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Magneto-structural Dependencies for Asymmetrically Bridged Cu(II) Dimers

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Abstract

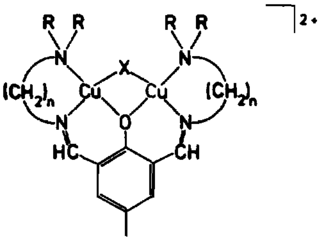
This article reports a magneto-structural comparison of six asymmetrically bridged Cu(II) dimers (structural data of one compound and magnetic data of four complexes are given). All dimers are obtained using a five-dentate macrocyclic ligand with a central phenolate group acting as the endogenous bridge. An exchangeable exogenous ligand (OH^- or end-on bound N_3^-) completes the tetragonal coordination geometry of the copper centers. The structural comparison of all Cu(II) dimers points out that the small chemical variations which are applied to the macrocycle changes only the bridging angles Cu–O(phenolate)–Cu and, more significantly, Cu–X(exogenous, X = N, O)–Cu. So exogenous and endogenous bridging angles vary by up to 6° for the same compound (98°–104°). From the magnetic susceptibility measurements all Cu(II) dimers have been found to show an antiferromagnetic exchange coupling. The calculated exchange integrals range between $2J = -84$ cm^{-1} and $2J = -852$ cm^{-1}. The present data allow us for the first time to establish a magneto-structural dependency for asymmetrically bridged Cu(II) dimers. A linear correlation can be assumed when the average bridging angles are used so that the exchange interaction involves both bridges between the copper centers. The asymmetry of the binuclear bridged copper centers derived from different ligands and angles does not lead to drastic deviations from known magneto-structural correlations for symmetrically bridged Cu(II) dimers having similar structures.

Introduction

A frequently modelled protein center is that of the binuclear Cu(II) active site in the oxygen transport protein hemocyanin. Intensive investigations of this metalloprotein revealed that the two Cu(II) ions are bridged by an exogenous peroxogroup [1, 2] and an endogenous ligand for which a phenolate [3] or a hydroxide group [4] have been proposed. The tetragonal coordination geometry of both copper atoms is completed by two or three histidine ligands [2, 5, 6]. EXAFS data indicate a Cu–Cu distance of 3.6 Å leading to a bridging angle of about 145° at the endogenous ligand [7, 8].

Today low molecular weight models of this hemocyanin active site are not able to reproduce the symmetric peroxo-bridge, but the first successful attempts describing the reactivity of the protein center are known [9]. So most model compounds [10–18] deal with the relation between structural features and magnetic behaviour to understand the strong antiferromagnetic coupling between the two Cu(II) centers ($|2J| > 550$ cm^{-1}) in the native protein [19, 20].

To understand better the magneto-structural behaviour of asymmetrically bridged Cu(II) centers, in this paper we compare the crystal structures and the magnetic properties of six similar Cu(II) dimers. The general structure of these compounds is given below.



Compound	X	R	*n*	Reference
1	N_3	methyl	2	25
2	N_3	methyl	3	21
3	OH	methyl	2	11, 25
4	OH	ethyl	2	11
5	OH	methyl	3	23
6	OH	imidazolyl (R_2)	2	12, 24

The same type of macrocyclic ligand has been used in all our investigations with only slight modifications in R, X, and *n*. Hence our study includes the possibility of obtaining information on geometric and magnetic differences corresponding to changes in the alkyl substituents of two nitrogen ligands (R), the

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chelate rings (*n*), or in the endogenous ligand (X). The exogeneous bridges were formed by OH^-- and end-on bound N_3^--groups. Since the geometries of the complexes are generally very similar deviating significantly only in the bridging angles, a magneto-structural correlation for asymmetrically bridged binuclear Cu(II) complexes can be assumed in connection with the largely different exchange integrals. The structural data of **4** [21] and the magnetic data of **1**, **3**, **4** and **5** are reported in this study. The magneto-structural data of the remaining compounds have been published previously [22–26], but are included here for purposes of generalization.

Experimental

Materials and Analysis

All reagents and solvents used were commercially available and of reagent grade. Uncorrected melting points were obtained with a Mettler equipment for differential scanning calorimetry. Microanalyses were performed by the Service of Microanalyses of the Technische Hochschule Darmstadt.

Preparation

The dialdehyde 2-hydroxy-5-methylisophthalaldehyde was prepared according to the method described by Ullmann and Brittner [27]. Compounds **1**, **3**, **4** and **5** were prepared according to the method described by Okawa *et al.* [11]. The macrocyclic double Schiff base was obtained by reaction of 2-hydroxy-5-methylisophthalaldehyde with 1-amino-2-*N*,*N*-dimethylamino-ethane (compounds **1** and **3**), with 1-amino-2-amino-2-*N*,*N*-diethylaminoethane (compound **4**) or with 1-amino-3-*N*,*N*-dimethylamino-propane (compound **5**).

1: Supplementary to the known method [11] an equimolar amount of NaN_3 was slowly added yielding a green precipitate; upon twofold recrystallization from absolute methanol green, needlelike crystals were obtained. *Anal.* (calc.) for $C_{17}H_{27}Cl_2Cu_2N_7O_9$: C, 30.13 (30.41); H, 3.89 (4.05); N, 14.18 (14.60)%.

3: Twofold recrystallization from water yielded dark green, needlelike crystals. *Anal.* (calc.) for $C_{17}H_{28}Cl_2Cu_2N_4O_{10} \cdot H_2O$: C, 30.61 (30.73); H, 4.23 (4.55); N, 8.39 (8.43)%.

4: Upon recrystallization from water violet, prismatic crystals were obtained from a blue-greenish solution. *Anal.* (calc.) for $C_{21}H_{36}Cl_2Cu_2N_4O_{10}$: C, 35.66 (35.90); H, 5.13 (5.17); N, 7.82 (7.98)%.

5: Recrystallization from water yielded blue, rhombohedral crystals. *Anal.* (calc.) for $C_{19}H_{32}Cl_2Cu_2N_4O_{10} \cdot H_2O$: C, 33.06 (32.96); H, 4.60 (4.95); N, 8.01 (8.09)%.

X-ray Crystallography (Structure of 4)

A preliminary diffractometer search using a crystal of the dimensions 0.1 × 0.1 × 3 mm revealed monoclinic symmetry. Observed systematic absences were consistent with the space group $P2_1/c$. Diffraction data were collected at room temperature on a computer controlled STOE-STADI-4 four circle diffractometer system using Cu Kα radiation (1.54178 Å). Precise lattice parameters and their estimated standard deviations were derived from a least-squares refinement of 50 strong reflections. The intensities were corrected for Lorentz-, polarization- and absorption effects, and showed no decay during the data collection. Crystal data, important details, and data collection are summarized in Table I.

TABLE I. Data Collection and Processing Parameters

Complex	4
Molecular formula	$C_{21}H_{36}Cl_2Cu_2N_4O_{10}$
Molecular weight	702.5
Temperature (K)	296
Space group	$P2_1/c$
Cell constants	
a (Å)	7.807(1)
b (Å)	23.232(3)
c (Å)	16.215(2)
β (°)	103.845(4)
V (Å^3)	2855.5
Z	4
δ (by flotation) (g cm^{-3})	1.62(4)
δ_{calc} (g cm^{-3})	1.630
Radiation	graphite-monochromatized Cu Kα radiation 1.54178 Å
Absorption coefficient (cm^{-1})	38.74
Scan type	$\omega:2\theta = 1:1$
Scan range	$6 \leq 2\theta \leq 46°$
Data measured	4899
Unique data with $\|F_o\| > 2\sigma(\|F_o\|)$	3952
R	0.063
R_w	0.068

The copper atom positions were determined by direct methods using the computer program SHELX-76 [28]. The remaining non-hydrogen atoms were located from a series of Fourier maps. The refinement was effected by full-matrix least-squares techniques. Atomic scattering factors are included in the computer-program package used [28] with the exception of Cu which was taken from Cromer and Mann [29].

The refinement using isotropic temperature factors converged at $R = 0.136$, by use of anisotropic temperature factors at 0.073. The resulting Fourier map revealed the disorder of the C atoms of both amino groups with *SOF* of 0.85 and 0.15, respectively. The C-bound hydrogen atoms were geometrically positioned (isotropic, C–H = 1.08 Å). The final *R* value was 0.063 ($R_w = 0.068$). All calculations were performed on an IBM 370/168 computer at the

TABLE II. Final Positional Parameters of $C_{21}H_{36}Cl_2Cu_2N_4O_{10}$ (4) (e.s.d.s in parentheses)

Atom	*x*	*y*	*z*
Cu(1)	0.42745(10)	0.41766(3)	0.24994(4)
Cu(2)	0.22659(10)	0.33239(3)	0.12234(4)
O(1)	0.3453(6)	0.3405(2)	0.2366(2)
O(2)	0.2993(5)	0.4137(1)	0.1304(2)
C(1)	0.7810(9)	0.3466(3)	0.3442(4)
C(2)[a]	0.6759(9)	0.3696(2)	0.4035(4)
C(2B)[b]	0.8032(73)	0.4039(19)	0.3872(31)
C(3)	0.2978(11)	0.3981(3)	0.4238(5)
C(4)[a]	0.4519(9)	0.4352(2)	0.4316(4)
C(4B)[b]	0.4958(49)	0.3918(14)	0.4346(20)
N(1)	0.5688(6)	0.4231(2)	0.3708(3)
C(5)[a]	0.6878(9)	0.4731(2)	0.3729(4)
C(5B)[b]	0.5719(47)	0.4886(14)	0.3987(20)
C(6)	0.5961(9)	0.5212(2)	0.3173(4)
N(2)	0.4932(6)	0.4958(2)	0.2373(3)
C(7)	0.4533(8)	0.5270(2)	0.1712(4)
C(8)	0.2766(7)	0.4541(2)	0.0708(3)
C(9)	0.3465(7)	0.5091(2)	0.0885(3)
C(10)	0.3197(8)	0.5509(2)	0.0227(2)
C(11)	0.2257(8)	0.5396(3)	−0.0572(3)
C(12)	0.1980(11)	0.5860(3)	−0.1262(4)
C(13)	0.1572(8)	0.4855(2)	−0.0747(3)
C(14)	0.1779(7)	0.4419(2)	−0.0131(3)
C(15)	0.1009(7)	0.3864(2)	−0.0409(3)
N(3)	0.1070(6)	0.3419(2)	0.0050(3)
C(16)	0.0276(9)	0.2880(2)	−0.0344(4)
C(17)[a]	0.1238(9)	0.2393(2)	0.0169(4)
C(17B)[b]	−0.0125(42)	0.2522(15)	0.0460(16)
N(4)	0.1519(6)	0.2488(2)	0.1092(3)
C(18)[a]	0.9853(9)	0.2376(2)	0.1347(4)
C(18B)[b]	0.1083(51)	0.2232(15)	0.1788(20)
C(19)	−0.0188(11)	0.2541(4)	0.2227(5)
C(20)[a]	0.2897(9)	0.2067(2)	0.1536(4)
C(20B)[b]	0.2611(65)	0.2100(21)	0.0784(25)
C(21)	0.4709(10)	0.2161(4)	0.1448(5)
Cl(1)	0.4841(2)	0.2963(1)	−0.1015(1)
O(3)	0.5379(11)	0.3024(3)	−0.0148(4)
O(4)	0.3842(8)	0.2443(2)	−0.1249(3)
O(5)	0.6231(9)	0.2992(4)	−0.1432(4)
O(6)	0.3658(8)	0.3429(2)	−0.1340(4)
Cl(2)	−0.0951(3)	0.4367(1)	−0.3242(1)
O(7)	0.1079(10)	0.5078(3)	0.2932(5)
O(8)	0.2553(10)	0.5886(4)	0.3606(7)
O(9)[c]	0.0282(18)	0.5634(7)	0.4003(5)
O(9B)[d]	0.1717(41)	0.5962(12)	0.2580(18)
O(10)	−0.0402(11)	0.5916(3)	0.2699(5)

Site occupation factor: [a]0.85; [b]0.15; [c]0.8; [d]0.2.

Technische Hochschule Darmstadt. The final positional and thermal parameters with their estimated standard deviations are listed in Table II. See also 'Supplementary Material'.

Magnetic Measurements

The magnetic susceptibility measurements of compounds **1**, **3**, **4** and **5** were carried out with a Faraday type magnetometer equipped with an evaporation cryostat [30] in the temperature range 5.1–313 K. The polycrystalline powder samples weighed 20–50 mg. The applied magnetic field was about 1 T. $Hg[Co(SCN)_4]$ was used as susceptibility standard [31]. The uncertainty in temperature is estimated to 0.1 K for the range 5–70 K and 0.3 K for higher temperatures. Magnetic molar susceptibility data were corrected for molar diamagnetism using Pascals increments [32]. Application of the fitting procedure discussed in the text allowed the separation of TIP and the amount of paramagnetic impurities, so that the paramagnetic molar susceptibility of the dimeric systems has been found reproductible with better than 1%.

Results and Discussion

Description of the Structure of 4

Compound **4** crystallizes as a binuclear Cu(II) cation with related two formula units of perchlorate anions in the asymmetric unit. Selected interatomic distances and angles are given in Table III. The binuclear cation is shown in Fig. 1 including the numbering system used. As found for many similar systems [10–14] the macrocycle acts as a five-dentate ligand. The two copper atoms are bridged by the oxygen atom O1 of the hydroxyl group and by the phenolate oxygen O2 of the multidentate ligand. Two amino nitrogens, N1 and N4, and two imino nitrogen atoms, N2 and N3, complete the coordination of the two copper atoms by the macrocycle. So each copper atom is coordinated by a square planar CuN_2O_2-sphere.

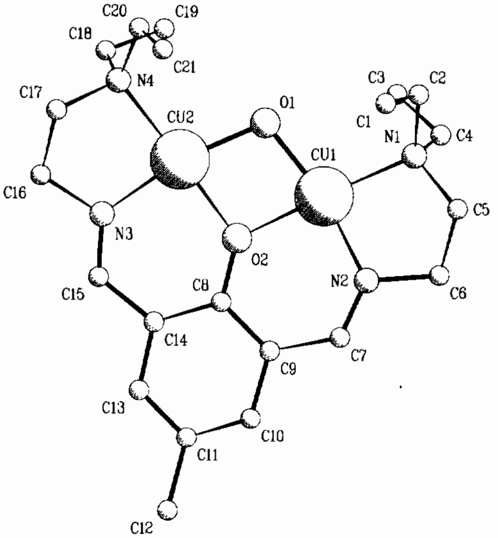

Fig. 1. Basic structure of all binuclear cations (except **2**) using complex **4** as an example.

TABLE III. Selected Bond Distances (Å) and Bond Angles (°) (with e.s.d.s in parentheses)

Cu(1)–Cu(2)	3.018(1)		
Cu(1)–O(1)	1.900(4)	Cu(2)–O(1)	1.873(3)
Cu(1)–O(2)	1.958(3)	Cu(2)–O(2)	1.965(3)
Cu(1)–N(1)	1.908(4)	Cu(2)–N(2)	1.911(4)
Cu(1)–N(3)	2.009(4)	Cu(2)–N(4)	2.014(4)
N(3)–C(16)	1.522(5)	N(4)–C(18)	1.478(5)
N(3)–C(16B)	1.640(56)	N(4)–C(18B)	1.471(37)
C(16)–C(17)	1.506(8)	C(18)–C(19)	1.481(8)
C(16B)–C(17)	1.493(46)	C(18B)–C(19)	1.537(40)
N(3)–C(10)	1.486(4)	N(4)–C(13)	1.477(4)
N(3)–C(10B)	1.572(32)	N(4)–C(13B)	1.459(28)
C(9)–C(10)	1.505(5)	C(12)–C(13)	1.497(6)
C(9)–C(10B)	1.575(33)	C(12)–C(13B)	1.639(32)
N(3)–C(14)	1.519(4)	N(4)–C(20)	1.506(4)
N(3)–C(14B)	1.485(35)	N(4)–C(20B)	1.523(56)
C(14)–C(15)	1.459(8)	C(20)–C(21)	1.476(8)
C(14B)–C(15)	1.578(37)	C(20B)–C(21)	1.588(48)
Cu(1)–O(1)–Cu(2)	106.3(2)		
Cu(1)–O(2)–Cu(2)	100.6(2)		
O(1)–Cu(1)–O(2)	76.8(1)	O(1)–Cu(2)–O(2)	76.8(1)
O(1)–Cu(1)–N(1)	167.7(2)	O(1)–Cu(2)–N(2)	167.6(2)
O(1)–Cu(1)–N(3)	105.1(2)	O(1)–Cu(2)–N(4)	105.2(2)
O(2)–Cu(1)–N(1)	91.5(2)	O(2)–Cu(2)–N(2)	91.1(2)
O(2)–Cu(1)–N(3)	177.3(2)	O(2)–Cu(2)–N(4)	177.8(2)
N(1)–Cu(1)–N(3)	87.0(2)	N(2)–Cu(2)–N(4)	86.9(2)
C(14)–N(3)–C(16)	106.9(3)	C(13)–N(4)–C(18)	109.3(3)
C(14B)–N(3)–C(16B)	108.4(2.1)	C(13B)–N(4)–C(18B)	107.1(2.3)
C(10)–N(3)–C(16)	110.1(3)	C(13)–N(4)–C(20)	107.7(3)
C(10B)–N(3)–C(16B)	104.5(1.9)	C(13B)–N(4)–C(20B)	104.5(2.0)
C(10)–N(3)–C(14)	108.0(3)	C(18)–N(4)–C(20)	109.1(3)
C(10B)–N(3)–C(14B)	104.2(1.9)	C(18B)–N(4)–C(20B)	107.5(2.4)

Structural Comparison of Six Asymmetrically Bridged Cu(II) Dimers

The basic structure for all dimers is illustrated above using compound **4** as a representative example. The structures of **2** [22], **5** [23] and **6** [24] have been published previously from our group, whereas **1** and **3** have been characterized recently by Kahn *et al.* [25], confirming our results [26]. Table IV compares the bond distances, bond angles, and special features of the coordination geometry for the copper cores of the six structurally characterized compounds.

The basic structure of all the binuclear Cu(II) complexes is a nearly planar Cu_2OX-core (X = N, O) which becomes evident from the small deviations of the atomic positions compared to the calculated best planes (see Table IV). Therefore the copper coordination spheres show distorted square planar geometry.

Oxygen atoms from perchlorate anions or water molecules coordinate perpendicular to the basis planes (with the exception of **4**) and are more elongated (Cu–O > 2.5 Å) leading to a tetragonal pyramid with an oxygen atom at its apex. The resulting coordination polyhedra around the copper centers are assigned as 4 + 1 or 4 + 2.

The chelating ligand bridges the two copper atoms with a phenolate group leading to a ligand backbone which contains six-membered chelate rings. So the resulting constraints are too small to push the copper atoms to a separation of >3.1 Å. Therefore the exogenous azido-bridges in **1** and **2** are bound end-on.

The bond distances Cu–O (exogenous bridge) are generally shorter than Cu–O (phenolate). Steric effects resulting from larger alkyl substituents at the outer amino ligands (**3**: R = Me; **4**: R = Et) lead to an increased Cu–Cu distance in connection with likewise enlarged Cu–O(X)–Cu bridging angles. The same effect has been found by changing the five-membered outer chelate rings (**1**, **3**) to six-membered ones (**2**, **5**). Remarkably, the bridging angle at the exogenous ligand is much more affected than at the endogenous phenolate group, particularly significant for **3**, **4** and **5**. This can be understood considering the extended conjugated system including the endogenous bridge

TABLE IV. Important Crystallographic Features of the Cu(II) Dimers Studied

Compound	1	2	3	4	5	6
Bond distances (Å)						
Cu–Cu	2.952(1)	3.120(1)	2.932(2)	3.019(1)	3.021(1)	3.014(2)
Cu–X(exogenous)	1.928(5) 1.928(5)	1.973(6) 1.972(7)	1.893(7) 1.940(7)	1.899(4) 1.872(3)	1.915(3) 1.898(3)	1.939(8) 1.958(8)
Cu–O(phenolate)	1.959(4) 1.951(4)	1.987(5) 2.003(4)	1.954(7) 1.937(7)	1.959(3) 1.968(3)	2.001(2) 1.980(2)	1.939(6) 1.969(7)
Cu–N(amino)	2.035(5) 2.018(5)	1.969(7)[a] 1.927(7)[a]	2.038(9) 2.000(9)	2.009(4) 2.023(4)	2.071(3) 2.050(3)	2.001(9) 2.012(10)
Cu–N(imino)	1.936(5) 1.927(5)	1.965(6) 1.973(7)	1.909(9) 1.926(9)	1.910(4) 1.922(4)	1.951(3) 1.929(3)	1.929(11)[b] 1.961(10)[b]
Bond angles (°)						
	99.2(2) 98.1(2)	104.5(4) 102.9(3)	99.8(3) 97.8(3)	106.4(2) 100.5(2)	104.7(1) 98.7(1)	101.3(4) 100.9(3)
Copper coordination features						
Cu coordination	4 + 2 4 + 2	4 + 1 4 + 2	4 + 2 4 + 2	4 4	4 + 1 4 + 1	4 + 1 4 + 2
Maximum deviation from best plane of the CuN_2OX-core (Å)	0.07 0.07	0.10 0.10	0.04 0.04	0.03 0.03	0.14 0.27	0.01 0.04
Dihedral angle between the CuN_2OX-cores (°)	0.5	7.8	2.0	3.5	19.4	7.8

[a] Cu–N(azido). [b] Cu–N(imidazolato).

as the rigid part of the ligand. Reduction of the C=N double bond (compound **6**) leads to two nearly identical bridging angles.

Compounds **1** and **3** have very similar molecular structures. Although the exogenous bridge is different for both complexes the angles at the exogenous and endogenous bridging ligands are identical within the e.s.d.s for both structures.

It has been established for all structures that the bond distance Cu–N(amino) is distinctly longer than Cu–N(non-amino). The generalization of this fact can be demonstrated with compound **6**, in which the imino groups are reduced to amines and the outer amino groups are replaced by imidazolyl residues (Cu–N(imidazolyl) < Cu–N(amino)) [24].

The only distinct difference between the molecular structures of the six compounds studied concerns the coordination of solvent molecules or perchlorate anions to the copper centers. In complexes **1** and **3** the copper atoms are bridged by two perchlorate groups resulting in a 4 + 2 coordination sphere (Cu–O(perchlorate)) between 2.491(10) and 3.088(12) Å. A 4 + 1 coordination geometry of the copper centers has been determined for compound **5** involving a water molecule and a perchlorate oxygen in the apical positions [23]. Only complex **4** shows a simple square planar coordination sphere of the copper cores. In the crystal structure of compounds **1**, **3**, **4** and **5**, the binuclear subunits appear well separated so that they can be considered as structurally isolated units.

The crystal structure of **6** reveals that one perchlorate group bridges two copper atoms of different asymmetric units leading to a one-dimensional chain structure of Cu(II) dimers along the *c*-axis (Cu–O-(perchlorate): 2.712(13) and 2.644(17) Å) [24]. In addition, a water molecule coordinates to the fifth coordinating position of the second copper atom.

The molecular structure of **2** is significantly different from those of other compounds studied. The macrocycle only acts as a tridentate ligand, because the outer amino groups of the multidentate ligand are replaced by two azido-groups. Two dimeric subunits inverted by a center of symmetry form a step-like tetrameric molecule. Since the interdimeric bond distances (Cu–N(azido): 2.858(6) and 2.466(7) Å) are significantly larger than the intradimeric ones (Cu–N(azido): 1.973(6) and 1.972(7) Å), **2** can be assumed as a transition type between dimeric and tetrameric clusters [22]. The molecular structure of **2** is completed by one perchorate group coordination to the sixth position of one copper atom.

Magnetic Susceptibility Data

The magnetic susceptibility data of the discussed Cu(II) dimers have been partly published. But either the magnetic data have been determined only for $T >$ 78 K (compounds **3**, **4** [11], and **6** [12]) or the paramagnetic impurities are higher for more than one order of magnitude as found in our measurements (compounds **1** and **3** [25]). So we measured the magnetic susceptibility data for these compounds in the temperature range 5.1–313 K to obtain more precise values for the exchange integrals.

The magnetic behaviour of all compounds studied is compared in Fig. 2 using a χ_M *versus* T presentation. Generally, χ_M increases with increasing temperature passing through a maximum for **1** (80 K) and **3** (261 K). The appearance of a maximum is characteristic of an antiferromagnetic coupling between the Cu(II) ions stabilizing the singlet state with regard to the triplet state.

The magnetic susceptibility of two interacting Cu(II) ions can be calculated using the isotropic Heisenberg–Dirac–van Vleck (HDvV) model resulting in eqn. (1) [33].

$$\chi_M = \frac{N_L g^2 \mu_B^2}{kT} \, \frac{1}{3 + \exp(-2J/kT)} \qquad (1)$$

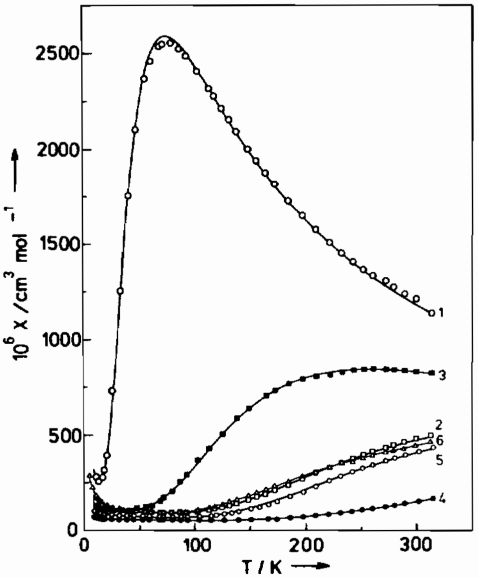

Fig. 2. χ_M *vs.* T plots of all studied complexes.

where N_L, μ_B, g, and k have their usual meanings and $2J$ is the singlet–triplet energy gap. The exchange integral $2J$, the g factor, the amount x of the paramagnetic impurities χ_{para}, and the temperature independent paramagnetism N_α were fitted by least-squares techniques using eqn. (2):

$$\chi_{calc} = (1 - x)\chi_M + x\chi_{para} + \chi N_\alpha \qquad (2)$$

The paramagnetic impurities are described by the Curie law. The function minimized was $\Sigma|\chi_{exp} - \chi_{calc}|/\chi_{exp}$. The resulting parameters are listed in Table V.

The applied calculation procedure involves dependencies between the fit parameters leading to the estimated uncertainties which are indicated in parentheses in Table V. To fit the magnetic susceptibility data of **2**, **5**, and **6** it was found necessary to keep the g factor fixed. Variation of the g factor in different calculations shows that the tabulated values are the best ones.

The calculated susceptibility values are in very good agreement with the experimental data (See Fig. 2), so that all of the compounds studied can be described as magnetically isolated dimers showing antiferromagnetic spin coupling. The different g factors result from spin-orbit coupling which is included in the g factors. Deviations from spin-only magnetism depend mainly on the ligand field splitting based on the different copper coordination geometry (4, 4 + 1, 4 + 2). The exchange integrals range between −84 and −852 cm^{-1} pointed out by the different temperature dependencies of the magnetic susceptibility. Attempts to include the structural particularities of **2** (step-like tetramer) and **6** (one-dimensional chain compound) into the magnetic models establish no interdimeric interactions [22, 24]. Hence, these complexes can also be understood as magnetically isolated dimers.

Although the molecular structures of **1** and **3** are very similar, differing only in the nature of the exogenous bridge, the resulting exchange integrals vary from $2J = -84$ cm^{-1} to −288 cm^{-1}. This comparison reveals that the only influence of electronic factors to exchange coupling is the modification of the bridging ligand from N_3^- to OH^-, while geometric factors, which will be discussed later as magneto-structural dependencies, remain constant.

TABLE V. Comparison of the Magnetic Parameters of the Studied Asymmetrically Bridged Binuclear Cu(II) Complexes

Compound	1	2	3	4	5	6
g factor	2.01(3)	2.25	2.02(3)	2.21(3)	2.25	2.10
$2J$ (cm^{-1})	−84(2)	−534(10)	−288(5)	−852(15)	−569(10)	−516(6)
x	0.0063(1)	0.0019(1)	0.0007(1)	0.0037(1)	0.0011(1)	0.0026(1)

Magneto-structural Dependencies of Asymmetrically Bridged Cu(II) Dimers

Investigations on dimeric Cu(II) complexes [34–37] point out that the strength of the antiferromagnetic exchange interaction depends on the bridging angles Cu–X–Cu, the copper coordination geometry (planarity), the dihedral angle between the copper cores and other geometrical factors (e.g. bond length). Symmetrically hydroxo- and alkoxo-bridged Cu(II) dimers are known to show a linear correlation between the exchange integral $2J$ and the bridging angle Cu–O–Cu in the range 95°–105° [34, 35]. In such magneto-structural correlations, it is necessary to vary only one geometric parameter while the other factors have to be held constant. The X-ray structure analysis of the asymmetrically bridged dimers studied here show comparable values for all important geometric factors with the exception of the bridging angles. Therefore it was possible for the first time to study magneto-structural dependencies of this class of Cu(II) dimers.

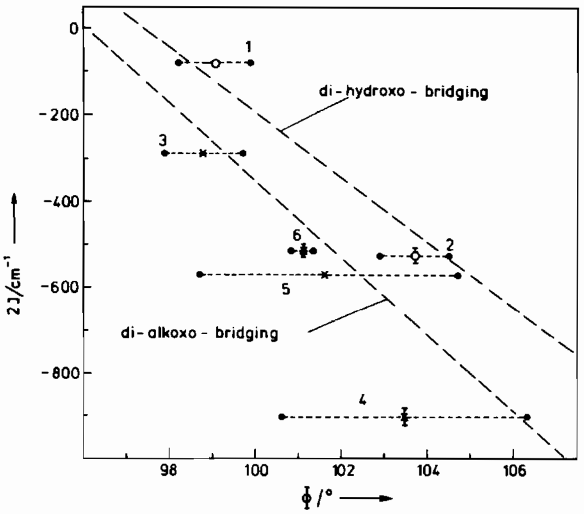

Fig. 3. Plot of the exchange integral ($2J$) as a function of the bridging angle (Φ).

Figure 3 presents a plot of the exchange integral ($2J$) *versus* the bridging angle (Φ) for these compounds. For every dimer the two different bridging angles and the average angle are shown. It is evident that the angles at the endogenous and exogenous bridges of **4** and **5** differ significantly (maximum difference 6.0°).

From Fig. 3 it becomes evident that no magneto-structural correlation for the compounds with exogenous hydroxo-group (**3**–**6**) can be obtained when the bridging angles either of the exogenous or of the endogenous bridges are used. Thus, as a first approximation we have averaged the values for exogenous and endogenous bridge angles which then lead to a reasonable dependence between the exchange integral and the average bridging angle. Distinctly different are the corresponding values for **1** and **2** with exogenous azido-groups (see Fig. 3).

The experimental results point out that asymmetrically bridged Cu(II) dimers with comparable structures can be assumed to show a linear dependence between the exchange integral and the average bridging angle. Since the magneto-structural correlation involves averaged values from both bridging angles, it would appear that the magnetic pathway includes both bridges. Another important fact is that the asymmetry of the bridges (from different ligands and angles) does not lead to drastic deviations from known magneto-structural correlations for symmetrically bridged Cu(II) dimers with similar structure [34, 35]. The similarity in both the basic structures and their magnetic properties of all dimers suggest that the same ligand orbitals are involved in the overlap with the d_{xy}-orbitals of the copper centers leading to antiferromagnetic spin-coupling. However, the exogenous bridge influences the resulting correlation so that every magneto-structural dependence is related to only one type of bridging ligand.

Supplementary Material

The F_o/F_c lists, anisotropic temperature factors, and the H atom positional parameters are available from the authors on request.

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