	0.912(3)	0.077(2)
C(4)	0.909(2)	0.111(3)	0.556(2)				

Table 3 Selected bond distances (Å) and angles (°) for complex **1**

Cu(1)–N(1)	2.03(2)	Cu(2)–N(3)	1.94(2)
Cu(1)–N(2)	1.99(2)	Cu(2)–N(4)	1.99(2)
Cu(1)–O(3)	1.96(2)	Cu(2)–N(5)	1.93(2)
Cu(1)–O(6)	1.89(2)	Cu(2)–N(6)	1.98(2)
Cu(1)–O(7)	2.26(2)	Cu(2)–O(8)	2.32(2)
N(1)–Cu(1)–N(2)	74.9(8)	N(3)–Cu(2)–N(4)	78.2(9)
N(1)–Cu(1)–O(3)	155.8(8)	N(3)–Cu(2)–N(5)	172.6(9)
N(1)–Cu(1)–O(6)	92.4(8)	N(3)–Cu(2)–N(6)	103.8(9)
N(2)–Cu(1)–O(3)	84.8(8)	N(4)–Cu(2)–N(5)	97.0(9)
N(2)–Cu(1)–O(6)	163.0(8)	N(4)–Cu(2)–N(6)	167.5(8)
O(3)–Cu(1)–O(6)	104.4(7)	N(5)–Cu(2)–N(6)	79.6(8)
O(7)–Cu(1)–N(1)	94.2(7)	O(8)–Cu(2)–N(3)	89.4(7)
O(7)–Cu(1)–N(2)	92.3(7)	O(8)–Cu(2)–N(4)	90.5(7)
O(7)–Cu(1)–O(3)	99.7(6)	O(8)–Cu(2)–N(5)	96.4(7)
O(7)–Cu(1)–O(6)	100.0(7)	O(8)–Cu(2)–N(6)	101.9(7)

equatorial bonds to Cu(2) lie in the range 1.93–1.99 Å and they are common for in-plane Cu–N(oxime) distances.[1j,3a,13] The four equatorial donor atoms around each copper are nearly coplanar [maximum deviation is 0.026 at N(2) and 0.055 Å at N(4)]. The Cu(1) and Cu(2) atoms stick out of their mean least-squares basal planes by 0.240 and 0.158 Å in the direction of the axially-bound water molecules. The dihedral angle between the mean basal planes is 26.1 °. Large deviations from the ideal value of 90 ° are observed in the angles subtended at the copper atoms due to the occurrence of five- [74.9(8), 78.2(9) and 79.6(8)° for N(1)–Cu(1)–N(2), N(3)–Cu(2)–N(4) and N(5)–Cu(2)–N(6), respectively] and six-membered [104.4(7) and 103.8(9)° for O(3)–Cu(1)–O(6) and N(3)–Cu(2)–N(6), respectively] chelate rings. The central six-membered Cu(1)O(3)N(3)Cu(2)N(6)O(6) ring in this species exhibits a boat conformation, Cu(1) and Cu(2) being 0.373 and 0.227 Å above the mean plane towards the axially-co-ordinated water molecules.

Charge-balance considerations dictate that two of the six protons from the three dimethylglyoxime ligands have been lost in forming the complex. However, only one oxime hydrogen [H(5)] was found. In the light of the reported dimethylglyoxime-containing copper(II) complexes,[3a,4] it may be anticipated that the O(3) and O(6) oxime protons are ionized [O(3) ··· O(6) 3.00 Å] and consequently, the remaining three oxime hydrogens would be attached to the O(1), O(2) and O(4) atoms. In fact, H(4) is most likely involved in hydrogen bonding between O(4) and O(5) because of the short O(4) ··· O(5) separation [2.69 Å]. This value is similar to that observed for hydrogen-bonded oxygen–oxygen oxime distances in structures of other metal(II)–oxime complexes.[13–15] From these considerations, it can be concluded that neutral H_2dmg is co-ordinated to Cu(1), whereas two monodeprotonated $Hdmg^-$ groups are bound to Cu(2).

The H_2dmg and $Hdmg^-$ ligands co-ordinate to the copper(II) ions in a chelating fashion through the oxime nitrogen atoms, each five-membered ring being almost exactly planar [largest deviation 0.081 Å at N(2) for the Cu(1)N(1)C(1)C(2)N(2) ring]. The six $C(sp^2)$–$C(sp^3)$ bond lengths average 1.53 Å, in good agreement with a carbon–carbon single bond value. However, the related three $C(sp^2)$–$C(sp^2)$ single bond lengths average 1.45 Å, a somewhat reduced value compared to the average $C(sp^2)$–$C(sp^3)$ bond length because of the smaller single-bond radius for carbon in trigonal hybridization. As far as the carbon–nitrogen bonds are concerned, the average values for the H_2dmg (1.26 Å) and $Hdmg^-$ groups (1.30 Å) reveal a significant percentage of double-bond character in both ligands. Finally, the nitrogen–oxygen bonds lie in the range 1.32(2)–1.41(2) Å.

The perchlorate anions have the expected tetrahedral geometry, with the Cl–O bond lengths and the intraanion O–Cl–O bond angles averaging 1.39 Å and 109.4 °, respectively. The value of the O(7) ··· O(8) separation [2.79(2) Å] suggests the occurrence of hydrogen bonding between both water molecules, interactions that stabilize their *cis* arrangement with regard to the mean plane of the dinuclear complex. Other probable hydrogen bonds occur between O(5) ··· O(17^{II}) [2.46(3) Å] (II = $\frac{1}{2} + x, \frac{3}{2} - y, z - \frac{1}{2}$), O(8) ··· O(10) [2.89(3) Å] and O(8) ··· O(9^{III}) [2.90(3) Å] (III = $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$). The intramolecular Cu(1) ··· Cu(2) separation is 3.526(4) Å whereas the shortest intermolecular Cu(1) ··· Cu(2^{I}) (I = $2 - x, 1 - y, 1 - z$) distance is 4.272(6) Å.

Infrared Spectra.—Infrared spectra of complexes **1**–**3** have been compared with that of $[Cu(Hdmg)_2]$ and $Cu(H_2dmg)Cl_2$ in order to establish the co-ordination modes of the oxime ligands in **1**–**3**. The more relevant OH, C=N and NO absorption bands are listed in Table 4.

The compound $[Cu(Hdmg)_2]$ shows two IR peaks near 2600 and 862 cm^{-1} which may be assigned to the ν(OH) stretching and γ(OH) (out-of-plane) deformation modes of the hydrogen-bonded O–H ··· O group, respectively.[16] The lack of these bands in the spectra of structurally characterized oximate polynuclear complexes which were synthesized using $[Cu(Hdmg)_2]$ as a ligand, have been attributed to the breakdown of the hydrogen bond present in $[Cu(Hdmg)_2]$ by its full deprotonation {to afford the $[Cu(dmg)_2]^{2-}$ anion},[3–5] as

Table 4 Structurally important IR data (cm ^{1})^{a}

Compound	ν(OH)	ν(C=N)	ν(NO)	γ(OH)
$[Cu(Hdmg)_2]$	2600m (br)	1535s (sp)	1210s (sp)	862m (sp)
$[Cu(H_2dmg)Cl_2]$	3300, 3216s (sp)	1395s (sp)	1087, 1064s (sp)	
1	*b*	1576w (br)	1206m (sp)	907m (sp)
	b	1383s (sp)	*c*	
2	2600m (br)	1584m (sp)	1208s (sp)	871w (br)
	b	1381s (sp)	*c*	
3		1584s (sp)	1202s (sp)	
	3603, 3527m (sp)	1378m (sp)	*c*	

^{a} sp = sharp. ^{b} Obscured by superposition with a strong band in the region 3429–3467 cm^{-1} from water. ^{c} Obscured by superposition with a very strong band near 1090–1100 cm^{-1} from perchlorate anion (antisymmetric stretch).

observed in complex **3**. On the other hand, the presence of these bands in complexes **1** and **2**, showing nearly the same shape although lower intensity, clearly indicates the persistence of a hydrogen-bonded structure in these complexes.

Additional structural information comes from the observation of the ν(CN) stretching vibration in $[Cu(Hdmg)_2]$ and $Cu(H_2dmg)Cl_2$. It is located at 1535 cm^{-1} in the former compound whereas it appears at 1395 cm^{-1} in the latter one. Infrared spectra of complexes **1**–**3** exhibit both ν(CN) vibrations with varying relative intensities near the positions quoted above for $[Cu(Hdmg)_2]$ and $Cu(H_2dmg)Cl_2$. That is what could be expected from the structure of **1** (Fig. 1), in which the $[Cu(H_2dmg)]^{2+}$ unit is present, and by logical extrapolation the same may well apply to complexes **2** and **3**. These IR data together with the structure of **1** allow us to propose dinuclear (**B**) and trinuclear (**C**) structures for complexes **2** and **3**, respectively (see Scheme 1). Finally, it is noteworthy that the ν(C=N) and ν(NO) vibrations are shifted towards the higher and lower frequency regions, respectively, when $[Cu(Hdmg)_2]$ co-ordinates to metal ions to yield polynuclear metal complexes.

Magnetic Properties.—At room temperature the values of $\chi_M T$ (where χ_M is the molar magnetic susceptibility) for complexes **1** and **2** are 0.040 and 0.038 cm^3 mol^{-1} K, respectively. They vanish on cooling. These low values of $\chi_M T$ are indicative of a very strong antiferromagnetic coupling between the copper(II) ions and the spin coupling is practically complete at room temperature. Due to their dimeric nature, the magnetic data were treated with a simple Bleaney–Bowers expression obtained from the spin Hamiltonian $\hat{H} = -J\hat{S}_A \cdot \hat{S}_B$. In the light of the reduced values of χ_M for complexes **1** and **2** at room temperature, it is clear that the diamagnetic susceptibility as well as the temperature-independent paramagnetism (t.i.p) are of the same order of magnitude, and consequently, accurate values of J and g cannot be obtained. For typical values of the diamagnetic susceptibility (Pascal's constants) and t.i.p. (60 × 10^{-6} cm^3 mol^{-1} per Cu^{II}), a least-squares fit of the experimental data leads to $J \approx -1000$ cm^{-1} and $g \approx 2.1$ for both compounds. The exchange integral obtained is similar or even stronger than that reported for other non-centrosymmetric oximate-bridged dicopper(II) complexes (such as **B**).[1j] The singlet–triplet energy gap for these complexes is *ca.* 850 cm^{-1}. This lower value of $-J$ could be due to their bent structure at the edge. In fact, this distortion would lead to a decrease in the overlap between the $d_{x^2-y^2}$ magnetic orbitals centered on the copper(II) ions. A series of centrosymmetric oximate-bridged dicopper(II) systems (such as **D**) where a coplanar structure is retained have been shown to be perfectly spin-coupled at room temperature ($|J| > 1000$ cm^{-1}).[17,18] The effect in these complexes is even more pronounced than in complex **1**, because the two magnetic orbitals have the same energy when the dimer is centrosymmetric, thus favouring their overlap.

The variation of $\chi_M T$ with temperature for complex **3** is depicted in Fig. 2. Its value at room temperature (*ca.* 0.65 cm^3 mol^{-1} K) is very low with respect to what is expected for three uncoupled copper(II) ions. As the temperature is lowered $\chi_M T$ decreases and reaches a plateau (0.42 cm^3 mol^{-1} K) at 90 K which corresponds well to the spin-only value expected for one unpaired electron. These results reveal that a very strong antiferromagnetic coupling between the copper(II) ions operates in complex **3**, a spin-doublet state being achieved at liquid-nitrogen temperature. The magnetic data are consistent with the assumed trinuclear nature of complex **3** and are analysed on the basis of the isotropic model $\hat{H} = -\Sigma J_{ij}\hat{S}_i \cdot \hat{S}_j$ for a linear trinuclear Cu^2–Cu^1–Cu^3 system assuming that the exchange integrals for the neighbouring copper ions are identical and neglecting the exchange between the terminal copper ions. A least-squares fit to the corresponding equation leads to $J = -360$ cm^{-1}, $g = 2.12$. The agreement factor defined as $\Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma(\chi_M T)_{obs}{}^2$ is then equal to 1.2 × 10^{-4}. The magnitude of the antiferromagnetic interaction in complex **3** is smaller than that of complexes **1** and **2**. This reduction of the exchange coupling is common to other trinuclear oximate-bridged copper(II) complexes[1i,3a,4] and it could be due to greater structural distortions in the trimers with respect to the related dimers.

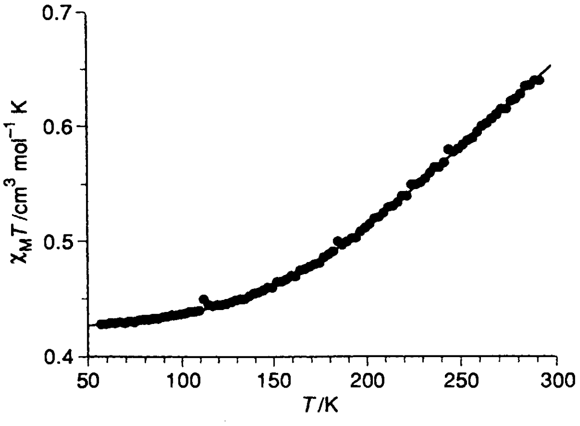


Fig. 2 Temperature dependence of $\chi_M T$ for complex **3**

Spectrophotometric Study.—Spectrophotometric data for a series of ethanolic solutions containing 2 × 10^{-4} mol dm^{-3} $[Cu(Hdmg)_2]$ and variable amounts of copper(II) perchlorate were treated to determine the number and nature of the species existing in solution. A change of colour from brown to red occurs upon addition of the copper(II) perchlorate to the initial solutions of $[Cu(Hdmg)_2]$. The shoulder at 470 nm of $[Cu(Hdmg)_2]$ vanishes and a new band appears at 500 nm [Fig. 3(*a*)]. The intensity of this band increases on addition of Cu^{2+} and attains its maximum value for a 1:2 Cu^{2+}:$[Cu(Hdmg)_2]$ molar ratio [Fig. 3(*b*)]. Further addition of Cu^{2+} is accompanied by a change in colour from red to pale green, the absorption band at 500 nm vanishing and a new absorption

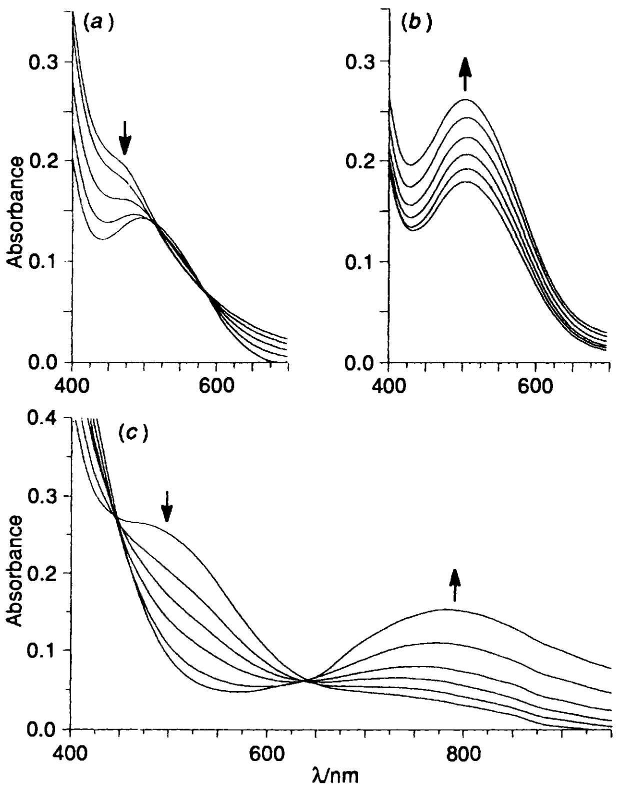


Fig. 3 Visible absorption spectra of ethanolic solutions of $[Cu(Hdmg)_2]$ (2×10^{-4} mol dm^{-3}) and variable amounts of copper(II) perchlorate: $0 \leqslant Cu^{2+}:[Cu(Hdmg)_2] \leqslant 1:3$ (*a*), $1:3 < Cu^{2+}:[Cu(Hdmg)_2] \leqslant 1:2$ (*b*) and $Cu^{2+}:[Cu(Hdmg)_2] > 1:2$ (*c*)

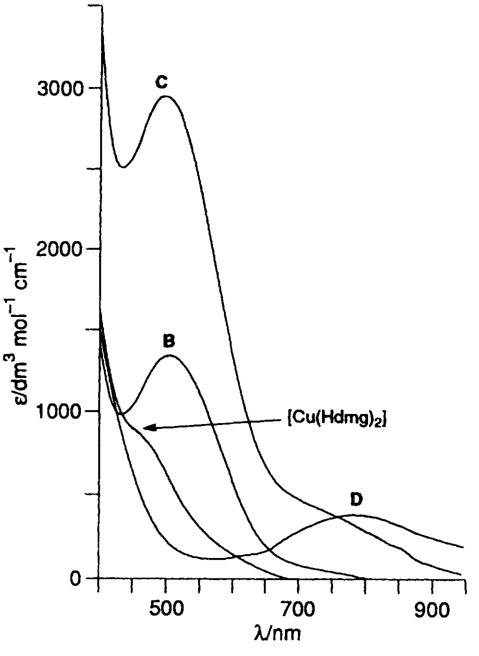
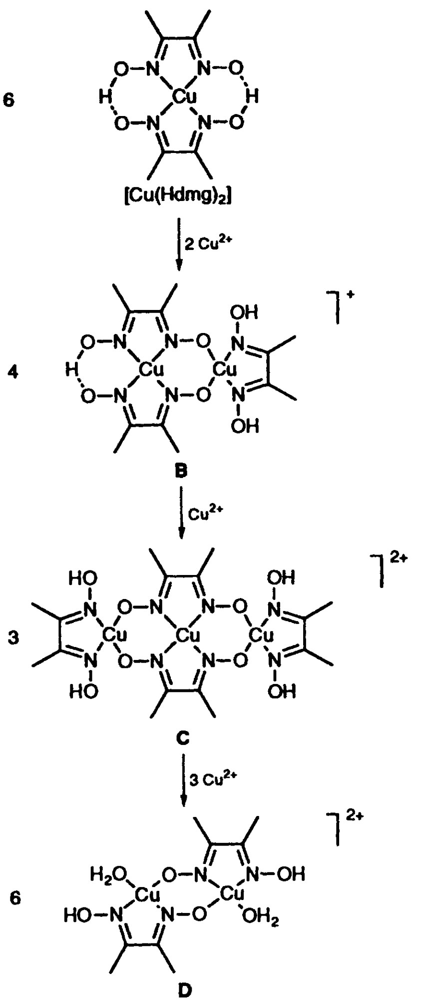


Fig. 4 Electronic spectra of the species $[Cu(Hdmg)_2]$ **B**, **C** and **D** (see Scheme 1)



Scheme 1

arising at 790 nm [Fig. 3(*c*)]. The intensity of this latter band increases as the $Cu^{2+}:[Cu(Hdmg)_2]$ molar ratio is increased. Taking into account that ethanolic solutions of Cu^{2+} absorb at $\lambda > 650$ nm ($\lambda_{max} = 790$ nm, $\varepsilon = 10$ dm^3 mol^{-1} cm^{-1}), the corrected values of absorbance were used in this wavelength range.

The occurrence of isosbestic points in the $0 \leqslant Cu^{2+}:[Cu(Hdmg)_2] \leqslant 1:3$ [Fig. 3(*a*)] and $Cu^{2+}:[Cu(Hdmg)_2] > 1:2$ [Fig. 3(*c*)] molar ratio ranges is indicative of the presence of two absorbing species. No isosbestic point is observed in the range $1:3 < Cu^{2+}:[Cu(Hdmg)_2] \leqslant 1:2$ [Fig. 3(*b*)]. However, linear plots were obtained by applying Coleman *et al.*'s test[19] to the spectrophotometric data of each concentration range assuming the coexistence of two absorbing species. Moreover, solutions containing variable concentrations of $[Cu(Hdmg)_2]$ and Cu^{2+} in 3:1 and 2:1 molar ratios, strictly obey the Beer–Lambert law for the absorption maxima at 500 nm ($\varepsilon = 1330$ and 2940 dm^3 mol^{-1} cm^{-1}, respectively) (Fig. 4). Consequently, relatively strong complexes of 3:1 and 2:1 $[Cu(Hdmg)_2]:Cu^{2+}$ stoichiometry are formed. The new species occurring at $Cu^{2+}:[Cu(Hdmg)_2] > 1:2$ should be a weak complex because its total formation was not observed up to as high a $Cu^{2+}:[Cu(Hdmg)_2]$ molar ratio as 25:1 (Fig. 4). The molar absorption coefficient of this species at 790 nm will be greater than 400 dm^3 mol^{-1} cm^{-1}. In the light of these spectral data the following pattern of complex formation is proposed [equations (1)–(3)] (Scheme 1). In fact, species **B** and **C** have been isolated

$$3[Cu(Hdmg)_2] + Cu^{2+} \rightleftharpoons 2\mathbf{B} \qquad (1)$$

$$2[Cu(Hdmg)_2] + Cu^{2+} \rightleftharpoons \mathbf{C} \qquad (2)$$

$$[Cu(Hdmg)_2] + Cu^{2+} \rightleftharpoons \mathbf{D} \qquad (3)$$

from their solutions and they correspond to complexes **2** and **3**, respectively (see Experimental). The stoichiometry of species **D** could not be determined from spectrophotometric data. We have proposed a species of 1:1 stoichiometry such as **D** {or the related monomeric $[Cu(Hdmg)]^+$}, whose stability would be much lower than that of the trimer **C** and correspondingly a great excess of Cu^{2+} would be required to achieve its total formation. Although the fully protonated species $[Cu(H_2dmg)]^{2+}$ also exhibits an absorption maximum at 790 nm, it can be discarded because its molar absorption coefficient at this wavelength is *ca.* 50 $dm^3\ mol^{-1}\ cm^{-1}$. The reaction of $[Cu(Hdmg)_2]$ with Cu^{2+} will lead to the formation of $[Cu(Hdmg)]^+$. The coexistence of both species is at the heart of the formation of the polynuclear species **2** and **3** described above where H_2dmg acts as an end-cap ligand. The formation of complex **1** does not occur because it implies an addition of H^+. Formally, this species issues from the protonation of complex **2** [equation (4)].

$$[Cu_2(dmg)(Hdmg)(H_2dmg)]^+ + H^+ \rightleftharpoons [Cu_2(Hdmg)_2(H_2dmg)]^{2+} \quad (4)$$

To conclude, in this work we show that $[Cu(dmg)(Hdmg)]^-$ and even $[Cu(Hdmg)_2]$ are able to co-ordinate to metal ions in a chelating fashion whereas $[Cu(dmg)_2]^{2-}$ can act as a bis(chelating) ligand.[3-5]

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