

## Formation in Solution, Synthesis, Crystal Structure, and Magnetic Properties of $\mu$ -Hydroxo- $\mu$ -perchlorato-bis[(diethylenetriamine)perchloratocopper(II)]<sup>†</sup>

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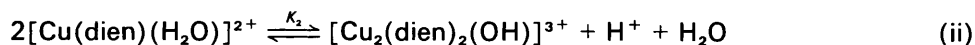
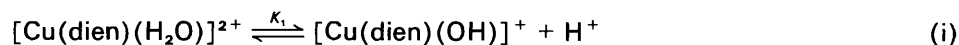
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A new binuclear complex  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  (dien = diethylenetriamine) has been synthesized and its crystal and molecular structure determined by X-ray diffraction. It crystallizes in the monoclinic space group  $P2_1$ , with  $Z = 2$ ,  $a = 11.896(7)$ ,  $b = 9.424(3)$ ,  $c = 11.468(7)$  Å, and  $\beta = 117.97(4)^\circ$ . The structure consists of discrete binuclear molecules where the two copper(II) ions are bridged by a single hydroxo group with a  $\text{Cu}(1)\text{—OH—Cu}(2)$  angle of  $128.1(4)^\circ$ , the intramolecular copper—copper separation being  $3.435(1)$  Å. A pseudo-mirror plane passes through the copper atoms, hydroxo bridge, and central nitrogen atom of the dien ligands. The co-ordination geometry around each copper(II) ion is approximately elongated tetragonal octahedral. The hydroxo group and the three nitrogen atoms of dien occupy the equatorial sites. The apical sites are filled by perchlorate oxygen atoms. Two perchlorate anions act as unidentate ligands whereas the third bridges the copper atoms through one of its oxygen atoms. The solid-state magnetic behaviour has been investigated in the temperature range 4.2—300 K. There is a large antiferromagnetic interaction between the two copper(II) ions [ $J(\text{singlet-triplet gap}) = -374 \text{ cm}^{-1}$ ]. The formation of hydroxo complexes of  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$  has been studied by potentiometry in aqueous solutions [equations (i) and (ii);  $\log K_1 = -9.168(2)$  and  $\log K_2 = -8.26(1)$  (25 °C, 0.1 mol dm<sup>-3</sup> NaNO<sub>3</sub>)].



Interest in binuclear copper(II) complexes has focussed mainly on the study of the exchange coupling between the two paramagnetic centres ( $S = \frac{1}{2}$ ) by bulk susceptibility and electron spin resonance (e.s.r.) measurements. Successful correlations between structural and electronic parameters and the extent of coupling have been established on the basis of such studies.<sup>1</sup> The best established correlation has been observed with the dihydroxo-bridged copper(II) complexes.<sup>2</sup> In this case, a linear relationship has been observed between the singlet-triplet energy gap,  $J$ , and the  $\text{Cu—OH—Cu}$  bridging angle,  $\theta$ . E.s.r. studies have been performed on such complexes in order to check a similar relationship for the anisotropic exchange.<sup>3,4</sup>

While numerous examples of di- $\mu$ -hydroxo binuclear copper(II) complexes are known, copper(II) complexes containing a single hydroxo bridge are rare.<sup>5–10</sup> The available X-ray diffraction structures show distorted octahedral, square-pyramidal, and trigonal-bipyramidal stereochemistries around the copper(II) ion. Antiferromagnetic interaction is predicted on the basis of the relatively large  $\text{Cu—OH—Cu}$  angles observed, and values for the singlet-triplet gap ranging from  $-322$  to  $-850 \text{ cm}^{-1}$  have been measured. It would be desirable to extend the correlation found in the di- $\mu$ -hydroxo binuclear copper(II) complexes to this series. Furthermore it is well known that binuclear copper(II) complexes are implicated in a wide variety of biochemical processes with strongly antiferromagnetically coupled di-copper(II) centres present in met- and oxy-haemocyanine,

laccase, and related proteins.<sup>11</sup> Tyrosine or oxo oxygen atoms have been proposed as bridging ligands but their precise nature remains unknown.

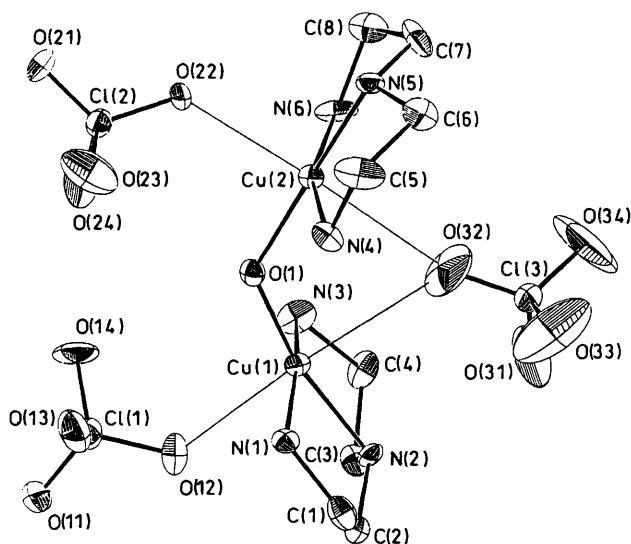
Herein we report the synthesis, crystal structure, and magnetic properties of a new binuclear diethylenetriamine (dien)-containing copper(II) complex bridged by a single hydroxo group,  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$ . The stability constants of the hydroxo complexes in aqueous solution are also reported.

### Experimental

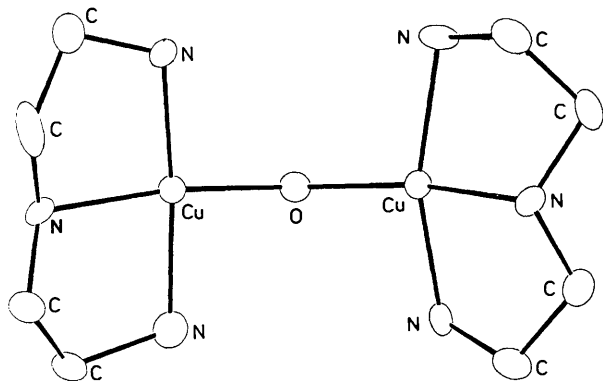
**Synthesis.**—An aqueous solution (10 cm<sup>3</sup>) of dien (1 mmol) was added, with stirring, to an aqueous solution (15 cm<sup>3</sup>) containing  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1 mmol). The resulting blue solution turned blue-violet on adding  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  (ca. 4 mmol) dissolved in water (20 cm<sup>3</sup>). Dark blue-violet crystals of  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  were obtained by slow evaporation at room temperature. They were filtered off, washed with cold water, and dried *in vacuo* over  $\text{CaCl}_2$  (Found: C, 15.25; H, 4.25; Cl, 15.60; Cu, 19.90; N, 13.00. Calc. for  $\text{C}_8\text{H}_{27}\text{Cl}_{13}\text{Cu}_2\text{N}_6\text{O}_{13}$ : C, 14.80; H, 4.15; Cl, 16.40; Cu, 19.60; N, 12.95%).

<sup>†</sup> Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed:  $G = 10^{-4} \text{ T}$ .



**Figure 1.** ORTEP drawing of  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  showing the atom labelling. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability level



**Figure 2.** Projection of the  $[\text{Cu}_2(\text{dien})_2(\text{OH})]^{3+}$  unit showing pseudo-symmetry

**Physical Techniques.**—Infrared spectra were recorded on a Perkin-Elmer 1750 FTIR spectrophotometer as KBr pellets in the  $4000\text{--}250\text{ cm}^{-1}$  region, and electronic spectra on a Perkin-Elmer Lambda 9 spectrophotometer with magnesium oxide as the reference for the solid spectrum. Magnetic susceptibility measurements were carried out in the range  $4.2\text{--}300\text{ K}$  with a previously described Faraday-type magnetometer<sup>12</sup> equipped with a helium continuous-flow cryostat. The uncertainty in the data is lower than  $0.1\text{ K}$  for temperatures and  $2 \times 10^{-5}\text{ cm}^3\text{ mol}^{-1}$  for susceptibilities. Experimental susceptibilities were corrected for diamagnetic contribution estimated from Pascal's tables to be  $-288 \times 10^{-6}\text{ e.m. units mol}^{-1}$  (1 e.m. unit =  $\text{S.I.} \times 10^6/4\pi$ ). X-Band e.s.r. spectra were recorded with a Bruker ER 200 spectrometer equipped with a helium continuous-flow cryostat.

Potentiometric titrations were performed with a previously described titration assembly<sup>13</sup> at  $25.0 \pm 0.1^\circ\text{C}$  at constant ionic strength:  $0.1\text{ mol dm}^{-3}\text{ NaNO}_3$  was used as background electrolyte. Carbonate-free NaOH standardized against dried potassium hydrogen phthalate was used as titrant. The equilibrium constants for the reaction of  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$  and  $\text{OH}^-$  were determined by titrating aqueous solutions of  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  (previously acidified with  $\text{HNO}_3$  to pH 7) with NaOH. The initial concentration of copper(II),  $c_M$ , was varied in the range  $(1.0\text{--}2.5) \times 10^{-2}\text{ mol dm}^{-3}$ . The sets

of data from three different experiments, carried out in the range pH 7.0–11.0, were merged and treated simultaneously by the computer program SUPERQUAD<sup>14</sup> to characterize the equilibrium scheme (see below). E.m.f. data from the range pH 8.0–10.0 were considered in the last refinement cycle. The formation constant of the binuclear species [equation (3)] has been refined with the potentiometric data corresponding to the higher  $c_M$  value because significant amounts of such species exist only at this concentration level.

**Crystallography.**—*Crystal data.*  $\text{C}_8\text{H}_{27}\text{Cl}_3\text{Cu}_2\text{N}_6\text{O}_{13}$ ,  $M = 648.5$ . Monoclinic,  $a = 11.896(7)$ ,  $b = 9.424(3)$ ,  $c = 11.468(7)\text{ \AA}$ ,  $\beta = 117.97(4)^\circ$ ,  $U = 1135(1)\text{ \AA}^3$  (by least-squares refinement on diffractometer angles for nine automatically centred reflections), space group  $P2_1$ ,  $Z = 2$ ,  $D_c = 1.897\text{ g cm}^{-3}$ ,  $D_m = 1.91\text{ g cm}^{-3}$ , dark blue crystals,  $0.7 \times 0.5 \times 0.2\text{ mm}$ ,  $\mu(\text{Mo-K}\alpha) = 23.80\text{ cm}^{-1}$ .

**Data collection and processing.** Diffraction data for  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  were collected at 294 K with a laboratory-made diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation ( $\lambda = 0.7107\text{ \AA}$ ). The intensities of two standard reflections measured every 100 reflections showed no significant variations. Intensity data were collected by the  $\theta\text{--}2\theta$  scan technique in the  $2\theta$  range  $3\text{--}46^\circ$  with scan range  $1.6^\circ + 0.345 \tan \theta$  and scan speed  $1.5^\circ\text{ min}^{-1}$ . Background 10 s was used in fixed position, before and after every scan. Reflections were measured in two octants,  $hkl$ ,  $\bar{h}k\bar{l}$ . Of the 2048 measured independent reflections, 1851 reflections were unique with  $I \geq 3\sigma(I)$  and were used for the structure refinement.

**Structure analysis and refinement.** The structure was solved by direct methods<sup>15</sup> (Cu and Cl atoms) followed by successive Fourier syntheses and least-squares refinements (CRYSTALS).<sup>16</sup> MULTAN statistical tests did not clearly show whether the system was in space group  $P2_1$  or  $P2_1/m$ . First, refinement was carried out in the  $P2_1/m$  space group, for which the Fourier map exhibited at least two peaks instead of one for each oxygen atom around the two chlorine atoms of both perchlorate anions. This feature suggests a disorder of these perchlorate oxygen atoms. Many attempts to describe this disorder failed; it appeared intractable to build two realistic disordered tetrahedral sets of oxygens around non-disordered chlorine atoms. Upon lowering the symmetry to the  $P2_1$  space group  $[\text{Cu}_2(\text{dien})_2(\text{OH})]^{3+}$  was found to be pseudo-centrosymmetrical while the three perchlorate groups were not. This induced correlations the effect of which was avoided by using restraints ( $\text{Cl}\text{--}\text{O} = 1.40 \pm 0.02\text{ \AA}$  and  $\text{O}\text{--}\text{Cl}\text{--}\text{O} = 109 \pm 3^\circ$ ). The final refinement was carried out without restraints, but using four blocks of variables, putting only non-correlated atoms in the same block. Hydrogen atoms were added in calculated positions, with isotropic thermal parameters 20% larger than those of the parent atoms. An absorption correction was performed by use of DIFABS.<sup>17</sup> No weighting scheme was applied and the average shift/estimated standard deviation (e.s.d.) was 0.26 for the last cycle;  $F(000)$  660. Number of reflections/number of variable parameters = 6.3. Final  $R$  and  $R'$  values were 0.053 and 0.054 respectively. The molecular structure is illustrated in Figures 1 and 2.<sup>18</sup> The fractional atomic co-ordinates are given in Table 1 and selected intramolecular bond lengths and angles in Table 2.

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

## Results and Discussion

**Description of the Structure.**—Figure 1 shows a perspective view of the compound. Its structure is made up of neutral

**Table 1.** Final atomic co-ordinates for  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu(1)	0.762 2(1)	0.250 0(1)	0.606 0(1)	Cl(1)	0.512 6(2)	0.250(1)	0.696 3(3)
Cu(2)	0.665 3(1)	0.249 0(4)	0.272 8(1)	Cl(2)	0.331 6(2)	0.249(1)	0.141 0(2)
O(1)	0.639 5(6)	0.267(2)	0.425 1(7)	Cl(3)	1.041 8(2)	0.256 1(9)	0.520 9(3)
N(1)	0.762 2(9)	0.458(1)	0.632 3(9)	O(11)	0.477 1(8)	0.250(3)	0.799 8(9)
N(2)	0.920 7(7)	0.253(2)	0.780 1(8)	O(12)	0.647 1(8)	0.235(2)	0.755(1)
N(3)	0.765(1)	0.031(1)	0.637(1)	O(13)	0.470(1)	0.378(2)	0.621(1)
N(4)	0.693(1)	0.455(1)	0.274(1)	O(14)	0.461(1)	0.130(1)	0.612(1)
N(5)	0.686 2(8)	0.261(2)	0.106 8(8)	O(21)	0.215 4(9)	0.236(4)	0.035(1)
N(6)	0.691(1)	0.037(1)	0.269(1)	O(22)	0.433 2(8)	0.226(3)	0.117 9(9)
C(1)	0.878(1)	0.507(1)	0.745(2)	O(23)	0.325(2)	0.405(2)	0.144(2)
C(2)	0.928(1)	0.389(2)	0.841(1)	O(24)	0.348(1)	0.211(2)	0.260(1)
C(3)	0.922(1)	0.122(2)	0.857(1)	O(31)	1.089(1)	0.216(3)	0.649(1)
C(4)	0.895(1)	0.008(2)	0.755(1)	O(32)	0.914(1)	0.253(4)	0.460(2)
C(5)	0.692(2)	0.498(1)	0.143(2)	O(33)	1.074(3)	0.394(2)	0.511(3)
C(6)	0.755(2)	0.388(1)	0.103(2)	O(34)	1.097(3)	0.189(3)	0.470(3)
C(7)	0.745(2)	0.122(2)	0.108(1)	H(1)	0.57(1)	0.214(7)	0.41(1)
C(8)	0.690(2)	-0.005(2)	0.148(1)				

**Table 2.** Main interatomic distances (Å) and bond angles (°) for  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  with e.s.d.s in parentheses

Cu(1)–O(1)	1.903(7)	Cu(2)–O(1)	1.917(7)
Cu(1)–N(1)	1.98(1)	Cu(2)–N(4)	1.97(1)
Cu(1)–N(2)	2.002(8)	Cu(2)–N(5)	2.036(8)
Cu(1)–N(3)	2.09(1)	Cu(2)–N(6)	2.02(1)
Cu(1)–O(12)	2.64(1)	Cu(2)–O(22)	2.495(8)
Cu(1)–O(32)	2.97(2)	Cu(2)–O(32)	2.72(1)
N(1)–C(1)	1.46(2)	N(4)–C(5)	1.55(2)
N(2)–C(3)	1.51(2)	N(5)–C(6)	1.47(2)
N(2)–C(2)	1.44(2)	N(5)–C(7)	1.48(3)
N(3)–C(4)	1.51(2)	N(6)–C(8)	1.44(2)
C(1)–C(2)	1.47(2)	C(5)–C(6)	1.47(2)
C(3)–C(4)	1.50(2)	C(7)–C(8)	1.54(3)
N(1)–Cu(1)–O(1)	91.7(5)	N(4)–Cu(2)–O(1)	90.5(6)
N(2)–Cu(1)–N(1)	84.5(7)	N(5)–Cu(2)–N(4)	81.7(7)
N(3)–Cu(1)–O(1)	102.0(6)	N(6)–Cu(2)–O(1)	101.1(6)
N(3)–Cu(1)–N(2)	84.9(7)	N(6)–Cu(2)–N(5)	87.1(7)
C(1)–N(1)–Cu(1)	112.4(8)	C(5)–N(4)–Cu(2)	109.2(9)
C(2)–N(2)–Cu(1)	107.8(11)	C(6)–N(5)–Cu(2)	112.6(10)
C(3)–N(2)–Cu(1)	108.6(9)	C(7)–N(5)–Cu(2)	102.2(10)
C(3)–N(2)–C(2)	117.7(9)	C(7)–N(5)–C(6)	117.1(11)
C(4)–N(3)–Cu(1)	102.7(9)	C(8)–N(6)–Cu(2)	111.0(9)
C(2)–C(1)–N(1)	107.6(11)	C(6)–C(5)–N(4)	109.9(12)
C(1)–C(2)–N(2)	113.5(11)	C(5)–C(6)–N(5)	101.2(13)
C(4)–C(3)–N(2)	101.1(10)	C(8)–C(7)–N(5)	115.0(11)
C(3)–C(4)–N(3)	110.7(11)	C(7)–C(8)–N(6)	105.3(13)
Cu(2)–O(1)–Cu(1)	128.1(4)		

$[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  binuclear units, with a pseudo-mirror plane through the  $[\text{Cu}_2(\text{dien})_2(\text{OH})]^{3+}$  cation (Figure 2). The two copper atoms are bridged by a hydroxo group with a Cu(1)–OH–Cu(2) angle of 128.1(4)° and an intramolecular copper–copper separation of 3.435(1) Å.

The co-ordination geometry around each copper atom is 4 + 1 + 1. Equatorial positions are occupied by the three nitrogen atoms of dien and the oxygen atom of the bridge. The dien terminal nitrogens are *trans* to each other with bond distances and angles within the ligand in agreement with previously reported values for other dien-containing copper(II) complexes.<sup>19–23</sup> All Cu–N distances are very similar, contrasting with those reported for bis(diethylenetriamine)-copper(II) complexes<sup>19,20</sup> where the copper–central nitrogen bond length is shorter than copper–terminal nitrogen distances. Furthermore angles between *cis* nitrogen atoms around the copper(II) ions lie in the range 78–81° in these bis complexes

*cf.* an average value of 84.5° in our complex. Both bridging Cu–O distances [1.903(7) and 1.917(7) Å for Cu(1)–O(1) and Cu(2)–O(1), respectively] are very close to those reported for the related complex  $[\text{Cu}_2(\text{terpy})_2(\text{OH})(\text{ClO}_4)_3(\text{H}_2\text{O})]^{10}$  (terpy = 2,2':6',2''-terpyridine) [1.902(4) and 1.909(4) Å].

Both basal planes around copper atoms are distorted; the deviations from both square planes including copper atoms are 0.18 and 0.13 Å for Cu(1) and Cu(2), respectively. The dihedral angle between these two mean basal planes is 123.3°. Semi-co-ordinated perchlorate anions occupy the apical positions in both metal surroundings: O(12) and O(22) from unidentate perchlorates and O(32) from the third perchlorate which also bridges the two copper atoms. The tetragonal distortion is greater for Cu(1) than for Cu(2) owing to longer apical Cu–O distances (the calculated tetragonalities<sup>24</sup> are 0.71 and 0.76, respectively).

**Infrared and Electronic Spectra.**—The i.r. spectrum of the complex shows a medium-intensity sharp band at 3 600 cm<sup>-1</sup> which is assigned to the O–H stretching vibration of the hydroxide bridging group in full accordance with the literature.<sup>5,6,10</sup> A medium-intensity band is observed at 560 cm<sup>-1</sup> which could be attributed to the Cu–O stretching vibration in the bridge. These spectral data support the presence of a single hydroxo-bridge between copper(II) ions. The  $\nu(\text{N–H})$  vibrations of dien appear in the region 3 360–3 140 cm<sup>-1</sup>. The slight splitting of the  $\nu_3$  (1 100 cm<sup>-1</sup>) and  $\nu_4$  (626 cm<sup>-1</sup>) perchlorate bands (Figure 3) suggests the presence of weakly co-ordinated perchlorate anions<sup>25,26</sup> as evidenced by the crystallographic structure.

The visible region of the solid-state electronic spectrum is dominated by a very broad band with an absorption maximum centred at 15 700 cm<sup>-1</sup>, attributable to the non-resolved *d–d* transitions of the two  $\text{CuN}_3\text{OO}'\text{O}''$  chromophores.<sup>27</sup> The shift of this maximum to higher energy in aqueous (16 700 cm<sup>-1</sup>) and in acetonitrile (17 100 cm<sup>-1</sup>) solutions can be interpreted as arising from the substitution of perchlorate ligands by solvent molecules and by the dissociation of the binuclear unit into  $[\text{Cu}(\text{dien})(\text{OH})]^+$  and  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$  as shown by the solution study (see below). Intense metal–ligand charge-transfer bands appear at 34 500 cm<sup>-1</sup> in the reflectance spectra and at 41 300 and 40 000 cm<sup>-1</sup> in aqueous and acetonitrile solutions, respectively.

**Magnetic Properties.**—The temperature dependence of the magnetic susceptibility,  $\chi_M$ , for the binuclear unit  $[\text{Cu}_2(\text{dien})_2-$

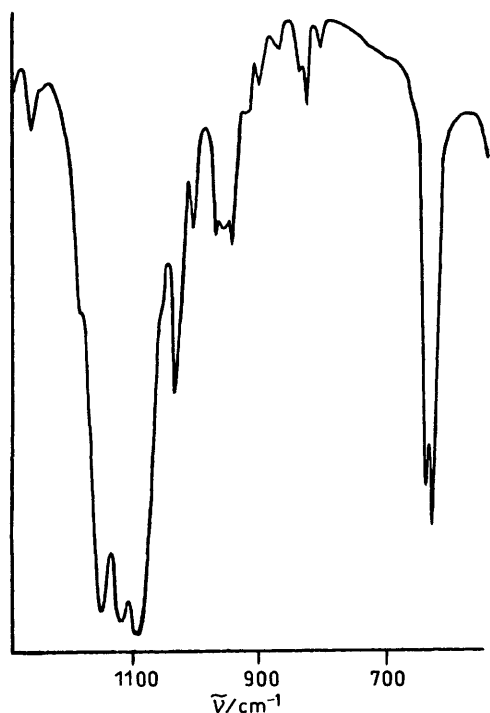


Figure 3. Infra-red spectrum of  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  in the range 1200–600  $\text{cm}^{-1}$

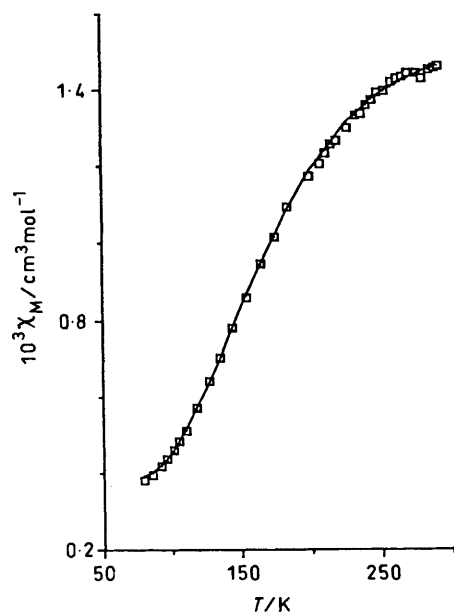


Figure 4. Thermal dependence of the magnetic susceptibility per dicopper(II) unit. The solid line corresponds to the best theoretical fit to the experimental points

$(\text{OH})(\text{ClO}_4)_3]$  is shown in Figure 4. The curve is characteristic for antiferromagnetically coupled copper(II) pairs with a rounded maximum in the susceptibility occurring at temperatures higher than 300 K. The susceptibility data were fitted by least-squares methods to the modified Bleaney–Bowers equation (1) where  $N$ ,  $\beta$ ,  $k$ , and  $g$  have their usual meanings and

$$\chi_M = \frac{2N\beta^2 g^2}{kT} [3 + \exp(-J/kT)]^{-1} (1 - \rho) + \frac{N\beta^2 g^2}{2kT} \rho + 2N\alpha \quad (1)$$

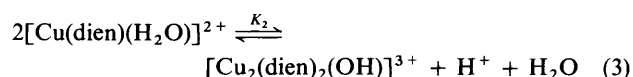
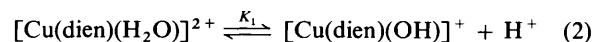
$\rho$  is the mass portion of uncoupled species assumed to follow a Curie law. The last term is the temperature-independent paramagnetism (t.i.p.) assumed to be  $120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for two copper(II) ions. The best-fitting parameters are  $J = -374 \text{ cm}^{-1}$ ,  $g = 2.18$ , and  $\rho = 0.0195$  with an agreement factor  $R = \sum_i [\chi_{\text{obs.}}(i) - \chi_{\text{calc.}}(i)]^2 / \sum_i \chi_{\text{obs.}}(i)^2$  of  $4.07 \times 10^{-5}$ .

The uncoupled species are detected in the X-band polycrystalline powder e.s.r. spectrum as a weak axial signal with  $g_{\parallel} = 2.19(1)$  and  $g_{\perp} = 1.99(1)$ . The  $g_{\parallel}$  component is split by a nuclear hyperfine interaction ( $I = \frac{3}{2}$ ), with  $A_{\parallel} = 194 \text{ G}$ . This signal is superimposed on a broad weak feature centred near  $g = 2.0$ . Such a feature together with a half-field forbidden transition ( $\Delta M_s = 2$ ) at 1690 G can be attributed to triplet transitions in the binuclear unit.

Magnetic and selected structural data for monohydroxo-bridged binuclear copper(II) complexes are summarized in Table 3. Strong antiferromagnetic exchange interactions are present in this series of compounds exhibiting different copper(II) stereochemistries and Cu–OH–Cu bridging angles ranging from 128.1 to 145.7° and Cu...Cu intramolecular separations varying between 3.384 and 3.645 Å. These data enable us to anticipate that a simple correlation of  $J$  with the bridging angle,  $\theta$ , such as that reported for the dihydroxo-bridged copper(II) complexes, cannot be expected in this series of compounds. The distortions of the metal environments as well as the different magnetic orbitals which are involved ( $d_{x^2-y^2}$  for distorted octahedral and square planar geometry, and  $d_{z^2}$  for trigonal bipyramidal geometry) precludes a simple correlation between the singlet–triplet energy gap and the bridging angle  $\theta$ .

The only complex which is structurally related to the present species is  $[\text{Cu}_2(\text{terpy})_2(\text{OH})(\text{ClO}_4)_3(\text{H}_2\text{O})]$ , both showing a distorted tetragonal octahedral geometry around the metal centres. For these the highest occupied magnetic orbital for copper(II) is basically  $d_{x^2-y^2}$  according to their structures for which the hydroxide anion occupies an equatorial position. It is well known that the copper(II)  $d_{x^2-y^2}$  magnetic orbitals are more favourably positioned to overlap in a  $\sigma$  fashion through the hydroxo bridge when  $\theta$  approaches 180°. Nevertheless, the opposite trend is observed when comparing the dien and terpy complexes: the former with a shorter bridging angle ( $\theta = 128.1^\circ$ ) shows a  $J$  value greater than that of the latter ( $\theta = 145.7^\circ$ ). This *a priori* unexpected result can be understood by taking into account the differences observed in the geometry around the metal ion in both complexes. First, larger Cu–O axial distances are observed in the dien complex leading to a larger tetragonality in this case and secondly, the *cis* N–Cu–O and N–Cu–N angles in the equatorial plane are closer to 90° in the dien complex. The rigidity of the terpy ligand is at the origin of such differences for the *cis* N–Cu–N angles. A larger  $d_{z^2}$  contribution to the copper(II) ground state is thus expected in the terpy complex, decreasing the  $d_{x^2-y^2}$  character,<sup>10</sup> and yielding a smaller antiferromagnetic interaction.

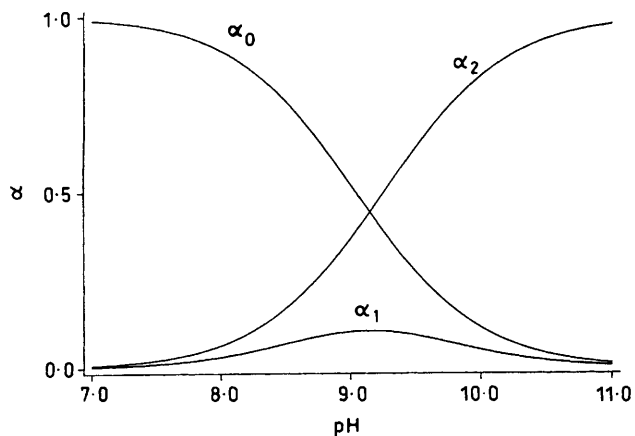
**Solution Study.**—Series of aqueous solutions of the complex  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  (previously acidified with nitric acid to pH 7) were titrated with sodium hydroxide, in order to investigate the formation of hydroxo complexes of  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$ . The data analysis allowed us to determine the equilibrium constants of equations (2) and (3):  $\log K_1 = -9.168(2)$  and  $\log K_2 = -8.26(1)$ . Since equilibrium (4) may



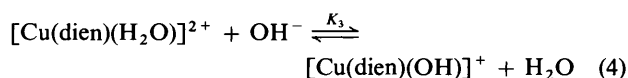
**Table 3.** Selected structural data and isotropic exchange parameters for binuclear copper(II) complexes with a single hydroxo bridge<sup>a</sup>

Complex	$-J/\text{cm}^{-1}$	$\text{Cu}\cdots\text{Cu}/\text{\AA}$	$\text{Cu}-\text{OH}-\text{Cu}/^\circ$	Geometry <sup>b</sup>	Ref.
$[\text{Cu}_2(\text{bipy})_4(\text{OH})][\text{ClO}_4]_3$	322	3.645	141.6	t.b.	6
$[\text{Cu}_2(\text{phen})_4(\text{OH})][\text{ClO}_4]_3$ <sup>c</sup>	354			t.b.	6
$[\text{Cu}_2(\text{tren})_2(\text{OH})][\text{ClO}_4]_3$ <sup>c</sup>	700			t.b.	5
$[\text{Cu}_2(\text{tren})_2(\text{OH})][\text{PF}_6]_3$ <sup>c</sup>	760			t.b.	5
$[\text{Cu}_2\text{L}^1(\text{OH})][\text{BF}_4]_3$	820	3.384	132.2	s.p.	7
$[\text{Cu}_2\text{L}^2(\text{OH})(\text{ClO}_4)][\text{ClO}_4]_2\cdot\text{CHCl}_3$	1 000	3.642	143.7	s.p.	8
$[\text{Cu}_2\text{L}^3(\text{OH})(\text{ClO}_4)(\text{H}_2\text{O})][\text{ClO}_4]_2$	240	3.57	141.6	s.p.	9
$[\text{Cu}_2(\text{terpy})_2(\text{OH})(\text{ClO}_4)_3(\text{H}_2\text{O})]$	303	3.642	145.7	d.o.	10
$[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$	374	3.435	128.1	d.o.	d

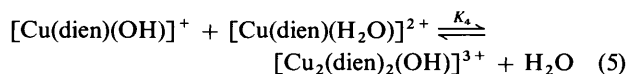
<sup>a</sup> Abbreviations used for ligands: bipy = 2,2'-bipyridine; phen = 1,10-phenanthroline; tren = tris(2-aminoethyl)amine; L<sup>1</sup> = 1,4-bis(1-oxa-4,10-dithia-7-azacyclododec-7-ylmethyl)benzene; L<sup>2</sup> = decadentate N<sub>6</sub>O<sub>4</sub> macrocyclic ligand obtained by reaction of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine; L<sup>3</sup> = 1,13-dioxa-4,7,10,16,19,29-tetra-azacyclotetrasane. <sup>b</sup> t.b. = Trigonal bipyramidal, s.p. = square pyramidal, d.o. = distorted octahedral. <sup>c</sup> X-Ray structural data have not been reported. Geometry is inferred from e.s.r. data. <sup>d</sup> This work.



**Figure 5.** Distribution diagram for the system  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+} - \text{OH}^-$ :  $\alpha_0 = [\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$ ,  $\alpha_1 = [\text{Cu}_2(\text{dien})_2(\text{OH})]^{3+}$ , and  $\alpha_3 = [\text{Cu}(\text{dien})(\text{OH})]^+$ . Concentration  $c_M = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$



be written in terms of equilibrium (2) and  $K_w$  for water,  $K_3$  may be expressed as  $K_2/K_w$ , from which a value of  $\log K_3 = 4.54$  was calculated. Analogously, the dimerization equilibrium (5)



may be written in terms of equilibria (2) and (3) leading to a value of  $\log K_4 = 0.9$ . The distribution diagram,  $\alpha$  versus pH, for the species existing in solution is plotted in Figure 5. The mononuclear species  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$  is predominant in the range pH 7.0–9.2. At pH 9.2,  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$  and  $[\text{Cu}(\text{dien})(\text{OH})]^+$  show the same degree of formation, with the latter complex being predominant at higher pH values. At pH 11 the monohydroxo species  $[\text{Cu}(\text{dien})(\text{OH})]^+$  is the only one existing. The monohydroxo-bridged species  $[\text{Cu}_2(\text{dien})_2(\text{OH})]^{3+}$  shows its highest degree of formation at pH 9.2 ( $\alpha_2 = 0.11$ ). This species vanishes at lower  $c_M$  values. However, if this species is not considered in the equilibrium scheme a poor fit of the potentiometric data is obtained. Several models involving its substitution for other species were ruled out by the SUPERQUAD program in the process of refinement and only the above mentioned species fitted well the experimental data. Our data show that the degree of formation of the binuclear species increases upon increasing  $c_M$  which enabled us to isolate

it from more concentrated solutions as crystals in this study. The formation of the binuclear species had not been observed in previous studies on the  $\text{Cu}^{2+}$ -dien system.<sup>29–31</sup> This can be rationalized taking into account that such studies were carried out at  $c_M$  values for which its concentration was negligible. Generally, higher values of  $c_M$  cannot be used because of the limited solubility of the starting complexes and/or mononuclear monohydroxo-species, which explains the lack of data concerning the formation of such binuclear monohydroxo-complexes in analogous systems. In our case, the high solubility of  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$  and  $[\text{Cu}(\text{dien})(\text{OH})]^+$  as nitrate salts allowed us to study the formation of  $[\text{Cu}_2(\text{dien})_2(\text{OH})]^{3+}$  at  $c_M > 10^{-2} \text{ mol dm}^{-3}$ .

The value of  $\log K_3$  is in fair agreement with a previously reported value of 4.86<sup>29</sup> but somewhat smaller than a more recent one of 5.17.<sup>31</sup> These differences are probably due to the fact that different ionic strengths were used in both cases. The value of the hydroxo stability constant is significantly smaller than that for  $[\text{Cu}(\text{terpy})(\text{OH})]^+$  (5.64).<sup>32</sup> The presumed structure of both hydroxo-species is one in which the hydroxo and the three nitrogen donor atoms occupy the four positions of a square plane as illustrated by the structure of  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$  and  $[\text{Cu}_2(\text{terpy})_2(\text{OH})(\text{ClO}_4)_3]$ . Both dien and terpy ligands are bound to copper(II) ion through a  $\sigma$ -donor bond yielding cationic species with the same charge and five-membered chelate rings. However, the greater stability of the hydroxo-complex with terpyridine is probably due to the  $\pi$ -acceptor character of this ligand<sup>33</sup> which enhances the Lewis-acid character of the metal ion.

## Conclusion

We have synthesized and characterized by spectroscopic and X-ray diffraction methods the binuclear copper(II) complex of formula  $[\text{Cu}_2(\text{dien})_2(\text{OH})(\text{ClO}_4)_3]$ . Its magnetic properties have been studied as a function of temperature and compared to the reported magnetic properties for other monohydroxo-bridged copper(II) complexes. This solid-state study has been complemented with the determination of the stability constants for the hydroxo-complexes of  $[\text{Cu}(\text{dien})(\text{H}_2\text{O})]^{2+}$  in aqueous solution. The formation of the monohydroxo-bridged species has been observed in solution for the first time.

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