Synthesis, *X*-Ray Structure, and Magnetic Properties of Di-μ-chloro-bis-[*N*-(2-hydroxy-2-phenylethyl)salicylideneiminatocopper(II)]†

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The crystal and molecular structure of $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$ [L = *N*-(2-hydroxy-2-phenylethyl)-salicylideneiminate; dmf = dimethylformamide] has been determined and refined to a final *R* value of 0.0329 (R' = 0.0257) using 3 979 independent reflections. The dinuclear units crystallize in the monoclinic space group $P2_1/c$ with dimensions a = 8.771(1), b = 13.440(2), c = 29.060(4) Å, and β = 97.113(4)°. Each copper atom is co-ordinated in a distorted square-planar manner by one tridentate Schiff-base anion and one chlorine atom, with normal copper–chlorine distances (mean 2.261 ± 0.002 Å). The chlorine atoms also form long bonds (mean 2.824 ± 0.019 Å) with the second copper atom. The magnetic susceptibilities measured from 5.1 K show a weak antiferromagnetic spin coupling. Fitting of the experimental data by the Bleaney–Bowers equation yielded the parameters g = 2.09(2), $2J_{12}$ = −7.1(4) cm^{-1}, and $N\alpha$ = 131(10) × 10^{-6} c.g.s. units. The contribution of intramolecular hydrogen bonds to the overall antiferromagnetic exchange interaction is discussed. The temperature-dependent e.s.r. spectra are reported.

Syntheses, *X*-ray structures, and magnetic properties of several oligomeric exchange-coupled copper(II) complexes with Schiff bases derived from aminoalcohols have been reported.[1–12] When prepared from copper(II) acetate monohydrate, alkoxo-bridged complexes are formed in which the Schiff-base ligands are dianions. The comparatively weak co-ordination properties of the acetate anion, due to its basicity, are apparently such that in addition to the formation of an enolato or a phenolato group, deprotonation of the considerably less acidic aliphatic hydroxy group also occurs. The formation of a dimeric complex with a Cu_2O_2 ring or of a tetrameric one with a Cu_4O_4 core occurs *via* the copper–alkoxide-oxygen bond. A great number of magnetic investigations on such iminoalcoholato-, but also on amino-alcoholato-bridged copper(II) complexes have shown that the spin coupling depends strongly on the geometric and electronic properties of the bridging group and also on the properties of the non-bridging co-ordinating atoms.[9–14]

In addition to several tetrameric copper(II) complexes derived from pyridoxal and different aminoalcohols,[9–12] attempts to obtain crystals suitable for *X*-ray measurements from the analogous salicylaldehyde derivative failed using copper(II) acetate for the synthesis.

Magnetic investigations on di-μ-chloro-bis[*N*-(2-hydroxy-2-phenylethyl)salicylideneiminato]copper(II), $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$ (dmf = dimethylformamide), prepared from copper(II) chloride dihydrate pointed to an oligo- or poly-nuclear arrangement different from that expected for alkoxo-bridged species, since the magnetic moment decreases below 50 K. Dimeric and polymeric alkoxo-bridged copper(II) complexes are normally strongly antiferromagnetically coupled,[14] whereas tetrameric alkoxo-bridged copper(II) complexes with Schiff bases as ligands show usually a weak ferromagnetic coupling.[5,9–12] In contrast, chloro-bridged copper(II) complexes are normally weakly antiferromagnetically coupled.[15] We report here the synthesis and structural and magnetic properties of the copper(II) complex $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$.

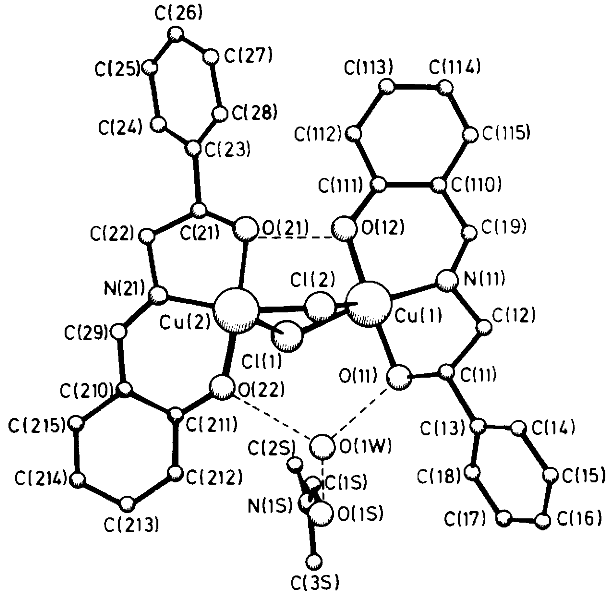

Figure 1. PLUTO drawing of $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$; projection on the plane defined by C(17), C(27), and C(214)

Results and Discussion

Description of the Structure.—The final structural data are presented in Tables 1 and 2 and in Figure 1. The structure consists of dinuclear units with a central non-planar Cu_2Cl_2 ring [dihedral angle between the planes defined by Cu(1),Cl(1),Cl(2) and by Cu(2),Cl(1),Cl(2) is 24.9°]. Within the pseudo-monomeric subunit each copper atom Cu(*n*) is co-ordinated in a distorted square-planar manner by a chlorine atom Cl(*n*) and by the tridentate Schiff-base anion with the aminoethanol oxygen O(*n*1), the deprotonated phenolato oxygen O(*n*2), and the nitrogen N(*n*1). The ligand–copper distances agree well with those found for comparable substances.[9–12,15] The increase in the co-ordination at the copper atom to (4 + 1) is achieved by two longer copper–chlorine bonds [Cu(1)–Cl(2), Cu(2)–Cl(1)] which are approximately

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† *Supplementary data available* (No. SUP 56497, 7 pp.): H-atom co-ordinates, thermal parameters, experimental and calculated magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Positional parameters with estimated standard deviations in parentheses for $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$

Atom	*x*	*y*	*z*
Cu(1)	0.204 4(1)	0.652 3(1)	0.031 9(1)
Cu(2)	0.350 4(1)	0.887 9(1)	0.020 2(1)
Cl(1)	0.090 6(1)	0.796 3(1)	0.048 9(1)
Cl(2)	0.492 3(1)	0.747 1(1)	0.028 3(1)
O(11)	0.288 8(2)	0.623 0(1)	0.097 4(1)
O(12)	0.138 5(2)	0.670 2(1)	−0.032 6(1)
O(21)	0.264 1(2)	0.846 3(1)	−0.045 6(1)
O(22)	0.411 3(2)	0.935 2(1)	−0.081 4(1)
N(11)	0.255 3(3)	0.513 4(2)	−0.024 3(1)
N(21)	0.274 9(2)	1.015 6(1)	−0.002 3(1)
C(11)	0.401 4(3)	0.545 5(2)	−0.098 7(1)
C(12)	0.324 6(3)	0.465 5(2)	−0.067 1(1)
C(13)	0.451 7(3)	0.506 3(2)	0.146 8(1)
C(14)	0.577 2(3)	0.444 0(2)	0.153 1(1)
C(15)	0.625 2(4)	0.403 4(2)	0.196 1(1)
C(16)	0.548 3(4)	0.424 1(2)	0.232 9(1)
C(17)	0.424 1(4)	0.486 1(2)	0.226 8(1)
C(18)	0.375 5(3)	0.527 4(2)	0.184 0(1)
C(19)	0.226 5(3)	0.462 3(2)	−0.013 0(1)
C(110)	0.154 9(3)	0.499 2(2)	−0.056 9(1)
C(111)	0.115 8(3)	0.600 6(2)	−0.064 8(1)
C(112)	0.048 5(3)	0.627 4(2)	−0.109 4(1)
C(113)	0.020 0(4)	0.558 0(3)	−0.143 7(1)
C(114)	0.0576 (4)	0.459 2(2)	−0.136 1(1)
C(115)	0.124 2(4)	0.430 6(2)	−0.093 3(1)
C(21)	0.155 1(3)	0.918 1(2)	−0.066 8(1)
C(22)	0.226 1(3)	1.017 9(2)	−0.052 3(1)
C(23)	0.127 0(3)	0.909 5(2)	−0.118 8(1)
C(24)	0.001 9(3)	0.958 4(2)	−0.142 2(1)
C(25)	−0.021 7(4)	0.958 2(2)	−0.190 1(1)
C(26)	0.077 6(4)	0.908 1(2)	−0.214 6(1)
C(27)	0.199 9(4)	0.858 8(2)	−0.191 9(1)
C(28)	0.225 1(3)	0.859 3(2)	−0.144 0(1)
C(29)	0.262 1(3)	1.094 0(2)	0.022 2(1)
C(210)	0.307 6(3)	1.102 0(2)	0.071 1(1)
C(211)	0.378 4(3)	1.023 5(2)	0.098 1(1)
C(212)	0.414 7(3)	1.041 3(2)	0.145 9(1)
C(213)	0.385 8(4)	1.131 0(3)	0.165 5(1)
C(214)	0.318 3(4)	1.207 9(2)	0.138 7(1)
C(215)	0.280 5(4)	1.193 2(2)	0.092 5(1)
O(1S)	0.152 3(3)	0.788 8(2)	0.198 6(1)
N(1S)	−0.106 9(3)	0.795 9(2)	0.189 4(1)
C(1S)	0.029 4(5)	0.791 5(2)	0.174 7(1)
C(2S)	−0.244 9(6)	0.805 5(4)	0.157 3(2)
C(3S)	−0.115 1(6)	0.804 1(4)	0.238 8(2)
O(1W)	0.386 8(3)	0.776 2(2)	0.144 3(1)

Table 2. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$

Cu(1)–Cu(2)	3.448(1)	Cu(2)–O(21)	2.046(2)
Cu(1)–Cl(1)	2.260(1)	Cu(2)–O(22)	1.902(2)
Cu(1)–Cl(2)	2.841(1)	Cu(2)–N(21)	1.925(2)
Cu(1)–O(11)	1.993(2)	O(21)–C(21)	1.441(3)
Cu(1)–O(12)	1.908(2)	O(22)–C(211)	1.328(3)
Cu(1)–N(11)	1.938(2)	N(21)–C(22)	1.464(3)
O(11)–C(11)	1.432(3)	N(21)–C(29)	1.284(3)
O(12)–C(111)	1.319(3)	O(12) ··· O(21)	2.658(4)
N(11)–C(12)	1.464(3)	O(11) ··· O(1W)	2.560(4)
N(11)–C(19)	1.281(3)	O(22) ··· O(1W)	2.838(4)
Cu(2)–Cl(2)	2.261(1)	O(1S) ··· O(1W)	2.748(4)
Cu(2)–Cl(1)	2.806(1)		
Cl(1)–Cu(1)–Cl(2)	92.4(1)	Cl(2)–Cu(2)–O(21)	90.3(1)
Cl(1)–Cu(1)–O(11)	94.7(1)	Cl(2)–Cu(2)–O(22)	95.4(1)
Cl(1)–Cu(1)–O(12)	91.1(1)	Cl(2)–Cu(2)–N(21)	160.7(1)
Cl(1)–Cu(1)–N(11)	164.5(1)	Cl(1)–Cu(2)–O(21)	86.5(1)
Cl(2)–Cu(1)–O(11)	84.1(1)	Cl(1)–Cu(2)–O(22)	90.7(1)
Cl(2)–Cu(1)–O(12)	94.0(1)	Cl(1)–Cu(2)–N(21)	103.6(1)
Cl(2)–Cu(1)–N(11)	102.1(1)	O(21)–Cu(2)–O(22)	173.8(1)
O(11)–Cu(1)–O(12)	174.0(1)	O(21)–Cu(2)–N(21)	81.6(1)
O(11)–Cu(1)–N(11)	81.7(1)	O(22)–Cu(2)–N(21)	93.7(1)
O(12)–Cu(1)–N(11)	93.2(1)	Cu(1)–Cl(1)–Cu(2)	85.0(1)
Cl(1)–Cu(2)–Cl(2)	93.3(1)	Cu(1)–Cl(2)–Cu(2)	84.2(1)

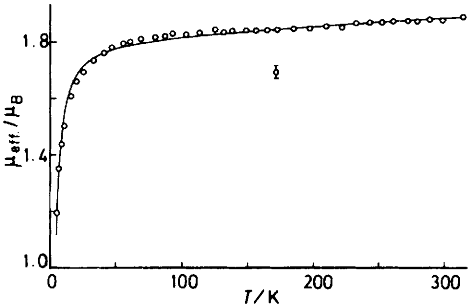

Figure 2. Temperature dependence of the magnetic moments of $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$. The solid line represents the best fit with the parameters $g = 2.09$ and $2J_{12} = -7.1$ cm^{-1} (see text)

perpendicular to the planes defined by each copper atom and its four main ligand atoms, leading to a step-like structure of the dimeric unit. This arrangement is stabilized by three hydrogen bonds [O(21) ··· O(12), O(11) ··· O(1W) ··· O(22)]. Another hydrogen bond exists between the water molecule and the dmf molecule [O(1W) ··· O(1S)]. There are no connections between the $[Cu_2Cl_2L_2]\cdot H_2O\cdot dmf$ units.

Magnetic Properties.—The temperature dependence of the magnetic moment is shown in Figure 2; it is characteristic of weakly spin-coupled copper(II) complexes with a singlet ground state. Fitting the experimental susceptibilities by use of the Bleaney–Bowers equation (1) (corrected for the temperature-independent paramagnetic susceptibility, $N\alpha$), we obtained the parameters $g = 2.09(2)$, $2J_{12} = -7.1(4)$ cm^{-1}, and $N\alpha = 131(10) \times 10^{-6}$ c.g.s. units. The uncertainties given in parentheses are taken from correlation effects within the non-linear optimization; for $N\alpha$ the error in $\chi_{\text{diam.}}$ is assumed to be $-216(10) \times 10^{-6}$ c.g.s. units. Figure 2 shows the good agreement between the experimental and calculated magnetic moments. The value of $N\alpha$ is distinctly higher than that normally observed (60×10^{-6} c.g.s. units), but the use of a fixed value yielded only moderate agreements especially at higher temperatures (> 200 K).

$$\chi_{\text{dimeric}}/2 = \frac{N_A g^2 \mu_B^2}{kT}\left[\frac{1}{3 + \exp(-2J_{12}/kT)}\right] + N\alpha \quad (1)$$

The *X*-band powder e.s.r. spectra are significantly dependent on the temperature (Figure 3). At 252.0 K the spectrum is typical of non-interacting copper(II) ions, yielding $g_{\parallel} = 2.29(2)$ $g_{\perp} = 2.15(2)$, and $g_{\text{av.}} = 2.20$. There is little change until *ca.* 70 K. Below this temperature, signals of the triplet state are superimposed on the previous ones as clearly seen at 40.0 K. Only the $\Delta M_s = \pm 1$ transitions of the triplet state are observed at 4.2 K, with a distinct *g* anisotropy [$g_1 = 2.28(2)$, $g_2 = 2.09(2)$, and $g_{\text{av.}} = 2.16$], showing that the single ion states are no longer populated. Careful scans in the $\Delta M_s = \pm 2$ region revealed no additional signals.

A comparison of the structural and magnetic data with the

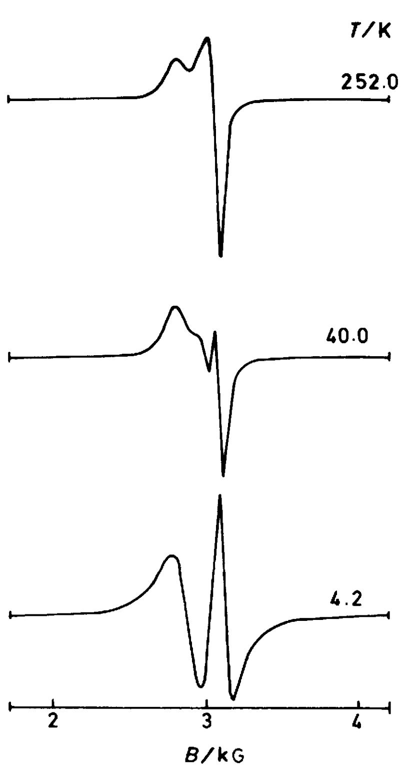

Figure 3. *X*-Band powder e.s.r. spectra of $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$

magnetostructural correlation found by Marsh *et al.*[15] shows at first sight a good agreement. According to this correlation the variable Cu–Cl distances, *R* [in our case Cu(1)–Cl(2) and Cu(2)–Cl(1)], and the bridging angle φ at the chlorine atoms are the important geometrical parameters by which the exchange constant $2J_{12}$ is determined. When $\varphi/R = 30° \text{ Å}^{-1}$ (estimated for the present complex from the mean values) a $2J_{12}$ value of about -12 cm^{-1} is expected, and indeed the value found experimentally is $-7.1(4)$ cm^{-1}. On the other hand, there are serious doubts as to whether this agreement is only another new confirmation of an existing magnetostructural correlation or whether especially in this case more than one term is important, combining to give accidentally the value expected.

First the deviation of the Cu_2Cl_2 ring from planarity (dihedral angle = 24.9°) must be taken into account. In Figure 4 the orbital scheme deemed by Marsh *et al.*[16] to be important for the exchange coupling in chloro-bridged copper(II) complexes is given, it is only valid for parallel planar dimers. It shows the symmetric and antisymmetric combinations ψ_{B_u} and ψ_{A_g} which essentially involve the $d_{x^2-y^2}$ metal orbitals and the p_x and p_z orbitals of the chlorine. Starting from this model, a dihedral angle in the four-membered M_2L_2 ring can be achieved by simultaneously moving the metal atoms along the *y*-axis. Primarily, since no spherical ligand *s*-orbitals are involved in the exchange process (according to extended-Hückel molecular-orbital calculations, between these and the metal orbitals a relatively large difference in energy exists), the overlap should change drastically with increasing dihedral angle. It is known that the exchange interaction in oligonuclear metal complexes is extremely sensitive to such changes. Secondly the hydrogen-bond bridges must not be excluded from an analysis of the magnetic behaviour. Bertrand *et al.*[7,17,18] showed that within some dimeric copper(II) complexes with the bridging unit represented in Figure 5 antiferromagnetic spin coupling occurs, in all cases to a distinctly greater extent than in the present complex ($-2J_{12} = 56-94$ cm^{-1}). Even though in $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$ one possible hydrogen bridge exchange pathway is elongated by the water molecule, the contribution of these bridges should be far from being negligible. Recently we found that even in a dimeric copper(II) complex with a longer copper–copper distance (5.46 Å), dimeric [*NN'*-2-hydroxypropane-1,3-diylbis(3-t-butyl-5-methylsalicylideneiminato)]-copper(II), a weak antiferromagnetic spin coupling exists which reduces the magnetic moment at temperatures below 20 K [$2J_{12} = -2.8(4)$ cm^{-1}].[19] The role of such $O\cdots H\cdots O$ hydrogen bonds in the magnetic exchange interaction has been discussed by Nieuwpoort *et al.*[20] Consequently, further investigations on copper(II) dimers of this type are necessary in order to determine the geometrical factors involved in the exchange interaction within this group of compounds.

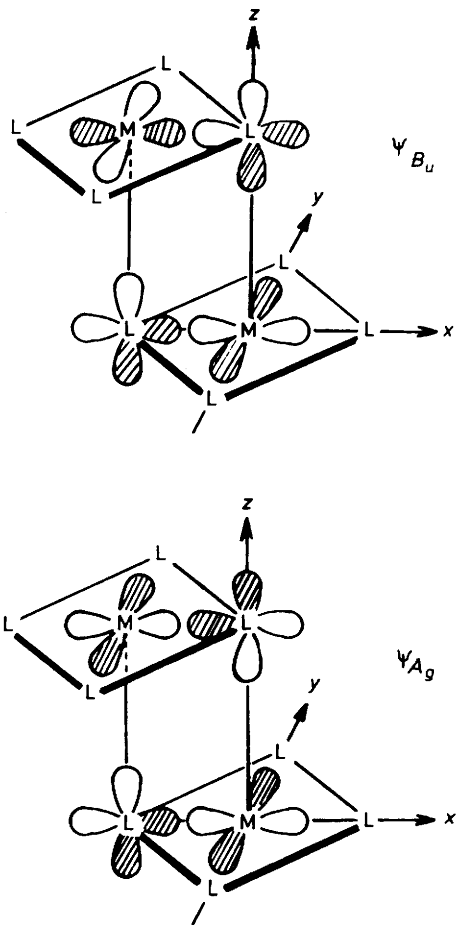

Figure 4. σ-Antibonding orbitals for parallel planar dimers showing the symmetric and antisymmetric combinations (from ref. 16)

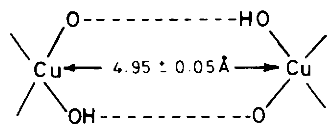

Figure 5. Exchange pathway *via* hydrogen bonds (see text)

Experimental

Preparation.—To a mixture of salicylaldehyde (1.22 g, 10 mmol) and 2-amino-1-phenylethanol (1.37 g, 10 mmol) in methanol (100 cm^3) a solution of copper(II) chloride dihydrate (1.70 g, 10 mmol) in methanol (100 cm^3) was added. The resulting mixture was stirred and solid sodium hydroxide (0.2 g, 5 mmol) was added. After 30 min a dark brown precipitate was collected by filtration. It was dried in air and recrystallized from dmf. After some weeks crystals suitable for *X*-ray analysis were obtained.

Crystallography.—Crystal data. $C_{33}H_{37}Cl_2Cu_2N_3O_6$, M = 769.7, monoclinic, a = 8.771(1), b = 13.440(2), c = 29.060(4) Å, β = 97.113(4)°, U = 3 399.23 Å^3 (by least-squares refinement with 64 strong reflections, λ = 0.710 69 Å), space group $P2_1/c$ (no. 14),[21] D_m(flotation) = 1.35(3) g cm^{-3}, Z = 4, D_c = 1.367 g cm^{-3}, $F(000)$ = 1 592. Dark brown, multifaceted crystals. Crystal dimensions (distances to faces from centre): 0.212($10\bar{2}$) × 0.192($1\bar{1}\bar{2}$) × 0.146($00\bar{1}$) × 0.196($11\bar{2}$) × 0.192($0\bar{1}\bar{1}$) × 0.208($1\bar{1}0$) × 0.212(110) × 0.196($1\bar{8}4$) × 0.216($01\bar{1}$) × 0.204($\bar{1}1\bar{2}$) × 0.219($0\bar{1}1$) × 0.204($\bar{1}12$) × 150(001) × 0.196($\bar{1}10$) mm, μ(Mo-K_α) = 13.87 cm^{-1}.

Data collection and processing. Stoe-Siemens AED2 diffractometer, scan $2\theta:\omega = 1:1$ in the range $6 < 2\theta < 45°$, graphite-monochromated Mo-K_α radiation; 8 451 reflections measured, 4 309 unique [merging R = 0.0221 after absorption correction (maximum, minimum transmission factors 0.684, 0.565)], giving 3 979 with $F > 3\sigma(F)$. Three strong reflections (108, $22\bar{5}$, $2\bar{2}\bar{5}$) measured every hour showed constant intensity.

Structure analysis and refinement. The structure was solved by direct methods which led to the positions of the copper and chlorine atoms. The positions of the remaining non-hydrogen atoms were found from several Fourier maps. Full-matrix least-squares refinement with isotropic thermal parameters converged to an R value of 0.1610. Refinement with anisotropic parameters yielded the positions of nearly all hydrogen atoms. These were included in further refinement cycles ($U_{iso.}$ fixed), the remaining hydrogen atoms being geometrically positioned; after some least-squares cycles these could also be included in the final cycles in which all hydrogen atoms including those of the water molecule and the dmf molecule were refined. This led to the final R value of 0.0329 (R' = 0.0257). The weighting scheme used was $w = 1/\sigma^2(F_o)$ with $\sigma(F_o)$ from counting statistics. For all parameters including those of the hydrogen atoms the shift-to-error ratio was less than 0.03 within the last least-squares cycle. The highest peak in the final difference map was at 0.28 e Å^{-3}.

Magnetic Measurements.—The magnetic susceptibilities of the complex $[Cu_2Cl_2L_2]\cdot dmf\cdot H_2O$ were measured by the Faraday method at *ca.* 6×10^6 G^2 cm^{-1} (G = 10^{-4} T) using $Hg[Co(SCN)_4]$ as a susceptibility standard. Experimental susceptibility data were corrected for underlying diamagnetism. Magnetic moments were calculated using the formula $\mu = 2.828(\chi T)^{\frac{1}{2}}$. To convert into S.I. units χ should be multiplied by $4\pi \times 10^{-6}$ and μ is then given by the expression $\mu = 797.74(\chi T)^{\frac{1}{2}}$.

E.s.r. spectra of a powder sample were recorded at different temperatures (252—4.2 K) on a Varian E-Line spectrometer.

Calculations.—The structure calculations were carried out with the program SHELX 76;[22] the scattering factors for Cu were those of Cromer and Mann;[23] the others are stored in the program. The exchange parameters were obtained using a modified simplex routine.[24] The function minimized was $\Sigma(\chi_{expt.} - \chi_{calc.})^2 T^2$. All calculations were performed on the IBM 3081 D computer at the Technische Hochschule Darmstadt.

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