

Crystal and Molecular Structures and Magnetic Properties of Bromo(3-dimethylaminopropan-1-olato)copper(II), Chloro(3-dimethylaminopropan-1-olato)copper(II), and (3-Diethylaminopropan-1-olato)isocyanatocopper(II)†

Leonhard Walz, Helmut Paulus, and Wolfgang Haase,*

Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 20, D-6100 Darmstadt, West Germany

The crystal and molecular structures of the title compounds have been determined using three-dimensional X-ray diffractometer data and refined to a final R value of 0.0263 for bromo(3-dimethylaminopropan-1-olato)copper(II) (**1**), 0.0349 for chloro(3-dimethylaminopropan-1-olato)copper(II) (**2**), and 0.0268 for (3-diethylaminopropan-1-olato)isocyanatocopper(II) (**3**). The compounds crystallize in the monoclinic space group $P2_1/c$. The unit-cell dimensions are $a = 6.273(3)$, $b = 10.282(5)$, $c = 12.403(5)$ Å, $\beta = 99.62(2)^\circ$, $Z = 4$ for (**1**); $a = 7.484(3)$, $b = 6.145(3)$, $c = 17.152(6)$ Å, $\beta = 101.55(2)^\circ$, $Z = 4$ for (**2**); and $a = 7.363(3)$, $b = 12.422(5)$, $c = 11.117(5)$ Å, $\beta = 96.37(2)^\circ$, $Z = 4$ for (**3**). The structures of (**1**) and (**2**) consist of infinite chains of alkoxo-bridged copper(II) dimers connected by halogen bridges with long halogen-copper bonds [3.127(1) Å for (**1**) and 2.905(1) Å for (**2**)]. Neglecting these additional fifth co-ordination sites the co-ordination of the copper ions is distorted square planar. The structure of (**3**) consists of discrete dimeric molecules. The copper-copper distances are 3.063(1) for (**1**), 3.060(1) for (**2**), and 3.044(1) Å for (**3**). The magnetic susceptibilities measured from 11.1 K show very strong antiferromagnetic spin coupling for all three compounds. The magnetic behaviour can be explained using the Bleaney-Bowers equation. By fitting the experimental data to the Bleaney-Bowers equation good agreement can be obtained with the parameters $g = 2.18(2)$, $2J_{12} = -1\ 065(20)$ cm⁻¹, $x = 0.004(1)$, $N_\alpha = 63(5) \times 10^{-6}$ c.g.s.u. for (**1**), $g = 2.21(2)$, $2J_{12} = -1\ 020(20)$ cm⁻¹, $x = 0.003(1)$, $N_\alpha = 54(5) \times 10^{-6}$ c.g.s.u. for (**2**) and $g = 2.26(2)$, $2J_{12} = -1\ 056(20)$ cm⁻¹, $x = 0.013(3)$, $N_\alpha = 108(5) \times 10^{-6}$ c.g.s.u. for (**3**). The evident differences between these results and those expected from magnetostructural correlations for related compounds are discussed. A magnetostructural correlation is presented which shows the influence of the co-ordination geometry at the copper atom on the exchange interaction in spin-coupled alkoxo-bridged copper(II) complexes.

A great number of alkoxo-bridged oligomeric and polymeric copper(II) complexes derived from 2-aminoethanols are known and have been structurally as well as magnetically investigated.¹⁻⁹ The copper(II) ion which is three-co-ordinated in the pseudomonomeric unit by the deprotonated aminoalcohol and a halogen (Cl or Br) or a pseudohalogen anion (NCO or NCS) can increase its co-ordination by three different ways. (a) The oxygen of one monomeric complex co-ordinates to the copper ion of a second monomer leading to isolated dimeric molecules with a central Cu₂O₂ unit [Figure 1(a)] (Cu-O and Cu-O' = 1.85-2.00 Å). (b) Two dimers are tied together by the co-ordination of the two oxygen atoms of one dimer to the two copper atoms of the other. This leads to the tetrameric copper(II) complexes of the cubane type. If the bonds within the pseudodimeric units are strong (Cu-O and Cu-O' = 1.85-2.00 Å) then the bonds between them are weak (Cu-O'' = 2.40-2.60 Å), these are the so-called type I complexes¹⁰ with an antiferromagnetic ground state. If the distances between the two pseudomonomeric units within the pseudodimeric unit are large (Cu-O' = 2.40-2.75 Å) then the Cu-O'' distances are small (Cu-O and Cu-O'' = 1.90-2.00 Å) and these so-called type II complexes exhibit ferromagnetic ground states [Figure 1(b)]. Nevertheless it should be noted that there is a large number of tetrameric complexes with Cu₄O₄ cores which lie between these

extreme types. (c) The dimers are connected into infinite alternating chains by the halogen or the pseudohalogen anion which forms a second weak bond between two dimers [Figure 1(c)].

While for complexes of the types (a) and (b) equations for the magnetic susceptibilities are known, alternating chains (c) can be treated only approximately. The simplest case occurs if the coupling within the pseudodimeric units is large and the coupling between them is negligible due to relatively long distances. This is realized for example in β -bromo(2-diethylaminoethanolato)copper(II) where the copper-bromine distance between the pseudodimeric units is 3.660(2) Å.¹¹ The situation becomes more difficult if these distances become smaller as then the magnetic behaviour does not follow the Bleaney-Bowers equation. This occurs in some complexes with isothiocyanate ligands. Ugglä *et al.*,¹² who studied the magnetism of (2-diethylaminoethanolato)isothiocyanatocopper(II), found by fitting the magnetic susceptibilities a g factor of 1.93 for this compound. The reason for this small value (normally 2.10-2.25) can be explained by assuming an exchange interaction between the dimers *via* the thiocyanate groups which connect the different dimeric units. The copper-sulphur distances along the isothiocyanate pathway are 2.851(4) Å.⁵

Using the various results on this group of copper(II) complexes Merz¹³ was able to correlate the exchange constants of the dimeric and tetrameric complexes with geometrical parameters. Contrary to the many investigations on oligomeric and polymeric copper(II) complexes with 2-aminoethanol and its derivatives the corresponding homologues with 3-amino-propan-1-ols are not well known. Hein and Rittersdorf¹⁴

† Supplementary data available (No. SUP 56155, 8 pp.): thermal parameters, H-atom co-ordinates, 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.

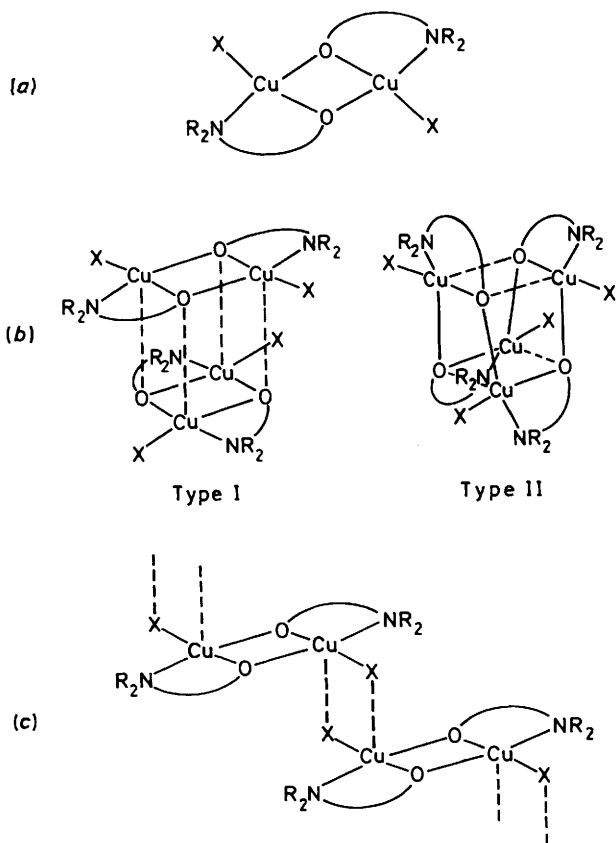


Figure 1. Schematic representation of alkoxy-bridged copper(II) complexes. (a) Dimeric molecule; (b) tetrameric molecules of the cubane type; (c) alternating chain formed by dimeric molecules

described in 1961 the syntheses of two modifications of chloro(3-diethylaminopropan-1-olato)copper(II) and postulated from cryoscopic measurements an alkoxy-bridged dinuclear structure. Okuda and Weiss¹⁵ observed the nuclear quadrupole resonances (n.q.r.) of some alkoxy-bridged copper(II) complexes. By analogy to the preparation method given by Hein and Beerstecher¹ they synthesized chloro(3-dimethylaminopropan-1-olato)copper(II) and studied the ³⁵Cl and ⁶³Cu resonance frequencies as a function of temperature. Lindgren *et al.*^{16,17} prepared and characterized some complexes with different 3-aminopropan-1-ol derivatives and reported the u.v.-visible and i.r. spectra. Using these results they proposed different structures in the solid state and in solution. Mikuriya *et al.*¹⁸ have investigated copper(II) complexes with amides derived from 3-aminopropan-1-ol and various amino-acids and described the crystal and molecular structure of the complex derived from α -aminopropan-1-ol and various amino-acids, and described the crystal and molecular structure of the complex derived from α -aminoisobutyric acid. The magnetic measurements show strong antiferromagnetic spin coupling for all compounds. Furthermore two copper(II) complexes are known in which 3-aminopropan-1-ol is used as the amine component of Schiff bases with acetylaceton¹⁹ and with pyrrole-2-carbaldehyde;²⁰ both complexes are dimeric.

The present work is devoted to two copper(II) complexes derived from 3-dimethylaminopropan-1-ol, (1) and (2), and to one copper(II) complex derived from 3-diethylaminopropan-1-ol, (3). While for (2) n.q.r. studies were reported by Okuda and Weiss¹⁵ no investigation for the bromine analogue, (1), and for (3) have been reported until now. The three complexes have been isolated during our investigations on the influence of co-

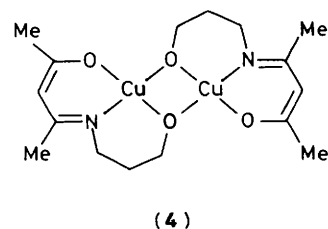
ordination effects on the exchange interaction in spin-coupled copper(II) complexes.

Results and Discussion

Description of the Structures.—The final structural data are presented in Tables 1 and 2 and in Figure 2. All three structures consist of alkoxy-bridged dimers with planar Cu₂O₂ units which are very similar. The co-ordination geometry around the copper ions is distorted square planar. The square plane is formed by two alkoxy-oxygen atoms, one amino-nitrogen atom, and one (pseudo)halogen anion. The distances and angles within the Cu₂O₂ cores are comparable with those of other alkoxy-bridged copper(II) complexes.^{9,18}

In addition to the normal copper-halogen distances [2.395(1) Å in (1) and 2.256(1) Å in (2)], the halogen atoms in [$\{\text{CuBr}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_n\}_n$] (1) and [$\{\text{CuCl}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2)_n\}_n$] (2) form a weak bond to the copper atom of the next dimeric unit. Within (1) the bromine atom is bonded to the copper atom on the position 1-x, 2-y, -z with a copper-bromine distance of 3.127(1) Å. This leads to an infinite chain of dimers along the a axis. The same connection occurs in (2) along the b axis with a copper-chlorine distance of 2.905(1) Å, the copper atom of the next dimer being on the position 1-x, 1-y, -z. Although these bonds are very long compared to normal copper-halogen bonds they are comparable with those found in di- μ -halogeno-bridged dimers,²¹ some of which with comparable copper-halogen distances show weak spin coupling.

In contrast to (1) and (2) the structure of [$\{\text{Cu}(\text{NCO})(\text{OCH}_2\text{CH}_2\text{CH}_2\text{NEt}_2)_2\}_2$] (3) consists of discrete dimeric molecules. While at least five different molecular structures of (2-diethylaminoethanolato)isocyanatocopper(II) are known in which the complex is always tetrameric,^{22,23} no dimeric modification of this compound has been found until now. Compound (3) is a new example of the fact that copper(II) complexes derived from 3-aminopropan-1-ols tend to build up dimeric molecules or alternating chains. The same behaviour was found for the copper(II) complexes of the Schiff bases formed from acetylaceton and aminoalcohols. Two tetrameric forms of the 2-aminoethanol derivative are known,^{19,24} whereas the 3-aminopropan-1-ol derivative (4) is dimeric.¹⁹ This is due



to the flatter structure of the dimeric unit which prevents the build up of a tetrameric molecule. A dimeric structure was also proposed by Hein and Rittersdorf¹⁴ for chloro(3-diethylaminopropan-1-olato)copper(II), but this was not confirmed until now. However, from the corresponding 2-aminoethanol derivatives two different structures with tetrameric molecules are known.^{4,25,26}

An interesting feature can be observed by comparing the distances and angles involving the copper atoms in (1)–(4) with the corresponding ones in dimeric and polymeric copper(II) complexes derived from different 2-aminoethanols (Table 3). While for the distances Cu–Cu', Cu–O, Cu–O' as well as for the angles Cu–O–Cu', O–Cu–O', O–Cu–X, and O'–Cu–N no large deviations between the two groups of complexes can be found, the angles O'–Cu–X and N–Cu–X show marked differences.

Table 1. Positional parameters with estimated standard deviations in parentheses for complexes (1)–(3)

Atom	(1)			(2)			(3)		
	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
Cu(1)	0.218 0(1)	0.930 1(1)	0.026 6(1)	0.398 4(1)	0.216 7(1)	0.484 5(1)	1.033 9(1)	0.581 5(1)	0.102 3(1)
Br(1)	0.536 2(1)	0.972 8(1)	0.157 7(1)	—	—	—	—	—	—
Cl(1)	—	—	—	0.344 4(1)	0.486 8(1)	0.565 8(1)	—	—	—
O(1)	−0.057 2(4)	0.919 8(3)	−0.068 9(2)	0.468 1(3)	−0.033 1(3)	0.430 2(1)	0.870 6(2)	0.470 2(1)	0.043 3(1)
O(2)	—	—	—	—	—	—	1.442 4(3)	0.811 9(2)	0.094 2(2)
N(1)	0.295 4(6)	0.738 9(4)	−0.004 7(3)	0.196 5(3)	0.299 3(3)	0.387 6(2)	0.934 7(3)	0.604 1(2)	0.266 4(1)
N(2)	—	—	—	—	—	—	1.192 8(3)	0.703 3(2)	0.125 3(2)
C(1)	−0.079 9(7)	0.860 8(5)	−0.173 8(3)	0.493 7(4)	−0.021 0(5)	0.350 4(2)	0.715 6(3)	0.428 0(2)	0.091 8(2)
C(2)	−0.010 4(8)	0.721 7(5)	−0.165 6(4)	0.319 3(5)	0.041 8(5)	0.294 6(2)	0.653 8(3)	0.499 6(2)	0.188 4(2)
C(3)	0.222 3(8)	0.698 0(5)	−0.120 2(3)	0.252 8(5)	0.268 0(4)	0.309 5(2)	0.802 7(3)	0.518 6(2)	0.292 9(2)
C(4)	0.529 6(8)	0.710 7(5)	0.017 4(4)	0.040 9(4)	0.157 0(5)	0.394 2(2)	1.094 0(3)	0.601 7(2)	0.362 5(2)
C(5)	0.186 7(9)	0.662 7(5)	0.069 8(4)	0.133 3(5)	0.528 0(5)	0.389 0(2)	1.217 5(5)	0.506 0(3)	0.355 5(2)
C(6)	—	—	—	—	—	—	0.848 1(4)	0.714 6(2)	0.262 6(2)
C(7)	—	—	—	—	—	—	0.760 1(5)	0.748 3(3)	0.373 1(3)
C(8)	—	—	—	—	—	—	0.317 1(3)	0.755 5(2)	0.109 8(2)

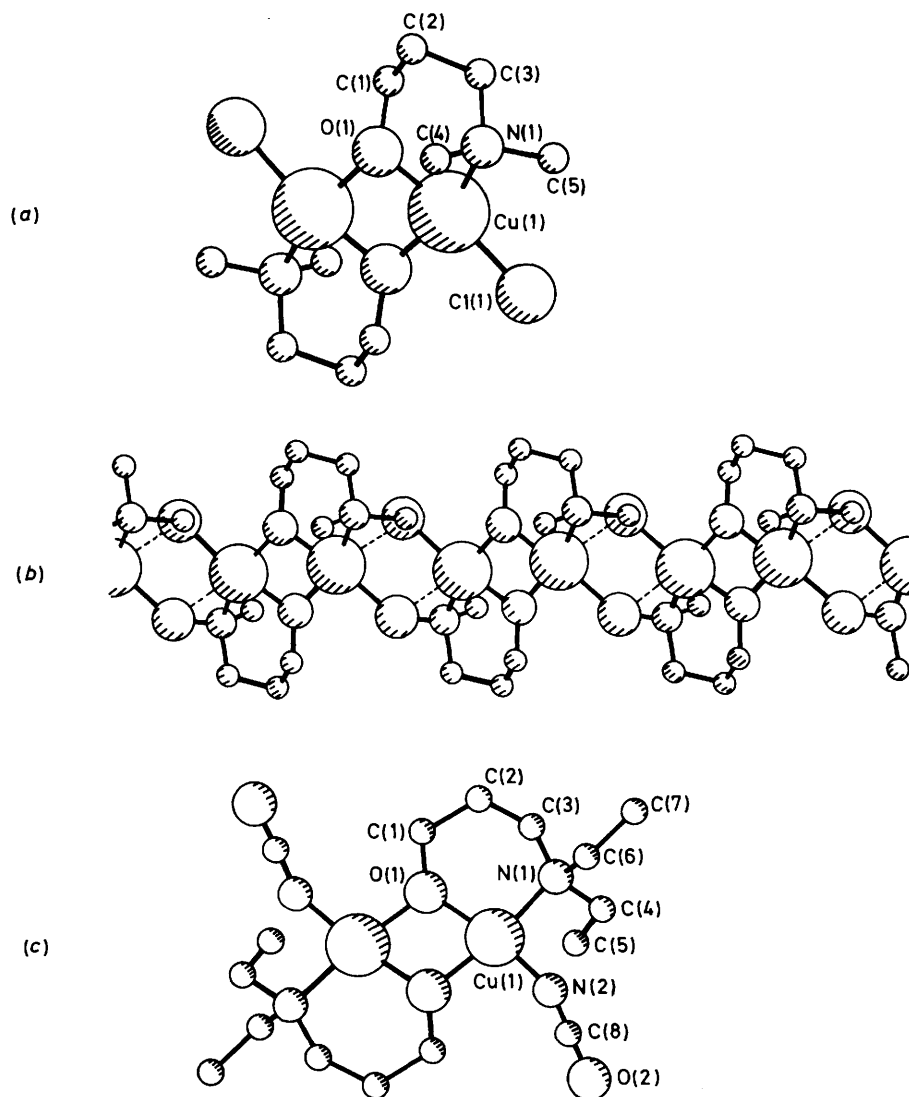
**Figure 2.** PLUTO drawings of (2) and (3). (a) View of the dimeric unit in (2); (b) view of the alternating chain in (2), the connection to polymeric chains along [010] is shown by the dashed Cu–Cl bonds; (c) view of the dimeric unit in (3)

Table 2. Distances (Å) and angles (°) with estimated standard deviations in parentheses for complexes (1)–(3)

	(1)	(2)	(3)
Cu(1)–Cu(1)*	3.063(1)	3.060(1)	3.044(1)
Cu(1)–Br(1)	2.395(1)	—	—
Cu(1)–Br(1)*	3.127(1)	—	—
Cu(1)–Cl(1)	—	2.256(1)	—
Cu(1)–Cl(1)*	—	2.905(1)	—
Cu(1)–O(1)	1.927(3)	1.921(2)	1.900(2)
Cu(1)–O(1)*	1.963(3)	1.957(2)	1.944(2)
Cu(1)–N(1)	2.077(4)	2.073(2)	2.058(2)
Cu(1)–N(2)	—	—	1.913(2)
O(1)–C(1)	1.420(5)	1.422(3)	1.416(3)
C(1)–C(2)	1.494(7)	1.506(4)	1.502(3)
C(2)–C(3)	1.494(6)	1.515(4)	1.525(3)
C(3)–N(1)	1.490(5)	1.494(4)	1.491(3)
N(1)–C(4)	1.478(5)	1.479(4)	1.497(3)
N(1)–C(5)	1.463(6)	1.485(3)	—
N(1)–C(6)	—	—	1.513(3)
C(4)–C(5)	—	—	1.505(4)
C(6)–C(7)	—	—	1.510(4)
N(2)–C(8)	—	—	1.150(3)
C(8)–O(2)	—	—	1.186(3)
Cu(1)–O(1)–Cu(1)*	103.9(1)	104.2(1)	104.7(1)
Cu(1)–N(2)–C(8)	—	—	155.7(2)
O(1)–Cu(1)–N(1)	92.6(1)	91.8(1)	97.6(1)
Br(1)–Cu(1)–O(1)	170.8(1)	—	—
Br(1)–Cu(1)–O(1)*	94.7(1)	—	—
Br(1)–Cu(1)–N(1)	96.1(1)	—	—
Cl(1)–Cu(1)–O(1)	—	170.9(1)	—
Cl(1)–Cu(1)–O(1)*	—	95.1(1)	—
Cl(1)–Cu(1)–N(1)	—	97.1(1)	—
O(1)*–Cu(1)–N(1)	160.2(1)	157.3(1)	168.5(1)
O(1)–Cu(1)–N(2)	—	—	167.4(1)
O(1)*–Cu(1)–N(2)	—	—	95.8(1)
N(1)–Cu(1)–N(2)	—	—	92.6(1)
Cu(1)–O(1)–C(1)	121.9(3)	121.8(2)	130.1(2)
Cu(1)–O(1)*–C(1)*	127.1(3)	127.1(2)	125.2(2)
O(1)–C(1)–C(2)	111.3(4)	111.0(2)	112.0(2)
C(1)–C(2)–C(3)	115.9(4)	113.6(3)	112.8(2)
Cu(1)–N(1)–C(3)	113.7(3)	113.3(2)	112.4(1)
Cu(1)–N(1)–C(4)	114.0(3)	114.6(2)	107.7(1)
Cu(1)–N(1)–C(5)	103.9(3)	113.7(2)	—
Cu(1)–N(1)–C(6)	—	—	106.8(1)
C(3)–N(1)–C(4)	105.1(4)	111.1(2)	108.7(2)
C(3)–N(1)–C(5)	110.8(4)	106.6(2)	—
C(3)–N(1)–C(6)	—	—	111.7(2)
N(1)–C(4)–C(5)	—	—	114.1(2)
N(1)–C(6)–C(7)	—	—	116.5(2)
C(4)–N(1)–C(6)	—	—	109.4(2)
N(2)–C(8)–O(2)	—	—	178.1(3)

Atoms indicated by * are related by a centre of symmetry.

For (1)–(4) these angles are nearer to 90° than the 2-aminoethanolato-complexes. The same is valid for the O–Cu–N angle within (1) and (2). In addition, taking into account that the O'–Cu–N angle is slightly larger in (1) and drastically larger in (3) and (4) than in the other complexes it is clear that (1)–(4) are less distorted from an ideal square-planar co-ordination than the other complexes. This will be of great importance in order to understand the stronger antiferromagnetic spin coupling observed than that expected. Until now only the influence of the geometry within the Cu₂O₂ core was considered to be an important factor in the size of the exchange interaction. Since this geometry does not differ significantly and since the ligands are the same, thus cancelling out effects due to different ligand properties, the effect of co-ordination geometry on the exchange interaction within alkoxo-bridged copper(II) complexes can be studied.

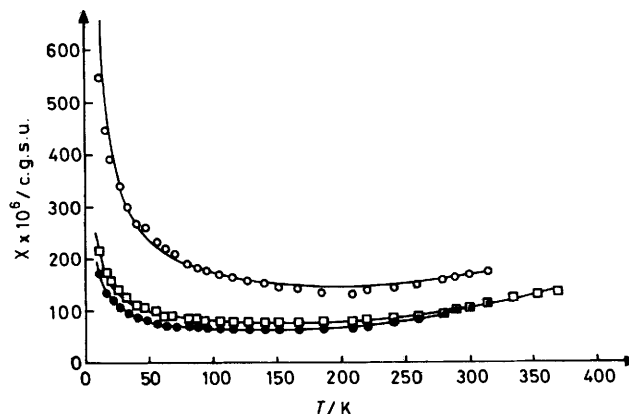


Figure 3. Temperature dependence of the magnetic susceptibility of (1) (□), (2) (●), and (3) (○). The solid lines represent the fits to equation (i) with the parameters given in Table 4

With the knowledge of the structures of (1) and (2) the interpretation of u.v.–visible spectra of some related compounds can be confirmed. Lindgren *et al.*^{16,17} proposed, on the basis of the different intensities of the band in the region of 25 000 cm⁻¹, dimeric structures in solution and higher aggregates in the solid state. Interpreting the n.q.r. spectra of (2) Okuda and Weiss¹⁵ proposed intermolecular interactions from the positive dv/dT for the ³⁵Cl n.q.r. frequency. With increasing temperature the long copper–chlorine bond becomes weaker, thereby the resonance frequency increases. On the contrary, the temperature dependence in chloro(2-diethylaminoethanolato)copper(II) is characterized by a negative dv/dT . This complex builds up a lattice of tetrameric units with a central Cu₄O₄ core, no connections between them exist.

Magnetic Properties.—The temperature dependence of the magnetic susceptibility of the three complexes is shown in Figure 3. Measurements for (1) and (3) were carried out in the temperature range 11.1–313 K and for (2), 11.1–368 K. The temperature dependence of the magnetic susceptibility is characteristic of strongly spin-coupled copper(II) complexes with a small amount of paramagnetic impurities. Fitting the experimental susceptibilities to the Bleaney–Bowers equation (i)

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

(corrected for the presence of paramagnetic impurities and the temperature independent paramagnetism, $N\alpha$) we obtained the parameters given in Table 4. The uncertainties given in parentheses for g , $2J$, and x are taken from correlation effects within the non-linear optimization, for $N\alpha$ the error in $\chi_{\text{diam.}}$ is assumed.

Figure 3 shows the good agreement between the experimental and calculated values. The temperature independent paramagnetism agrees well with that of related compounds for copper(II) dimers; with isocyanato-ligands it is larger than 60×10^{-6} c.g.s.u.¹³ An interesting feature can be observed by comparing the fitted exchange constants with those expected from magnetostructural correlations for related compounds. By analogy to the linear relationship between the Cu–O–Cu' angle Φ and the observed exchange constant in hydroxide-bridged copper(II) dimers given by Hatfield,²⁷ Merz¹³ found a different

Table 3. Selected distances (Å) and angles (°) with estimated standard deviations in parentheses for dimeric and polymeric alkoxy-bridged copper(II) complexes

	(5)	(6)	(7)	(8)	(9)	(10)
Symmetry	C_i	C_i	C_i	C_1	C_1	C_1
Cu-Cu'	3.033(5)	3.003(2)	3.010(1)	3.019(4)	2.903(3)	2.950(1)
Cu-O	1.873(13)	1.900(4)	1.891(2)	1.920	1.916	1.903
Cu-O'	1.949(13)	1.914(4)	1.924(2)	1.920	1.933	1.924
Cu-O-Cu'	105.0(6)	103.9(2)	104.2(1)	103.8	97.9	100.9
Cu-X (polymer)	—	3.660(2)	—	—	—	2.979
O-Cu-O'	75.0(6)	76.1(1)	75.8(1)	76.2	76.8	77.5
O-Cu-N	83.1(5)	84.2(1)	83.8(1)	82.2	84.1	84.5
O-Cu-X	171.3(4)	169.2(1)	172.2(1)	171.7	173.7	171.0
O'-Cu-X	100.7(4)	101.4(1)	99.0(1)	99.0	99.6	98.3
N-Cu-X	101.7(3)	100.6(1)	102.0(1)	102.6	99.3	98.3
O'-Cu-N	157.4(5)	155.4(1)	158.5(1)	158.5	160.7	160.0
Ref.	4	11	<i>b</i>	<i>c</i>	7	<i>d</i>

	(11)	(12)	(1)	(2)	(3)	(4)
Symmetry	C_i	C_i	C_i	C_i	C_i	C_i
Cu-Cu'	2.981(2)	2.956(2)	3.063(1)	3.060(1)	3.044(1)	3.026(6)
Cu-O	1.913(8)	1.902(6)	1.927(3)	1.921(2)	1.900(2)	1.86(1)
Cu-O'	1.937(8)	1.930(10)	1.963(3)	1.957(2)	1.944(2)	1.92(1)
Cu-O-Cu'	101.5(3)	101.0(5)	103.9(1)	104.2(1)	104.7(1)	106.4(6)
Cu-X (polymer)	2.851(4)	2.846(6)	3.127(1)	2.905(1)	—	—
O-Cu-O'	78.5(3)	79.0(5)	76.1(1)	75.8(1)	75.2(1)	73.6(6)
O-Cu-N	84.9(4)	83.5(4)	92.6(1)	91.8(1)	97.6(1)	99.6(6)
O-Cu-X	175.2 ^a	175.2(5)	170.8(1)	170.9(1)	167.4(1)	165.4 ^a
O'-Cu-X	97.0 ^a	97.9(5)	94.7(1)	95.1(1)	95.8(1)	91.8(6)
N-Cu-X	99.9 ^a	100.8(5)	96.1(1)	97.1(1)	92.6(1)	95.0(7)
O'-Cu-N	149.6 ^a	149.5(3)	160.2(1)	157.3(1)	168.5(1)	173.1(6)
Ref.	5	<i>e</i>	This work	This work	This work	19

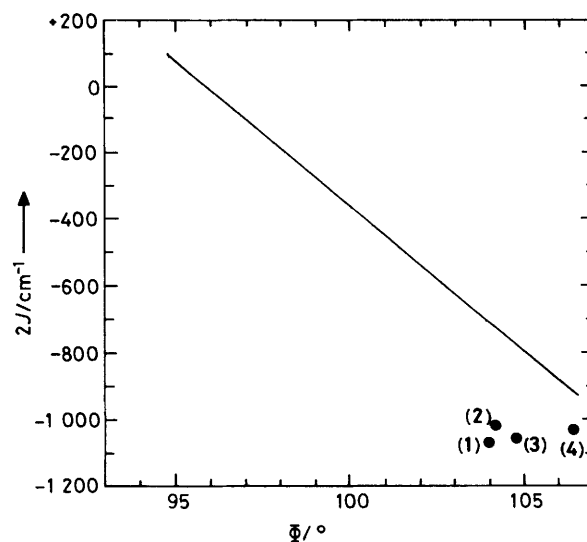
The compounds (5)—(12) are: (5) = α -bromo(2-diethylaminoethanolato)copper(II), (6) = β -bromo(2-diethylaminoethanolato)copper(II), (7) = (2-dipropylaminoethanolato)isocyanatocopper(II), (8) = bromo(2-dibutylaminoethanolato)copper(II), (9) = chloro(3-diethylaminopropan-2-olato)copper(II), (10) = (2-dimethylaminoethanolato)isothiocyanatocopper(II), (11) = (2-diethylaminoethanolato)isothiocyanatocopper(II), (12) = (2-dipropylaminoethanolato)isothiocyanatocopper(II). Complexes (1)—(3) are reported in this paper and (4) is a copper(II) complex of a tridentate ligand which is the dianion of the Schiff base derived from acetylacetonate and 3-aminopropan-1-ol. The primed atoms belong to the second monomeric unit. If the molecular symmetry is C_i mean values are given without standard deviations. X represents the (pseudo)halogen anion, in the case of (4) it is the enolate oxygen of the Schiff base. Cu-X (polymer) represents the distances Cu...SCN and Cu...halide in polymeric complexes (fifth coordination).

^a Angles are not given in the literature. ^b L. Merz and W. Haase, *Acta Crystallogr., Sect. B*, 1978, **34**, 2128. ^c R. Mergehenn and W. Haase, *Z. Naturforsch., Teil B*, 1975, **30**, 155. ^d W. Haase, R. Mergehenn, and W. Haase, *Z. Naturforsch., Teil B*, 1976, **31**, 86. ^e M. Mikuriya, Y. Nishida, S. Kida, T. Mechi, and I. Meda, *Acta Crystallogr., Sect. B*, 1977, **33**, 538.

Table 4. Exchange parameters resulting from the isotropic Heisenberg-Dirac-von Vleck model for (1), (2), and (3)

Complex	<i>g</i>	$-2J_{12}/\text{cm}^{-1}$	<i>x</i>	$10^6 N\alpha/\text{c.g.s.u.}$
(1)	2.18(2)	1 065(20)	0.004(1)	63(5)
(2)	2.21(2)	1 020(20)	0.003(1)	54(5)
(3)	2.26(2)	1 056(20)	0.013(3)	108(5)

relationship which was valid to describe the geometry dependence of the exchange interaction in alkoxy-bridged copper(II) complexes derived from different 2-aminoethanols. Both linear relationships have almost the same slope, $\delta J_{12}/\delta\Phi$, but the cross-over angle is slightly different. This is due to the different electronegativities of the bridging ligands. This effect was also estimated theoretically by Hay *et al.*²⁸ Figure 4 shows the Merz straight line together with the corresponding points for (1), (2), and (3). The expected exchange constants are considerably smaller than those observed. Since the copper-oxygen distances do not differ from related distances within the copper(II) complexes derived from 2-aminoethanols and since the additional CH_2 group will surely not change the coordinating properties of the oxygen, another reason for the difference in expected and observed exchange constants must be

**Figure 4.** Relationship between $2J$ and the Cu-O-Cu' bridging angle (Φ) in alkoxy-bridged copper(II) complexes (—)^{9,13} together with the corresponding values for (1)—(4)

found. First, the influence of the halogen bridges must be discussed.

These bridges transform the idealized system of non-interacting dimers into a many-spin system. If, as in case of (1) and (2), two different exchange interactions are possible, then the exact Hamiltonian becomes equation (ii), where J is the

$$\hat{H} = -2J \sum_{i=1}^{\frac{N}{2}} [S_{2i} S_{2i-1} + \alpha S_{2i} S_{2i+1}] \quad (\text{ii})$$

exchange constant between a spin and one of its nearest neighbours and αJ is the exchange constant between this spin and the other nearest neighbour in the chain. This problem has been studied by many authors;²⁹⁻³³ since exact solutions of the Hamiltonian (ii) do not exist, expressions for the properties of short alternating rings containing an increasing number of spins were deduced and extrapolations to infinite chains were carried out. The same procedures cannot be applied to (1) and (2). The spin coupling is very strong ($2J/kT > 0.2$ at room temperature) and leads to a very unresponsive temperature dependence of the magnetic susceptibility. The part of the χ versus T curves which is characterized by an initial population of $S \neq 0$ states ($T > 200$ K) does not allow the determination of two parameters (α and J), especially since the exchange interaction *via* the halogen bridges should be much smaller compared with that *via* the oxygen bridges.

If we compare the geometry of the pathway between the dimeric molecules with halogen-bridged dimeric copper(II) complexes which have also been magnetically investigated^{21,34,35} we can see that the exchange constants are considerably smaller than those in strongly-coupled alkoxo-bridged copper(II) complexes. Marsh *et al.*²¹ reported the magnetic properties of di- μ -chloro-bis(N,N,N' -triethylethylenediamine)copper(II). The geometry of the Cu_2Cl_2 unit compares rather well with that in (2). Magnetic susceptibility measurements show a typical single-ion behaviour. An empirical correlation, $2J = f(\Phi/R)$,²¹ where Φ is the angle at the chlorine atom and R the copper-chlorine distance between the pseudomonomeric units, predicts only a very small exchange interaction for (2). The same is to be expected for (1) from related compounds.^{34,36} The fact that the polymer bridging cannot be a very important factor in the higher than expected exchange interaction in (1) and (2) is also supported by the stronger spin coupling in (3). The singlet-triplet splitting energy is more than 250 cm^{-1} larger than that expected from the correlation found by Merz.¹³ This suggests that the differences within the co-ordination at the copper atom between the complexes derived from 2-aminoethanols and 3-aminopropan-1-ols are responsible for the very strong spin coupling within (1)–(3).

To illustrate the influence of the co-ordination geometry around the copper atom on the exchange interaction it is necessary to find a parameter dependent on the size of the distortion from an ideal square-planar co-ordination. Since the distortion always leads to a partial tetrahedral co-ordination geometry, the sum, A , given by equation (iii) was calculated for

$$A = \sum_{j=1}^6 |\Phi_j - \Phi_{j,id}| \quad (\text{iii})$$

the compounds (1)–(8), where Φ_j are the six actual angles in which the copper atom is involved (see Table 3) and $\Phi_{j,id}$ are the angles of an ideal square planar co-ordination ($4 \times 90^\circ$, $2 \times 180^\circ$). Figure 5 shows a plot $2J$ vs. A . Neglecting complex (7) the dependence of the exchange interaction on A for these alkoxo-bridged copper(II) complexes is approximately linear. Complex (4) has a slightly smaller exchange constant ($2J = -1030 \text{ cm}^{-1}$)³⁷ than that expected from this magnetostructural

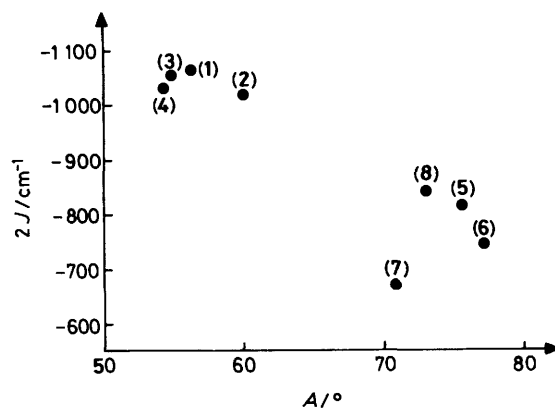


Figure 5. Plot $2J$ vs. A [see equation (iii) and Table 3]

Table 5. Elemental analyses (%) for (1)–(3)

	(1)		(2)		(3)	
	Found	Calc.	Found	Calc.	Found	Calc.
C	24.30	24.45	29.35	29.85	39.85	40.75
H	5.05	4.90	6.00	6.00	6.80	6.85
N	5.55	5.70	6.80	6.95	11.50	11.90

correlation, but it should be emphasized that (4) is a complex with a Schiff-base ligand. Recently we were able to show³⁸⁻⁴⁰ that the exchange interaction within these complexes is smaller than expected from magnetostructural correlations. This is due to hybridization and conjugation effects which lower the electron density at the co-ordinating atoms.

The possibility of correlating the singlet-triplet splitting with the parameter A arises from the fact that the bridging angle, which normally plays an important role, is very similar in all the compounds; except for (4), where the angle is $106.4(6)^\circ$ they lie in the range $103.8(4)$ – $105.0(1)^\circ$. The only deviation given by (7) cannot be explained easily. Since no geometrical parameter differs significantly from those of the other compounds the discrepancy must be due to an effect of the isocyanate ion. However, a comparison with (3), whose experimental singlet-triplet gap agrees well with the predicted one, shows no distinct differences. Consequently additional copper(II) dimers with isocyanate ions are necessary to investigate the important geometrical factors on the exchange interaction within this group of compounds.

Experimental

Preparations.—The preparations of (1) and (2) were carried out according to the procedure described in ref. 1. Suitable crystals of (1) were obtained by recrystallization from methanol whereas single crystals of (2) can only be obtained by slow evaporation of the mother-liquor. The preparation of (3) closely followed the procedure given by Lehtonen *et al.*⁴¹ KOCN was used instead of KSCN. Since it is very sparingly soluble in methanol, solid KOCN was added to the methanolic solution of copper(II) acetate monohydrate and 3-diethylaminopropan-1-ol (mol ratio 1:2). Crystals suitable for X-ray analysis were obtained by recrystallization from methanol. Table 5 shows the results of the C, H, and N analyses.

Crystal Data.—Complex (1). $\text{C}_5\text{H}_{12}\text{BrCuNO}$, $M = 245.59$, monoclinic, $a = 6.273(3)$, $b = 10.282(5)$, $c = 12.403(5)$ Å, $\beta =$

99.62(2)°, $U = 788.73 \text{ \AA}^3$ (by least-squares refinement of 67 strong reflections, $\lambda = 0.71069 \text{ \AA}$), space group $P2_1/c$ (no. 14),⁴² $Z = 4$, D_m (floatation) = 2.03(4) g cm⁻³, $D_c = 2.07 \text{ g cm}^{-3}$, $F(000) = 484$. Green columns. Crystal dimensions (distance to faces from centre): 0.134 (011,0 $\bar{1}\bar{1}$) \times 0.134 (01 $\bar{1}$,0 $\bar{1}\bar{1}$) \times 0.350 (100, $\bar{1}$ 00) mm, $\mu(\text{Mo-K}\alpha) = 75.82 \text{ cm}^{-1}$.

Complex (2). C₅H₁₂ClCuNO, $M = 201.15$, monoclinic, $a = 7.484(3)$, $b = 6.145(3)$, $c = 17.152(6) \text{ \AA}$, $\beta = 101.55(2)^\circ$, $U = 772.83 \text{ \AA}^3$ (by least-squares refinement of 48 strong reflections, $\lambda = 0.71069 \text{ \AA}$), space group $P2_1/c$ (no. 14),⁴² $Z = 4$, D_m (floatation) = 1.71(4) g cm⁻³, $D_c = 1.73 \text{ g cm}^{-3}$, $F(000) = 412$. Flat green crystals. Crystal dimensions (distance to faces from centre): 0.400 (100, $\bar{1}$ 00) \times 0.124 (001,00 $\bar{1}$) \times 0.572 (010,0 $\bar{1}$ 0) mm, $\mu(\text{Mo-K}\alpha) = 29.86 \text{ cm}^{-1}$.

Complex (3). C₈H₁₆CuN₂O₂, $M = 235.77$, monoclinic, $a = 7.363(3)$, $b = 12.422(5)$, $c = 11.117(5) \text{ \AA}$, $\beta = 96.37(2)^\circ$, $U = 1010.42 \text{ \AA}^3$ (calculated from the orienting matrix using 16 strong reflections, $\lambda = 0.71069 \text{ \AA}$), space group $P2_1/c$ (no. 14),⁴² $Z = 4$, D_m (floatation) = 1.55(4) g cm⁻³, $D_c = 1.55 \text{ g cm}^{-3}$, $F(000) = 492$. Blue-green columns. Crystal dimensions (distances to faces from centre): 0.347 (100, $\bar{1}$ 00) \times 0.290 (011,0 $\bar{1}\bar{1}$) \times 0.177 (0 $\bar{1}\bar{1}$,01 $\bar{1}$) mm, $\mu(\text{Mo-K}\alpha) = 20.54 \text{ cm}^{-1}$.

Data Collection and Processing.—Complex (1). Stoe-STADI 4 diffractometer, scan $\omega:\theta = 1:1$ in the range $3 \leq 2\theta \leq 45^\circ$, graphite-monochromated Mo-K α radiation; 1609 reflections measured, 1021 unique [merging $R = 0.022$ after absorption correction (max., min. transmission factors = 0.207, 0.134)], giving 979 with $F > 3\sigma(F)$; three strong reflections monitored every 50 reflections showed constant intensity.

Complex (2). Stoe-STADI 4 diffractometer, scan $\omega:\theta = 1:1$ in the range $3 \leq 2\theta \leq 50^\circ$, graphite-monochromated Mo-K α radiation; 2633 reflections measured, 1362 unique [merging $R = 0.037$ after absorption correction (max., min. transmission factors = 0.488, 0.104)], giving 1355 with $F > 2\sigma(F)$; three strong reflections measured every 50 reflections showed constant intensity.

Complex (3). Stoe-STADI 4 diffractometer, scan $\omega:\theta = 1:1$ in the range $3 \leq 2\theta \leq 50^\circ$, graphite-monochromated Mo-K α radiation; 3016 reflections measured, 1761 unique [merging $R = 0.032$ after absorption correction (max., min. transmission factors = 0.512, 0.323)], giving 1718 with $F > 2\sigma(F)$; three strong reflections measured every 50 reflections showed constant intensity.

Structure Analysis and Refinement.—All three structures were solved by direct methods, which led to the positions of the copper and halogen atoms. The positions of the remaining atoms were found by Fourier maps. Full-matrix least-squares refinement with isotropic thermal parameters converged to the R values of 0.0984 for (1), 0.1009 for (2), and 0.0966 for (3). Refinement with anisotropic thermal parameters and geometrical positioning of all hydrogen atoms (C–H distance = 1.08 Å) led to the final R values 0.0263 ($R' = 0.0269$) for (1), 0.0349 ($R' = 0.0374$) for (2), and 0.0268 ($R' = 0.0294$) for (3). The weighting scheme was $w = 1/\sigma^2(F_o)$ with $\sigma(F_o)$ from counting statistics. For all parameters of the three structures the shift to error ratio was always smaller than 0.01 within the last least-squares cycles. The final difference map showed the highest peak at 0.45 for (1), 0.61 for (2), and 0.27 e Å⁻³ for (3).

Magnetic Measurements.—The magnetic susceptibilities of the samples were measured by the Faraday method at ca. $6 \times 10^6 \text{ G}^2 \text{ cm}^{-1}$ ($G = 10^{-4} \text{ T}$) using Hg[Co(SCN)₄] as a susceptibility standard. Experimental susceptibility data were corrected for underlying diamagnetism. To convert into S.I. units χ should be multiplied by $4\pi \times 10^{-6}$.

Calculations.—The structure calculations were carried out with the program SHELX-76;⁴³ the scattering factors for Cu were taken from Cromer and Mann,⁴⁴ the others are stored in the program.

The exchange parameters were obtained using a modified simplex-routine.⁴⁵ The function minimized was $\Sigma(|\chi_{\text{calc.}} - \chi_{\text{expt.}}|)/\chi_{\text{expt.}}$.

All calculations were performed on the IBM 3081 K computer at the Technische Hochschule Darmstadt.

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