Exchange Interaction in Tetrameric Oxygen-bridged Copper(II) Clusters of the Cubane Type †

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The magnetic properties of the tetrameric oxygen-bridged copper(II) complexes [{CuX(OCH$_2$CH$_2$NR$_2$)}$_4$] (1) (R = Me, X = NCO; R = Pr^n, X = NCO; and R = Bu^n, X = NCO or NCS) have been determined in the temperature range 3.4—300 K. The cubane-type complexes exhibit magnetic interactions between the single copper(II) ions, which can be explained on the basis of the isotropic Heisenberg–Dirac–van Vleck model. The magnetism of (1; R = Me, X = NCO) can be explained on the basis of four non-interacting ' dimeric ' units with the exchange integrals $J_1 = -65 \pm 3$, $J_2 = -0.6 \pm 2$, $J_3 = -0.3 \pm 2$, and $J_4 = -0.9 \pm 2$ cm^{-1}. A linear relationship between the exchange integral and the Cu–O–Cu bridge angle has been established for symmetric bridged complexes. The magnetic properties of (1; R = Pr^n, X = NCO; R = Bu^n, X = NCO or NCS) could be fitted with a theoretical equation assuming C_{2v} symmetry. The resulting exchange integrals $J_{12} = -30 \pm 1$, $J_{34} = -53 \pm 3$, $J_{13} = 8 \pm 4$ (1; R = Pr^n, X = NCO), $J_{12} = -28 \pm 2$, $J_{34} = -84 \pm 10$, $J_{13} = 21 \pm 10$ (1; R = Bu^n, X = NCO), and $J_{12} = -27 \pm 2$, $J_{34} = -72 \pm 5$, and $J_{13} = +15 \pm 10$ cm^{-1} (1; R = Bu^n, X = NCS) reveal the existence of antiferromagnetic interaction within the ' dimeric ' units and ferromagnetic interaction between them.

RECENTLY, structural investigations [1-3] of copper(II) complexes with *N,N*-dialkylated amino-alcohols [{CuX(OCH$_2$CH$_2$NR$_2$)}$_4$] (1; R = Me, Et, Pr^n, or Bu^n; X = Cl, Br, NCO, or NCS) showed the existence of a great number of tetrameric oxygen-bridged clusters of the cubane type. The variation of the structural parameters within the Cu$_4$O$_4$ core in this class of compounds, *i.e.* Cu–Cu and Cu–O bond distances and Cu–O–Cu bridging angles, offers the unique opportunity of studying correlations between structural details and the magnitude of the magnetic exchange interaction between the single copper(II) centres with only slight changes in the ligands. These correlations allow a better understanding of the exchange mechanism.

In contrast to dimeric complexes, which are also verified in this group of complexes [1,3] and show a strongly reduced magnetic moment at room temperature, the normal magnetic moment of the tetrameric clusters ($\mu \sim 1.7$—1.9 B.M.‡) indicates only small magnetic interactions between the magnetic centres. A normal Curie–Weiss law behaviour is obeyed in the temperature range 100—300 K with a non-zero Weiss constant.[4,5] Magnetic investigations in the temperature range 2.6—300 K of (1; R = Et, X = Cl; R = Bu^n, X = Cl or Br) [6] and (1; R = Et, X = NCO)[2] revealed the existence of antiferromagnetic ($S' = 0$) or ferromagnetic ($S' = 2$) ground states, which are exclusively populated at low temperature. A detailed analysis of the susceptibility data by use of the isotropic Heisenberg–Dirac–van Vleck (HDVV) model showed the simultaneous presence of ferromagnetic and antiferromagnetic exchange interactions within the same molecule.

In this work we report the magnetic properties of (1; R = Me, X = NCO; R = Pr^n, X = NCO; and R = Bu^n, X = NCO or NCS) in the temperature range 3.4—300 K. The magnetic data are interpreted with the isotropic HDVV model and the exchange parameters are determined. Their relation to structural features is discussed.

EXPERIMENTAL

Preparation.—The preparation of (1; R = Pr^n, X = NCO; and R = Bu^n, X = NCO or NCS) followed the procedure given in ref. 1. The complex (1; R = Me, X = NCO) was prepared by a slightly modified procedure which is generally useful for the complexes with X = NCO.

Equimolar amounts (0.025 mol) of copper(II) acetate monohydrate, potassium cyanate, and 2-dimethylaminoethanol were dissolved in methanol (50 cm^3) by heating on a water-bath. A solution of potassium hydroxide (0.025 mol) in absolute methanol (25 cm^3) was added to the warm solution in small portions. Upon standing overnight, blue-green crystals resulted, which were filtered off and recrystallized from ethanol.

Magnetic Measurements.—Magnetic susceptibilities of powdered samples were recorded in the temperature range 3.4—300 K by the Faraday method at *ca.* 10 kG. The system included a Bruker electromagnet BE-20va connected to a stabilized 6-kW power supply. Change of weight was registered by a Cahn RG electrobalance. Quartz sample holders were suspended by a quartz fibre. The sample amount was in the range 30—40 mg. Temperatures were held constant by a Leybold–Heraeus flow-type helium cryostat by means of a carbon resistor in the range 3.4—70 K and by a thermistor in the range 70—300 K. Temperature calibration was achieved by a vapour pressure thermometer and an Au(Fe)-chromel thermocouple. The salt Hg[Co(SCN)$_4$] was used as a field-calibrating standard.[7] The overall accuracy of the magnetic data is estimated to be 1—2%. Experimental susceptibility data were corrected for the underlying diamagnetism. Magnetic moments were calculated using the formula $\mu = 2.828 (\chi T)^{\frac{1}{2}}$.§

RESULTS

Structure of the Complexes.—The general structure of the complexes is shown in Figure 1. The complexes

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† This work is part of the dissertation of L. M., Darmstadt, D17.

‡ Throughout this paper: 1 B.M. = 9.274×10^{-24} A m^2; 1 G = 10^{-4} T.

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

TABLE 1

Mean values (according to symmetry C_{2v}) of some important, with regard to the magnetic properties, bond lengths (Å) and interbond angles (°) with estimated standard deviations in parentheses

Compound	Symmetry	Cu–Cu [a]	Cu–O [a,b]	Cu–O [a]	Cu–Cu [c]	Cu–O [c]	Cu–O–Cu [a]	ϕ [d]	Ref.
(1; R = Me, X = NCO)									
Molecule I	C_1	2.910(3)	1.93(1)	1.98(1)	3.457(3)	2.50(1)	96.1(5)	22.4	3
		2.904(4)	1.95(1)	1.97(1)			95.8(5)	23.0	
Molecule II	C_1	2.941(3)	1.95(1)	1.96(1)	3.428(3)	2.46(1)	97.5(5)	25.5	
		2.911(3)	1.94(1)	2.01(1)			95.2(5)	18.6	
(1; R = Pr^n, X = NCO)	C_2	3.155(4)	1.932(8)	2.214(8)	3.202(2)	2.154(8)	98.9(2)	11.8	1
		3.181(3)	1.913(8)	2.244(8)			99.5(2)	11.6	
(1; R = Bu^n, X = NCO)	C_1	3.053(5)	1.91(2)	2.12(1)	3.257(4)	2.27(1)	98.4(5)	15.0	8
		3.051(4)	1.93(1)	2.12(2)			98.0(7)	12.0	
(1; R = Bu^n, X = NCS)	C_1	3.034(4)	1.93(1)	2.09(1)	3.242(3)	2.25(1)	98.1(4)	15.1	8
		3.034(3)	1.93(1)	2.11(1)			97.4(6)	13.7	

[a] Within the 'dimers.' [b] Chelate-bonded copper–oxygen distance. [c] Between the 'dimers.' [d] The CuO_2Cu dihedral angle within the 'dimeric' unit.

may be thought of as two 'dimers' held together by out-of-plane Cu–O bonds. The symmetry of the clusters is

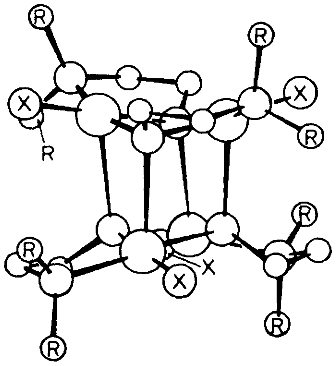

FIGURE 1 General structure of the tetrameric complexes $[\{CuX(OCH_2CH_2NR_2)\}_4]$

C_2 for (1; R = Pr^n, X = NCO)[1] and C_1 in the other cases;[3,8] it may be approximated as C_{2v}. In the case of (1; R = Me, X = NCO) the structure essentially consists of two different tetrameric molecules. The mean values according to symmetry C_{2v} of some bond lengths and interbond angles, which are important in regard to the magnetic properties, are given in Table 1.

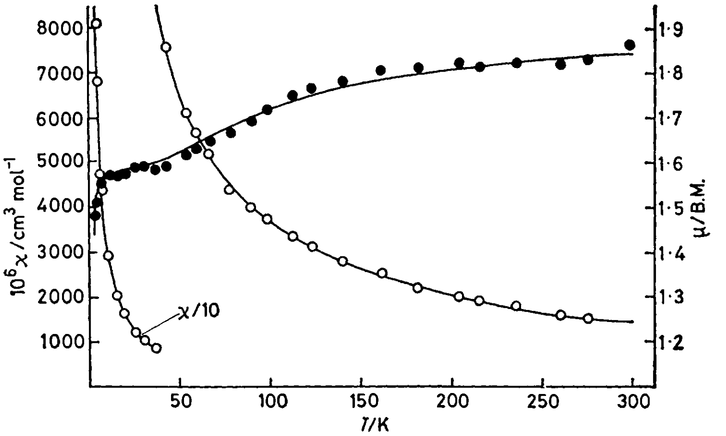

FIGURE 2 Temperature dependence of the magnetic susceptibility (○) and magnetic moment (●) of (1; R = Me, X = NCO). Experimental points are compared with values calculated (—) from equation (5) with $g = 2.135$, $J_1 = -65$, $J_2 = -0.6$, $J_3 = -0.3$, and $J_4 = -0.9$ cm^{-1} (see text)

Magnetic Properties.—The magnetic susceptibility of the complexes under investigation in the temperature range 3.4—300 K is shown in Figures 2 and 3. Experimental and calculated susceptibility data are available as Supplementary Publication No. SUP 22710 (3 pp.).*

The susceptibility of (1; R = Me, X = NCO) as a function of temperature is shown in Figure 2. The susceptibility increases steadily with decreasing temperature and reaches no maximum in the investigated temperature range. The magnetic moment decreases with decreasing temperature, reaches a constant value of 1.59 B.M. at 10—50 K, and then decreases again.

The general behaviour of (1; R = Pr^n, X = NCO; R = Bu^n, X = NCO or NCS) (Figure 3) is very similar, but opposite to that of (1; R = Me, X = NCO). The susceptibility increases with decreasing temperature, reaches a maximum at *ca.* 70 K, and then decreases rapidly. At still lower temperatures the susceptibility increases again probably due to various amounts of a monomeric paramagnetic impurity. This behaviour is consistent with an overall antiferromagnetic exchange interaction resulting in an $S' = 0$ ground state, which is exclusively populated at very low temperature.

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

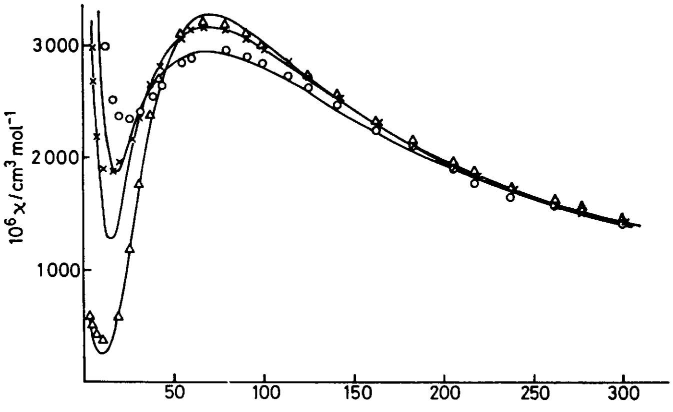

FIGURE 3 Temperature dependence of the magnetic susceptibility of (*a*) (**1**; R = Pr^n, X = NCO) (△), (*b*) (**1**; R = Bu^n, X = NCO) (○), and (*c*) (**1**; R = Bu^n, X = NCS) (×). Calculated values (–) from equations (3) and (4) (see text) with $g = 2.15, 2.16, 2.17$, $J_{12} = -30, -28, -27$, $J_{34} = -53, -84, -72$, $J_{13} = 8, 21, 15$ cm^{-1}, and $x = 0.004, 0.055, 0.03$ for (*a*), (*b*), and (*c*) respectively

EVALUATION OF THE EXCHANGE INTEGRALS

Theory.—The magnetic properties of exchange-coupled copper(II) complexes in most circumstances may well be described with the isotropic HDVV model.[9-13] In this model the Hamiltonian of the spin system takes the form (1) where J_{ij}, the exchange integral, describes the interaction between the centres i and j. In an arrangement of copper(II) ions with point symmetry C_{2v} (Figure 4), the Hamiltonian becomes (2). The energy values corresponding to this Hamiltonian are:[13] $E_1 = -\frac{1}{2}J_{12} - \frac{1}{2}J_{34} - 2J_{13}$, $S' = 2$; $E_2 = -\frac{1}{2}J_{12} - \frac{1}{2}J_{34} + 2J_{13}$, $S' = 1$; $E_3 = \frac{3}{2}J_{12} - \frac{1}{2}J_{34}$, $S' = 1$; $E_4 = \frac{3}{2}J_{34} - \frac{1}{2}J_{12}$, $S' = 1$; $E_5 = \frac{3}{2}J_{12} + \frac{3}{2}J_{34}$, $S' = 0$; and $E_6 = -\frac{1}{2}J_{12} - \frac{1}{2}J_{34} + 4J_{13}$, $S' = 0$. The general susceptibility expression as derived from the general van Vleck equation is given in equation (3) (per mole Cu^{II}) where all quantities have their usual meaning. The presence of a small monomeric impurity (mole fraction x) may be taken into account using equation (4). In the case of (**1**; R = Me, X = NCO) the substance may be thought of as consisting of four 'dimeric' moieties with no interaction between the 'dimeric' units. Copper–copper distances (3.44 Å) and Cu–O distances (2.48 Å) (Table 1) probably do not allow for any detectable 'interdimer' interaction. The susceptibility equation in this case becomes (5) where J_1, J_2, J_3, and J_4 are the exchange integrals within the 'dimeric' units.

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

$$\mathscr{H} = -2J_{12}S_1S_2 - 2J_{34}S_3S_4 - 2J_{13}(S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4) \qquad (2)$$

$$\chi_{\text{tet.}} = \frac{Ng^2\beta^2}{4\boldsymbol{k}T}\,\frac{10\cdot\exp(-E_1/\boldsymbol{k}T) + 2[\exp(-E_2/\boldsymbol{k}T) + \exp(-E_3/\boldsymbol{k}T) + \exp(-E_4/\boldsymbol{k}T)]}{5\cdot\exp(-E_1/\boldsymbol{k}T) + 3[\exp(-E_2/\boldsymbol{k}T) + \exp(-E_3/\boldsymbol{k}T) + \exp(-E_4/\boldsymbol{k}T)] + \exp(-E_5/\boldsymbol{k}T) + \exp(-E_6/\boldsymbol{k}T)} \qquad (3)$$

$$\chi_{\text{calc.}} = (1 - x)\chi_{\text{tet.}} + (xNg^2\beta^2/4\boldsymbol{k}T) + N\alpha \qquad (4)$$

$$\chi_{\text{calc.}} = \frac{Ng^2\beta^2}{4\boldsymbol{k}T}\left[\frac{1}{3 + \exp(-2J_1/\boldsymbol{k}T)} + \frac{1}{3 + \exp(-2J_2/\boldsymbol{k}T)} + \frac{1}{3 + \exp(-2J_3/\boldsymbol{k}T)} + \frac{1}{3 + \exp(-2J_4/\boldsymbol{k}T)}\right] + N\alpha \qquad (5)$$

Calculation.—The exchange integrals J_{ij} are evaluated by fitting equations (4) and (5) to the experimental susceptibility data. The calculations were performed on the IBM 370/168 computer of the Technische Hochschule Darmstadt with a modified version of the simplex routine given by Olsson.[14] The g factor was allowed to vary in the range 2.0—2.2 and the temperature-independent paramagnetism, $N\alpha$, was taken as 60×10^{-6} cm^3 mol^{-1}. As a fitting criterion the magnitude $\Sigma(\chi_{\text{obs.}} - \chi_{\text{calc.}})^2$ was used in the cases (**1**; R = Pr^n, X = NCO; and R = Bu^n, X = NCS or NCO). Since the data below 10 K are mainly determined by the monomeric impurity, these points have been omitted in the fitting procedure. For (**1**; R = Me, X = NCO) the magnitude $\Sigma(\chi_{\text{obs.}} - \chi_{\text{calc.}})^2T^2$ was used in the fitting process in order to prevent an overestimation of the low-temperature data. The resulting exchange integrals are given in Table 2 and the agreement between experimental and calculated data can be seen in Figures 2 and **3**.

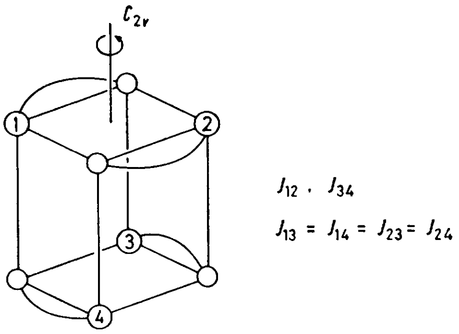

FIGURE 4 Principal structure of the Cu_4O_4 core of [{CuX(OCH$_2$CH$_2$NR$_2$)}$_4$] and relations between the exchange integrals J_{ij}

DISCUSSION

The calculated exchange integrals of (**1**; R = Me, X = NCO) show one rather strong antiferromagnetic interaction ($J_1 = -65$ cm^{-1}) (Table 2) within one 'dimeric' unit, whereas the interaction within the other three 'dimerics' is essentially zero. The result of the magnetic calculations confirms the existence of two structurally different tetrameric molecules. Whereas in one molecule there is considerable exchange interaction within one 'dimeric' unit, the interactions within the other molecule are all approximately zero. The magnetic properties can thus be explained on the basis of four non-interacting 'dimeric' units. Furthermore, as the

TABLE 2

Exchange integrals J_{ij} (cm^{-1}) of the investigated compounds resulting from the HDVV model with estimated errors (see text for explanation)

Compound	g	x	J_1	J_2	J_3	J_4
(1; R = Me, X = NCO)	2.135	0.0	-65 ± 3	-0.6 ± 2	-0.3 ± 2	-0.9 ± 2
	g	x	J_{12}	J_{34}		J_{13}
(1; R = Pr^n, X = NCO)	2.15	0.004	-30 ± 1	-53 ± 3		$+8 \pm 4$
(1; R = Bu^n, X = NCO)	2.16	0.055	-28 ± 2	-84 ± 10		$+21 \pm 10$
(1; R = Bu^n, X = NCS)	2.17	0.030	-27 ± 2	-72 ± 5		$+15 \pm 10$

The J values can be related to the corresponding copper(II) ions of the original structural studies in the following way: (1; R = Me, X = NCO), J_1 = Cu(5)–Cu(6), J_2, J_3, J_4 = Cu(1)–Cu(2), Cu(3)–Cu(4), or Cu(7)–Cu(8); (1; R = Pr^n, X = NCO), J_{12} = Cu(1)–Cu(1′), J_{34} = Cu(2)–Cu(2′); (1; R = Bu^n, X = NCO or NCS), J_{12} = Cu(3)–Cu(4), J_{34} = Cu(1)–Cu(2). J_{13} is the 'inter-dimer' interaction.

interaction in three of these 'dimerics' is very small, one can treat them as monomers. When fitting the susceptibility data with a modified equation (6) very good agreement between experimental and calculated data

$$\chi_{\text{calc.}} = \frac{Ng^2\beta^2}{4kT}\left[\frac{1}{3 + \exp(-2J_1/kT)}\right] + \frac{3Ng^2\beta^2}{16k(T - \theta)} + N\alpha \quad (6)$$

for $J_1 = -66$ cm^{-1} and $\theta = -0.55$ K results. The small Weiss constant, θ, results from either little exchange interaction within the three 'dimers' or between the 'dimers'. The very small value of θ further confirms the existence of only weak interaction in the three 'dimers' and this explains the stepwise decrease in the magnetic moment.

The structural origin for this behaviour can be found in the fact that one Cu–O–Cu bridging angle (97.5°) deviates appreciably from the Cu–O–Cu bridging angles in the other three 'dimerics' (96.1, 95.8, and 95.2°) (Table 1). A linear relation between the Cu–O–Cu bridging angle and the singlet–triplet splitting in dimeric hydroxide-bridged copper(II) complexes with a planar Cu_2O_2 ring has been found.[11] An increase of the Cu–O–Cu bridging angle parallels an increase of the antiferromagnetic exchange integral. This fact explains very well the deviation of one exchange integral from the other three in (1; R = Me, X = NCO).

A similar situation has been found in (1; R = Et, X = Cl),[6] which has much the same structure as (1; R = Me, X = NCO) and can also be thought of as two non-interacting 'dimeric' moieties. The exchange integrals -17.4 cm^{-1} (Cu–O–Cu 95.7°) and -93 cm^{-1} (Cu–O–Cu 97.6°)[15,16] are exactly in the range observed in this work. Furthermore, in dimeric complexes [{CuX(OCH$_2$CH$_2$NR$_2$)}$_2$] (2) with a planar Cu_2O_2 four-membered ring the following exchange integrals have been evaluated: $2J = -670$ cm^{-1} for (2; R = Pr^n, X = NCO) with Cu–O–Cu 104.2°[1] and $2J = -800$ cm^{-1} for (2; R = Et, X = Br) with Cu–O–Cu 105.0°.[4,16] Recently the structure of [{Cu(OMe)(2,4,6-Cl$_3$C$_6$H$_2$O)(MeOH)}$_4$] has been determined and shown to have much the same structure as (1; R = Me, X = NCO).[17] The exchange integral was calculated to be $2J = -245$ cm^{-1}[18] (Cu–O–Cu 99.1°, mean value).

In Figure 5 the exchange integrals for the above mentioned compounds are plotted as a function of the Cu–O–Cu bridging angle. A linear relation is obeyed within experimental error, which is mainly determined by the uncertainty of the bridging angle.

The extrapolated transition angle ($2J = 0$) of the linear plot is 95.7° and agrees very well with the mean value of 95.7° for the three weakly interacting 'dimeric' moieties in (1; R = Me, X = NCO). The transition angle found for the alkoxide-bridged copper(II) complexes is thus noticeably smaller than the value of 97.6° found for hydroxide-bridged complexes. This difference must be caused by the different electronic structure of hydroxide and alkoxide oxygen. However, the slope is the same in both cases (82.1 cm^{-1} degree^{-1}).

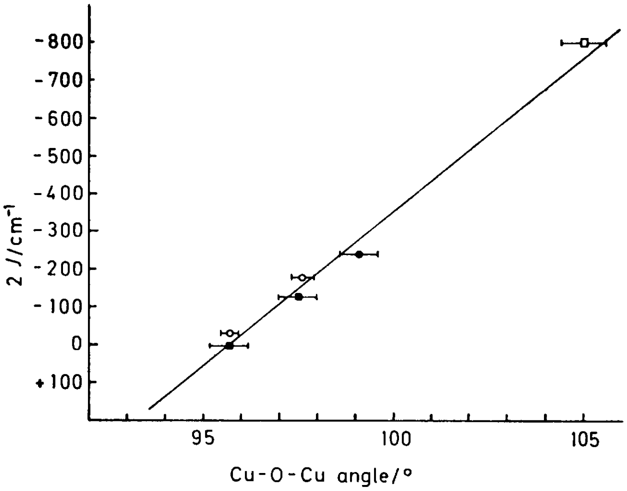

FIGURE 5 Relation between $2J$ and the Cu–O–Cu bridging angle in symmetric alkoxide-bridged copper(II) complexes: (1; R = Me, X = NCO) (■); (1; R = Et, X = Cl) (○); (2; R = Et, X = Br) (□); (2; R = Pr^n, X = NCO) (▲); [{Cu(OMe)(2,4,6-Cl$_3$C$_6$H$_2$O)(MeOH)}$_4$] (●) (see text)

The fact that planar and bent dimeric complexes with symmetric Cu–O–Cu bridges fit the straight line in Figure 5 means that a slight bending of the Cu_2O_2 four-membered ring is of minor importance with regard to the magnitude of the exchange integral.

The susceptibilities of (1; R = Pr^n, X = NCO; and R = Bu^n, X = NCO or NCS) (Figure 3) are very similar and so are the exchange integrals (Table 2). In all cases the magnetic properties can be satisfactorily explained with a model of C_{2v} symmetry [equations (3) and (4)]. Lowering of the symmetry to C_2 does not much improve the fit. Fitting with the model of two non-interacting ' dimerics ', on the other hand, does not provide good agreement. This means that in contrast to (1; R = Me, X = NCO) there is considerable interaction between the out-of-plane bonded copper(II) ions, which is caused by the shortening of the out-of-plane Cu–O bond from 2.48 (1; R = Me, X = NCO) to 2.27 (1; R = Bu^n, X = NCO), 2.25 (1; R = Bu^n, X = NCS), and 2.15 Å (1; R = Pr^n, X = NCO). This out-of-plane interaction (the interaction between the ' dimerics ') in all cases turns out to be ferromagnetic (Table 2), but there is no striking relation to the structural detail. The reason for this may be the fact that this parameter is the least accurate in the calculation, as it influences the susceptibility data only to a minor degree. Furthermore, correlations in the fitting procedure between J_{13}, J_{34}, and the g factor cause inaccuracy in these parameters. If one changes g from 2.15 to 2.18 in (1; R = Pr^n, X = NCO), J_{13} changes from 8.3 to 3.2 cm^{-1}. But it seems certain that the out-of-plane interaction is ferromagnetic.

Recently the magnetism of (1; R = Et, X = NCO) has been described and antiferromagnetic in-plane and ferromagnetic out-of-plane interactions have been discussed.[2] The value of J_{13} = 12.3 cm^{-1} with a Cu–O out-of-plane bond distance of 2.113 Å lies in the range found in the present work. In the compound (1; R = Bu^n, X = Cl or Br) the ferromagnetic interaction (J_{13} *ca.* 30 cm^{-1}, Cu–O *ca.* 1.99 Å) dominates and the ground state becomes ferromagnetic. In ref. 2 the symmetry of the magnetic planes (*i.e.* the planes of the unpaired electrons) is suggested as being the determining factor.[19]

The magnitude of the antiferromagnetic in-plane interaction (within the ' dimerics ') can be understood in terms of the Cu–O–Cu bridging angle and the non-chelate-bonded Cu–O bond distance. Although the Cu–O–Cu bridging angles in (1; R = Pr^n, X = NCO) (98.9, 99.5°) are greater than in (1; R = Bu^n, X = NCO) (98.4, 98.0°), and (1; R = Bu^n, X = NCS) (98.1, 97.4°), the exchange parameters are of equal magnitude, as the diminution of the Cu-O-Cu bridging angle is accompanied by a shortening of the non-chelate-bonded Cu–O bond distance from 2.23 Å (1; R = Pr^n, X = NCO) to 2.12, 2.10 Å (1; R = Bu^n, X = NCO or NCS). The chelate-bonded Cu–O distance remains nearly constant. For (1; R = Et, X = NCO) a value of J_{12} = −22.4 cm^{-1} is found (Cu–O–Cu 99.4°, Cu–O 2.243 Å), which is in the range found for the present compounds. As the uncertainty in the measured Cu–O–Cu bond angles for (1; R = Bu^n, X = NCO or NCS) is rather large (±0.7°) a more quantitative discussion at the present stage is not possible.

It is apparent from the above discussion that with symmetric alkoxide-bridged copper(II) clusters of the cubane type with only weak out-of-plane interaction there is a linear relation between the Cu–O–Cu bridging angle and singlet–triplet splitting. If bridging becomes unsymmetric, the exchange interaction is determined by the Cu–O–Cu bridging angle and the non-chelate-bonded Cu–O bond distance. The out-of-plane interaction (if present) in all cases is ferromagnetic and rather small.

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