Crystal Structure† and Magnetic Properties of Dimeric [2-Hydroxypropane-1,3-diylbis(3′-t-butyl-5′-methylsalicylideneiminato)]copper(II)

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The crystal and molecular structure of the title compound has been determined from single-crystal *X*-ray diffraction data and refined to a final *R* value of 0.0882 (*R*′ = 0.0521) using 2 527 independent reflections. The copper(II) complex crystallizes in the tetragonal space group $I4_1/a$ with dimensions a = 14.740(2) and c = 47.512(8) Å. The copper atom is co-ordinated in a distorted square planar fashion by the deprotonated phenolic oxygens and the Schiff-base nitrogen atoms. Discrete dimeric units are built up by an additional weak co-ordination of the hydroxy oxygen [Cu(1)–O(2′) 2.697(5) Å] approximately perpendicular to the plane defined by the four chelate ligand donor atoms. This arrangement is also stabilized by three hydrogen bond bridges per dimer. Despite the long copper–copper distance [Cu(1)–Cu(1′) 5.457(2) Å] and unusual bridging units the e.s.r. spectra and the temperature dependence of the magnetic moment show a weak antiferromagnetic spin coupling with a singlet–triplet splitting of about 3 cm^{-1}.

Our recent work[1] on the kinetics of metal exchange in [*N,N*′-ethylenebis(salicylideneiminato)]copper(II) led us to the preparation of a series of analogous complexes with a modified ethylene bridge and to their kinetic investigation.[2] In the course of this work 1,3-diamino-2-hydroxypropane was reacted with two moles of 3-t-butyl-5-methylsalicylaldehyde to form the corresponding Schiff base, which yields the green complex [2-hydroxypropane-1,3-diylbis(3′-t-butyl-5′-methylsalicylideneiminato)]copper(II), (**1**). Our interest in this complex was three-fold, concerning the following questions: (*i*) do the bulky t-butyl groups in the 3-position force (**1**) to become tetrahedrally distorted, (*ii*) is (**1**) more soluble than the corresponding complex lacking the hydroxy group in the propane-1,3-diyl bridge, and (*iii*) does the hydroxy group in (**1**) lead to structural effects in the sense that monomeric units of (**1**) interact in the solid state?

In the present paper we report the single-crystal *X*-ray diffraction analysis of (**1**) as well its magnetic and e.s.r. spectroscopic properties.

Table 1. Selected distances (Å) and angles (°) with estimated standard deviations in parentheses for (**1**)*

Cu(1)–Cu(1′)	5.457(2)	O(2)–O(2′)	2.867(7)
Cu(1)–O(1)	1.904(4)	O(2)–C(14)	1.333(10)
Cu(1)–O(2′)	2.697(5)	O(3)–C(27)	1.315(8)
Cu(1)–O(3)	1.941(4)	N(1)–C(12)	1.293(9)
Cu(1)–N(1)	1.973(5)	N(1)–C(13)	1.483(7)
Cu(1)–N(2)	1.960(5)	N(2)–C(15)	1.463(9)
O(1)–C(1)	1.307(8)	N(2)–C(16)	1.286(11)
O(1)–Cu(1)–O(3)	84.7(2)	O(3)–Cu(1)–N(1)	168.7(3)
O(1)–Cu(1)–N(1)	91.9(2)	O(3)–Cu(1)–N(2)	91.5(3)
O(1)–Cu(1)–N(2)	166.8(3)	N(1)–Cu(1)–N(2)	94.1(4)

* Primed atoms on the symmetry related position $1-x$, $1.5-y$, z.

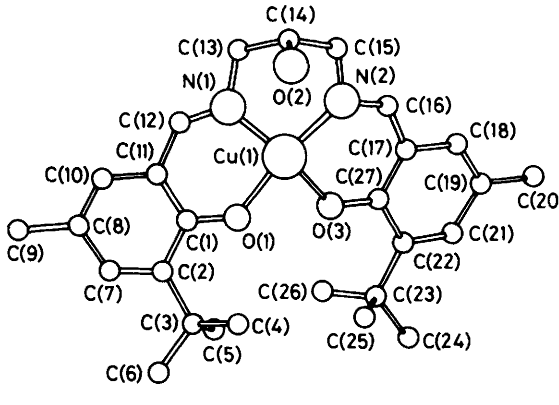

Figure 1. Molecular structure of (**1**) (view along [100])

Results and Discussion

Description of the Structure.—The final structural data are presented in the Tables 1—3 and in Figures 1 and 2. The copper atom is co-ordinated in a distorted square planar fashion by the two deprotonated phenolic oxygen atoms and by the two Schiff-base nitrogen atoms. The considerable tetrahedral distortion shows that the crystallographically possible higher symmetry with a mirror plane through Cu(1), C(14), and O(2) is found only as a rough approximation with pseudo-symmetry. The two six-membered rings formed by Cu(1), the azomethine groups, the phenolic oxygen atoms and the carbon atoms belonging to the phenyl rings are essentially planar. These rings are known to be aromatic.[3,4] The ring formed by Cu(1) and the atoms of the diamine, however, is corrugated due to its saturated character. In addition to the distorted planar co-ordination core a long Cu(1)–O(2′) bond exists [2.697(5) Å] which is approximately perpendicular to the co-ordination plane. This weak interaction leads to the formation of dimers. Figure 2 shows the central bridging unit within these dimeric aggregates which are additionally stabilized by three hydrogen bridges [O(2)–O(2′) 2.867(7), O(2)–O(3′) and O(2′)–O(3) 2.956(7) Å]. It follows from symmetry considerations that

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† *Supplementary data available* (No. SUP 56605, 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.

Non-S.I. units employed: G = 10^{-4} T, $\chi_{c.g.s.} = (10^6/4\pi)\chi_{S.I.}$.

Table 2. Deviations from best planes (Å) and interplanar angles (°) for (**1**)

Plane	Atom/deviation
1	Cu(1)/0.011, O(1)/−0.203, O(3)/0.197, N(1)/0.177, N(2)/−0.182
2	Cu(1)/−0.065, O(1)/0.054, N(1)/0.047, C(1)/0.012, C(11)/−0.062, C(12)/0.015
3	Cu(1)/−0.052, O(3)/0.033, N(2)/0.048, C(16)/0.000, C(17)/−0.049, C(27)/0.019
4	N(1)/−0.027, N(2)/0.178, C(13)/−0.012, C(14)/0.318, C(15)/−0.367

Angles (°) between planes: 1–2, 10.1; 1–3, 9.0; 1–4, 21.3; 2–3, 19.1; 2–4, 19.4; 3–4, 26.9

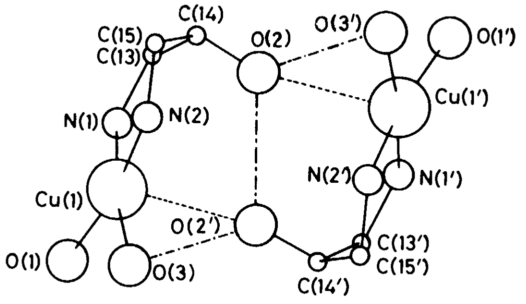

Figure 2. Pair arrangement *via* the O(2) atoms in (**1**), [001]. The primed atoms are related to those in Table 3 by the symmetry operation 1 − *x*, 1.5 − *y*, *z*

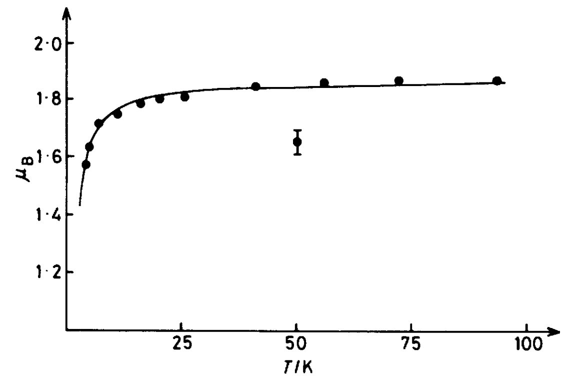

Figure 3. Temperature dependence of the magnetic moment of (**1**). Solid line calculated on the basis of $g = 2.14$, $2J_{12} = -2.8$ cm^{-1}

these three hydrogen bridges have to be dynamic in the sense that the bridge combination O(2)–O(2′) plus O(2)–O(3′) is in equilibrium with the combination O(2)–O(2′) plus O(2′)–O(3). For the interpretation of the magnetic data it is necessary to emphasize that the dimers are not actually connected, a fact which prevents long-range order phenomena.

Recently several dimeric copper(II) complexes derived from Schiff bases of different carbonyl compounds (pyridine-2-carbaldehyde, salicylaldehyde, acetylacetone, *etc.*) with 1,3-diamino-2-hydroxypropane or 1,5-diamino-3-hydroxypentane were reported.[5–8] In some of these dimeric complexes the two copper atoms are bridged asymmetrically by the deprotonated hydroxy group and an additional anion (Cl$^-$, OH$^-$, pyrazolate, acetate). The Cu–Cu distances (3.2—3.6 Å) are considerably smaller than in (**1**), which is obviously due to the presence of the additional anions which are also responsible for the stronger spin coupling observed for these compounds.

Magnetic Properties.—The temperature dependence of the magnetic moment (Figure 3) is characteristic of very weakly spin-coupled copper(II) complexes with a singlet ground state.

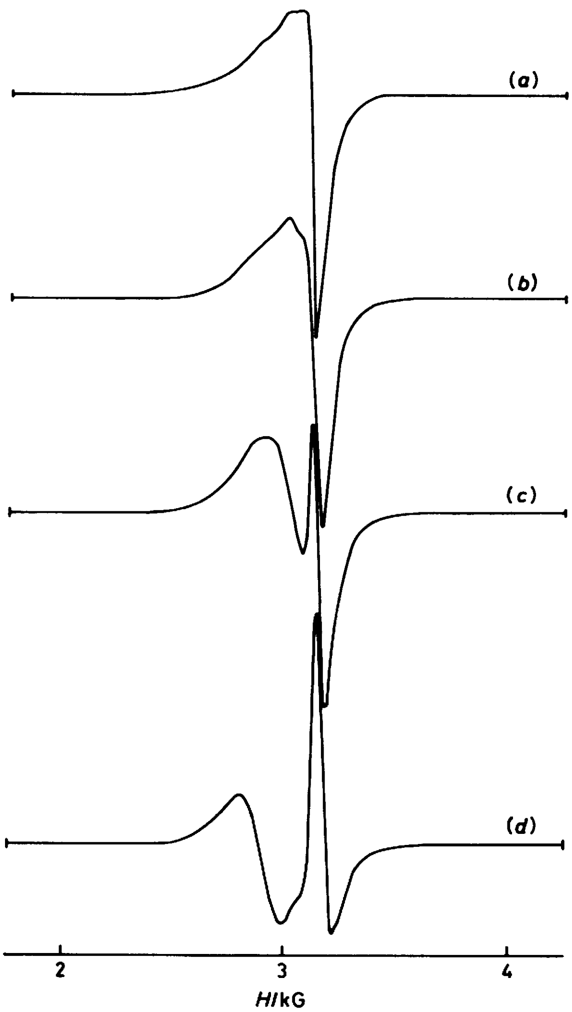

Figure 4. *X*-Band powder e.s.r. spectra of (**1**) at (*a*) 278, (*b*) 37.5, (*c*) 13.7, and (*d*) 4.1 K

Fitting the experimental susceptibilities to the Bleaney–Bowers equation (1), we obtained the parameters $g = 2.14(2)$ and

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

$2J_{12} = -2.8(4)$ cm^{-1} (uncertainty values given were taken from correlation effects); $N\alpha$ was fixed at 60×10^{-6} cm^3 mol^{-1}. A greater uncertainty may arise from neglecting the Zeeman term in the Hamiltonian (2) used, since an exact evaluation of J_{12} can

$$\mathscr{H} = -2J_{12}\hat{S}_1\hat{S}_2 \quad (2)$$

Table 3. Fractional co-ordinates with estimated standard deviations in parentheses for (**1**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	0.323 2(1)	0.695 2(1)	0.202 4(1)	C(12)	0.279 2(4)	0.763 7(4)	0.147 1(1)
O(1)	0.263 3(3)	0.603 9(2)	0.181 0(1)	C(13)	0.366 1(5)	0.870 7(4)	0.170 1(2)
O(2)	0.500 5(3)	0.847 3(4)	0.194 8(1)	C(14)	0.422 5(5)	0.892 9(5)	0.194 3(2)
O(3)	0.342 3(3)	0.599 1(2)	0.229 7(1)	C(15)	0.369 8(5)	0.882 8(5)	0.221 3(2)
N(1)	0.322 1(3)	0.780 2(3)	0.170 3(1)	C(16)	0.375 6(4)	0.770 9(5)	0.255 8(2)
N(2)	0.359 8(3)	0.787 8(4)	0.229 7(1)	C(17)	0.376 3(4)	0.686 6(4)	0.270 3(2)
C(1)	0.225 7(4)	0.607 4(4)	0.156 1(1)	C(18)	0.394 5(4)	0.689 2(6)	0.299 3(2)
C(2)	0.179 9(4)	0.529 6(4)	0.145 2(1)	C(19)	0.402 6(5)	0.612 7(8)	0.314 8(2)
C(3)	0.174 3(5)	0.442 3(4)	0.162 3(2)	C(20)	0.422 8(5)	0.614 2(5)	0.346 0(1)
C(4)	0.124 0(4)	0.460 5(4)	0.190 0(2)	C(21)	0.392 0(5)	0.531 4(6)	0.300 8(2)
C(5)	0.270 8(4)	0.408 4(4)	0.169 1(1)	C(22)	0.374 9(4)	0.521 0(4)	0.272 6(1)
C(6)	0.125 1(5)	0.365 9(4)	0.147 2(2)	C(23)	0.367 2(5)	0.426 1(4)	0.259 0(1)
C(7)	0.139 2(4)	0.537 7(5)	0.119 5(2)	C(24)	0.386 8(5)	0.348 3(4)	0.279 7(1)
C(8)	0.140 0(4)	0.616 4(6)	0.102 6(1)	C(25)	0.271 3(4)	0.412 6(4)	0.247 6(1)
C(9)	0.090 5(4)	0.619 4(5)	0.074 6(1)	C(26)	0.436 0(4)	0.418 0(4)	0.234 8(1)
C(10)	0.184 6(4)	0.688 7(4)	0.112 9(1)	C(27)	0.363 0(4)	0.603 4(4)	0.256 6(1)
C(11)	0.228 9(4)	0.686 3(4)	0.139 1(1)				

only be carried out by fitting the magnetization instead of the magnetic susceptibility. Nevertheless it remains certain that a small antiferromagnetic spin coupling reduces the magnetic moment at low temperatures. Figure 3 shows good agreement between experimental and calculated magnetic moments.

The e.s.r. spectra recorded at different temperatures confirm the existence of an intradimeric exchange interaction. Four spectra are presented in Figure 4. No significant change can be observed in the temperature range from 300 to 35 K in which typical single-ion spectra are obtained corresponding to the fact $kT \gg |2J_{12}|$. The shoulders observed between 2.75 and 3.05 kG result from axial symmetry and hyperfine coupling and are not sufficiently resolved to evaluate *g* values. Below 35 K a broad line appears which becomes more and more intense and at 4.1 K two separate lines show clearly the anisotropic spectrum of the triplet state with the *g* values: $g_{\parallel} = 2.29(2)$, $g_{\perp} = 2.07(2)$, $g_{\text{av.}} = 2.14$. The value for $g_{\text{av.}}$ is in good agreement with the one obtained by fitting the magnetic susceptibility data to equation (1).

A pathway for the observed spin coupling could be Cu(1)–N(1)–C(13)–C(14)–O(2)–Cu(1′) [alternatively *via* N(2) and C(15); see Figure 2]. This bridge contains four strong chemical bonds (of which at least two are pure σ bonds) and a weak fifth one.

Another possible pathway is Cu(1)–O(2′)–O(2)–Cu(1′), consisting of two weak copper–oxygen bonds and a hydrogen bridge. A clear assignment to one of the two pathways cannot be made. Coupling *via* the hydrogen bridge, however, would be in line with similar systems as studied by Bertrand *et al.*[9,10] and Nieuwpoort *et al.*[11] In addition, the alternative pathway with coupling through a four-membered σ-bonded bridge would be very unusual and a novel route.

Experimental

Preparation.—A solution of 1,3-diamino-2-hydroxypropane (1.80 g, 0.02 mol) (Aldrich; Steinheim, West Germany) in ethanol (50 cm^3) was added dropwise to a stirred solution of 3-t-butyl-5-methylsalicylaldehyde (7.69 g, 0.04 mol; as prepared from commercially available 2-t-butyl-4-methylphenol according to a published procedure[12]) in ethanol (100 cm^3). The mixture was then heated to 70 °C for 5 min. After cooling the solvent was distilled off and the solid Schiff base crystallized from light petroleum (b.p. 40—80 °C), m.p. 145—146 °C.

A solution of $Cu(O_2CMe)_2 \cdot H_2O$ (1.0 g, 0.005 mol) (reagent grade; Merck Darmstadt) in water (20 cm^3) was added dropwise to a solution of the Schiff base (2.19 g, 0.005 mol) in ethanol (200 cm^3). After that another portion of ethanol (50 cm^3) was added and the mixture heated to 70 °C, filtered, and then cooled. The dark green crystals formed were sucked off and recrystallized from toluene, m.p. 275—285 °C (decomp.) (Found: C, 64.95; H, 7.25; N, 5.60. Calc. for $C_{27}H_{36}CuN_2O_3$: C, 64.85; H, 7.25; N, 5.60%).

Crystal Data.—$C_{27}H_{36}CuN_2O_3$, $M = 500.14$, tetragonal, $a = 14.740(2)$, $c = 47.512(8)$ Å, $U = 10\,322.82$ Å^3 (by least-squares refinement with 56 strong reflections), space group $I4_1/a$ (no. 88),[13] $Z = 16$, D_m (flotation) = 1.28(3), $D_c = 1.287$ g cm^{-3}, $F(000) = 4\,240$, $\mu(\text{Mo-}K_\alpha) = 8.3$ cm^{-1}. Dark green bipyramids {101}; crystal dimensions (distances to faces from centre), 0.081 $(01\bar{3})$ × 0.119 (101) × 0.135 $(\bar{1}01)$ × 0.146 $(0\bar{1}1)$ × 0.150 $(10\bar{1})$ × 0.185 mm (011).

Data Collection and Processing.—Stoe-Siemens AED2 diffractometer, scan $2\theta:\omega = 1:1$ in the range $6.2 < 2\theta < 45.0°$; graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å); 6 999 reflections measured, 3 358 unique [merging $R = 0.064$ for 6 983 after absorption correction (max., min. transmission factors 0.857, 0.815)], giving 2 527 with $F > 2\sigma(F)$; three strong reflections measured every 60 min showed constant intensity.

Structure Analysis and Refinement.—The structure was solved by direct methods which led to the position of the copper atom. The positions of the remaining non-hydrogen atoms were found by a Fourier map. Least-squares refinement with isotropic thermal parameters converged to the *R* value of 0.1345. Least-squares refinement with anisotropic non-hydrogen atoms and isotropic hydrogens in fixed calculated positions (C–H 0.96 Å) gave the final *R* value of 0.0882 ($R' = 0.0521$). The weighting scheme was $w = 1/\sigma^2(F_o)$. For all parameters the ratio of shift to estimated standard deviation was <0.04 within the last least-squares cycle. A final difference map showed the highest peak (e Å^{-3}) at 0.59.

Magnetic Measurements.—The magnetic susceptibilities of (**1**) were measured by the Faraday method at *ca.* 6 × 10^6 G^2 cm^{-1} using $Hg[Co(SCN)_4]$ as a susceptibility standard. Experimental susceptibility data were corrected for underlying diamagnetism ($\chi_{\text{dia}} = -314.6 \times 10^{-6}$ cm^3 mol^{-1}). Magnetic moments were calculated using the formulae $\mu = 2.828(\chi_{\text{c.g.s.}}T)^{\frac{1}{2}}$, $\mu = 797.74(\chi_{\text{S.I.}}T)^{\frac{1}{2}}$.

Electron spin resonance spectra of a powder sample of (**1**) were recorded at different temperatures (4.1—278 K) on a Varian E-Line spectrometer.

Calculations.—Structure calculations were performed on a Data General Eclipse S 140 computer using a program package developed by Stoe and Cie, Darmstadt; scattering factors are stored in the program.

The exchange parameters were obtained using a modified simplex routine.[14] The function minimized was $\Sigma(\chi_{\mathrm{expt.}} - \chi_{\mathrm{calc.}})^2 T^2$. These calculations were performed on the IBM 3081 K computer at the Technische Hochschule Darmstadt.

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