Crystal and Molecular Structure and Magnetic Properties of Tetrakis[(2-diethylaminoethanolato)isocyanatocopper(II)]

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The crystal and molecular structure of the title complex has been determined from single-crystal X-ray diffraction data and refined to R 0.068 for 1 423 independent reflections. Four oxygen-bridged cubane-type molecules with a Cu_4O_4 core, having crystallographically imposed S_4 point symmetry, occupy a tetragonal unit cell, space group $I\bar{4}2d$, of dimensions a = 17.85(1) and c = 11.92(1) Å. The four copper atoms in the tetranuclear cluster are situated in an almost tetrahedral arrangement, the two independent copper–copper separations being 3.194(2) (× 2) and 3.193(2) Å (× 4). Copper–oxygen distances within the Cu_4O_4 framework [1.936(6) (× 4), 2.243(6) (× 4), and 2.113(6) Å (× 4)] are different and show unsymmetric bridging of the copper atoms. The co-ordination around copper (amine nitrogen, isocyanate nitrogen, and three alkoxide triply bridging oxygens) may be described as between distorted square pyramidal and distorted trigonal bipyramidal. The magnetic susceptibility measured over the range 2.6—300 K shows a maximum at *ca.* 35 K and thus indicates overall antiferromagnetic spin coupling. The magnetism of the complex can be explained on the basis of the isotropic Heisenberg–Dirac–van Vleck model. The resulting values for the magnetic exchange integrals: [J_{12} −21.4 ± 0.5 (× 2), J_{13} 12.3 ± 1.0 cm^{-1} (× 4)] indicate the simultaneous presence of antiferromagnetic and ferromagnetic interactions between copper atoms within the same molecule.

STRUCTURAL and magnetic investigations[1-7] of alkoxo-bridged copper(II) complexes $[\{CuX(OCH_2CH_2NR_2)\}_n]$ (R = Me, Et, Pr^n, or Bu^n; X = Cl, Br, NCO, or NCS) showed the existence of di-, tetra-, and poly-meric structures, and intramolecular magnetic interactions between the single copper(II) ions. The magnetic moment at room temperature of the dimeric complexes is strongly reduced and decreases further with decreasing temperature. This behaviour can be satisfactorily explained by the widely applied Bleaney–Bowers equation on the basis of the isotropic Heisenberg–Dirac–van Vleck (HDVV) model (for reviews see refs. 8—11). If two of the dimeric molecules come together to build-up cubane-type tetramers $[\{CuX(OCH_2CH_2NR_2)\}_4]$ (1) the situation becomes more complicated since the number of exchange parameters increases and the complexes show normal magnetic moments at room temperature. Magnetic investigations in the range 80—300 K indicated a non-zero Weiss constant and thus the presence of overall antiferromagnetic or ferromagnetic spin coupling.[2,3]

For a determination of the exchange parameters in cubane-type tetramers it is necessary to extend susceptibility measurements to liquid-helium temperature, since the magnetic interactions between the single copper(II) ions become smaller compared to those in the dimeric complexes. Such studies have already been made for the cases in which R = Et, X = Cl and R = Bu^n, X = Cl or Br.[12] We report here the crystal and molecular structure of (1; R = Et, X = NCO) and its magnetic properties down to 2.6 K. The exchange parameters have been determined on the basis of the HDVV model and their relations to the structure are discussed.

EXPERIMENTAL

Preparation.—The preparation of the complex followed closely the procedure described by Lehtonen *et al.*;[13] K[OCN] was used instead of K[SCN]. Since it is very sparingly soluble in methanol, solid K[OCN] was added to the methanolic solution of copper(II) acetate monohydrate and 2-(dipropylamino)ethanol (mol ratio 1 : 2). It dissolved on heating the reaction mixture on a water-bath. On standing overnight a light green precipitate resulted [Found: C, 37.8; H, 6.30; N, 12.8. Calc. for $(C_7H_{14}CuN_2O_2)_4$: C, 37.9; H, 6.35; N, 12.65%]. Crystals suitable for X-ray analysis were obtained by recrystallization from methanol.

Magnetic Measurements.—The magnetic susceptibility of a powdered sample was recorded over the range 2.6—300 K with a Foner-type vibrating sample magnetometer at 10 kG † as cited in ref. 12. Experimental susceptibility data were corrected for the underlying diamagnetism. Magnetic moments were calculated using the formula $\mu = 2.828(\chi T)^{\frac{1}{2}}$.‡

Crystal Data.—$(C_7H_{14}CuN_2O_2)_4$, M = 886.96, Tetragonal, a = 17.85(1), c = 11.92(1) Å, U = 3 798 Å^3, D_m (by flotation) = 1.53(2) g cm^{-3}, Z = 4, D_c = 1.551 g cm^{-3}, $F(000)$ = 1 808, space group $I\bar{4}2d$ from the systematic absences hkl for $h + k + l = 2n + 1$ and hhl for $2h + l = 4n + 2$ and successful structure determination, Mo-K_α radiation, graphite monochromatized, λ = 0.710 69 Å, μ(Mo-K_α) = 21.8 cm^{-1}. Cell constants were obtained from

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† Throughout this paper: 1 G = 10^{-4} T; 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

‡ To convert into S.I. units, χ is multiplied by $4\pi \times 10^{-6}$ and the magnetic moment is then given by the expression $\mu = 797.74(\chi T)^{\frac{1}{2}}$.

[1] E. Uhlig and K. Staiger, *Z. anorg. Chem.*, 1966, **346**, 21.

[2] E. Uhlig and K. Staiger, *Z. anorg. Chem.*, 1968, **360**, 39.

[3] Y. Nishida and S. Kida, *J. Inorg. Nuclear Chem.*, 1976, **38**, 451.

[4] R. Mergehenn and W. Haase, *Acta Cryst.*, 1977, **B33**, 1877.

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[6] L. Merz and W. Haase, *Acta Cryst.*, in the press.

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[11] W. E. Hatfield, in 'Theory and Applications of Molecular Paramagnetism,' eds. E. A. Boudreaux and L. N. Mulay, Wiley-Interscience, New York, 1976, p. 349.

[12] L. Merz, W. Haase, and G. Keller, *Ber. Bunsengesellschaft Phys. Chem.*, 1976, **80**, 305.

[13] M. Lehtonen, E. Luukkonen, and R. Uggla, *Suomen Kem.*, 1971, **B44**, 399.

precession photographs and refined by least-squares fit to the positions of 16 reflections (2θ 21.5°) on a computer-controlled STOE four-circle-diffractometer.

Intensity Data.—A crystal with dimensions *ca.* 0.17 × 0.17 × 0.32 mm was orientated along the *c* axis and transferred to a Weissenberg-geometry computer-controlled STOE diffractometer equipped with a scintillation counter. Intensity data were collected (ω scan) in the range $5 \leqslant 2\theta \leqslant 50°$. The variable-range technique was used, $\Delta\omega = 1.2 + 0.5(\sin \mu/\tan \theta')°$. Measuring time for background: 30 s; measuring times for the reflections: 0.5 s per step of width 0.01° (= 60 s for zero-layer reflections). Of 1 702 independent reflections, 1 423 having $I \geqslant 3\sigma(I)$ were considered observed and used in the analysis. The intensity data were corrected for Lorentz, polarization, and absorption effects.

Structure Determination.—The position of the copper atom was determined from a sharpened Patterson map. This partial structure refined well and the remaining non-hydrogen atoms could be located after several ΔF syntheses and successive least-squares calculations. The concluding refinement with anisotropic temperature factors for all the atoms (except hydrogen, for which no allowance was made) with blocked full-matrix least squares reduced R to 0.068. The choice of the weighting scheme was justified by the fact that the weighted errors showed no systematic dependence on sin θ or intensity. A three-dimensional ΔF syntheses at this stage showed one peak (1.7 e Å^{-3}) with no reasonable connections to atoms of the molecule [shortest distance is to C(12), 1.69 Å] and another peak (1.3 e Å^{-3}) near Cu (distance, 0.73 Å). These peaks may arise from a slight statistical disorder. The existence of this disorder can be seen from the higher-level precession photographs which show lines between the reflections perpendicular to the tetragonal axis. The disorder was also observed for a different crystal. At the end of the refinement all the shifts were less than the estimated standard deviation.

The final fractional co-ordinates and their standard deviations are listed in Table 1. Observed and calculated structure-factor amplitudes and anisotropic thermal parameters are available as Supplementary Publication No. SUP 22330 (12 pp.).* All the calculations were performed with the program SHELX-76 [14] on an I.B.M. computer 370/168 at the Technische Hochschule, Darmstadt. The scattering factor for Cu^{II}, which is not stored in the program, was taken from Cromer and Mann.[15]

TABLE 1

Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu(1)	121(1)	886(1)	−947(1)
O(1)	754(3)	11(3)	−804(5)
N(1)	884(5)	1 225(4)	−2 148(6)
N(2)	−585(5)	1 677(5)	−1 127(9)
C(2)	−990(7)	2 062(6)	−1 513(11)
O(2)	−1 423(8)	2 523(7)	−1 903(12)
C(11)	1 403(5)	33(5)	−1 466(8)
C(12)	1 252(7)	522(6)	−2 501(9)
C(21)	565(8)	1 621(7)	−3 101(11)
C(22)	−79(8)	1 215(8)	−3 757(10)
C(31)	1 492(6)	1 707(7)	−1 565(13)
C(32)	1 181(7)	2 415(8)	−1 060(14)

RESULTS AND DISCUSSION

Structure of the Complex.—The final structural information is presented in Tables 1 and 2 and in Figures 1 and 2. The unit cell of $[\{Cu(NCO)(OCH_2CH_2NEt_2)\}_4]$ contains four cubane-type clusters with a Cu_4O_4 core. The symmetry of the cluster is S_4. The complex is thus the first structurally known member in the group of complexes of Cu^{II} with *NN*-dialkylaminoethanols which reaches the highest possible symmetry. Further members of this series $[\{CuX(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ (X =

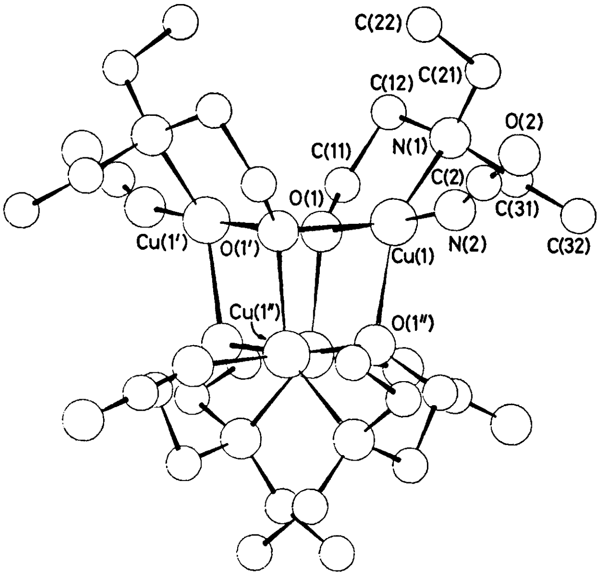

FIGURE 1 Molecular structure of the complex (1; R = Et, X = NCO)

TABLE 2

Bond length (Å) and angles (°), with estimated standard deviations in parentheses *

(*a*) Distances

Cu(1) ··· Cu(1′)	3.194(2)	C(2)–O(2)	1.220(18)
Cu(1) ··· Cu(1″)	3.193(2)	O(1)–C(11)	1.403(10)
Cu(1)–O(1)	1.936(6)	N(1)–C(12)	1.476(13)
Cu(1)–O(1′)	2.243(6)	N(1)–C(21)	1.455(15)
Cu(1)–O(1″)	2.113(6)	N(1)–C(31)	1.550(15)
Cu(1)–N(1)	2.066(8)	C(11)–C(12)	1.535(14)
Cu(1)–N(2)	1.903(9)	C(21)–C(22)	1.568(19)
N(2)–C(2)	1.100(15)	C(31)–C(32)	1.506(19)

(*b*) Angles

O(1)–Cu(1)–O(1′)	79.8(3)	Cu(1)–O(1)–C(11)	114.2(5)
O(1)–Cu(1)–O(1″)	83.5(3)	Cu(1)–N(2)–C(2)	161.1(11)
O(1)–Cu(1)–N(1)	85.0(3)	N(2)–C(2)–O(2)	176.2(14)
O(1)–Cu(1)–N(2)	174.0(3)	Cu(1)–N(1)–C(12)	104.0(6)
O(1″)–Cu(1)–O(1′)	76.5(3)	Cu(1)–N(1)–C(21)	115.2(7)
O(1″)–Cu(1)–N(1)	142.2(3)	Cu(1)–N(1)–C(31)	108.3(7)
O(1″)–Cu(1)–N(2)	96.9(3)	C(12)–N(1)–C(21)	111.4(8)
N(1)–Cu(1)–O(1′)	136.1(3)	C(12)–N(1)–C(31)	106.7(8)
N(1)–Cu(1)–N(2)	98.1(4)	C(21)–N(1)–C(31)	110.7(9)
N(2)–Cu(1)–O(1′)	94.5(3)	O(1)–C(11)–C(12)	108.9(8)
Cu(1)–O(1)–Cu(1′)	99.4(2)	N(1)–C(12)–C(11)	109.4(8)
Cu(1)–O(1)–Cu(1″)	104.0(2)	N(1)–C(21)–C(22)	116.8(10)
Cu(1′)–O(1)–Cu(1″)	94.2(2)	N(1)–C(31)–C(32)	112.7(9)

* Symmetry code: (′) = $\bar{x}, \bar{y}, z$; (″) = $\bar{y}, x, \bar{z}$.

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[14] SHELX-76, Program for Crystal Structure Determination, G. M. Sheldrick, Cambridge, 1976.

[15] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

Cl or Br)[16] attain the same symmetry as does a closely related complex of Cu^{II} containing a Schiff base formed by condensation of aminoethanol and pentane-2,4-dione, α-[{$\overline{Cu(OCH_2CH_2NCMeCHCMeO)}$}$_4$].[17]

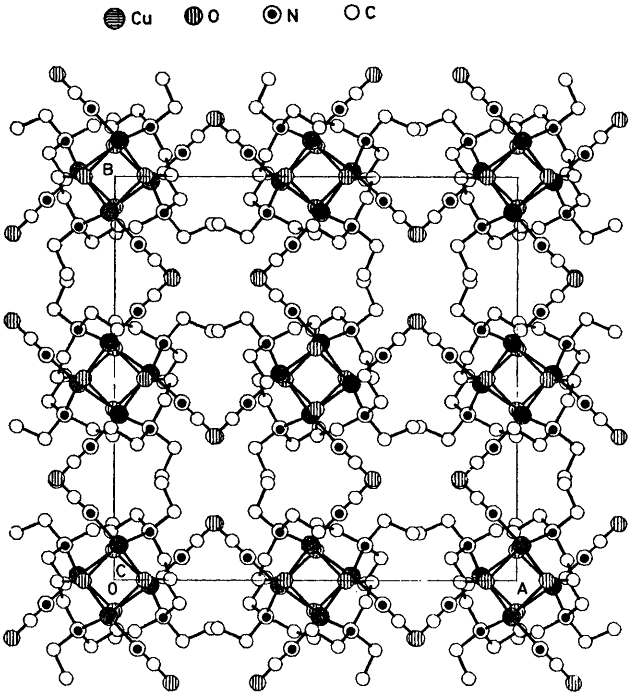

FIGURE 2 Projection of the unit cell of the complex along the tetragonal axis

The four copper(II) ions of the cluster constitute a nearly regular tetrahedron with Cu–Cu separations of 3.194(2) (× 2) and 3.193(2) Å (× 4). This geometry is thus very similar to those of the complexes [{CuX-($OCH_2CH_2NPr^n{}_2$)}$_4$] (X = Cl[18] or NCO[6]) which only possess point symmetry C_2 [Cu–Cu distances (mean values): 3.228 (× 2), 3.214 (× 4) (X = Cl), 3.168 (× 2), and 3.202 Å (× 4) (X = NCO)]. Although all the intramolecular Cu–Cu separations are equal within experimental error, the complex may be thought of as two ' dimers ' held together by out-of-plane Cu–O bonds (parallel to the tetragonal axis, Figure 1). The geometry within the Cu_2O_2 four-membered rings shows unsymmetric bridging (Table 2, Figure 2). Whereas the chelate-bonded Cu–O distance is of normal Cu–O bond length, the non-chelate-bonded Cu–O bond length within the pseudo-dimeric unit is elongated and longer than the out-of-plane Cu–O bond distance, which lies between these values. The extent of bending of the Cu_2O_2 four-membered ring within the pseudo-dimer is given by the dihedral angle between the O–Cu–O planes of 12.4°. The deviations of some atoms from the plane defined by Cu(1), O(1), Cu(1'), O(1') are given in Table 3.

The copper atoms are five-co-ordinated by amine and isocyanate nitrogen and three alkoxide triply bridging oxygens. The co-ordination may be described as between distorted tetragonal and distorted trigonal bipyramidal, as may be seen from the interbond angles around copper (Table 2).

TABLE 3

Distances (Å) of some atoms from the plane defined by Cu(1), O(1), Cu(1'), O(1')

Cu(1)	−0.086	N(2)	−0.299
O(1)	+0.086	C(2)	−0.760
Cu(1'')	2.172	O(2)	−1.225
O(1'')	2.001	C(11)	−0.704
N(1)	−1.517		

A summary of the known structures of all the copper(II) complexes containing *NN*-dialkylaminoethanols was given recently by Mergehenn and Haase[4] and the complexes have been classified into groups. Two extreme types exist, which may be distinguished by the arrangement of the Cu–Cu and Cu–O bond distances. One extreme type may be represented by [{Cu(NCO)-($OCH_2CH_2NMe_2$)}$_4$][4] [two short (mean 2.92 Å) and four long (mean 3.44 Å) intramolecular Cu–Cu separations] and the other by [{CuBr($OCH_2CH_2NBu^n{}_2$)}$_4$][19] [two long (mean 3.45 Å) and four intermediate (mean 3.18 Å) intramolecular Cu–Cu separations]. Besides these extreme types there are intermediate types where Cu–C separations tend to become equal. The present complex is the ideal intermediate type having all the Cu–Cu bond distances equal and with the highest possible point symmetry S_4, and is therefore of special interest in regard of its magnetic properties.

Magnetic Properties.—Results. The magnetic susceptibility in the range 2.6—300 K is shown in Figure 3. The susceptibility increases with decreasing temperature to a maximum at *ca.* 35 K and then decreases rapidly. At <8 K the susceptibility increases again, probably due to a small paramagnetic impurity [*e.g.* a small

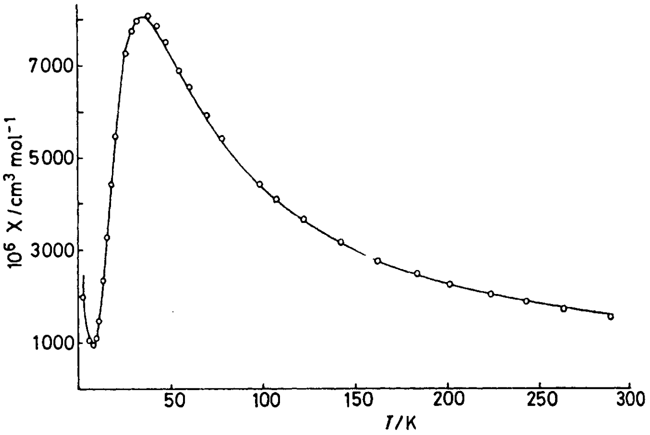

FIGURE 3 Temperature dependence of the magnetic susceptibility of (1; R = Et, X = NCO). Experimental points are compared with values (full line) calculated from equations (3) and (4) with $g = 2.19$, $J_{12} = -21.4$ cm^{-1}, $J_{13} = 12.3$ cm^{-1}, and $x = 0.014$ (see text)

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[16] R. Mergehenn, personal communication.

[17] J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, 1970, **4**, 203.

[18] N. Matsumoto, I. Ueda, Y. Nishida, and S. Kida, *Bull. Chem. Soc. Japan*, 1976, **49**, 1308.

[19] R. Mergehenn, W. Haase, and R. Allmann, *Acta Cryst.*, 1975, **B31**, 1847.

portion of a monomeric copper(II) complex]. This behaviour shows the presence of an overall antiferromagnetic interaction. The reciprocal susceptibility follows very closely a Curie-law behaviour with deviations becoming important only at <120 K. An extrapolation from the range 120—300 K gives a Weiss constant $\theta = 1°$. At >120 K our complex thus behaves like a normal paramagnet, although an overall antiferromagnetic interaction occurs at lower temperatures.

Theory and calculation. The magnetic properties of spin-coupled cubane-type copper(II) complexes may be described with help of the Heisenberg spin–spin exchange Hamiltonian (1) where the isotropic exchange integral

$$\mathscr{H} = -2 \sum_{i<j} J_{ij} S_i S_j \qquad (1)$$

J_{ij} describes the interaction between the magnetic centres i and j. In the case of an arrangement of the copper(II) ions with point symmetry S_4 (Figure 4) the Hamiltonian becomes (2). The energy values corresponding to this Hamiltonian can be obtained by standard procedures.[8-11] The appropriate susceptibility equation per mol of Cu^{II} then results from the van Vleck equation as (3) where $u = J_{13}/kT$, $v = J_{12}/kT$, and all the quantities have their usual meaning.

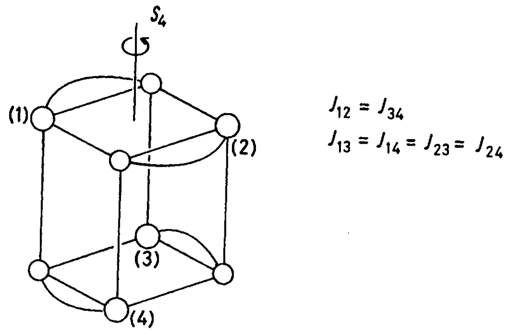

FIGURE 4 Principal structure of the Cu_4O_4 core of (1; R = Et, X = NCO) and relations between the exchange integrals J_{ij}

$$\mathscr{H} = -2J_{12}(S_1S_2 + S_3S_4) - 2J_{13}(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) \qquad (2)$$

$$\chi_{\text{tet}} = \frac{N\beta^2g^2}{4kT} \cdot \frac{10e^{2u} + 2e^{-2u} + 4e^{-2v}}{5e^{2u} + 3e^{-2u} + e^{-4u} + 6e^{-2v} + e^{-4v}} \qquad (3)$$

To allow for the presence of a small amount of monomeric impurity it was assumed that this impurity follows a Curie-law behaviour. The same g factor and temperature-independent paramagnetism (N_α) were taken as for the tetrameric complex, and a molecular weight of one quarter of that of the tetramer was assumed. The susceptibility is thus given by (4) where $\chi_{\text{mono}} = N\beta^2g^2/4kT$ and x = mol fraction of impurity.

$$\chi_{\text{calc.}} = (1 - x)\chi_{\text{tet}} + x\chi_{\text{mono}} + N_\alpha \qquad (4)$$

The exchange integrals J_{12} and J_{13} are evaluated by fitting equations (3) and (4) to the experimental susceptibility values. The g factor was allowed to vary in the range 2.0—2.2 and N_α was fixed at 60×10^{-6} cm^3 mol^{-1}. In order to evenly distribute the error the criterion for the best fit was calculated from $\Sigma|(\chi_{\text{calc.}} - \chi_{\text{obs.}})/\chi_{\text{obs.}}|$. Data at <12 K were omitted because the susceptibility in this range is mainly determined by the monomeric impurity. The following values were obtained from the fitting procedure: $J_{12} = -21.4 \pm 0.5$ cm^{-1}, $J_{13} = 12.3 \pm 1.0$ cm^{-1}, $g = 2.19$, and $x = 0.014$. The excellent agreement between the experimental and calculated values is shown in Figure 3 and Table 4.

TABLE 4

Calculated and observed magnetic moments (B.M.) for (1; R = Et, X = NCO) [a]

T/K	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$ [b]	T/K	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$ [b]
2.6	0.204	0.227	54.3	1.728	1.730
5.9	0.222	0.232	60.4	1.781	1.764
8.0	0.248	0.247	69.7	1.817	1.802
9.4	0.286	0.279	78.0	1.842	1.825
11.1	0.361	0.350	98.0	1.865	1.860
13.5	0.502	0.495	106.5	1.870	1.870
15.5	0.638	0.635	121.6	1.893	1.883
17.8	0.793	0.796	141.9	1.898	1.895
20.0	0.934	0.937	161.9	1.903	1.903
26.1	1.231	1.242	183.2	1.909	1.910
28.7	1.333	1.336	201.3	1.910	1.915
31.4	1.414	1.416	223.5	1.911	1.920
37.7	1.560	1.551	242.8	1.904	1.924
42.4	1.632	1.621	263.0	1.904	1.927
47.5	1.688	1.676	289.0	1.891	1.931

[a] $\mu = 2.828(\chi T)^{\frac{1}{2}}$. [b] Calculated for $g = 2.19$, $J_{12} = -21.4$ cm^{-1}, $J_{13} = 12.3$ cm^{-1}, and $x = 0.014$.

Discussion. Complex (1) exhibits both antiferromagnetic and ferromagnetic interactions within the same molecule. At high temperatures the effects nearly compensate and normal paramagnetic behaviour results, indicated by a very small Weiss constant. Thus the magnetism is very similar to the cubane-type complex α-[{Cu(OCH$_2$CH$_2$NCMeCHCMeO)}$_4$] [10,17,20] having S_4 point symmetry, which also shows the effect of antiferromagnetic and ferromagnetic exchange interactions within the same molecule. The other complexes investigated to low temperatures in the series [{CuX(OCH$_2$CH$_2$NR$_2$)}$_4$] have R = Et, X = Cl and R = Bu^n, X = Cl or Br.[12] Whereas (1; R = Et, X = Cl) shows antiferromagnetism, which can be explained by the HDVV model, the complexes (1; R = Bu^n, X = Cl or Br) exhibit ferromagnetism which cannot be explained by the HDVV model due to their low symmetry.

Although the copper(II) ions constitute, within experimental error, a regular tetrahedron, the different signs of the exchange constants J_{12} and J_{13} for (1; R = Et, X = NCO), rule out direct interactions between the copper(II) ions. The only possible interaction is superexchange *via* oxygen bridges. A correlation between the exchange constants and structural features within the Cu_2O_2 four-membered rings is not easy. A linear relation between the Cu–O–Cu bridging angle and the singlet–triplet splitting in dimeric hydroxide-bridged copper(II) complexes having a planar Cu_2O_2 ring has been found and mechanisms have been discussed.[11] On going from dimeric to tetrameric complexes the

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[20] L. Merz and W. Haase, *Z. Naturforsch.*, 1976, **A31**, 177.

magnetism cannot be explained exclusively by the variations in the bridging angle. Other features also become important, *e.g.* unsymmetric bridging, the dihedral angle between O–Cu–O planes, and out-of-plane bonding. The bridging angle Cu(1)–O(1)–Cu(1′) within the present pseudo-dimeric unit (99.4°) (Figure 1) is greater than in (1; R = Et, X = Cl) (95.9 and 96.7°),[21] but the corresponding exchange integral (J_{12}) is smaller than the value of -93 cm^{-1} assigned to the angle of 96.7° in the latter complex.[12] The only reason for this reduction of antiferromagnetic interaction seems to be the elongation of the non-chelate-bonded Cu–O bond distance and thus the reduction of overlap between Cu 3*d* and O 2*s* orbitals. In the complexes (1; R = Bu^n, X = Cl or Br) having a non-chelate-bonded Cu–O separation of *ca.* 2.5 Å and a Cu–O–Cu interbond angle within the pseudo-dimeric unit of *ca.* 101° this interaction becomes zero.[12]

The magnitude of J_{13} is more difficult to explain, since only a few structurally related dimers with out-of-plane oxygen bridges have been investigated.[11] The bridging angles Cu–O–Cu (Table 2) are different, 94.2 (Cu–O 2.113 and 2.243 Å) and 104.0° (Cu–O 1.936 and 2.113 Å). Although one angle (94.2°) would be compatible with ferromagnetic coupling, if one applies the relation between singlet–triplet splitting and Cu–O–Cu bond angle, the other would give rise to a large antiferromagnetic interaction. Thus it seems that for the ferromagnetic interaction between the copper(II) ions, with out-of-plane oxygen bridges, the angles and bond lengths are of minor importance. The orientation of the magnetic planes (the planes of the unpaired electron) seems to be the determining factor.[22] Structurally related oxygen-bridged dimeric complexes all exhibit ferromagnetic spin coupling.[11]

The existence of antiferromagnetic spin coupling for the in-plane bridged, and ferromagnetic spin coupling for the out-of-plane bridged, copper(II) ions seems to be true for all the tetrameric clusters of Cu^{II} with *NN*-disubstituted amino-alcohols. This is in contrast to the results of Hall *et al.*[23] for (1; R = Et, X = Cl) which indicated a rather large antiferromagnetic interaction (-36.2 cm^{-1}) between out-of-plane bridged Cu^{II}. However, in an earlier work [12] the magnetism of the complex was investigated and a very weak ferromagnetic out-of-plane interaction was found. The reason for this discrepancy may be the fact that the measured susceptibilities in ref. 23 are too low. This would result in an unreasonably low *g* factor of 1.96 in the fitting procedure, if no out-of-plane interaction is assumed. The out-of-plane interaction must become antiferromagnetic if one is to obtain a *g* factor of 2.11, which is expected for a copper(II) ion.[23] A remeasurement of the susceptibilities of (1; R = Et, X = Cl) in our laboratory confirmed the values given in ref. 12.

The main conclusion which can be drawn from the magnetic investigations of oxygen-bridged cubane-type copper(II) clusters is the fact that, depending on the relative magnitudes of the antiferromagnetic and ferromagnetic interactions, which are related to structural features, overall antiferromagnetic or ferromagnetic behaviour results. It is apparent that no single structural parameter can account for the magnetic properties. While for the antiferromagnetic in-plane interaction the Cu–O–Cu bridging angle and Cu–O bond distances seem to be of most importance, the symmetry of the magnetic planes seems to give rise to ferromagnetic out-of-plane interactions, the magnitude of which is not easily explained.

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