Crystal and Molecular Structures and Magnetic Properties[†] of Four New Exchange-coupled Copper(II) Complexes derived from Different 3-*N*,*N*-Dialkylamino-1-propanols and Pseudohalogens

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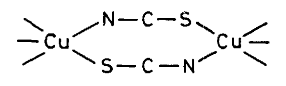
The crystal and molecular structures of (3-*N*,*N*-dimethylamino-1-propanolato)isocyanatocopper(II) (**1**), (3-*N*,*N*-dimethylamino-1-propanolato)isothiocyanatocopper(II) (**2**), (3-*N*,*N*-diethylamino-1-propanolato)isothiocyanatocopper(II) (**3**), and (3-*N*,*N*-di-n-butylamino-1-propanolato)isothiocyanatocopper(II) (**4**) have been determined using three-dimensional *X*-ray diffractometer data. Final *R* values were 0.0237 for (**1**), 0.0250 for (**2**), 0.0297 for (**3**), and 0.0464 for (**4**). Compounds (**1**) and (**2**) crystallize in monoclinic lattices (space group $P2_1/c$), (**3**) and (**4**) in triclinic ones (space group $P\bar{1}$). The structure of (**1**) consists of an infinite two-dimensional network of alkoxo-bridged dimers connected by cyanato-groups in the plane (100); the three remaining structures consist of infinite chains of alkoxo-bridged dimers connected by the thiocyanato-groups. Within the dimeric units the copper atoms have distorted square-planar co-ordination.The connection between the dimers leads to a fifth co-ordination with longer copper–ligand bonds. The magnetic susceptibilities measured from 11.1 K show for all four compounds very strong antiferromagnetic spin coupling ($|2J| > 850$ cm^{-1}). A correlation between the exchange constants and the Cu–O–Cu′ bridging angles within the dimers for all known (3-*N*,*N*-dialkylamino-1-propanolato)-halogenocopper(II) and -pseudohalogenocopper(II) complexes is given and shows that these complexes are systematically more strongly coupled than the related complexes derived from analogous aminoethanols.

A great number of oligomeric and polymeric copper(II) complexes derived from several aminoethanols has been structurally and magnetically investigated.[1] However, studies involving 3-amino-1-propanol derivatives are limited to only a few examples. Recently we gave a short summary of the known complexes[2] and described the structures and the magnetic properties of three complexes of this type. In order to obtain more information about this group of compounds we synthesized the four complexes [Cu^{II}(OCH$_2$CH$_2$CH$_2$NMe$_2$)(NCO)] (1), [Cu^{II}(OCH$_2$CH$_2$CH$_2$NMe$_2$)(NCS)] (2), [Cu^{II}(OCH$_2$CH$_2$CH$_2$NEt$_2$)(NCS)] (3), and [Cu^{II}(OCH$_2$CH$_2$CH$_2$NBu$^n{}_2$)(NCS)] (4). In this paper we discuss the significant differences between the copper(II) complexes derived from aminoethanols and 3-amino-1-propanols.

Results and Discussion

Description of the Structures.—The final structural data for (1)—(4) are presented in Tables 1 and 2 and in Figure 1(*a*)—(*c*). All four structures consist of alkoxo-bridged dimers with planar Cu$_2$O$_2$ units, which are connected by the pseudohalogen (NCO or NCS) groups. The bond lengths and angles within the dimeric units show no significant differences to those in similar complexes. While (1) forms a two-dimensional network in the plane (100), complexes (2)—(4) develop infinite chains with bridges as shown below. These chains are along [101] in (2), along [001] in (3), and along [100] in (4). The equivalent connection with halogen bridges was also observed in [Cu^{II}(OCH$_2$CH$_2$CH$_2$NMe$_2$)Br] (5) along [100] and in [Cu^{II}(OCH$_2$CH$_2$CH$_2$NMe$_2$)Cl] (6) along [010].[2] In this class of compounds only [Cu^{II}(OCH$_2$CH$_2$CH$_2$NEt$_2$)(NCO)] (7) consists of discrete dimeric molecules.[2] Among the seven copper(II) complexes (1)—(7) only homologues for (2) and (3) exist in the series of complexes derived from aminoethanols,[3,4] while the analogues of (1), (4), and (7) form tetrameric species with a central Cu$_4$O$_4$ core.[5–8] A comparable polymeric structure to (1) has not been observed in the (*N*,*N*-dialkylaminoethanolato)isocyanatocopper(II) series of complexes, although eight different complexes of the type [{Cu^{II}(OCH$_2$CH$_2$NR$_2$)(NCO)}$_n$] are known [$n = 2$, R = Pr^n;[9] $n = 4$, R = Me,[7] Et (five different structures, three with crystal solvents),[5,6] Pr^n,[9] or Bu^n [8]]. In the case of (1)—(7) the flat structure of the dimeric units, which is due to the additional CH$_2$ group, prevents a connection of two dimers to form a tetramer. However, the connection to form polymeric species elevates the co-ordination number at the copper atom.



Magnetic Properties.—The temperature dependence of the magnetic susceptibility for the complexes (1)—(4) is shown in Figure 2. Measurements for (1) were carried out over the temperature range 11.1—368 K, and for (2)—(4), over the range 11.1—313 K. Fitting the experimental susceptibilities to the Bleaney–Bowers equation (1) corrected for the presence of paramagnetic impurities and the temperature-independent paramagnetism $N\alpha$ (using the Hamiltonian $\mathcal{H} = -2J_{12}\hat{S}_1\hat{S}_2$) the parameters presented in Table 3 are obtained. The values for

$$\chi_{\mathrm{dim}}/2 = (1 - x)\left(\frac{N_A \cdot g^2 \cdot \beta^2}{kT}\right)\left[\frac{1}{3 + \exp(-2J_{12}/kT)}\right] + x\left(\frac{N_A \cdot g^2 \cdot \beta^2}{4kT}\right) + N\alpha \quad (1)$$

[†] *Supplementary data available* (No. SUP 56201, 9 pp.): H-atom co-ordinates, thermal parameters, experimental and calculated magnetic susceptibilities. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

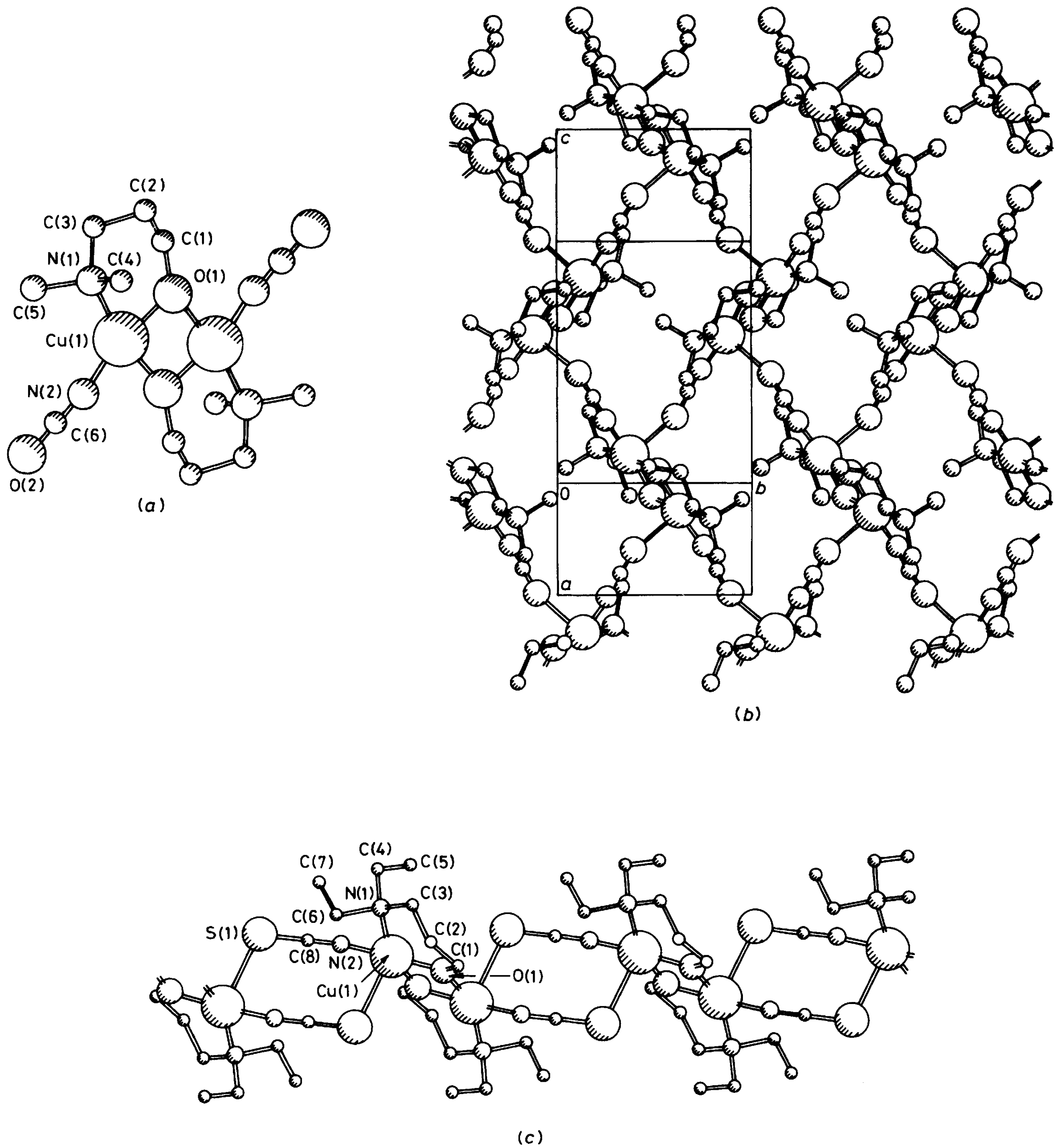


Figure 1. PLUTO drawings of (**1**) and (**3**): (*a*) view of the dimeric unit in (**1**) (projection along [010]); (*b*) view of the two-dimensional connection in (**1**) [projection on (100)]; (*c*) view of the alternating chain in (**3**) along [001] (projection along [010]). The equivalent connection in (**2**) and (**4**) occurs along [101] and [100], respectively

$2J_{12}$ show a strong antiferromagnetic spin coupling. The fitting for (**1**) leads only to a moderate agreement which is obtained with an abnormally high $N\alpha$ value. Although the temperature dependence of strongly coupled polymeric copper(II) complexes ($|2J| > 850$ cm^{-1}) is too unspecific to point out deviations from the Bleaney–Bowers equation, it appears that for (**1**), in addition to the exchange interaction within the dimers, an interdimer interaction exists which may be the real reason for the deviations and the high $N\alpha$ value. For (**2**)—(**4**) interdimer interactions are also possible (these compounds are so-called alternating chains) but the results of the fitting procedures do not allow such interactions to be demonstrated.

An interesting feature can be observed by comparing the pathways between the dimeric units for (**1**)—(**6**). In this series, only the dimers of (**1**) are connected to four other dimers *via* the isocyanato-bridges, the others having only two neighbouring dimers.

The geometry of the pathway in (**1**) is also different. Let us assume sp^3 hybridization at the bromine atom in (**5**) and at the chlorine atom in (**6**), and sp^2 hybridization at the oxygen atom

Table 1. Positional parameters with estimated standard deviations in parentheses for (**1**)—(**4**)

	Compound (**1**)			Compound (**2**)		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.949 5(1)	0.129 7(1)	0.563 9(1)	0.772 3(1)	0.033 3(1)	0.866 5(1)
S(1)	—	—	—	0.125 1(1)	−0.087 5(1)	0.390 0(1)
O(1)	0.868 8(2)	0.013 3(2)	0.424 2(1)	1.058 1(3)	0.062 0(1)	1.073 3(3)
O(2)	1.192 8(3)	0.393 8(3)	0.872 1(2)	—	—	—
N(1)	0.748 9(2)	0.289 5(3)	0.519 3(2)	0.620 8(4)	0.133 6(1)	0.867 5(4)
N(2)	1.069 7(2)	0.256 6(3)	0.699 9(2)	0.494 6(5)	−0.016 4(2)	0.688 8(4)
C(1)	0.707 1(2)	−0.032 8(3)	0.358 1(2)	1.138 1(6)	0.136 4(2)	1.131 1(5)
C(2)	0.599 5(3)	0.128 9(3)	0.337 0(2)	0.978 6(6)	0.186 8(2)	1.139 7(5)
C(3)	0.598 2(3)	0.203 3(4)	0.437 9(2)	0.770 1(5)	0.200 7(2)	0.952 4(5)
C(4)	0.778 8(4)	0.458 5(4)	0.476 3(3)	0.438 8(6)	0.156 1(2)	0.676 6(5)
C(5)	0.722 6(4)	0.333 3(5)	0.615 6(3)	0.527 9(7)	0.114 7(3)	0.975 8(7)
C(6)	1.129 0(3)	0.323 5(4)	0.783 8(2)	0.340 5(5)	−0.045 4(2)	0.565 9(5)

	Compound (**3**)			Compound (**4**)		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	0.586 8(1)	0.049 9(1)	0.293 6(1)	0.350 6(1)	0.559 5(1)	0.434 5(1)
S(1)	0.671 7(1)	−0.186 2(1)	−0.154 5(1)	−0.043 4(2)	0.365 8(2)	0.350 6(1)
O(1)	0.530 0(3)	0.135 5(3)	0.484 3(3)	0.492 4(4)	0.636 2(4)	0.488 9(3)
N(1)	0.761 0(3)	0.229 6(4)	0.121 3(4)	0.282 2(6)	0.769 9(5)	0.309 4(4)
N(2)	0.631 2(3)	−0.072 1(4)	0.133 2(4)	0.223 7(6)	0.448 1(5)	0.393 3(4)
C(1)	0.545 5(6)	0.298 6(5)	0.465 1(6)	0.454 7(8)	0.791 8(6)	0.504 0(6)
C(2)	0.631 8(8)	0.410 4(5)	0.278 1(8)	0.325 6(9)	0.914 7(6)	0.437 1(5)
C(3)	0.768 6(6)	0.364 2(6)	0.187 5(7)	0.347 4(11)	0.897 2(8)	0.314 7(7)
C(4)	0.899 9(5)	0.148 8(7)	0.108 0(7)	0.085 4(7)	0.818 9(7)	0.314 0(5)
C(5)	0.910 4(6)	0.010 6(9)	0.304 0(7)	0.011 4(8)	0.964 2(7)	0.222 9(5)
C(6)	0.733 3(5)	0.311 0(5)	−0.082 1(6)	−0.170 3(10)	0.979 1(10)	0.218 0(7)
C(7)	0.855 2(6)	0.430 6(7)	−0.240 1(7)	−0.261 9(12)	1.118 9(11)	0.137 8(8)
C(8)	0.648 0(4)	−0.120 6(4)	0.014 7(4)	0.388 8(10)	0.722 1(10)	0.184 0(5)
C(9)	—	—	—	0.567 2(10)	0.612 6(11)	0.179 5(6)
C(10)	—	—	—	0.682 0(14)	0.586 2(13)	0.047 1(10)
C(11)	—	—	—	0.744 1(20)	0.731 7(15)	−0.009 2(13)
C(12)	—	—	—	0.113 9(6)	0.412 2(6)	0.375 3(4)

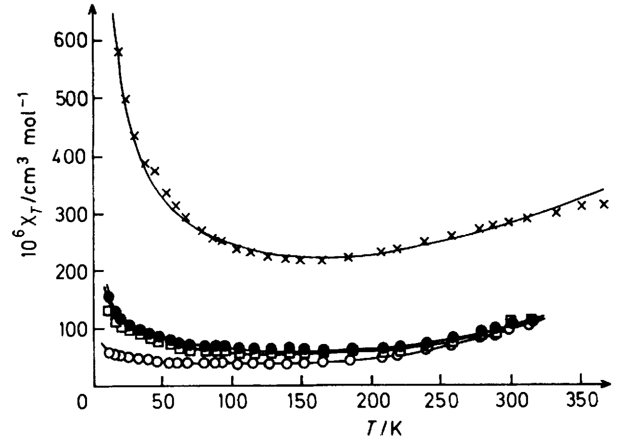


Figure 2. Temperature dependence of the magnetic susceptibility of (**1**) (×), (**2**) (○), (**3**) (●), and (**4**) (□). The solid lines represent the fits to equation (1) with the parameters given in Table 3

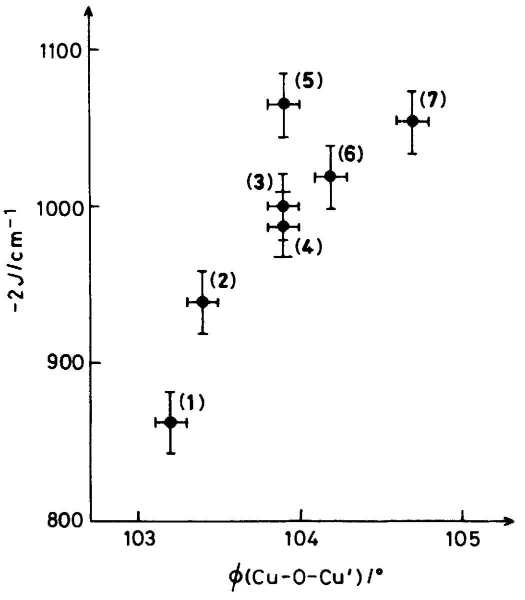


Figure 3. Plot of $-2J$ *versus* φ(Cu–O–Cu′) for (**1**)—(**7**)

of the isocyanato-group in (**1**) and at the sulphur atom of the isothiocyanato-groups in (**2**)—(**4**). Then the best overlap for Cu–X ··· Cu′, where X is the halogen atom, is expected for 109.5°. For the complexes with pseudohalogen groups the angle Cu ··· E–C [E = O in (**1**) and S in (**2**)—(**4**)] should be 120°. Since the Cu–X and the Cu–E bonds, respectively, are nearly perpendicular to the Cu_2O_2 plane an overlap between the $3d_{z^2}$ orbital of the copper atom and the hybrid orbital of the ligand is expected, because the pathway within the dimers is formed by the $3d_{xy}$ orbitals of the copper atoms and the $2p$ orbitals of the oxygen. Any deviation from the ideal angle should decrease this overlap. Table 4 shows that the best agreement between the

Table 2. Distances (Å) and angles (°) with estimated standard deviations in parentheses for (**1**)—(4)

	(**1**)	(**2**)	(**3**)	(**4**)
Cu(1)–Cu(1′)	3.024(1)	3.033(1)	3.035(1)	3.030(1)
Cu(1)–O(1)	1.907(1)	1.907(2)	1.905(2)	1.899(3)
Cu(1)–O(1′)	1.952(1)	1.957(2)	1.949(2)	1.949(3)
Cu(1)–S(1′)	—	2.893(1)	2.887(1)	3.013(2)
Cu(1)–O(2′)	2.581(3)	—	—	—
Cu(1)–N(1)	2.066(2)	2.069(3)	2.072(3)	2.074(4)
Cu(1)–N(2)	1.919(2)	1.936(3)	1.939(3)	1.934(4)
O(1)–C(1)	1.410(2)	1.389(4)	1.396(4)	1.393(6)
C(1)–C(2)	1.502(4)	1.504(5)	1.447(6)	1.474(7)
C(2)–C(3)	1.491(4)	1.496(5)	1.422(7)	1.486(8)
C(3)–N(1)	1.486(3)	1.480(4)	1.489(5)	1.462(7)
N(1)–C(4)	1.461(4)	1.478(4)	1.445(6)	1.485(6)
N(1)–C(5)	1.484(5)	1.486(4)	—	—
N(1)–C(6)	—	—	1.559(5)	—
N(1)–C(8)	—	—	—	1.587(8)
C(4)–C(5)	—	—	1.565(7)	1.519(7)
C(5)–C(6)	—	—	—	1.453(8)
C(6)–C(7)	—	—	1.503(6)	1.470(8)
C(8)–C(9)	—	—	—	1.428(9)
C(9)–C(10)	—	—	—	1.612(12)
C(10)–C(11)	—	—	—	1.479(8)
N(2)–C(6)	1.133(3)	1.146(4)	—	—
N(2)–C(8)	—	—	1.155(4)	—
N(2)–C(12)	—	—	—	1.154(6)
C(6)–O(2)	1.193(3)	—	—	—
C(6)–S(1)	—	1.626(3)	—	—
C(8)–S(1)	—	—	1.682(3)	—
C(12)–S(1)	—	—	—	1.619(5)
O(1)–Cu(1)–N(1)	94.0(1)	95.2(1)	95.3(1)	94.0(1)
O(1′)–Cu(1)–N(1)	168.5(1)	166.8(1)	159.7(1)	157.6(1)
O(1)–Cu(1)–N(2)	167.8(1)	167.3(1)	170.6(1)	170.8(2)
C(1′)–Cu(1)–N(2)	94.4(1)	93.9(1)	94.6(1)	94.8(2)
O(1)–Cu(1)–O(1′)	76.8(1)	76.6(1)	76.1(1)	76.1(2)
N(1)–Cu(1)–N(2)	93.6(1)	92.5(1)	93.1(1)	94.9(2)
S(1′)–Cu(1)–O(1)	—	90.4(1)	89.2(1)	89.1(1)
S(1′)–Cu(1)–O(1′)	—	94.0(1)	94.4(1)	99.2(1)
S(1′)–Cu(1)–N(1)	—	96.4(1)	104.0(1)	100.7(1)
S(1′)–Cu(1)–N(2)	—	98.8(1)	92.9(1)	91.2(1)
O(2′)–Cu(1)–O(1)	90.5(1)	—	—	—
O(2′)–Cu(1)–O(1′)	100.5(1)	—	—	—
O(2′)–Cu(1)–N(1)	86.3(1)	—	—	—
O(2′)–Cu(1)–N(2)	99.5(1)	—	—	—
Cu(1)–S(1′)–C(6′)	—	92.0(1)	—	—
Cu(1)–S(1′)–C(8′)	—	—	97.8(1)	—
Cu(1)–S(1′)–C(12′)	—	—	—	101.3(1)
Cu(1)–O(2′)–C(6′)	122.5(1)	—	—	—
Cu(1)–O(1)–Cu(1′)	103.2(1)	103.4(1)	103.9(1)	103.9(1)
Cu(1)–O(1)–C(1)	124.5(2)	126.9(2)	128.9(2)	127.0(3)
Cu(1)–O(1′)–C(1′)	124.9(2)	127.6(2)	126.5(1)	126.4(3)
Cu(1)–N(1)–C(3)	114.1(2)	114.1(2)	113.2(2)	113.1(3)
Cu(1)–N(1)–C(4)	106.2(2)	111.5(2)	108.2(3)	110.4(3)
Cu(1)–N(1)–C(5)	111.4(1)	105.4(2)	—	—
Cu(1)–N(1)–C(6)	—	—	107.8(2)	—
Cu(1)–N(1)–C(8)	—	—	—	104.8(4)
O(1)–C(1)–C(2)	111.6(2)	111.8(3)	113.5(3)	113.8(4)
C(1)–C(2)–C(3)	113.9(2)	113.1(3)	120.5(5)	116.3(5)
C(2)–C(3)–N(1)	116.1(2)	115.7(3)	118.4(4)	115.0(5)
C(3)–N(1)–C(4)	111.1(2)	107.4(3)	112.1(3)	114.7(5)
C(3)–N(1)–C(5)	105.5(2)	109.8(3)	—	—
C(3)–N(1)–C(6)	—	—	107.3(3)	—
C(3)–N(1)–C(8)	—	—	—	106.2(5)
C(4)–N(1)–C(5)	108.6(3)	108.4(3)	—	—
C(4)–N(1)–C(6)	—	—	108.1(3)	—
C(4)–N(1)–C(8)	—	—	—	106.7(4)
N(1)–C(4)–C(5)	—	—	112.6(4)	118.3(4)
C(4)–C(5)–C(6)	—	—	—	113.3(5)
C(5)–C(6)–C(7)	—	—	—	119.1(7)
N(1)–C(6)–C(7)	—	—	117.9(4)	—
N(1)–C(8)–C(9)	—	—	—	115.2(5)
C(8)–C(9)–C(10)	—	—	—	113.8(7)
C(9)–C(10)–C(11)	—	—	—	104.2(11)
Cu(1)–N(2)–C(6)	172.3(2)	169.6(3)	—	—
Cu(1)–N(2)–C(8)	—	—	167.6(3)	—
Cu(1)–N(2)–C(12)	—	—	—	163.9(4)
N(2)–C(6)–O(2)	179.4(4)	—	—	—
N(2)–C(6)–S(1)	—	178.7(3)	—	—
N(2)–C(8)–S(1)	—	—	179.2(3)	—
N(2)–C(12)–S(1)	—	—	—	178.7(5)

Primed atoms are related by a centre of symmetry with the co-ordinates given in Table 1.

Table 3. Results of the fits to equation (1) for (**1**)—(**4**)

Compound	g	$-2J$/cm^{-1}	x	$10^6 N\alpha$/ c.g.s.u.
(**1**)	2.20*	863(20)	0.018(4)	169(5)
(**2**)	2.12(2)	940(20)	0.001(1)	37(5)
(**3**)	2.20*	1 001(20)	0.003(1)	52(5)
(**4**)	2.20*	988(20)	0.003(1)	49(5)

* Fixed parameter.

Table 4. Angles (°) at the bridging atoms between two dimeric units in (**1**)—(**6**)

Compound		
(**5**)	Cu(1)–Br(1) ··· Cu(1′)	91.1(1)
(**6**)	Cu(1)–Cl(1) ··· Cu(1′)	93.8(1)
(**1**)	C(6)–O(2) ··· Cu(1′)	122.5(1)
(**2**)	C(6)–S(1) ··· Cu(1′)	92.0(1)
(**3**)	C(7)–S(1) ··· Cu(1′)	97.8(1)
(**4**)	C(12)–S(1) ··· Cu(1′)	101.3(1)

ideal angle and the real one is observed for (**1**). Of course, an exchange interaction through such a pathway requires that the unpaired electron is partially in the copper $3d_{z^2}$ orbital.

If we connect these observations with the correlation between $2J$ and the Cu–O–Cu′ angle (φ) presented in Figure 3, we see that the smaller than expected exchange constant ($2J$) for (**1**) can be explained by a weak interdimer interaction. Figure 3 shows an equivalent correlation to those given by Hatfield for hydroxo-bridged[10] and by Merz and Haase[1] for alkoxo-bridged copper(II) complexes. The differences between the three $2J = f(\varphi)$ correlations are due to differences in the electronegativity (hydroxo-bridged/alkoxo-bridged) and to co-ordination effects (aminoethanolato/aminopropanolato). Recently we showed, that for the similar Cu–O–Cu′ bridging angles, alkoxo-bridged complexes with less distorted square-planar co-ordination are stronger coupled than more distorted ones.[2] Since complexes derived from 3-*N*,*N*-dialkylamino-1-propanols are systematically less distorted than the corresponding aminoethanolato-complexes, two different correlations for alkoxo-bridged copper(II) complexes exist.

Experimental

Preparations.—Compound (**1**) was prepared by a similar procedure to that described by Merz and Haase;[5] (**2**)—(**4**) were prepared according to the procedure given by Lehtonen *et al.*[11]

Table 5. Analytical data (%) for (**1**)—(**4**) *

	(**1**)	(**2**)	(**3**)	(**4**)
C	33.65 (34.70)	31.95 (31.20)	37.90 (38.15)	46.40 (46.80)
H	5.65 (5.80)	5.49 (5.40)	6.40 (6.40)	8.00 (7.85)
N	13.00 (13.50)	12.35 (12.50)	10.95 (11.10)	9.10 (9.10)

* Calculated values are given in parentheses.

Crystals suitable for *X*-ray analysis were obtained by recrystallization from methanol. Analytical data are in Table 5.

Crystal Data for (**1**).—$C_6H_{12}CuN_2O_2$, M = 207.72, monoclinic, a = 9.426(2), b = 7.356(2), c = 13.696(3) Å, β = 117.35(1)°, U = 843.49 Å^3 (by least-squares refinement of 50 strong reflections, λ = 0.710 69 Å), space group $P2_1/c$ (no. 14),[12] D_m (flotation) = 1.63(3) g cm^{-3}, Z = 4, D_c = 1.64 g cm^{-3}. Blue-green, plate-like crystals; crystal dimensions (distances to faces from centre) 0.297 $(100,\bar{1}00)$ × 0.188 $(011,0\bar{1}\bar{1})$ × 0.413 mm $(0\bar{1}1,01\bar{1})$, μ(Mo-K_α) = 24.55 cm^{-1}.

Crystal Data for (**2**).—$C_6H_{12}CuN_2OS$, M = 223.78, monoclinic, a = 7.403(2), b = 17.317(4), c = 8.702(2) Å, β = 124.605(5)°, U = 918.22 Å^3 (by least-squares refinement of 46 strong reflections, λ = 0.710 69 Å), space group $P2_1/c$ (no. 14),[12] D_m (flotation) = 1.60(3) g cm^{-3}, Z = 4, D_c = 1.62 g cm^{-3}. Blue-green, short columns; crystal dimensions (distance to faces from centre) 0.279 $(11\bar{1},\bar{1}\bar{1}1)$ × 0.118 (010) × 0.275 $(\bar{1}11)$ × 0.115 $(0\bar{1}0)$ × 0.298 $(1\bar{1}\bar{1})$ × 0.317 $(00\bar{1})$ × 0.317 mm (101), μ(Mo-K_α) = 24.60 cm^{-1}.

Crystal Data for (**3**).—$C_8H_{16}CuN_2OS$, M = 251.83, triclinic, a = 9.186(2), b = 8.840(2), c = 7.910(2) Å, α = 66.32(1), β = 75.84(1), γ = 88.23(1)°, U = 568.73 Å^3 (by least-squares refinement of 50 strong reflections, λ = 0.710 69 Å), space group $P\bar{1}$ (no. 2),[12] D_m (flotation) = 1.47(3) g cm^{-3}, Z = 2, D_c = 1.47 g cm^{-3}. Blue-green, cube-shaped crystals; crystal dimensions (distance to faces from centre) 0.099 $(0\bar{1}0)$ × 0.130 $(\bar{1}0\bar{1})$ × 0.118 (010) × 0.179 (111) × 0.130 (101) × 0.156 (100) × 0.210 $(00\bar{1})$ × 0.217 $(\bar{1}00)$ × 0.152 mm (001), μ(Mo-K_α) = 19.90 cm^{-1}.

Crystal Data for (**4**).—$C_{12}H_{24}CuN_2OS$, M = 307.94, triclinic, a = 8.131(2), b = 9.102(2), c = 12.120(3) Å, α = 72.400(5), β = 70.930(5), γ = 68.840(5)°, U = 773.09 Å^3 (by least-squares refinement of 74 strong reflections, λ = 0.710 69 Å), space group $P\bar{1}$ (no. 2),[12] D_m (flotation) = 1.34(3) g cm^{-3}, Z = 2, D_c = 1.32 g cm^{-3}. Dark blue-green, plate-like crystals; crystal dimensions 0.182 $(111,\bar{1}\bar{1}\bar{1})$ × 0.089 $(010,0\bar{1}0)$ × 0.096 mm $(001,00\bar{1})$, μ(Mo-K_α) = 14.71 cm^{-1}.

Data Collection and Processing.—The data collections for all four complexes were carried out using a computer-controlled STOE-STADI 4 diffractometer with graphite-monochromated Mo-K_α radiation, λ = 0.710 69 Å. The $\omega:\theta$ = 1:1 mode was applied in the range $3 \leqslant 2\theta \leqslant 45°$. Three strong reflections were monitored at measured intervals and showed consistency throughout the measurements.

Compound (**1**). 2 690 Reflections measured, 1 458 unique [merging R = 0.028 after absorption correction (max., min. transmission factors = 0.297, 0.159)], giving 1 435 with $I > 2\sigma(I)$.

Compound (**2**). 1 295 Reflections measured, 1 186 unique [merging R = 0.014 after absorption correction (max., min. transmission factors = 0.578, 0.305)], giving 1 149 with $I > 2\sigma(I)$.

Compound (**3**). 2 996 Reflections measured, 1 493 unique [merging R = 0.017 after absorption correction (max., min. transmission factors = 0.705, 0.615)], giving 1 462 with $I > 2\sigma(I)$.

Compound (**4**). 2 194 Reflections measured, 1 940 unique [merging R = 0.019 after absorption correction (max., min. transmission factors = 0.804, 0.745)], giving 1 859 with $I > 3\sigma(I)$.

Structure Analysis and Refinement.—Direct methods [Cu atoms for (**1**)—(**4**), S atom also for (**4**)]. The positions of the remaining atoms were found by Fourier maps. Full-matrix least-squares refinement with anisotropic non-hydrogen atoms and isotropic hydrogens in fixed calculated positions gave the final R values 0.0237 (R' = 0.0273) for (**1**), 0.0250 (0.0291) for (**2**), 0.0297 (0.0328) for (**3**), and 0.0464 (0.0491) for (**4**). The weighting scheme was $w = 1/\sigma^2(F_o)$. For all parameters of the four structures the ratio of shift to estimated standard deviation was smaller than 0.1 within the last least-squares cycles. A final difference map showed the highest peak (e Å^{-3}) at 0.22 for (**1**), 0.35 for (**2**), 0.55 for (**3**), and 0.35 for (**4**).

Magnetic Measurements.—The magnetic susceptibilities of the samples were recorded by the Faraday method at *ca.* 6.2 kG^2 cm^{-1} using mercury tetra(thiocyanato)cobaltate(II) as a susceptibility standard. Experimental susceptibility data were corrected for underlying diamagnetism. To convert into S.I. units χ/c.g.s.u. should be multiplied by $4\pi \times 10^{-6}$.

Calculations.—The structure calculations were carried out with the program SHELX 76;[13] scattering factors for Cu^0 were taken from Cromer and Mann,[14] the others are stored in the program.

The exchange parameters were obtained using a modified simplex routine.[15] The function minimized was $\Sigma(|\chi_{exp.} - \chi_{calc.}|/\chi_{exp.})$. The calculations were performed on an IBM 3081 K computer of the calculation centre of the Technische Hochschule Darmstadt.

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