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Crystal Structure and Magnetic Properties of an Asymmetric Bridged Binuclear Cu(II)-complex with a Macrocyclic Ligand Derived from 2-Hydroxy-5-methyl-isophthalaldehyde and Histamine

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Abstract

The Cu(II) complex $C_{19}H_{26}N_6O_{10}Cl_2Cu_2 \cdot 1.5H_2O$ using the macrocyclic amin derived from 2-hydroxy-5-methyl-isophthalaldehyde and histamine consists of asymmetric bridged binuclear cations having a phenolate and hydroxyl bridge. The X-ray crystal structure analysis (a = 42.153(8), b = 18.258(3), c = 7.534(1); space group *Ccc*2) shows the dimeric units linked by perchlorate groups to one-dimensional infinite chains along the c-axis. The coordination polyhedra around the copper atoms are 4 + 2 and 4 + 1, respectively, including one coordinating water molecule.

The magnetic susceptibility of the complex has been measured in the temperature range from 5.1 K to 313.7 K. The magnetic exchange interaction has been interpreted in terms of strong antiferromagnetic coupling within the binuclear cation. Magnetic exchange coupling along the one-dimensional chains has been neglected because of the large distance copper–perchlorate oxygen > 2.644 Å. The exchange integral has been calculated to 2 J about −516 cm^{-1}.

Structural and magnetic aspects of the title compound forming a saturated chelate system are compared to similiar compounds using Schiff base macrocyclic ligands in relation as models for the asymmetric bridging in the oxygen transport protein hemocyanin.

Introduction

An unresolved problem of the oxygen-transport protein hemocyanin is the unusual magnetic behaviour of the dinuclear copper(II)-active site [1, 2]. Asymmetric bridged dimeric Cu(II)-complexes are widely used as models [3–7], but complexes simulating the large Cu–Cu distance of 3.6 Å as well as the asymmetric bridges of hemocyanin are rare [8, 9]. As it has been pointed out in former studies, it is necessary to investigate the influence of asymmetric bridges to exchange coupling at first and then to relate the results to the large bridging angle [10].

Double Schiff base macrocycles are often used as five-dentate ligands leading to roughly square planar coordination polyhedra around the copper atoms [6, 7]. The influence of a fifth ligand, as assumed in the copper coordination sphere of the hemocyanin active site [11], to magnetic exchange coupling has already been studied by different coordinations of perchlorate groups to the copper atoms [12, 13].

Imino nitrogen atoms are not assumed to be coordinated to the copper atoms in hemocyanin, and additionally, macrocyclic Schiff base ligands from planar chelate rings with aromatic character. So it seems to be necessary to compare structural and magnetic features with similiar Cu(II)-complexes using saturated chelate systems.

Grzybowski *et al.* [5] described the preparation of this type of compound. We have determined the crystal structure of one of the Cu(II)-complexes. The macrocyclic ligand used, containing amino and imidazol nitrogen donor atoms, leads to a phenolate and a supplementary hydroxyl bridge. Because of unusual structural features we have decided to remeasure the magnetic susceptibility down to 5 K.

Experimental

Preparation

The title compound was prepared according to the method described by Grzybowski *et al.* [5]. The macrocyclic double Schiff base was obtained by reaction of 2-hydroxy-5-methyl isophtalaldehyde with histamine. Reduction of the Schiff base functions with sodium bore hydride yield the corresponding macrocyclic amin (L). Green needle-like crystals were obtained by twofold recrystallisation from water. The crystals were vacuum dried at 60 °C; m.p. >320 °C.

Elemental analysis results (%) for the crystalline product of the empirical formula $C_{19}H_{26}N_6O_{10}$-

0020-1693/85/$3.30

TABLE I. Data Collection and Processing Parameters.

Molecular formula	$C_{19}H_{26}N_6O_{10}Cl_2Cu_2 \times 1.5H_2O$
Molecular weight	723.46
Cell constants	a = 42.153(8) Å
	b = 18.258(3) Å
	c = 7.534(1) Å
	V = 5798.39 Å^3
	Z = 8
D_m (by flotation)	1.66(1) g/cm^3
D_c	1.653 g/cm^3
Space group	$Ccc2$
Radiation	graphite-monochromatized Mo K_α-radiation, λ = 0.71069 Å
Absorption coefficient	16.38 cm^{-1}
$F(000)$	2952
Scan type	$\omega:2\theta = 1:1$
Scan range	$3° \leq 2\theta \leq 50°$
Intensity variations	<3%
Unique data measured	2394
Observed data with $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$	2132
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.062

$Cl_2Cu_2 \cdot 1.5H_2O$ were as follows, with calculated values in parenthesis: C, 31.53(31.54); H, 4.09(4.04); N, 11.43(11.62).

X-Ray Crystallography

A needle-like crystal of approximate dimensions 0.1 × 0.1 × 1.5 mm was measured on a computer controlled STOE Stadi 4 four-circle-diffractometer system. The cell dimensions were obtained from least-squares refinement of the 2θ values of 48 strong reflections. The intensity data were corrected for Lorentz, polarization and absorption effects. The pertinent crystallographic data are summarized in Table I.

The systematic absences, hkl: $h + k = 2n + 1$, $0kl$: $l = 2n + 1$, $h0l$: $l = 2n + 1$, indicated the space groups $Ccc2$ or $Cccm$. The former was confirmed by the statistical distribution of E values and a successful refinement of the structure.

The crystal structure was solved by direct methods using SHELX-76 [14], which gave the positions of the two copper atoms. The remaining atoms, including the macrocyclic cation, one coordinating water molecule and the bridging perchlorate group, were recovered after several Fourier syntheses, ΔF syntheses and successive least-squares cycles. During the course of refinement a second perchlorate group was located with chlorine in the special position ¼ ¼ 0.2400. After least-squares refinement using isotropic (R = 0.111) and anisotropic (R = 0.090) temperature factors all C-bound H atoms were geometrically generated (C–H distance fixed at 1.08 Å) assigning isotropic thermal parameters. From the resulting ΔF map a second water molecule was located in a half-occupied site. The remaining perchlorate group indicated from elementary analysis [5] has been assumed within the large channels resulting from the crystal structure. Because no correlations between the positions from the ΔF map and the geometry of the perchlorate group could be found, the highest peak of the ΔF map was assigned as a half-positioned oxygen-atom of this group because of its coordination.

The highest peaks of the final difference map with residual extrema lying between 0.91 and −0.49 eÅ^{-3} were located in the region where the remaining perchlorate group was assigned. The missing correlation between these peaks indicated that the remaining part of this perchlorate group takes non fixed places in the lattice at the experimental temperature (299 K). All the atomic scattering factors were taken from 'International Tables for X-Ray Crystallography' [15] and ref. [16].

All calculations were performed on an IBM 370/168 computer in the Technische Hochschule Darmstadt. The final positional and thermal parameters with their estimated standard deviations are listed in (Table II). The F_o/F_c-lists, anisotropic temperature factors, and the H-atom positional parameters are available from the authors on request.

Magnetic Measurements

The magnetic susceptibility was recorded by the Faraday method as described previously [17] at *ca.* 10 kG (1T) in the temperature range from 5.1–313.7 K. Experimental susceptibility data were corrected for underlaying diamagnetism using Pascal's increments [18] and for temperature-independent paramagnetism. The calculation of the theoretical $\chi(T)$ curve was performed on a IBM 370/168 computer of the Technische Hochschule, Darmstadt.

Results and Discussion

Description of the Structure

The title compound crystallizes as a binuclear $(LCu_2{-}OH)^{2+}$-cation with related two formula-units of perchlorate anions and 1.5 water molecules in the asymmetric unit. Selected interatomic distances and angles are given in Table III.

The binuclear cation is represented (Fig. 1) including the numbering system used. The macrocycle L acts as a five-dentate ligand as known from literature [3–7]. The two copper atoms are bridged by the oxygen atom O2 of the hydroxyl group and by the phenolate oxygen O1 of the multidentate ligand. Two amino nitrogens, N3 and N4, and two imidazol nitrogen atoms, N1 and N6, complete the coordination of the two copper atoms by the macrocycle L.

TABLE II. Atomic Positional Parameters and Equivalent Temperature Factors (Å^2) for all Non-hydrogen Atoms with e.s.d.s in Parenthesis; $B_{eq} = 8/3\ \pi^2(U_{11} + U_{22} + U_{33})$.

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Cu1	0.08950(3)	0.21092(8)	0.57220	3.61
Cu2	0.14696(3)	0.30862(7)	0.59759(37)	3.75
N1	0.0437(2)	0.2282(7)	0.5519(21)	4.7
C1	0.0302(4)	0.2876(9)	0.5093(24)	5.9
N2	−0.0027(3)	0.2772(9)	0.5071(25)	7.4
C2	−0.0085(3)	0.2124(11)	0.5553(34)	6.5
C3	0.0210(3)	0.1769(10)	0.5811(28)	6.2
C4	0.0284(3)	0.0977(10)	0.6302(29)	6.8
C5	0.0553(3)	0.0694(8)	0.5228(25)	5.7
N3	0.0855(2)	0.1018(5)	0.5851(22)	3.8
C6	0.1119(3)	0.0664(7)	0.4871(21)	4.4
O1	0.1353(1)	0.2043(4)	0.5899(19)	3.6
O2	0.1011(2)	0.3136(4)	0.5586(20)	4.6
C7	0.1531(2)	0.1448(7)	0.6338(18)	3.3
C8	0.1432(2)	0.0756(6)	0.5809(23)	3.2
C9	0.1616(3)	0.0146(6)	0.6288(18)	3.6
C10	0.1906(3)	0.0224(7)	0.7195(21)	3.9
C11	0.2107(4)	−0.0431(9)	0.7573(25)	5.6
C12	0.1999(3)	0.0908(8)	0.7643(19)	3.8
C13	0.1815(3)	0.1533(7)	0.7308(19)	3.2
C14	0.1916(3)	0.2278(8)	0.7960(20)	4.2
N4	0.1923(2)	0.2841(6)	0.6565(16)	4.0
C15	0.2140(3)	0.3441(8)	0.7088(26)	5.1
C16	0.2121(3)	0.4082(8)	0.5807(32)	5.9
C17	0.1820(4)	0.4500(7)	0.6039(27)	5.1
C18	0.1776(5)	0.5228(10)	0.6280(30)	7.6
N5	0.1460(5)	0.5316(7)	0.6437(26)	8.9
C19	0.1310(4)	0.4646(10)	0.6349(26)	6.7
N6	0.1529(3)	0.4133(6)	0.6072(21)	5.1
Cl(1)	0.0982(1)	0.1823(2)	0.0555(6)	4.7
O3	0.1310(2)	0.1725(7)	0.0787(35)	9.0
O4	0.0842(3)	0.2048(8)	0.2137(17)	7.4
O5	0.0842(3)	0.1140(7)	0.0083(25)	10.7
O6	0.0903(4)	0.2297(10)	0.9201(23)	11.0
Cl(2)	0.2500	0.2500	0.2400(9)	5.6
O7	0.2373(4)	0.3080(8)	0.1365(24)	11.2
O8	0.2272(7)	0.2235(10)	0.3374(42)	23.9
O9	0.0585(5)	0.3666(11)	−0.1132(33)	5.8
O1W	0.1609(3)	0.3029(6)	0.2653(16)	6.6
O2W	0.0874(4)	0.3834(10)	0.2246(30)	5.0

So each copper atom is coordinated in a square planar CuN_2O_2-sphere.

The Cu–O distances in the Cu_2O_2-core range from 1.939(6) Å to 1.969(7) Å. In accordance with known asymmetric bridged binuclear copper(II) complexes the copper–amino nitrogen distances (mean value 2.007(10) Å) are found to be longer than the copper–non-amino nitrogen distances (1.929(11) Å and 1.961(10) Å).

All the four chelate rings formed by the macrocyclic ligand (Figs. 1, 2) are non planar. In comparison to this saturated ligand system the two inner chelate rings I and II are found nearly planar using

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

Cu1–Cu2	3.014(2)		
Cu1–O1	1.939(6)	Cu2–O1	1.969(7)
Cu1–O2	1.939(8)	Cu2–O2	1.958(8)
Cu1–N1	1.961(10)	Cu2–N6	1.929(11)
Cu1–N3	2.001(9)	Cu2–N4	2.012(10)
Cu1–O4	2.712(13)	Cu2–O1W	2.574(12)
Cu1–O6	2.644(17)		
O2W–N5[a]	2.981(15)	O2W–O9	2.838(15)
O2W–O2	2.880(15)	O9–N2[b]	3.002(15)
Cu1–O1–Cu2	100.9(3)		
Cu1–O2–Cu2	101.3(4)		
O1–Cu1–O2	79.3(3)	O1–Cu2–O2	78.1(3)
O1–Cu1–N1	174.3(4)	O1–Cu2–N6	173.0(4)
O1–Cu1–N3	91.0(3)	O1–Cu2–N4	91.6(4)
O1–Cu1–O4	98.5(5)	O1–Cu2–O1W	89.4(5)
O1–Cu1–O6	85.8(6)		
O2–Cu1–N1	95.1(4)	O2–Cu2–N6	95.1(4)
O2–Cu1–N3	170.2(3)	O2–Cu2–N4	168.9(4)
O2–Cu1–O4	90.5(5)	O2–Cu2–O1W	94.7(5)
O2–Cu1–O6	85.6(6)		
N1–Cu1–N3	94.7(4)	N6–Cu2–N4	95.1(5)
N1–Cu1–O4	81.2(5)	N6–Cu2–O1W	92.7(5)
N1–Cu1–O6	94.0(6)		
N3–Cu1–O4	90.0(6)	N4–Cu2–O1W	89.3(4)
N3–Cu1–O6	94.7(6)		
O4–Cu1–O6	173.5(5)		

[a] $x, -y, z + ½$. [b] $-x, y, z + ½$.

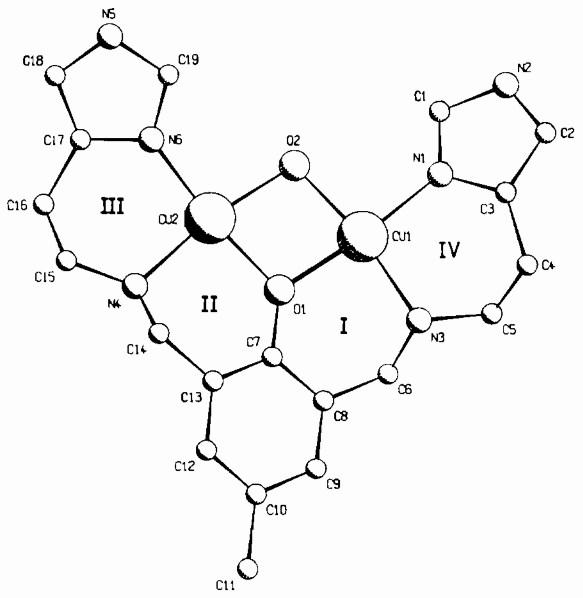

Fig. 1. Perspective view of the binuclear cation.

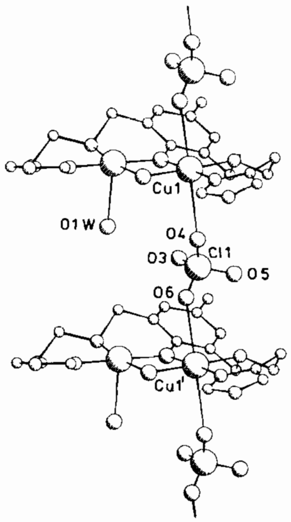

Fig. 2. One-dimensional infinite chain structure along the *c*-axis.

Schiff base ligands [7, 10]. The torsion angle between the best planes of the phenolate ring and the four-membered Cu_2O_2-core has been calculated to 24.6°. All distances and angles of the ligand show normal values.

One perchlorate group is situated between two binuclear cations. The perchlorate oxygens O4 and O6 are coordinated to Cu1-atoms from different subunits (Cu1–O4 2.712(13) Å; Cu1–O6 2.644(17) Å) leading to a sixfold coordination of Cu1. The resulting structure is interpreted as a one-dimensional infinite chain along –Cu1–O4–Cl(1)–O6–Cu1′– with Cu′ in x, y, $1 - z$. A representative part of this chain is shown (Fig. 2).

Therefore, the coordination polyhedron of Cu1 can be described as 4 + 2 having a square planar basis plane with two additional ligands perpendicular to this plane and more elongated. The related basis plane is extremely planar (max. deviation 0.01 Å) with the Cu1 situated in this plane. The coordination polyhedron around Cu2 can be assigned as 4 + 1 forming a distorted tetragonal pyramid with the water molecule O1W as its apex. The basis plane is also planar (max. deviation 0.02 Å) but the Cu2 atom is situated 0.05 Å above this plane slightly shifted towards the apex.

A projection of the unit cell is displayed (Fig. 3). The two-dimensional binuclear cations are placed in the (001) plane. Symmetry operations depending on the space group *Ccc*2 lead to structural features built up from four crystallographic different binuclear cations. A channel system parallel to the *c*-axis is formed around $x = 0, y = ½$ and $x = ½, y = 0$. Two binuclear cations related by a twofold axis (parallel to the *c*-axis and through the given positions) are connected by hydrogen bonds via N3–O2W–O9–N6 (see Table III). A supplementary hydrogen bond has been found between O1W and O2 from a third dimeric unit in $x, -y, z - ½$. So a three-dimensional network by hydrogen bonding is built up within this structural feature supplementary to perchlorate bridging along the *c*-axis.

The half-positioned perchlorate group within the channel system has not been located with the exception of the oxygen atom O9 coordinated by hydrogen bonding. In Fig. 3 a circle characterizes the region where the other atoms of this group are assumed and where the strongest peaks were found in the ΔF map. This can be explained by the assumption that the non localized part of the perchlorate group exhibits motions in relation to the fixed oxygen atom at the experimental temperature of 299 K.

The remaining perchlorate group with the chlorine atom in the special position ¼ ¼ 0.2400 separates the described structural features parallel to the (100) plane. No bonding contact between this perchlorate group and the dimeric subunits has been observed.

Magnetic Properties

The magnetic susceptibility of the crystalline samples has been measured in the temperature range

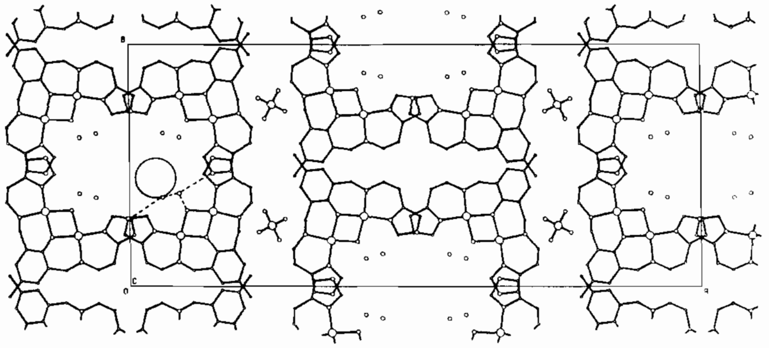

Fig. 3. Crystal structure of the title compound projected perpendicular to the (001) plane. Broken lines illustrate the network from hydrogen bonding. The bridging perchlorate group and the water molecule coordinated to Cu2 have been omitted for clarity.

TABLE IV. Experimental Magnetic Susceptibility (10^6 cm^3 mol^{-1}) in Comparison to the Values Calculated for the Low-temperature and High-temperature Region.

T (K)	χ_{exp}	χ_{calc} T < 220 K	χ_{calc} T > 240 K
5.1	283.1	287.9	287.9
7.9	220.8	213.2	213.2
11.2	177.8	173.1	173.1
13.2	162.1	158.6	158.6
16.2	146.3	143.5	143.5
20.3	130.0	130.1	130.1
25.8	115.6	118.8	118.8
33.4	105.3	109.3	109.3
41.1	99.1	103.3	103.3
47.4	97.1	99.8	99.8
55.9	95.1	96.4	96.4
61.3	89.6	94.8	94.8
69.1	87.5	93.3	93.1
72.1	86.8	92.9	92.7
79.9	87.5	92.8	92.2
87.2	89.6	93.8	92.8
93.2	93.7	95.7	94.1
103.4	101.1	101.2	98.4
113.7	115.6	110.1	105.7
118.3	121.7	115.2	109.9
125.2	132.0	124.1	117.5
131.8	143.6	134.0	126.0
138.4	153.9	145.1	135.7
149.2	176.4	165.6	153.8
156.5	190.7	180.7	167.4
164.6	207.8	198.6	183.5
172.5	224.2	216.7	200.1
184.9	250.2	245.9	227.1
197.5	276.1	275.7	255.1
209.6	299.4	303.9	281.9
222.0	323.4	331.6	308.5
232.9	345.5	354.7	330.9
243.2	355.6	375.3	351.1
252.4	370.3	392.4	368.0
261.0	385.2	407.5	383.0
272.9	401.2	426.6	402.2
279.9	412.2	436.9	412.7
289.5	422.0	450.0	426.1
300.2	437.2	463.2	439.7
313.7	454.0	477.8	454.9

5.1 K to 313.7 K (see Table IV and Fig. 4). With increasing temperature the magnetic susceptibility first decreases slightly because of the few paramagnetic impurities. At about 80 K the magnetic susceptibility begins to increase without reaching a maximum in the studied temperature range.

A quantitative theoretical analysis of the magnetic behaviour is given using the isotropic Heisenberg-Dirac-van Vleck (HDvV) model. The Hamiltonian is:

$$\mathcal{H} = -2 \sum_{i<j} J_{ij}\hat{S}_i\hat{S}_j \qquad (1)$$

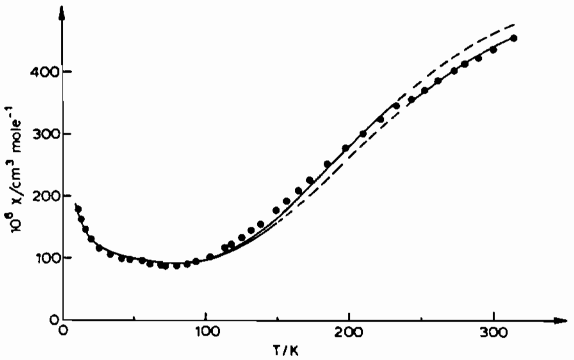

Fig. 4. Temperature dependence of the magnetic susceptibility with (●) experimental and (–) calculated values using eqn. (2). The upper fit represents a $2J$-value of -508 cm^{-1}, the lower one of -524 cm^{-1}.

J_{ij} is the exchange integral between the magnetic centers i and j. The magnetic behaviour of the title compound can be interpreted as an antiferromagnetic exchange coupling of discrete dimers. Any magnetic interaction along the one-dimensional infinite chains via the perchlorate groups can be neglected because of the large Cu1–perchlorate oxygen distance >2.64 Å (see Table III). It is known from literature [19, 20] that exchange interaction involving similiar large copper–oxygen distances can be assumed as zero. For the theoretical description we used the Bleaney-Bowers equation [21].

The exchange integral J_{12}, χ_{para} from the paramagnetic impurities and the temperature independent paramagnetism N_α were fitted by least-squares techniques using eqn. (2):

$$\chi_{exp} = (1 - x)\chi_{Mol} + x\chi_{para} + \chi_{N_\alpha} \qquad (2)$$

The function minimized was $\Sigma(\chi_{exp} - \chi_{calc})$. During the fitting procedure it became clear that the Bleaney-Bowers theory could not describe sufficiently the behaviour of the magnetic susceptibility in the whole temperature range. Separate fits of the low temperature (<220 K) and of the high temperature part (>240 K) gave each a good agreement between experiment and theory (see Table IV and Fig. 4). Table V shows the results of the fitting

TABLE V. Comparison of the Exchange Integral (cm^{-1}), g-Factor, Paramagnetic Impurities x and Temperature Independent Paramagnetism N_α (10^6 cm^3 mol^{-1}) for the Low-temperature and the High-temperature Region.

	T < 220 K	T > 240 K
J_{12}	−254(3)	−262(3)
g-factor	2.10 (fixed)	2.10 (fixed)
x	0.0026	0.0026 (fixed)
N_α	77.1	77.1 (fixed)

procedures for the low and the high temperature part and indicates the fixation of the different parameters. Because, in the applied calculation procedure the J-value depends on the chosen values of the g-factor and on the amount of the paramagnetic impurities, the g-factor has been kept fixed. Variation of the g-factor in different calculations indicated the used value as the best.

We explain the two data sets necessary for the description of the temperature dependence of the magnetic susceptibility in terms of a fixation of the perchlorate group within the channel system at about 230 K. The freezing of this group is assumed to cause a small perturbation to the bridging hydroxyl group connected by the system of hydrogen bonding. Small deviations of the magnetic pathway-system are known to influence the exchange integral drastically [22, 23].

The values calculated for the exchange integral are comparable with the data obtained by Grzybowski *et al.* [5] ($2J = -545$ cm^{-1}) who have taken measurements in the range from 78 K to room temperature. We explain the small differences to their values with our investigation on the magnetic susceptibility down to 5 K. Exact values for the paramagnetic impurities and the temperature-independent paramagnetism for the title compound can be calculated between 5 K and 80 K because the effect from exchange coupling can be neglected in this temperature region.

The value of the magnetic exchange integral is comparable to complexes with macrocyclic Schiff base ligands [5]. Different types of nitrogen atoms complexing the copper atoms seem to have no large effect on exchange coupling. The used ligand has been shown to form an extremely planar coordination sphere around the copper atoms despite the saturated chelate system. As the copper coordination spheres of the title compound and of similar complexes with Schiff base ligands are comparable, both types of compounds are suitable for modelling the asymmetric bridging in hemocyanin.

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