Magnetic and Electrochemical Studies on Binuclear Copper(II) Complexes derived from 2,6-Diacetyl-4-methylphenol: the *X*-Ray and Molecular Structure of an Acyclic, Binuclear Schiff-base Complex†

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The syntheses of binuclear copper(II) complexes derived from 2,6-diacetyl-4-methylphenol are reported. Magnetic susceptibility measurements in the temperature range 6—300 K establish that the two Cu^{2+} in bis(2,6-diacetyl-4-methylphenolato)dicopper(II) diperchlorate (**3**) and μ-[2,6-bis(5′-amino-1′-methyl-2′-azapent-1′-enyl)-4-methylphenolato]-μ-hydroxo-diperchloratodicopper(II) (**4**) are antiferromagnetically coupled with the singlet–triplet separation $2J = -460$ and -493 cm^{-1}, respectively. In bis[4-methyl-2,6-bis(1′-oxido-3′-oxobut-1′-enyl)phenol]dicopper(II) (**5**), on the other hand, the two Cu^{2+} are magnetically independent. Electrochemical studies of the three compounds in dimethyl sulphoxide solutions reveal highly irreversible behaviours due to chemical and/or stereochemical changes subsequent to electron transfer. Upon reduction, (**3**) and (**4**) give stable copper(I) species, but (**5**) is reduced directly to copper metal. The crystal structure of complex (**4**) is triclinic, $R = 0.0605$, for 3 074 reflections. The molecule comprises a binuclear copper(II) cation in which the metals are separated by 2.957 1(15) Å and asymmetrically bridged by an endogenous phenoxy-bridge and an exogenous hydroxy-bridge.

Since Robson's advocacy [1] of 2,6-diformyl-4-methylphenol as a building block for the construction of binucleating ligands there has been a considerable expansion of interest in this area of chemistry. A significant number of papers has been presented concerning ligands based on the diformyl phenol,[2] and, in contrast, little work has been concerned with the use of the corresponding diketone, 2,6-diacetyl-4-methylphenol.[3—6] Until recently this could have been attributed to the relative difficulty of ligand synthesis.

2,6-Diacetyl-4-methylphenol provides a versatile precursor for polynucleating species as it can act as a ligand in its own right, be converted into acyclic and macrocyclic Schiff bases, or provide a tetraketonic array after ligand extension *via* a modified Wittig condensation. We report here the magnetic and electronic properties of three complexes, representative of each of the above groups, together with the *X*-ray and molecular structure of μ-[2,6-bis(5′-amino-1′-methyl-2′-azapent-1′-enyl)-4-methylphenolato-*N*,*N*′,*N*″,*N*‴,μ-*O*]-μ-hydroxo-diperchloratodicopper(II).

Results and Discussion

Synthesis.—2,6-Diacetyl-4-methylphenol (**1**) was prepared by a procedure similar to that reported by Mandal and Nag,[5] and then extended to give the tetraketone (**2**) by application of the method of Wittig.[7] The tetraketone was found, by ^{1}H n.m.r. spectroscopy, to exist almost exclusively as the bis(enol) and reaction with an excess of copper(II) acetate, in the presence of lithium hydroxide, gave the dicopper(II) complex, (**5**). Attempts by us to prepare the binuclear copper(II) complex (**3**) by direct synthesis were unsuccessful, even though a variety of reaction conditions was used; the product recovered was always the mononuclear 1:2 complex of deprotonated (**1**). The binuclear complex was obtained when compound (**1**), 1,3-diamino-2-propanol, and copper(II) perchlorate were allowed to react in ethanol. The acyclic binuclear Schiff-base complex (**4**) was synthesised by the reaction of (**1**), sodium hydroxide, 1,3-diaminopropane, and copper(II) perchlorate in aqueous methanol.

The structure of complex (**4**) is illustrated in Figure 1 with the atom labelling used in the corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are given in Table 1. The molecule comprises a binuclear copper dication in which the metals are separated by 2.957 1(15) Å and are bridged by the deprotonated oxygen atom of the *p*-cresol fragment of the quinquedentate ligand (L), by a hydroxyl group, and by the two perchlorate anions which form weak bonds in the axial sites above and below the mean molecular plane. It has approximate C_s symmetry. The asymmetric unit is completed by a water molecule which is disordered unequally between two sites.

The equatorially co-ordinating atoms at each copper (an imine and a primary amine in addition to the oxygen bridging functions) show some tetrahedral distortion from coplanarity, particularly those around Cu(2) (8.7°), otherwise the binuclear core is fairly planar with little hinge about the bridging atoms (2.4°).

The six-membered chelate rings involving the 1-amino-3-imino fragments both have twisted boat conformations, that containing Cu(1) being markedly more twisted. The six-membered ring of the *p*-cresol fragment is fairly planar [root-mean-square (r.m.s.) deviation 0.044 Å] but its substituents deviate markedly from the mean plane (by up to 0.35 Å) leading to substantially non-planar (r.m.s. deviations 0.073 and 0.061 Å) and non-coplanar (11.1°) imine-containing chelate fragments from which the metals each deviate by approximately 0.78 Å. Thus the ligand backbone C(5)—C(13) curves away from the mean metal co-ordination plane to which the *p*-cresol ring is inclined at 36°. Despite these various molecular distortions from planarity, the trigonal

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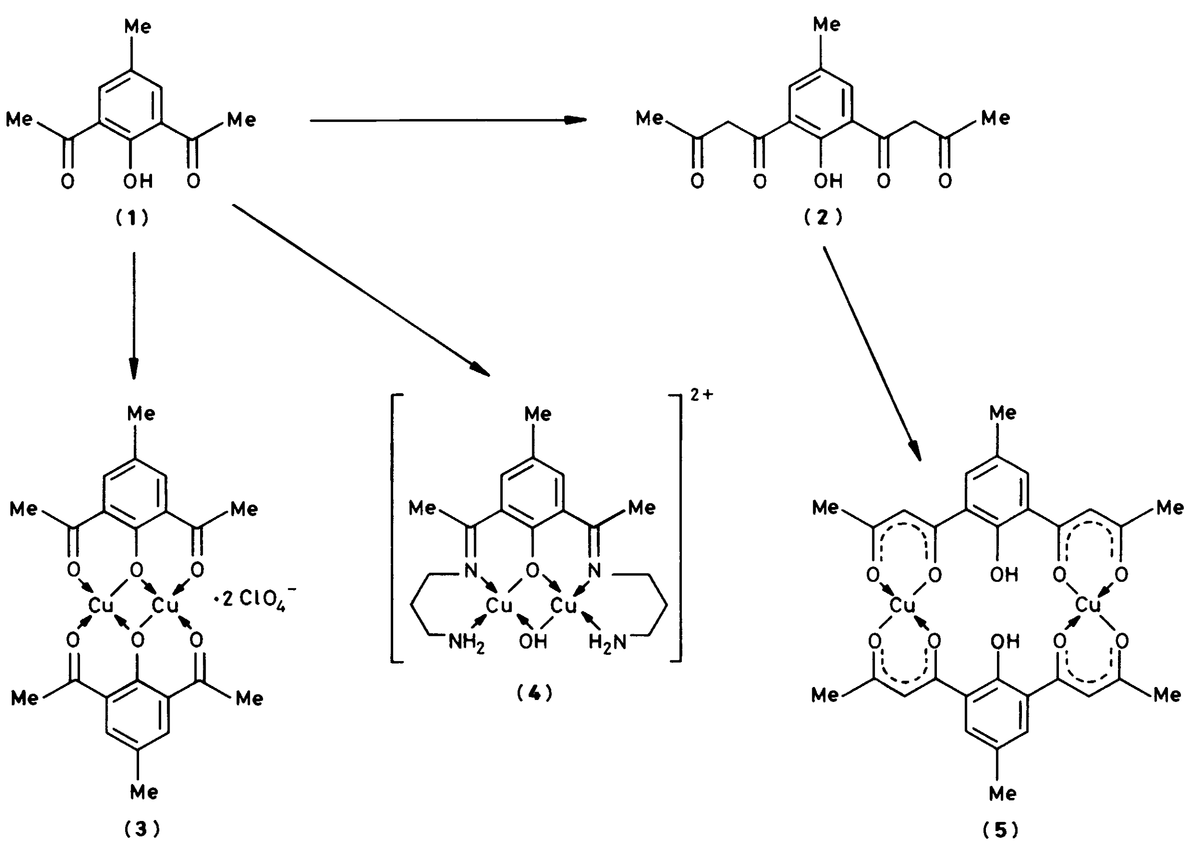
† *Supplementary data available* (No. SUP 56636, 5 pp.): thermal parameters, H-atom co-ordinates, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: B.M. $\approx 9.27 \times 10^{-24}$ A m^2, G = 10^{-4} T.



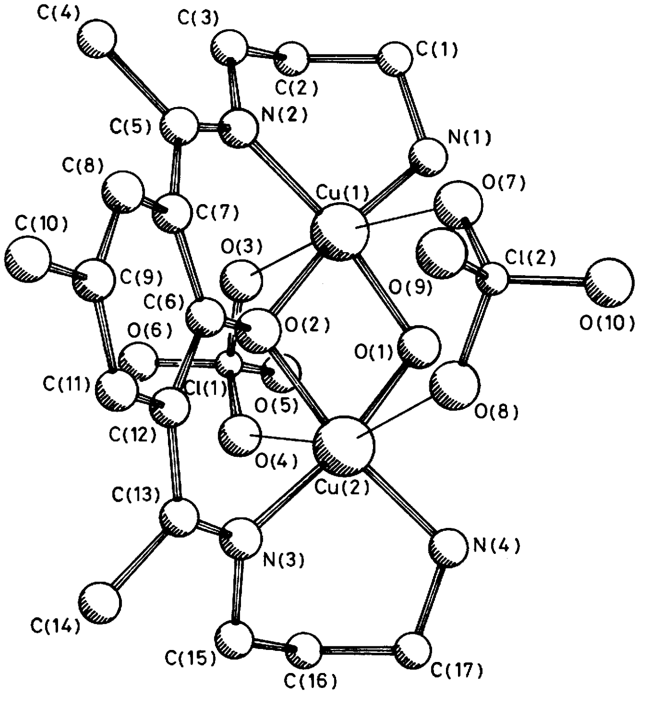


Figure 1. The structure of complex (4)

imines and adjacent trigonal carbon atoms remain in planar environments.

Of the two bidentate, intramolecularly bridging, anionic perchlorate ligands, that involving Cl(2) forms the stronger bonds to the coppers whereas for the other such ligand the two Cu–O interactions are longer and more dissimilar.

The two sites for the disordered water molecule show different degrees of hydrogen bonding in a manner consistent with their apparently different occupancies. One site, O(11), is linked to two oxygen atoms of different perchlorate groups in different molecules, one terminal, O(5), and one co-ordinated, O(7^{I}), and to the bridging hydroxyl ligand, O(1). The other site, O(12), is hydrogen bonded only to a primary amine, N(4), and is rather remote (3.17 Å) from the co-ordinated hydroxyl ligand. Additionally, intermolecular hydrogen bonds are formed between a primary amine, N(1), and the co-ordinated hydroxyl group and, much more weakly (3.15 Å), between the other primary amine, N(4), and a terminal oxygen of a perchlorate, O(10); the direction of the N–H bond supports the existence of this latter interaction.

The rather short skeletal bonds to atom C(2) and its higher thermal parameters and estimated standard deviations (e.s.d.s) denote a less well determined position but conformational disorder was not detected. One perchlorate bond [to O(5)] is very short and again high thermal motion and e.s.d.s are evident: otherwise the bond lengths and angles are unexceptional.

Magnetic Properties.—The magnetic properties of complex (**4**) are displayed in Figure 2 in the form of the molar susceptibility and effective magnetic moment *vs.* temperature over the range 6—300 K. The shape of the susceptibility plot reveals a behaviour typical of a strongly antiferromagnetically coupled binuclear compound with the maximum of the susceptibility occurring at a temperature higher than 300 K. The susceptibility increase at low temperature is indicative of the presence of a small amount of monomeric impurity. The susceptibility data were fitted with the expression (1) where all

Table 1. Selected bond lengths (Å) and angles (°) with estimated standard deviations for complex (**4**)*

Cu(1) ··· Cu(2)	2.957 1(15)	O(2)–C(6)	1.321(10)	N(1)–C(1)	1.492(15)	N(4)–C(17)	1.491(15)
Cu(1)–O(1)	1.951(6)	Cu(2)–O(1)	1.928(6)	N(2)–C(3)	1.488(12)	N(3)–C(15)	1.497(12)
Cu(1)–O(2)	1.954(6)	Cu(2)–O(2)	1.955(6)	N(2)–C(5)	1.266(11)	N(3)–C(13)	1.285(11)
Cu(1)–O(3)	2.773(11)	Cu(2)–O(4)	2.940(9)	O(11) ··· O(1)	2.77(2)	O(12) ··· N(4)	2.96(3)
Cu(1)–O(7)	2.612(8)	Cu(2)–O(8)	2.653(9)	O(11) ··· O(5)	2.86(3)	O(1) ··· N(1^{I})	3.08(1)
Cu(1)–N(1)	1.983(9)	Cu(2)–N(4)	1.989(9)	O(11) ··· O(7^{I})	3.02(2)	N(4) ··· O(10^{II})	3.15(1)
Cu(1)–N(2)	1.982(7)	Cu(2)–N(3)	1.947(7)				
O(1)–Cu(1)–O(2)	80.89(24)	O(1)–Cu(2)–O(2)	81.44(24)	O(3)–Cu(1)–N(2)	92.30(30)	O(4)–Cu(2)–N(3)	91.51(27)
O(1)–Cu(1)–O(3)	85.95(29)	O(1)–Cu(2)–O(4)	81.20(25)	O(7)–Cu(1)–N(1)	92.29(31)	O(8)–Cu(2)–N(4)	89.20(32)
O(1)–Cu(1)–O(7)	85.86(25)	O(1)–Cu(2)–O(8)	83.62(26)	O(7)–Cu(1)–N(2)	95.46(27)	O(8)–Cu(2)–N(3)	101.61(28)
O(1)–Cu(1)–N(1)	90.38(31)	O(1)–Cu(2)–N(4)	92.79(32)	N(1)–Cu(1)–N(2)	99.82(32)	N(4)–Cu(2)–N(3)	96.49(33)
O(1)–Cu(1)–N(2)	169.64(27)	O(1)–Cu(2)–N(3)	169.38(28)	Cu(1)–N(1)–C(1)	117.6(7)	Cu(2)–N(4)–C(17)	117.5(7)
O(2)–Cu(1)–O(3)	87.03(28)	O(2)–Cu(2)–O(4)	81.77(24)	Cu(1)–O(2)–C(6)	124.6(5)	Cu(2)–O(2)–C(6)	122.2(5)
O(2)–Cu(1)–O(7)	90.01(24)	O(2)–Cu(2)–O(8)	83.50(25)	Cu(1)–O(2)–Cu(2)	98.3(3)	Cu(1)–O(1)–Cu(2)	99.3(3)
O(2)–Cu(1)–N(1)	170.80(30)	O(2)–Cu(2)–N(4)	171.14(31)	Cu(1)–N(2)–C(3)	117.1(6)	Cu(2)–N(3)–C(15)	117.4(6)
O(2)–Cu(1)–N(2)	88.82(26)	O(2)–Cu(2)–N(3)	89.91(27)	Cu(1)–N(2)–C(5)	124.2(6)	Cu(2)–N(3)–C(13)	123.5(6)
O(3)–Cu(1)–O(7)	171.64(29)	O(4)–Cu(2)–O(8)	160.23(25)	C(3)–N(2)–C(5)	118.8(7)	C(15)–N(3)–C(13)	119.1(7)
O(3)–Cu(1)–N(1)	89.45(33)	O(4)–Cu(2)–N(4)	104.09(31)				

* Symmetry equivalents: I $-x, -y, -z$; II $-x, -1-y, -z$.

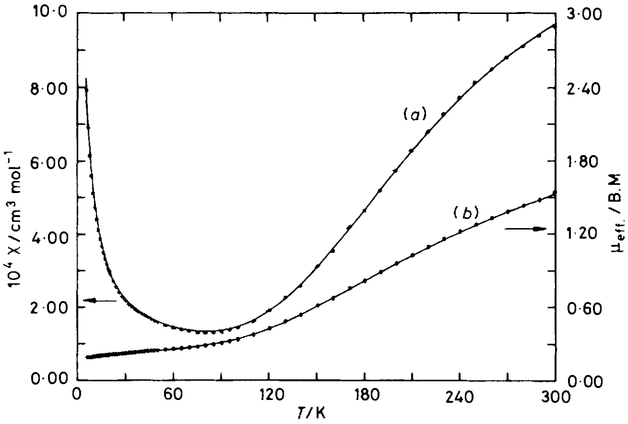


Figure 2. Plots of (*a*) the corrected molar susceptibility and (*b*) effective magnetic moment *vs.* absolute temperature for complex (**4**). The solid lines show the least-squares fit to the data using the parameters and equations described in the text

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

symbols have their usual meaning and P is the proportion of monomeric impurity. All four parameters were allowed to vary. Least-squares fitting of the χ_M *vs.* T data yielded $g = 2.19(1)$, $-J = 246(5)$ cm^{-1}, $P = 0.004\,9(1)$, and $2N\alpha = 70(5) \times 10^{-6}$ cm^3 mol^{-1}.

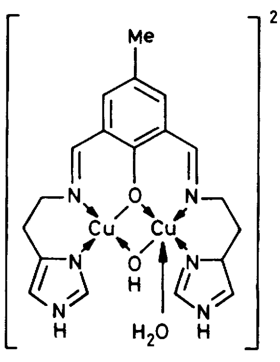
Following the early work of Robson[1] and Kida and co-workers[8] several studies have appeared that present the magnetic properties of binuclear copper chelates involving both hydroxy and phenoxy bridges.[6,9–20] However, many of these studies have been restricted to measurement of the room-temperature effective magnetic moment[1,6,9,11–13] and only in five cases (see below) are both magnetic and structural data available. Room-temperature magnetic moments in the range 0.6—1.4 B.M. per copper have been reported and the present compound lies in the middle of this range, $\mu = 1.06$ B.M. On the other hand, singlet–triplet separations (E_{ST}) span a wide range between 0 and -865 cm^{-1}.[8,10,14–20] Close examination of these data reveals that, except for the two extreme values, complexes whose quinquedentate ligands possess only two carbon atoms between the two nitrogens have an E_{ST} of -345 ± 25 cm^{-1}. Their analogues with an extra carbon between the nitrogens have a greater singlet–triplet separation, $E_{ST} = -465 \pm 80$ cm^{-1}. With $E_{ST} = -493$ cm^{-1}, complex (**4**) lies to the higher end of this range, which is consistent with its structure.

Table 2. Structure of the Cu_2O_2 core and singlet–triplet separations

Compound	Cu–Cu (Å)	CuOHCu (°)	CuOPhCu (°)	$-E_{ST}$ (cm^{-1})	Ref.
(**9**)	3.020	104.8	99.1	675	14
(**7**)	3.053	103.6	101.9	420	15
(**6**)[a]	3.05	102.5	101.4	525	11, *b*
(**10**)	3.014	101.3	100.9	516[c]	16
(**4**)	2.957	99.3	98.3	493	This work
(**8**)	2.872	96.5	91.7	0	19
	2.857	96.4	91.4		

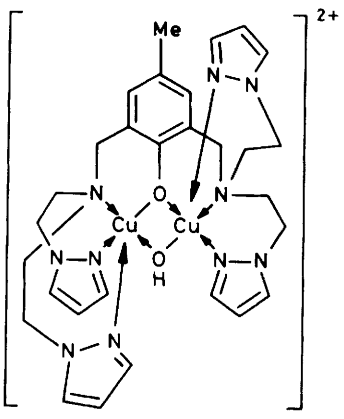
[a] Magnetic and structural studies have not been performed on the same salts of complex (**6**). This is probably not of major importance as the anions do not bind to the copper(II). [b] R. R. Gagne, M. W. McCool, and R. E. Marsh, *Acta Crystallogr., Sect. B*, 1980, **36**, 2420. [c] A value of $E_{ST} = -545$ cm^{-1} was reported in ref. 11.

To our knowledge, only five complexes (**6**)—(**10**) [apart from (**4**)] with mixed phenoxy hydroxy bridges have been structurally and magnetically characterised. Table 2 summarises the main geometrical features of the Cu_2O_2 core and the E_{ST} values of the five compounds. As noted by Sorrell *et al.*,[15] complex (**7**) follows the magneto-structural correlation established by Hatfield and co-workers[21] for copper hydroxy dimers. However, the five other compounds strongly depart from this correlation. No obvious pattern emerges from the data in Table 2. Nevertheless, the dramatic decrease in antiferromagnetic coupling of compound (**8**) may possibly be related to the low values of the angles CuOCu, as compared with the other five complexes, since a high antiferromagnetic coupling is generally associated with an obtuse CuOCu angle.[21] It is worth noting at this stage that the non-planarity of the phenoxide oxygen has little effect if any on the extent of the antiferromagnetic coupling. The dihedral angle between the Cu_2O_2 core and the phenyl ring amounts to about 45° in complex (**8**), and to a value approaching 36° in (**4**). This non-planarity appears to be a non-exceptional feature since it is also



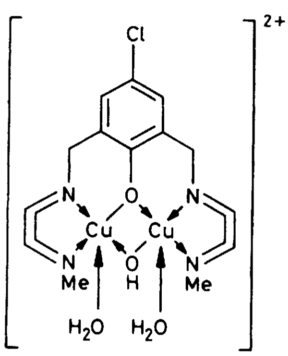
$[BF_4]\,1/2\,[SiF_6]\cdot 0{\cdot}42H_2O$

(6)



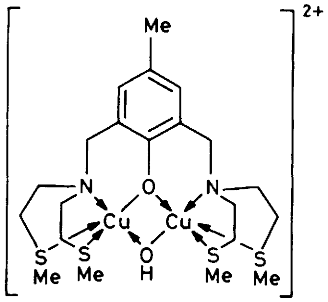
$[BF_4]_2$

(7)



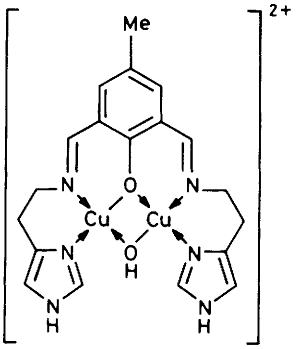
$[ClO_4]_2\cdot H_2O$

(8)



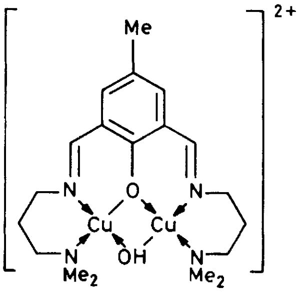
$[ClO_4]_2$

(9)



$Cl_2\cdot 1{\cdot}5H_2O$

(10)



$[ClO_4]_2\cdot H_2O$

(11)

present in a third related compound (**11**).[22] The magnetic study of the latter will prove interesting in assessing the influence of this structural property on the exchange process.

The five other compounds (**4**), (**6**), (**7**), (**9**), and (**10**) have comparable structural and magnetic properties. However, in Sorrell's complex (**7**) the two copper sites are not structurally equivalent: one is square pyramidal while the other is intermediate between a square pyramid and a trigonal bipyramid with the CuO(H) bond on the axial direction. Whatever the true structure of this copper site the copper-based magnetic orbital ($d_{x^2-y^2}$ for a tetragonal geometry or d_{z^2} for a trigonal one) points towards the hydroxide ion. The situation is different for the other bridging ligand: if the site structure is tetragonal the phenoxide will participate in the exchange pathway while it will not if the structure is trigonal. The structures of complexes (**4**) and (**6**) warrant that both bridging ligands will contribute to the exchange. This may be the reason for the higher E_{ST} exhibited by these compounds. The situation is similar in (**9**) where each copper has a trigonal-bipyramidal geometry.[14] This imposes d_{z^2} as the copper-based magnetic orbital and, thus, the exchange pathway involves only the hydroxide bridge. On the other hand, the structures of complexes (**4**), (**6**), and (**10**) warrant that both bridging ligands contribute to the exchange since both coppers are in tetragonal environments. It follows that inclusion of the phenoxide in the exchange pathway is not a requisite to high E_{ST}, but the latter is associated with obtuse CuO(H)Cu angles.

Figure 3 illustrates the temperature dependence of the molar susceptibilities of (**3**) and (**5**) in the range 6—300 K. The behaviour of complex (**3**) closely resembles that of (**4**) and can be fitted by equation (1). This procedure leads to $g = 2.14(1)$, $-J = 229(5)$ cm^{-1}, $P = 0.014(1)$, and $2N\alpha = 71(5) \times 10^{-6}$ cm^3 mol^{-1}. On the other hand, the data for (**5**) were satisfactorily accounted for through the use of the Curie–Weiss equation: $g = 2.075(5)$, $\theta = -0.90$ K, and $N\alpha = 96(5) \times 10^{-6}$ cm^3 mol^{-1}.*

A room-temperature magnetic moment of 1.05 B.M. has been reported for complex (**3**) by Mandal and Nag[4] who did not study its temperature dependence. Dicopper 1,3,5-triketonates, on the other hand, have been shown to exhibit strong antiferromagnetic couplings (E_{ST} *ca.* -700 cm^{-1}).[23,24] In the absence of structural data any reasoning on the causes of the decreased coupling of (**3**) ($E_{ST} = -460$ cm^{-1}) would be far too speculative. To our knowledge only one dicopper 1,3,5,7-tetraketonate has been reported so far.[25] Although its structure has not been

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* The data can be equally fitted to the Bleaney-Bowers equation [$P = 0$ in equation (1)]. The following parameters are obtained: $g = 2.06(1)$, $-J = 1$ cm^{-1}, $2N\alpha = 138(5) \times 10^{-6}$ cm^3 mol^{-1}.

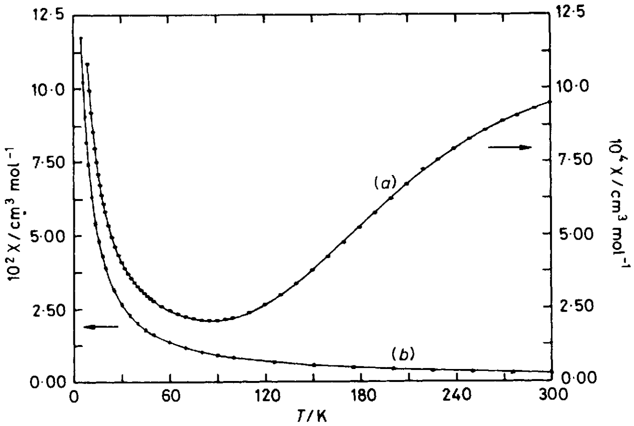


Figure 3. Plots of corrected molar susceptibility *vs.* absolute temperature for (*a*) complex (**3**) and (*b*) complex (**5**). The solid lines show the least-squares fit to the data using the parameters and equations described in the text

solved, contiguity of the two metal binding sites (as in 1,3,5-triketonates) was ruled out on the basis of its magnetic properties which do not show the strong antiferromagnetism of triketonates. Our results are in line with these observations since complex (**5**) does follow the Curie law.

Redox Properties.—Hydroxy derivative (**4**). In the recent past Urbach and co-workers[11] and Gagne *et al.*[12] have reported on the redox properties of hydroxo-bridged dicopper complexes similar to (**4**) but in which the terminal nitrogen belongs to a pyridine moiety. These complexes exhibit an irreversible behaviour and reduction generally leads to copper metal possibly through disproportionation of a copper(I) intermediate. The reason for such a behaviour probably lies in the poor co-ordinating ability of hydroxide for copper(I); this view is supported by the fact that replacing hydroxide with pyrazolate allows the isolation of stable copper(I) derivatives.[12] Mandal and Nag[6] reported that in acetonitrile at a hanging mercury drop electrode (h.m.d.e.) the diformyl analogue of complex (**4**) is reduced in two successive one-electron transfers at $E_{p_c}{}^1 = -0.15$ V and $E_{p_c}{}^2 = -0.58$ V *vs.* saturated calomel electrode (s.c.e.);* no stable mixed-valence copper(I,II) nor binuclear copper(I) species were obtained.

Figure 4 illustrates the cyclic voltammogram of complex (**4**) at a rate of 50 V s^{-1} on a platinum disc. The shape of the reduction peak changes after the first scan. Reduction of the compound appears as a single broad peak at $E_{p_c} = -0.60$ V *vs.* s.c.e. and exhaustive electrolysis at -0.8 V *vs.* s.c.e. consumes 2 F mol^{-1}. Two oxidation peaks are present at $E_{p_a}{}^1$ *ca.* -0.5 V and $E_{p_a}{}^2 = +0.14$ V *vs.* s.c.e. After a first reduction–oxidation cycle the shape of the reduction peak is altered and two overlapping peaks can be distinguished ($E_{p_c}{}^1 = -0.44$, $E_{p_c}{}^2 = -0.64$ V *vs.* s.c.e.). Moreover a new reduction peak has appeared at $E_{p_c}{}^3 = -0.06$ V *vs.* s.c.e. No new oxidation peak can be seen but the intensity of the main oxidation peak at $E_{p_a}{}^2$ has increased. The shape of the voltammogram does not change after the second cycle except for a slight increase of the main oxidation peak. This cyclic voltammetric study reveals a very complex redox behaviour whose analysis is complicated by the irreversibility of the electrode processes. Nevertheless several indications can be derived from these results. First, coulometric analysis of the reduction process indicates that two electrons per mol are transferred which suggests the formation of two copper(I) ions. Secondly, two oxidation peaks are present which may correspond to the sequential one-electron oxidation of the dicopper(I) species. Moreover, the huge difference between E_{p_c} and $E_{p_a}{}^2$ suggests that a chemical change is occurring with the electron transfer. It may be a structural reorganisation of the copper co-ordination sphere. Thirdly, the splitting of the reduction peak after the first cycle shows that complex (**4**) is not recovered upon a reduction–oxidation cycle, *i.e.* an irreversible process is associated with the electron transfer. We think that this process may be the loss of the hydroxy ligand. Fourthly, the small reduction peak $E_{p_c}{}^3$ associated with $E_{p_a}{}^2$ corresponds to the reduction of a different copper(II) form. We believe that this form may derive from some steric distortion of the copper environment. These interpretations of the experimental data are based on a very recent study of the occurrence of stereochemical changes[26] and the observation of ligand loss[12] induced by electron transfer in related complexes. We thus speculate that the reduction of (**4**) can be described by Scheme 1.†

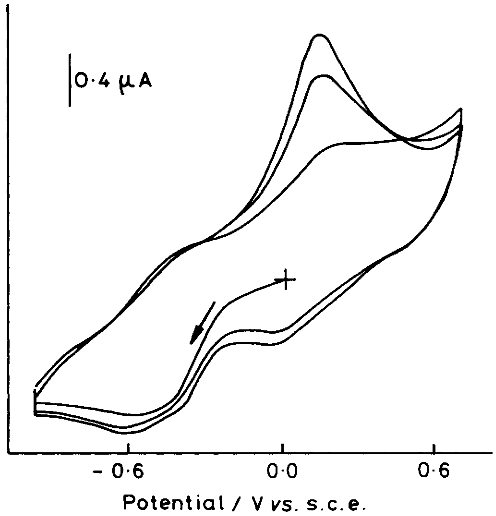
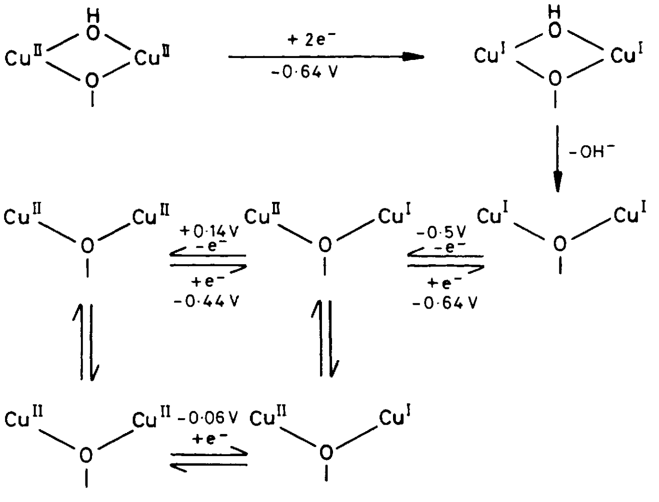


Figure 4. Cyclic voltammogram of complex (**4**) in dmso. The scan rate was 50 V s^{-1}



Scheme 1.

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* Potentials of the anodic (E_{p_a}) and cathodic (E_{p_c}) peaks estimated from Figure 1 of ref. 6.

† The reversibility of the electron transfers indicated has to be taken in a chemical (not electrochemical) sense.

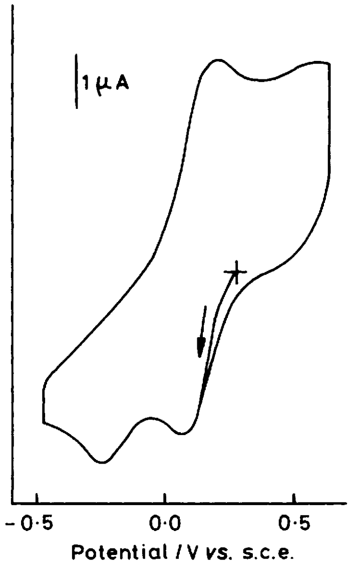

Figure 5. Cyclic voltammogram of complex (**3**) in dmso. The scan rate was 200 V s^{-1}

Bis(diacetylphenoxide) complex (**3**). Cyclic voltammetry of complex (**3**) in dimethylformamide (dmf) at the h.m.d.e. showed a single reduction peak at $E_{p_c} = -0.046$ V *vs.* s.c.e.[4] Coulometric analysis indicated that two electrons were transferred and from electronic spectroscopy it was deduced that the reduction product was the dicopper(I) compound. Figure 5 illustrates the cyclic voltammogram of (**3**) on platinum at 200 V s^{-1}. Two reduction peaks are observed at $E_{p_c}{}^1 = +0.06$ V and $E_{p_c}{}^2 = -0.25$ V *vs.* s.c.e. Only one oxidation peak is noted at $E_{p_a} = +0.18$ V *vs.* s.c.e. Exhaustive electrolysis at -0.15 V *vs.* s.c.e. requires one electron per mol and produces a stable solution which has been analysed by electronic and e.s.r. spectroscopies (see below). Coulometric analysis at -0.35 V *vs.* s.c.e. shows that the second transfer is also monoelectronic. Moreover, reoxidation of this solution at $+0.3$ V *vs.* s.c.e. consumes about two electrons per mol and regenerates the starting solution. A third electron transfer (not shown in Figure 5) is present at $E_{p_c}{}^3 = -0.70$ V *vs.* s.c.e. No oxidation peak is associated with this. Controlled-potential electrolysis at -0.85 V *vs.* s.c.e. consumes 2 F mol^{-1} and is accompanied by copper deposition onto the electrode; the resulting solution contains L^- [ligand anion of (**3**)] which is characterised by an irreversible oxidation process at $E_{p_a} = +0.3$ V *vs.* s.c.e. The redox properties of complex (**3**) are depicted in Scheme 2.

$$\begin{tikzcd} {[Cu^{II}{}_2L_2]^{2+}} \arrow[r, shift left, "+e^-"] & {[Cu^{II}Cu^{I}L_2]^+} \arrow[l, shift left] \arrow[d, shift left, "+e^-"] \\ 2Cu^0 + 2L^- & {[Cu^{I}Cu^{I}L_2]} \arrow[u, shift left] \arrow[l, "2e^-"'] \end{tikzcd}$$

Scheme 2.

This electrochemical study shows that one-electron reduction of complex (**3**) produces the corresponding mixed-valence compound $[Cu^{II}Cu^{I}L_2]^+$. Spectroscopic analysis of the electrogenerated solution supports this assignment. Electronic absorption spectroscopy reveals a change in the *d–d* transition region where the broad absorption centred at *ca.* 788 nm ($\varepsilon = 150$ dm^3 mol^{-1} cm^{-1}) associated with (**3**) shifts to *ca.* 685 nm ($\varepsilon = 90$ dm^3 mol^{-1} cm^{-1}). However, the most striking and significant changes are observed in the e.s.r. spectra. Figure 6 depicts the room-temperature spectra of (**3**) and its one-electron-reduced derivative and the spectrum of the latter at *ca.* 340 K. Comparison of spectra (*a*) and (*b*) undoubtedly demonstrates that a different copper(II) species has been obtained upon reduction. Moreover, careful examination of Figure 6(*c*) suggests that this species has a seven-line spectrum with separation of 33 G.* At low temperatures a four-line spectrum with axial symmetry is obtained. Such a behaviour corresponds to a class II compound in the nomenclature of Robin and Day[27] and has been studied in detail for related dicopper complexes by Long and Hendrickson.[28] The last authors were able to evaluate the intersite electron-exchange rate from the temperature dependence of the e.s.r. spectra. In the present case the low solubility of the products drastically hampers the realisation of an analogous study.

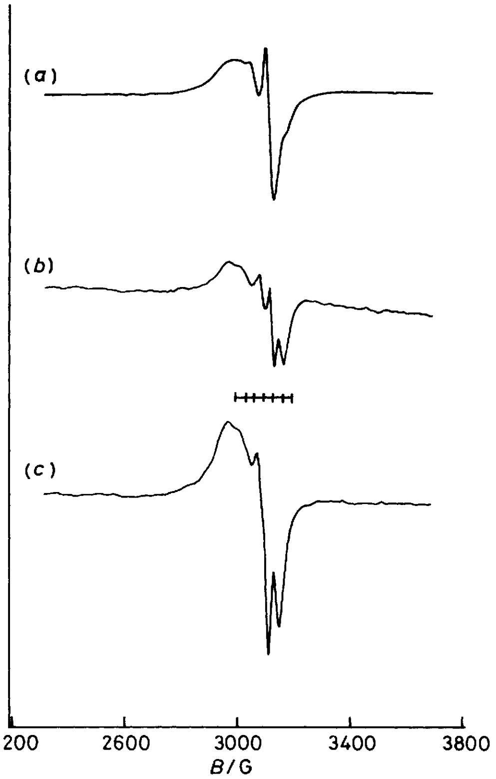

Figure 6. E.s.r. spectra of a 0.5 mmol dm^{-3} dmso solution of (*a*) complex (**3**) at room temperature, (*b*) the same after one-electron reduction, and (*c*) same as (*b*) but at 340 K. Instrumental settings: microwave power 20 mW; modulation amplitude 5 G; time constant 0.25 s; sweep rate *ca.* 20 G s^{-1}; number of scans 10; microwave frequency 9.12 GHz

A particular interest in complex (**3**) stems from the fact that it is intermediate between two main types of binuclear copper complexes: namely the triketonates[29] and the bis(iminophenolates).[5,28,30] The latter compounds are reduced in two reversible one-electron transfers in the range -0.4 to -1.3 V *vs.* s.c.e. On the contrary, the former are reduced at -0.48 to -0.65 V *vs.* s.c.e. in a two-electron process (which may be complicated, however, by some subsequent reactions).[29] The redox behaviour of (**3**) is analogous to the one of the bis(iminophenolates) in that two one-electron transfers occur, but differs from it since the transfers are not electrochemically reversible and occur at much higher potentials. We think that the reason for the last two discrepancies is unique and reflects the structural difference between the respective ligands. It is well known that copper(II)

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* Two overlapping spectra could possibly give rise to the same pattern. However no evidence of two species is found in the low-temperature spectrum.

Table 3. Atomic positional parameters with estimated standard deviations for complex (**4**)

Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.223 73(8)	0.120 23(10)	0.158 78(9)
Cu(2)	0.180 18(8)	−0.136 56(11)	0.288 35(9)
Cl(1)	0.238 33(26)	0.278 63(31)	0.479 75(26)
Cl(2)	0.150 32(21)	−0.254 74(26)	−0.045 55(24)
O(1)	0.095 9(5)	−0.034 0(6)	0.187 1(5)
O(2)	0.310 7(4)	0.021 6(6)	0.266 1(5)
O(3)	0.261 1(10)	0.314 3(10)	0.374 1(8)
O(4)	0.231 1(7)	0.126 6(8)	0.484 0(7)
O(5)	0.147 2(13)	0.298 9(19)	0.482 7(20)
O(6)	0.335 2(12)	0.387 3(11)	0.583 7(9)
O(7)	0.168 4(7)	−0.095 2(7)	−0.034 7(7)
O(8)	0.146 5(7)	−0.295 4(8)	0.071 2(7)
O(9)	0.239 9(9)	−0.278 1(12)	−0.065 2(12)
O(10)	0.042 4(8)	−0.349 6(10)	−0.141 4(8)
N(1)	0.116 2(7)	0.205 3(8)	0.060 7(8)
N(2)	0.371 8(5)	0.264 2(7)	0.152 7(6)
N(3)	0.288 5(6)	−0.201 4(7)	0.403 9(6)
N(4)	0.034 7(7)	−0.304 5(10)	0.282 7(8)
C(1)	0.168 9(9)	0.356 8(11)	0.028 4(11)
C(2)	0.283 1(10)	0.457 3(12)	0.123 2(14)
C(3)	0.382 3(8)	0.423 0(9)	0.136 5(10)
C(4)	0.568 6(8)	0.347 3(10)	0.159 0(10)
C(5)	0.457 4(7)	0.230 1(9)	0.163 9(7)
C(6)	0.395 1(6)	−0.008 8(8)	0.251 0(6)
C(7)	0.462 1(7)	0.081 1(8)	0.189 7(7)
C(8)	0.540 6(7)	0.035 1(9)	0.163 4(7)
C(9)	0.563 9(7)	−0.087 4(9)	0.202 6(7)
C(10)	0.650 0(9)	−0.134 6(12)	0.173 7(9)
C(11)	0.508 9(7)	−0.159 1(9)	0.276 8(7)
C(12)	0.427 8(6)	−0.123 1(8)	0.304 9(7)
C(13)	0.382 0(7)	−0.198 7(8)	0.393 9(7)
C(14)	0.456 0(8)	−0.267 8(10)	0.476 7(8)
C(15)	0.257 4(8)	−0.263 2(11)	0.506 1(8)
C(16)	0.147 5(9)	−0.264 2(12)	0.508 4(9)
C(17)	0.041 3(9)	−0.369 3(12)	0.394 8(10)
O(11)	−0.043(2)	0.048(2)	0.285(2)
O(12)	−0.063(3)	−0.086(3)	0.341(3)

Atoms O(11) and O(12) are the oxygen atoms of the disordered water molecule with occupancies of 60 and 40% respectively.

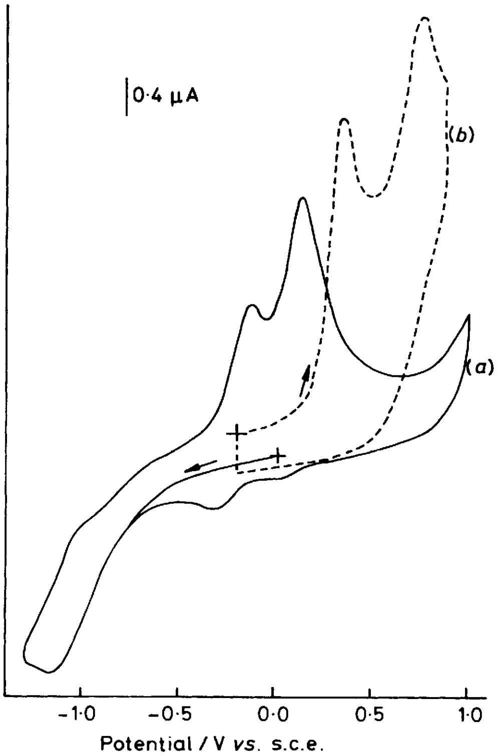

Figure 7. Cyclic voltammograms of a dmso solution of (*a*) complex (**5**) at 50 V s^{-1} and (*b*) the same solution after exhaustive electrolysis at −1.30 V *vs.* s.c.e. at a scan rate of 500 V s^{-1}

prefers co-ordination by four or five ligands, while copper(I) best suits environments consisting of three or four ligands in a trigonal or tetrahedral arrangement, respectively. So, upon reduction copper will tend to lose a ligand and distort its co-ordination sphere; both processes will lead to irreversible electrochemical reactions. This situation is not observed with the bis(iminophenolates) because the macrocyclic structure enforces a roughly square-planar environment on the coppers. In the case of a non-macrocyclic system, bond breaking and stereochemical changes are likely to occur leading to irreversible behaviour. Conversely, the latter events probably allow the copper(I) ion to be in a favourable environment which increases the potential of the copper(II)–copper(I) couple.

Tetraketonic complex (**5**). Figure 7(*a*) presents the cyclic voltammograms of complex (**5**) on a Pt disc. There is only one reduction peak at $E_{p_c} = -1.16$ V *vs.* s.c.e. and two couples at $E_{p_c}{}^1 = -0.12$, $E_{p_c}{}^2 = +0.14$ V *vs.* s.c.e. and $E_{p_c}{}^1 = +0.01$, $E_{p_c}{}^2 = -0.32$ V *vs.* s.c.e. The last peaks appear only after the reduction at −1.16 V *vs.* s.c.e. has occurred; their shape and position are extremely dependent on the potential sweep rate. Cyclic voltammetric studies after holding the potential at −1.30 V *vs.* s.c.e. suggest that $E_{p_a}{}^1$ and $E_{p_a}{}^2$ could correspond to copper dissolution. Exhaustive electrolysis at this potential requires 4 F mol^{-1} and is accompanied by copper deposition onto the platinum grid. The cyclic voltammogram of the electrolysed solution is depicted in Figure 7(*b*). It is constituted by two irreversible oxidations at $E_{p_a}{}^1 = 0.34$ V and $E_{p_a}{}^2 = 0.75$ V *vs.* s.c.e. This curve is identical to the one obtained after addition of 3 equivalents of tetrabutylammonium hydroxide to a solution of the ligand. This demonstrates that after electrolysis the solution only contains L^{3-} [ligand anion of (**5**)]. Several mechanisms could account for the present observations; in our view the most plausible one involves a two-electron reduction of the complex followed by a disproportionation of the resulting dicopper(I) derivative (Scheme 3).*

$$[Cu^{II}(HL)]_2 + 2e^- \longrightarrow [Cu^{I}(HL)]_2$$

$$[Cu^{I}(HL)]_2 \longrightarrow \tfrac{1}{2}[Cu^{II}(HL)]_2 + Cu^0 + L^{3-}$$

Scheme 3.

We do not have at the moment an explanation for the deprotonation of the ligand, except that reductive electrolyses generally increase the basicity of the medium. It is possible to redissolve the copper deposited on the electrode by applying

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* An alternative mechanism would involve the release of copper(I) ions and reduction of the resulting copper(I)–dimethyl sulphoxide (dmso) complex.[31]

positive potentials up to +0.85 V *vs.* s.c.e. After such a process, electrochemical and e.s.r. analyses of the resulting solution show that complex (**5**) has been partly regenerated but is contaminated by another species whose nature is unknown.

When looking at (**5**) one interesting question is whether the compound more closely resembles 1,3-diketonates or 1,3,5-triketonates. The present study provides a mixed answer to this question. Copper(II) bis(1,3-diketonates) are reduced in a two-electron process[30] leading to copper metal as is observed for (**5**). Moreover, copper(II) bis(1,3-diketonate), bearing methyl and phenyl substituents on the terminal carbons, is reduced at −0.38 V *vs.* s.c.e.[32] Compound (**5**) is reduced only at −1.18 V *vs.* s.c.e. This shift of the redox potential must be attributed to the fact that the high conjugation of the binucleating ligand strongly favours the planar structure suited to copper(II). A similar effect, although much less important, is observed for triketonates.[29]

Experimental

2,6-Diacetyl-4-methylphenol was prepared by a method similar to that reported by Mandal and Nag,[5] as was complex (**4**).

The Tetraketone (**2**).—Sodium (2.4 g) divided into small pieces was added to ethyl acetate (25 cm^3) whilst being vigorously stirred. To this was slowly added 2,6-diacetyl-4-methylphenol (3.85 g). The resulting mixture was stirred at room temperature for a few minutes until a red solid mass formed. This was gently heated at 100 °C eventually becoming liquid and then refluxed for 2 h. Upon cooling, diethyl ether (100 cm^3) was added resulting in precipitation of a large amount of the sodium salt of the tetraketone. This salt was then hydrolysed by dilute acetic acid (15%) resulting in a bright yellow powder. The powder was washed with water and dried under vacuum. Yield 3.3 g, m.p. 129 °C (Found: C, 65.2; H, 5.8; *m/z* 276. $C_{15}H_{16}O_5$ requires C, 65.2; H, 5.8%).

The Copper(II) *Complex of the Tetraketone*, (**5**).—The tetraketone (**2**) (1 mmol) was dissolved in ethanol (30 cm^3) and heated to reflux. To this was added a solution of $Cu(MeCO_2)_2$ (1 mmol) in ethanol (30 cm^3) and reflux continued for 1 h. The green powder precipitated was collected and purified by Soxhlet extraction with ethanol. Yield 70% (Found: C, 53.2, H, 4.1. $C_{30}H_{28}Cu_2O_{10}$ requires C, 53.3; H, 4.2%).

The Copper(II) *Complex of* 2,6-*Diacetyl*-4-*methylphenol*, (**3**).—The complex was isolated from an attempt to prepare a macrocyclic complex by a template technique.

Copper(II) perchlorate (1 mmol) and 1,3-diamino-2-propanol (1 mmol) were dissolved in ethanol (100 cm^3). The resulting solution was brought to reflux and 2,6-diacetyl-4-methylphenol (1 mmol) in ethanol (50 cm^3) was added dropwise; reflux was continued for 90 min. Upon cooling a blue powder was precipitated. This was found to be the copper amine complex $Cu\{H_2NCH_2CH(OH)CH_2NH_2\}_2(ClO_4)_2$. The green filtrate was reduced in volume to *ca.* 50 cm^3 and diethyl ether added, resulting in the precipitation of a green powder. This was collected, washed with ether, and dried under vacuum. Yield 30% (Found: C, 37.2; H, 3.2; Cl, 10.2. $C_{22}H_{22}Cl_2Cu_2O_{14}$ requires C, 37.3; H, 3.1; Cl, 10.0%).

Magnetic Measurements.—E.s.r. spectra were obtained with a Varian E9 instrument equipped with a Drusch RMN2 gaussmeter and an EIP 545 A microwave frequency counter and calibrated with tanol ($g = 2.0058$). Magnetic susceptibility measurements were done with a SHE 900 variable-temperature superconducting magnetometer operating at 5.6 kG in the range 6—300 K. Diamagnetic corrections were evaluated by using Pascal's constants. Data for complexes (**3**) and (**5**) were corrected for small amounts of saturated ferromagnetic impurities whose contributions were deduced from the field dependence of the samples' magnetic susceptibilities. The data were least-squares fitted by the equation (1). All parameters were allowed to vary; the quantity $[\chi_M(\text{obs.}) - \chi_M(\text{calc.})]^2$ was minimised. The quality of the fit was estimated through the statistical indicator $R = [\chi_M(\text{obs.}) - \chi_M(\text{calc.})]^2/N[\chi_M(\text{obs.})]^2$, where N is the number of measurements; R was 1.8×10^{-7}, 6.1×10^{-7}, and 8.4×10^{-8} for complexes (**3**), (**4**), and (**5**), respectively.

Electrochemistry.—The electrochemical apparatus consisted of a PAR 173 potentiostat/galvanostat driven by a PAR 175 universal programmer, a PAR 179 coulometer, and a Sefram TGM XY recorder. Electrochemical studies were performed in dimethyl sulphoxide (dmso) 0.1 mol dm^{-3} in tetrabutylammonium tetrafluoroborate using a conventional three-electrode cell with a saturated calomel reference electrode and a platinum working electrode. The reference electrode was connected to the solution through a bridge of 0.1 mol dm^{-3} NBu_4BF_4 in dmso. All potentials are referenced to the s.c.e. Under these conditions the oxidation potential of the ferrocene–ferrocenium couple calculated as $E_{\frac{1}{2}} = \frac{1}{2}(E_{p_c} + E_{p_a})$ was 0.43 V *vs.* s.c.e.

Crystal Data.—$C_{17}H_{30}Cl_2Cu_2N_4O_{11}$, $M = 664.43$, crystallises from water as black-purple plates, mean crystal dimensions 0.58 × 0.51 × 0.23 mm, triclinic, $a = 13.366(13)$, $b = 9.430(9)$, $c = 11.760(9)$ Å, $\alpha = 95.044(24)$, $\beta = 109.506(34)$, $\gamma = 111.245(8)^\circ$, $U = 1\,264.9(19)$ Å^3, $D_m = 1.74$ g cm^{-3}, $Z = 2$, $D_c = 1.745$ g cm^{-3}, space group $P\bar{1}$ (C_i, no. 2), graphite-monochromated Mo-K_α radiation ($\bar{\lambda} = 0.710\,69$ Å), μ(Mo-K_α) = 19.59 cm^{-1}, $F(000) = 680$.

Three-dimensional *X*-ray diffraction data were collected in the range $6.5 < 2\theta < 50^\circ$ on a Stoe Stadi-2 diffractometer by the ω-scan method. The 3 074 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Two alternative, and mutually incompatible, sites were found for partial occupancy water molecules: on the basis of peak heights and isotropic thermal parameters, occupancies of 0.60 and 0.40 were assigned to give a total of one water molecule of crystallisation. Hydrogen atoms, with the exception of those of the disordered water molecules, were located and were placed in calculated positions (C–H 0.98, N–H 1.01, and O–H 1.02 Å; C–C–H 111°); their contributions were included in structure-factor calculations ($B = 7.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at R 0.0605 with allowance for anisotropic thermal motion of all non-hydrogen atoms, with the exception of the partial occupancy water oxygens, and for the anomalous scattering of copper and chlorine. Table 3 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from ref. 33; unit weights were used throughout the refinement. Computer programs formed part of the Sheffield *X*-ray system.

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