Crystal and Molecular Structure and Magnetic Properties of Tetrakis[bromo(2-diethylaminoethanolato)copper(II)]–Tetrachloromethane (1/4), a Complex with a Ferromagnetic Ground State

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The crystal and molecular structure of $[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ (A) has been determined from three-dimensional *X*-ray diffractometer data and refined to *R* 0.061 using 1 581 independent reflections. The tetragonal unit cell of space group $I4_1/a$ with dimensions a = 19.47(2) and c = 15.78(1) Å contains four oxygen-bridged cubane-type clusters of symmetry S_4 with a Cu_4O_4 core. Copper–copper distances are 3.523(2) (×2), 3.176(2) Å (×4) and copper–oxygen distances 1.924(5) (×2), 2.524(5) (×2), and 1.982(5) Å (×4), respectively. The co-ordination around copper (amine nitrogen, bromine, three bridging alkoxide oxygens) is distorted square pyramidal. Sixteen molecules of tetrachloromethane act as solvent of crystallization in the unit cell. The isomorphic $[\{CuCl(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ (B) has cell dimensions a = 19.21(2) and c = 15.96(1) Å. The decomposition of (A) and (B) has been followed by Debye–Scherrer investigation. The magnetic susceptibility of (A) and (B) in the temperature range 3.4—300 K and of the α and β modifications of $[\{CuBr(OCH_2CH_2NEt_2)\}_n]$ (n = 2 or ∞) in the range 70—300 K have also been determined and interpreted in terms of the isotropic Heisenberg–Dirac–van Vleck model. Whereas the α and β modifications show strong antiferromagnetic exchange interaction [$2J = -817$ and -744 (± 20) cm^{-1}], there is simultaneous antiferromagnetic and ferromagnetic exchange interaction in compounds (A) and (B) with the latter interaction dominating. The evaluated exchange parameters are: $J_{12} = -4.5 \pm 3$, $J_{13} = 40.0 \pm 3$ cm^{-1} (A); $J_{12} = -5.2 \pm 3$, $J_{13} = 46.9 \pm 3$ cm^{-1} (B). These can be understood in terms of the Cu–O–Cu bridging angle and the Cu–O bond distances.

DIFFERENT types of structures in the solid state have been found in the series of copper(II) complexes with *NN*-dialkylated 2-aminoethanols $[\{CuX(OCH_2CH_2NR_2)\}_n]$ (X = Cl, Br, NCS, or NCO; R = Me, Et, Pr^n, or Bu^n).[1-4] There are dimeric ($n = 2$),[1,5,6] polymeric ($n = \infty$),[1,7,8] and tetrameric ($n = 4$) cubane-type molecules.[1-4] Different tetrameric Cu_4O_4 clusters exist, which exhibit different intramolecular magnetic interactions between the individual copper(II) ions.[4,9,10] A summary of all known structures has been given recently.[1] According to their structural properties, the tetrameric cubane-type molecules may be classified in terms of two extreme types (types I and II) and of intermediate types. Common to all these tetrameric molecules is the fact that they exhibit ferromagnetic and antiferromagnetic interactions between individual copper(II) ions within the same molecule. Depending on the relative magnitude of these exchange interactions, overall ferromagnetic or antiferromagnetic behaviour results.

In the case of $[\{CuBr(OCH_2CH_2NEt_2)\}_n]$ two isomeric crystal structures have been reported,[5-7] which are built-up from dimeric oxygen-bridged copper(II) clusters. In the β modification the dimeric molecules are further weakly bridged by bromine atoms to form infinite chains.[7] Recrystallization of both modifications revealed the existence of a third modification (A) with built-in tetrachloromethane $[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$. An isomorphic complex (B) is also formed, $[\{CuCl(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$.

In this work we report the crystal and molecular structure of (A) and the cell parameters of (B). The decomposition of (A) when standing in air has been followed by Debye–Scherrer investigations. Also, the magnetic susceptibility has been determined in the temperature ranges 3.4—300 [(A) and (B)] and 70—300 K (α and β modifications). The results are interpreted in terms of the isotropic Heisenberg–Dirac–van Vleck (HDVV) model and the exchange parameters evaluated are correlated with structural features.

EXPERIMENTAL

Preparation.—The preparation of the complexes followed the procedure described in ref. 5. The different modifications of $[\{CuBr(OCH_2CH_2NEt_2)\}_n]$ were obtained by recrystallization from various solvents. Recrystallization from methanol, ethanol, or benzene yields crystals of the monoclinic α modification if the hot solution is cooled slowly, *e.g.* by standing overnight at room temperature. Crystals of the triclinic β modification are obtained by rapid cooling of a saturated hot methanolic or ethanolic solution in an ice-bath. The needle-like triclinic crystals must immediately be removed from the solution, because they transform into the monoclinic α modification when standing in solution. Recrystallization of $[\{CuCl(OCH_2CH_2NEt_2)\}_4]$ from the above solvents always yields crystals of the known tetragonal modification.

Crystals suitable for *X*-ray analysis of $[\{Cu(Br,Cl)(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ (A,B) were obtained by recrystallization of the solvent-free modifications from tetrachloromethane. The crystals occur as light green square bipyramids with well developed faces.

Magnetic Measurements.—The magnetic susceptibility of powdered samples was recorded by the Faraday method at *ca.* 10 kG † in the temperature range 10—300 K and at *ca.* 2 kG at temperatures <10 K as cited in ref. 10. Experimental susceptibility data were corrected for the underlying diamagnetism. Magnetic moments were calculated using the formula $\mu = 2.828(\chi T)^{\frac{1}{2}}$.‡

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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 should be multiplied by $4\pi \times 10^{-6}$ and the magnetic moment is then given by the expression $\mu = 797.74(\chi T)^{\frac{1}{2}}$.

Crystal Data.—(A) $(C_6H_{14}BrCuNO)_4\cdot4CCl_4$, $M = 1\,653.83$, Tetragonal, $a = 19.47(2)$, $c = 15.78(1)$ Å, $U = 5\,981.9$ Å^3, D_m (by flotation) $= 1.82(2)$ g cm^{-3}, $Z = 4$, $D_c = 1.84$ g cm^{-3}, $F(000) = 3\,248$.

(B) $(C_6H_{14}ClCuNO)_4\cdot4CCl_4$, $M = 1\,476.02$, Tetragonal, $a = 19.21(2)$, $c = 15.96(1)$ Å, $U = 5\,889.6$ Å^3, D_m (by flotation) $= 1.66(2)$ g cm^{-3}, $Z = 4$, $D_c = 1.66$ g cm^{-3}.

The space group was shown to be $I4_1/a$ for both compounds from systematic absences hkl for $h + k + l = 2n + 1$, $hk0$ for $h(k) = 2n + 1$, and $00l$ for $l = 4n + 1$. Structure determination was only undertaken for (A). Graphite-monochromatized Mo-K_α radiation was used: $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 46.8$ cm^{-1}. Cell constants and the orientation matrix were obtained by a least-squares fit of 16 strong reflections to the setting angles on the computer-controlled Stoe STADI 4 four-circle diffractometer.

Debye–Scherrer Investigations.—Microcrystalline samples obtained by rapid cooling of both complexes in tetrachloromethane were investigated using a Philips PW 1051 *X*-ray diffractometer with a PW 1050 wide-range goniometer. Measurements in the range $7 \leqslant 2\theta \leqslant 18°$ (Cu-K_α radiation, $\lambda = 1.540\,56$ Å) were carried out every 2 h.

Intensity Data.—A crystal of (A) with faces {011} and {101} and distances from face to the inverse face of 0.18 mm was pasted in cyanoacrylate to prevent loss of crystal solvent during the measurement. Intensity data were collected (θ—2θ scan) on the Stoe four-circle diffractometer in the range $3 \leqslant 2\theta \leqslant 45°$. Two reference reflections were monitored every 50 reflections and indicated no decomposition during the measurement. Measuring time for background: 2×20 s; measuring time for the reflections, 40 s in 100 steps of width 0.01°. Of 5 587 reflections, 1 581 independent reflections 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 positions of the Cu, Br, and O atoms were derived by direct methods. This partial structure refined well and the remaining non-hydrogen atoms could be located after several ΔF syntheses and successive least-squares cycles. The chlorine atoms of tetrachloromethane located in a ΔF map constitute a distorted tetrahedron. An ideal tetrahedron was built up from these four positions by least-squares calculations, with a fixed distance C–Cl 1.70 Å. In the following refinement cycles CCl_4 was considered as a rigid group with one variable C–Cl distance for all Cl atoms. Refinement with isotropic thermal parameters for all atoms converged at $R = 0.165$. Continued refinement with anisotropic thermal parameters for all atoms and the site-occupation factor for the tetrachloromethane tied to a free variable reduced R to 0.114. The site-occupation factor for CCl_4 converged to 0.98(1) indicating that no significant loss of CCl_4 had taken place during the measurements. This is in accordance with the good stability of the reference reflections.

A ΔF synthesis calculated at this stage showed three significant peaks (*ca.* 3 e Å^{-3}) with a distance to the tetrachloromethane carbon in the range of a C–Cl bond length (*ca.* 1.70 Å). This indicated a disorder of the CCl_4 molecule, which may be interpreted as a free rotation around one fixed C–Cl axis or as a statistical occupation of 2×3 Cl positions.

In the region of the ethanolato-group and one ethyl group, two peaks (*ca.* 1 e Å^{-3}) indicated a disorder of the two carbon atoms bonded to the amine nitrogen. This may be interpreted as a statistical occupation of 2×2 carbon positions Two positions with a fixed site-occupation factor of 0.5 were assumed for the above peaks. Refinement, including the disordered carbon positions, reduced R to 0.098. The concluding refinement was done without geometric restrictions for the tetrachloromethane molecule. The site-occupation factors for 3×2 chlorine atoms and 2×2 carbon atoms were tied to two free variables so that the sum of the site-occupation factors for the disordered atoms equals unity. At the end of refinement with blocked full-matrix methods, R had reached a value of 0.061. Only a few thermal parameters had shifts slightly greater than the estimated standard deviation at this stage. The site-occupation factors of the disordered atoms were 0.527(7) for Cl(2), Cl(3), Cl(4), 0.473(7) for Cl(21), Cl(31), Cl(41), 0.52(1) for C(2), C(5), and 0.48(1) for C(21), C(51), respectively.

The final fractional co-ordinates and their standard deviations are listed in Table 1. Observed and calculated structure-factor amplitudes, thermal parameters, and magnetic susceptibilities are available as Supplementary Publication No. SUP 22786 (13 pp.).* All calculations were performed with the SHELX-76 [11] program on the IBM 370/168 computer at the Technische Hochschule Darmstadt. The scattering factors for Cu and Br, which are not stored in the program, were taken from Cromer and Mann.[12]

TABLE 1

Positional ($\times 10^4$) parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	745(1)	1 987(1)	626(1)
Br	1 874(1)	2 435(1)	413(1)
N	734(4)	1 318(4)	−378(5)
O	−229(3)	1 825(3)	671(3)
C(1)	−481(5)	1 343(5)	68(6)
C(2)	−77(11)	1 388(21)	−704(15)
C(21) *	118(11)	915(13)	−282(16)
C(3)	943(8)	1 673(7)	−1 160(7)
C(4)	909(8)	1 221(7)	−1 951(8)
C(5)	882(16)	627(13)	−99(17)
C(51) *	1 445(14)	796(12)	−291(14)
C(6)	1 570(7)	543(7)	443(10)
C	1 119(8)	927(7)	5 219(9)
Cl(1)	865(3)	680(3)	4 228(3)
Cl(2)	606(4)	461(4)	5 983(5)
Cl(21) *	1 136(8)	414(4)	5 964(9)
Cl(3)	1 165(8)	1 708(5)	5 415(9)
Cl(31) *	531(6)	1 669(6)	5 439(6)
Cl(4)	1 941(7)	593(10)	5 383(12)
Cl(41) *	1 858(4)	1 582(5)	5 094(7)

* The occupation factors of the atoms C(*n*1) and Cl(*n*1) are tied to those of the atoms C(*n*) [0.52(1)] and Cl(*n*) [0.527(7)] to a total of 1.0.

RESULTS

Description of the Structure.—A perspective view of [{CuBr(OCH$_2$CH$_2$NEt$_2$)}$_4$] is given in Figure 1. The unit cell contains four cubane-type clusters with a Cu_4O_4 core. The symmetry of each cluster is S_4. The complex is thus the first member in the series of copper(II) complexes with *NN*-dialkylated aminoethanols of molecular type II[1] which reaches the highest possible symmetry. The same symmetry is found in the closely related complexes [{Cu(NCO)(OCH$_2$CH$_2$NEt$_2$)}$_4$],[4] α-[{Cu(OCH$_2$CH$_2$NCMeCHCMeO)$_4$}] [13] [a complex of copper(II) with the Schiff base of acetylacetone and aminoethanol], and [{Cu[OCH$_2$CH$_2$NH(CH$_2$)$_3$NH$_2$]}$_4$]Cl$_4\cdot$4H$_2$O,[14] all having a Cu_4O_4 core. Copper–copper

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

distances of 3.523(×2) and 3.176 Å(×4) and copper–oxygen distances of 1.924(×2) and 2.524 Å(×2) within the pseudo-dimeric unit and 1.982 Å(×4) between the pseudo-dimeric units clearly demonstrate that the complex is of type II. The geometry within the Cu_4O_4 core is very similar to that of the other type II complexes $[\{Cu(Cl,Br)(OCH_2CH_2NBu^n{}_2)\}_4]$,[15] β-$[\{Cu(OCH_2CH_2NCMeCHCMeO)_4\}]\cdot 2C_6H_6$,[16] $[\{Cu[OCH_2CH_2NH(CH_2)_3NH_2]\}_4]$-$Cl_4\cdot 4H_2O$,[14] -$[NO_3]_4\cdot 2H_2O$,[17] -$Br_4\cdot 3H_2O$,[18] and $[\{Cu(O_2CCHCl_2)(OCH_2CH_2NEt_2)\}_4]$.[19]

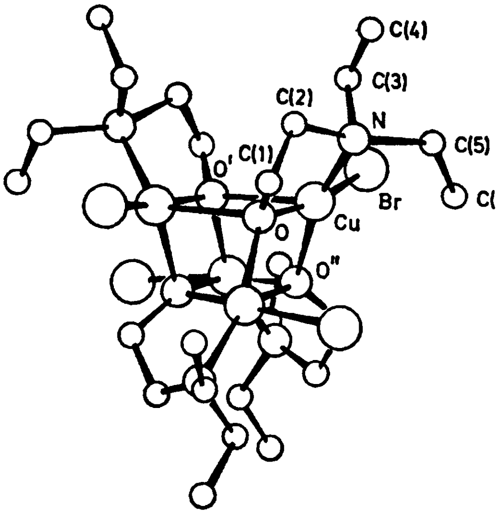

FIGURE 1 Perspective view of the tetrameric complex

The square-pyramidal co-ordination around copper is developed best in this molecule as compared with the other Cu_4O_4 cubane-type clusters of copper(II) with *NN*-dialkylated aminoethanols. The angles L–Cu–L (L = Br, N, O, or O″) with a mean value of 90.6°(×4) are very close to the ideal value of 86.6°. The angles N–Cu–O″ and Br–Cu–O (mean 161.5°) in the basal plane, as well as the angles from the apical O′ to the basal ligands O′–Cu–L [mean 91.7°(×4)], are slightly different from the ideal values of 151.9(×2) and 104.1°(×4). Thus copper is placed nearly in the basal plane.

TABLE 2

Distances (Å) with estimated standard deviations in parentheses *

Cu–Cu′	3.523(2)	Cu–Br	2.390(2)
Cu–Cu″	3.176(2)	N–C(2)	1.68(3)
Cu–O	1.924(5)	N–C(21)	1.44(3)
Cu–O′	2.524(5)	N–C(3)	1.47(1)
Cu–O″	1.982(5)	N–C(5)	1.44(3)
Cu–N	2.052(8)	N–C(51)	1.72(3)
O–C(1)	1.42(1)	C(1)–C(2)	1.45(3)
		C(1)–C(21)	1.54(3)
C(3)–C(4)	1.53(2)	C(5)–C(6)	1.60(3)
		C(51)–C(6)	1.28(3)
C–Cl(1)	1.71(2)	C–Cl(2)	1.81(2)
		C–Cl(21)	1.54(2)
C–Cl(3)	1.55(2)	C–Cl(4)	1.75(2)
C–Cl(31)	1.86(2)	C–Cl(41)	1.70(2)
C(2)–C(21)	1.20(4)	Cl(2)–Cl(21)	1.04(2)
C(5)–C(51)	1.18(4)	Cl(3)–Cl(31)	1.24(2)
C(5)–C(21)	1.62(4)	Cl(4)–Cl(41)	1.61(2)
		Cl(4)–Cl(21)	1.85(2)
		Cl(3)–Cl(41)	1.58(2)

* Symmetry code: single primes, $\bar{x}$, $0.5 - y$, z; double primes, $0.25 - y$, $0.25 + x$, $0.25 - z$.

The Cu–L distances (Table 2) as well as the distances and angles (Table 3) between the other atoms of the complex appear quite normal compared with molecules of the same type. The distances of the atoms from the best plane through the Cu_2O_2 unit of the pseudo-dimeric moiety are listed in Table 4. It should be noted that the basal plane of the square pyramids makes an angle of 51.2° with this plane.

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses

O–Cu–O′	75.8(3)	Cu–O–Cu′	104.1(3)
O–Cu–O″	86.7(3)	Cu–O–Cu″	108.8(3)
O–Cu–N	85.1(3)	Cu–O–C(1)	115.7(5)
O–Cu–Br	166.5(2)	Cu″–O–Cu′	88.8(3)
O″–Cu–O′	71.9(3)	Cu″–O–C(1)	119.7(5)
O″–Cu–N	156.4(3)	Cu′–O–C(1)	115.9(5)
O″–Cu–Br	95.6(2)		
O′–Cu–N	126.8(3)		
O′–Cu–Br	92.1(2)		
N–Cu–Br	97.6(2)		
Cu–N–C(2)	101.4(12)	Cu–N–C(21)	105.8(11)
Cu–N–C(3)	110.3(6)		
Cu–N–C(5)	110.7(11)	Cu–N–C(51)	107.8(10)
C(2)–N–C(3)	88.6(12)	C(21)–N–C(3)	125.1(12)
C(2)–N–C(5)	110.4(12)	C(21)–N–C(51)	107.3(13)
C(3)–N–C(5)	129.7(13)	C(3)–N–C(51)	98.2(12)
N–C(2)–C(1)	108(2)	C(2)–C(1)–O	109.6(11)
N–C(21)–C(1)	120(2)	C(21)–C(1)–O	109.7(11)
N–C(3)–C(4)	113.7(10)	N–C(5)–C(6)	115(2)
		N–C(51)–C(6)	115(2)
Cl(1)–C–Cl(2)	108.0(8)	Cl(1)–C–Cl(21)	121.4(10)
Cl(1)–C–Cl(3)	118.3(10)	Cl(1)–C–Cl(31)	102.1(8)
Cl(1)–C–Cl(4)	107.2(10)	Cl(1)–C–Cl(41)	106.6(9)
Cl(2)–C–Cl(3)	112.9(10)	Cl(21)–C–Cl(31)	111.7(10)
Cl(2)–C–Cl(4)	102.7(10)	Cl(21)–C–Cl(41)	114.0(11)
Cl(3)–C–Cl(4)	106.4(12)	Cl(31)–C–Cl(41)	97.9(8)

Four molecules of tetrachloromethane per cluster stabilize the crystal structure. There is no direct interaction with the complex: the shortest distance between copper and tetrachloromethane is 6.23 Å [Cu–Cl(1)]. The C–Cl distances vary between 1.55 and 1.86 Å (mean 1.70 Å).

TABLE 4

Distances (Å) of all atoms from the plane defined by Cu, O, Cu′, and O′

Cu	−0.035	C(1)	−0.920	C	7.189
O	0.035	C(2)	−2.113	Cl(1)	5.641
Br	−0.371	C(21)	−1.467	Cl(2)	8.440
N	−1.623	C(3)	−2.837	Cl(21)	8.312
O″	1.864	C(4)	−4.100	Cl(3)	7.477
		C(5)	−1.147	Cl(31)	7.561
		C(51)	−1.465	Cl(4)	7.341
		C(6)	−0.379	Cl(41)	7.079

The disorder of the *N*-bonded carbon atoms causes a rather bad description of this molecular fragment. Therefore the tabulated N–C and C–C distances as well as the affected angles are far from normal (Tables 2 and 3). A similar disorder has been found in the crystal structure of $[\{Cu(NCS)(OCH_2CH_2NEt_2)\}_\infty]$.[20]

Investigation of Decomposition.—The decomposition of both complexes was studied by taking Debye-Scherrer diagrams every 2 h. In the case of the chloro-complex complete decomposition, giving a new crystal structure, takes place in 6 h. The $(\sin\theta)/\lambda$ values and the relative intensities of the reflections in the range $7 \leqslant 2\theta \leqslant 18°$ (Table 5) are constant from this time. In parallel with the decomposition is loss of crystal solvent, as can be seen from the change in weight. The new crystal structure is stable for some days and not identical with the known structure [6] of the complex, which exhibits antiferromagnetic spin coupling in the ground state.[9]

In the case of the bromo-complex the decomposition is much more complicated. As can be seen in Table 6 (column b), the first crystal structure formed is probably isomorphic to the product of decomposition of the chloro-complex (Table 5, column b). This structure is not stable in the case of the bromo-complex, further decomposition resulting mainly in products of the monoclinic modification (Table 6). In addition to the typical reflections of the dimeric crystal structure, there are a few reflections which need further interpretation. Thus, two very weak reflections at $(\sin\theta)/\lambda = 0.061\ 3$ and $0.094\ 3$ may be explained in terms of the existence of a small amount of the polymeric β modification. One reflection with $(\sin\theta)/\lambda = 0.057\ 9$ may indicate a small amount of a structure isomorphic to the antiferromagnetic modification of the chloro-complex, whose strongest reflection (012) occurs at $(\sin\theta)/\lambda = 0.057\ 2$. The last two conclusions, the existence of polymeric and antiferromagnetic tetrameric bromo-complexes in the stable product of decomposition, will be investigated in more detail. It would be very interesting to know whether they are final products or intermediates of the decomposition process.

TABLE 5

Debye–Scherrer data for the decomposition of $[\{CuCl(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ in the range $7 \leqslant 2\theta \leqslant 18°$ (Cu-K_α radiation, $\lambda = 1.540\ 56$ Å).* The reflections of the known crystal structures are indexed. Column a gives values obtained after 2 h, column b those of the final product of decomposition

$[\{CuCl(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$		$(\sin\theta)/\lambda$		$[\{CuCl(OCH_2CH_2NEt_2)\}_4]$	
$(\sin\theta)/\lambda$	*hkl*	a	b	$(\sin\theta)/\lambda$	*hkl*
		0.045 3(25)	0.045 3(29)		
				0.047 8	101
0.052 1(48)	020	0.052 9(25)			
		0.055 5(92)	0.054 6(172)		
				0.057 2	012
			0.058 5(96)		
		0.063 0(64)	0.062 2(118)	0.063 0	110
0.066 1(57)	121	0.066 4(51)		0.065 6	111
		0.068 1(53)	0.068 1(64)		
				0.070 1	103
0.072 8(76)	220	0.072 8(43)		0.072 4	112
				0.083 3	113
0.084 2(24)	022	0.085 0(10)			
				0.088 7	200
		0.090 0(30)	0.090 0(57)		
0.096 8(96)	222	0.096 8(38)			
				0.101 0	211

* Relative intensities are given in parentheses.

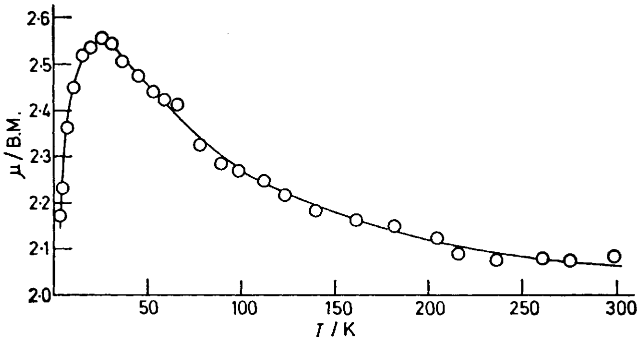

FIGURE 2 Temperature dependence of the magnetic moment of $[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$. Experimental points are compared with values (full line) calculated from equation (3) with $g = 2.17$, $J_{12} = -4.5$ cm^{-1}, $J_{13} = 40.0$ cm^{-1}, and $\theta = -1.74$ K (see text)

Magnetic Properties.—Results. The temperature dependence of the magnetic moment of (A) and (B) in the range 3.4—300 K is shown in Figures 2 and 3. The magnetic moment increases with decreasing temperature, reaching a constant value of 2.55 (A) and 2.49 B.M. (B) at *ca.* 15—40 K. Below 15 K the magnetic moment decreases again. The graph $1/\chi = f(T)$ is linear in the range 100—300 K and has an intercept at 25 (A) and 31 K (B). This behaviour is in accordance with an overall ferromagnetic exchange interaction. The magnetic properties of the solvent-free α and β modifications (Figure 4) are completely different and show strong magnetic interaction at room temperature. The susceptibility is strongly reduced, decreases further with decreasing temperature, and reaches a constant value

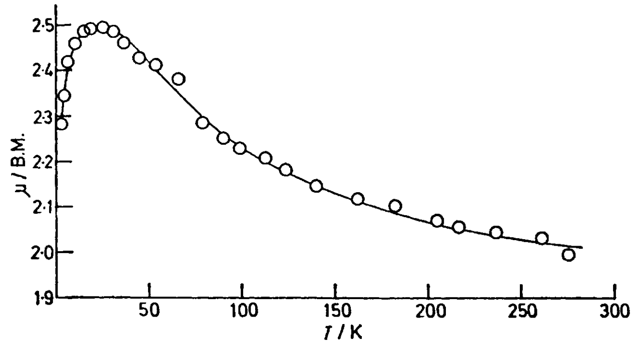

FIGURE 3 Temperature dependence of the magnetic moment of $[\{CuCl(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$. Experimental points are compared with values (full line) calculated from equation (3) with $g = 2.08$, $J_{12} = -5.2$ cm^{-1}, $J_{13} = 46.9$ cm^{-1}, and $\theta = -0.75$ K (see text)

below *ca.* 140 K, which is determined by the temperature-independent paramagnetism ($N\alpha$). Experimental and calculated susceptibility data are available in SUP 22786.

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

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

interaction between the magnetic centres *i* and *j*. The energy values corresponding to this Hamiltonian may be derived by standard procedures. The appropriate susceptibility equation then results from the general van Vleck equation.[4,21-23] In the case of two interacting copper(II) ions the well known Bleaney–Bowers equation (2) results, where all quantities have their usual meaning. The appropriate susceptibility equation for a system of four interacting copper(II) ions with point symmetry S_4 is (3) (per mol of Cu^{II}), where $u = J_{13}/kT$, $v = J_{12}/kT$, and θ is the Weiss constant to account for the decrease of the magnetic moment at very low temperature; J_{12} is the exchange integral between the copper(II) ions related by a C_2 axis and J_{13} the exchange integral between the copper(II) ions related by the S_4 axis.

TABLE 6

Debye–Scherrer data for the decomposition of $[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ obtained as in Table 5.* Values of the product with total loss of crystal solvent are given in column b, the decomposition from b to c requires 1 d

$[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$		$(\sin\theta)/\lambda$			α-$[\{CuBr(OCH_2CH_2NEt_2)\}_2]$		β-$[\{CuBr(OCH_2CH_2NEt_2)\}_\infty]$	
$(\sin\theta)/\lambda$	*hkl*	a	b	c	$(\sin\theta)/\lambda$	*hkl*	$(\sin\theta)/\lambda$	*hkl*
			0.044 4(22)					
0.051 2(33)	020	0.052 1(23)						
		0.054 6(62)	0.053 8(117)					
			0.057 2(56)	0.057 9(50)				
		0.060 5(43)	0.060 5(87)	0.061 3(9)			0.0605	010
0.065 6(27)	121	0.064 7(58)	0.063 9(113)					
				0.071 5(80)	0.0715	110		
0.072 4(108)	220	0.073 2(46)						
				0.074 1(111)	0.0741	011		
		0.079 1(23)	0.079 1(40)					
0.080 8(22)	022	0.081 6(16)						
				0.085 0(89)	0.0850	$\bar{1}11$	0.0850	$0\bar{1}1$
		0.089 2(8)	0.089 2(22)					
		0.094 2(17)	0.094 3(36)	0.094 3(10)			0.0934	101
0.096 0(54)	222	0.096 3(23)						
		0.098 4(14)	0.099 3(20)				0.0984	210
				0.101 8(99)	0.1018	120		
				0.102 7(163)	0.1035	021		

* Relative intensities are given in parentheses.

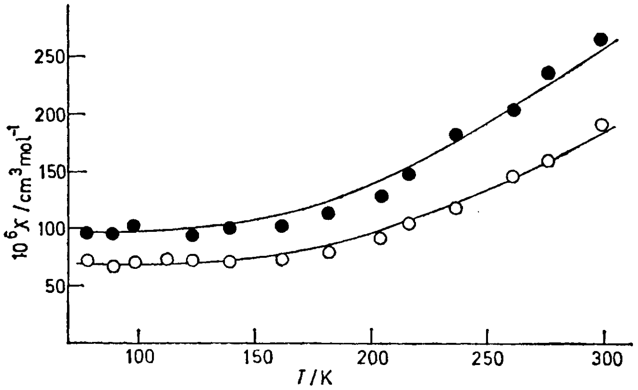

FIGURE 4 Temperature dependences of the magnetic susceptibilities of α-$[\{CuBr(OCH_2CH_2NEt_2)\}_2]$ (○) and β-$[\{CuBr(OCH_2CH_2NEt_2)\}_\infty]$ (●). Experimental points are compared with values (full lines) calculated from equation (2) with $2J = -817$ cm^{-1}, $N\alpha = 71 \times 10^{-6}$ cm^3 mol^{-1} (α modification) and $2J = -744$ cm^{-1}, $N\alpha = 98 \times 10^{-6}$ cm^3 mol^{-1} (β modification)

The exchange integrals are evaluated by fitting equations (2) and (3) to the experimental susceptibility data as

$$\chi_{\text{calc.}} = \frac{Ng^2\beta^2}{kT}\cdot\frac{1}{3+\exp(-2J/kT)} + N\alpha \qquad (2)$$

described in ref. 10. The temperature-independent paramagnetism $N\alpha$ was fixed at 60×10^{-6} cm^3 mol^{-1} for (A) and (B). In the case of the α and β modifications, $N\alpha$ was determined from the constant susceptibility data at low temperature. The function minimized was $\Sigma(\chi_{\text{obs.}} - \chi_{\text{calc.}})^2T^2$ for (A) and (B) and $\Sigma(\chi_{\text{obs.}} - \chi_{\text{calc.}})^2$ in the other cases.

$$\chi_{\text{calc.}} = \frac{Ng^2\beta^2}{4k(T-\theta)}\cdot\frac{10e^{2u} + 2e^{-2u} + 4e^{-2v}}{5e^{2u} + 3e^{-2u} + e^{-4u} + 6e^{-2v} + e^{-4v}} + N\alpha \qquad (3)$$

The resulting exchange parameters are given in Table 7. The agreement between experimental and calculated data can be seen in Figures 2—4.

DISCUSSION

The behaviour of the dimeric and polymeric α and β modifications is markedly different from that of the tetrameric modifications (A) and (B) (Figures 2—4). This is quite general when going from di- to tetra-meric clusters and has been investigated in the cases $[\{CuBr(OCH_2CH_2NBu^n{}_2)\}_n]$ [9,24] and $[\{Cu(NCO)(OCH_2CH_2NPr^n{}_2)\}_n]$ (n = 2 or 4).[3,10]

Uhlig and Staiger[24] and Lehtonen *et al.*[25] have evaluated the exchange integral of the α modification and found the values $2J = -800$ [24] and -799 cm^{-1}.[25]

As at this time the existence of the polymeric β modification was not known and both sets of authors did not exactly specify which modification they studied, a reinvestigation of the α modification, characterized by Debye–Scherrer diagrams, was undertaken. The resulting exchange integral ($2J = -817 \pm 20$ cm^{-1}) agrees well with the above values and indicates strong antiferromagnetic interaction between the individual copper(II) ions.

The susceptibility of the polymeric β modification (characterized by Debye–Scherrer diagrams) can satisfactorily be described by equation (2). This shows that there are no or only little interactions *via* the Cu–Br ··· Cu bridges, which may be understood in terms of the rather long Cu ··· Br distance [3.660(2) Å].[7] The exchange integral ($2J = -744 \pm 20$ cm^{-1}) shows that the antiferromagnetic exchange interaction is rather strong, but markedly less than with the α modification.

TABLE 7

Exchange integrals J_{ij} resulting from the HDVV model, with estimated errors in parentheses (see text for explanation)

Compound	g	θ/K	J_{12}/cm^{-1}	J_{13}/cm^{-1}	$10^6 N\alpha$/cm^3 mol^{-1}
$[\{CuBr(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$	2.17	−1.74	−4.5 (±3)	40.0 (±3)	60 *
$[\{CuCl(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$	2.08	−0.75	−5.2 (±3)	46.9 (±3)	60 *
			2 J/cm^{-1}		
α-$[\{CuBr(OCH_2CH_2NEt_2)\}_2]$	2.20 *		−817 (±20)		71
β-$[\{CuBr(OCH_2CH_2NEt_2)\}_\infty]$	2.20 *		−744 (±20)		98

* Held fixed in the fitting process.

The magnetic properties of the α and β modifications may be understood in terms of the Cu–O–Cu bridging angle. A linear relation between this angle and the magnetic exchange integral has been established with alkoxide-bridged copper(II) clusters[10] and strong antiferromagnetic interaction is to be expected when this angle becomes 104.7 (α modification, mean value from refs. 5 and 6) or 103.9(2)° (β modification).[7] The difference in the magnitudes of the exchange integral of the α and β modifications is a consequence of the different magnitudes of the Cu–O–Cu bridging angles.

The calculated exchange integrals of $[\{Cu(Br,Cl)(OCH_2CH_2NEt_2)\}_4]\cdot 4CCl_4$ (A,B) (Table 7) show the simultaneous presence of ferromagnetic and antiferromagnetic exchange interactions within the same molecule. Whereas the interaction within the pseudo-dimeric unit is slightly antiferromagnetic, that between the pseudo-dimeric units is strongly ferromagnetic and dominates, so that an overall ferromagnetic behaviour with an $S' = 2$ ground state results. The ground state is fully populated below *ca.* 30 K.

This behaviour is quite general for oxygen-bridged copper(II) clusters of the cubane type. In all cases so far investigated, antiferromagnetic interaction within the pseudo-dimeric unit and ferromagnetic interaction between the pseudo-dimeric units has been found.[4,9,10] The overall magnetic behaviour is then determined by the relative magnitudes of these two opposing effects and is a consequence of the structural details within the Cu_4O_4 core. Cubane-type copper(II) clusters with a ferromagnetic ground state have been found with the complexes $[\{Cu(Br,Cl)(OCH_2CH_2NBu^n{}_2)\}_4]$[9] and β-$[\{Cu(OCH_2CH_2NCMeCHCMeO)\}_4]\cdot 2C_6H_6$.[26] All these complexes have the same structure and are classified as type II complexes. The common structural feature is the rather elongated non-chelate-bonded Cu–O distance within the pseudo-dimeric unit (*ca.* 2.5 Å) and the rather short Cu–O distances (*ca.* 1.98 Å) between the pseudo-dimeric units.

The exchange integrals of 40.0 ± 3 (A) and 46.9 ± 3 cm^{-1} (B) are as far as we know the strongest ferromagnetic exchange integrals in this class of compounds. In the complexes $[\{Cu(Br,Cl)(OCH_2CH_2NBu^n{}_2)\}_4]$ this integral is estimated to be *ca.* 30 ± 10 cm^{-1}.[9]

The antiferromagnetic exchange interaction within the pseudo-dimeric unit may be understood in terms of the Cu–O–Cu bridging angle and the magnitude of the non-chelate-bonded Cu–O distance. Whereas the Cu–O–Cu bridging angle [104.1(3)°] would give rise to large antiferromagnetic exchange interaction, this interaction is largely diminished by the long Cu–O′ bond distance [2.524(5) Å]. The opposing effect of bridging angle and bond distance is also observed in the compounds $[\{Cu(NCO)(OCH_2CH_2NR_2)\}_4]$ where R = Et (99.4°, 2.243 Å), Pr^n (98.9°, 2.214 Å; 99.5°, 2.244 Å), and Bu^n (98.4°, 2.12 Å; 98.0°, 2.12 Å), and $[\{Cu(NCS)(OCH_2CH_2NBu^n{}_2)\}_4]$ (98.1°, 2.09 Å; 97.4°, 2.11 Å). In all these complexes the antiferromagnetic exchange interaction within the pseudo-dimeric unit is markedly less than would be expected from the linear relation between the exchange integral and the bridging angle.[10] Clearly the reduction of the exchange interaction in these compounds is caused by the elongation of the Cu–O bond distance. It should be emphasized that this class of compounds thus offers the unique opportunity of separating the influences of the bridging angle and the bond distance on the magnitude of the magnetic exchange integral.

The ferromagnetic exchange interaction between the pseudo-dimeric units is mainly determined by the Cu–O bond distance between the pseudo-dimeric units. There is no clear correlation with the Cu–O–Cu bridging angle. The strongest ferromagnetic exchange interaction in the present compounds parallels short Cu–O bonds between the pseudo-dimeric units [1.982(5) Å]. With the closely related complexes $[\{Cu(Br,Cl)(OCH_2CH_2NBu^n{}_2)\}_4]$ and a value of J_{13} *ca.* 30 ± 10 cm^{-1}, this distance becomes 1.98 Å (mean). On the other hand the ferromagnetic exchange interaction becomes approximately zero with the type I complexes $[\{CuCl(OCH_2CH_2NEt_2)\}_4]$ [9] and $[\{Cu(NCO)(OCH_2CH_2NMe_2)\}_4]$ [10] with 'interdimer' Cu–O bond lengths of 2.46 and 2.48 Å (means). In the intermediate complexes $[\{Cu(NCO)[OCH_2CH_2N(Et,Pr^n)_2]\}_4]$ with interdimer Cu–O bond lengths of 2.113 and 2.154 Å (means) the ferromagnetic interaction is 12.3 ± 1 [4] and 8 ± 4 cm^{-1}.[10]

The above discussion clearly shows that there are strong correlations between the magnetic exchange integrals and structural details for oxygen-bridged cubane-type copper(II) complexes. Whereas type I complexes with long 'interdimer' Cu–O bonds show antiferromagnetic exchange interactions, type II complexes with short 'interdimer' Cu–O bonds exhibit ferromagnetic exchange interaction in the $S' = 2$ ground state. In all complexes the interaction within the pseudo-dimeric unit is antiferromagnetic, whereas the 'interdimer' interaction is ferromagnetic. Depending on the relative magnitudes of these interactions, overall antiferromagnetism or ferromagnetism results. There is a continuous transition from type I to type II complexes, accompanied by a continuous change in the magnetic exchange integral.

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