Strong Antiferromagnetism in Isolated Anionic Dicopper(II) Methanoato *Paddle-wheel* Complex*

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Abstract. A new ionic compound $(C_5H_6NO)_2[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]$, **1** formed of 4-hydroxy-pyridinium cations and a complex anion was synthesized. The anion is a *paddle-wheel* dicopper carboxylate complex with four *syn,syn*-bridging and two axial anionic methanoato ligands. The XRD structure determination of **1** reveals that the molecular structure is stabilized by two H-bonds between the cations and the axial *paddle-wheel* anions (N–H···O 2.755(3), O–H···O 2.489(2) Å). The compound exhibits a very strong ($2J = 500$ cm^{-1}) *intra*-binuclear antiferromagnetic interaction noticed already at room temperature attributed to the methanoato *intra*-binuclear bridges. The typical EPR $S = 1$ spin system signals of the dicopper *paddle-wheel* complexes at 90 and 450–700 mT are found in the room temperature spectrum, but they are poorly seen in the 110 K spectrum. These signals are of very low intensity and are accompanied by a dominant signal at 320 mT, all closely related to a very strong antiferromagnetic interaction present in **1**.

Keywords: copper(II), methanoate, 4-hydroxypyridinium, dimer, antiferromagnet

INTRODUCTION

Bimetal tetracarboxylates are a large group of complexes with a very similar coordination central core of $[M_2(\mu\text{-}L1)_4]$ type, known as the *paddle-wheel* or the copper acetate hydrate type, after the first such crystal structure described in 1953.[1–3] The complexes with these building blocks are commonly with two identical metal ions in the binuclear unit, and are known for several metal ions, most often with copper and ruthenium. Additionally, they are found with two different metal ions bridged by four, usually the same L1 ligands.[4–11] The binuclear building blocks in copper(II) complexes are reported to be isolated or mutually arranged by spacer moieties, the last one as a rule *via* the axially coordinated ligands L2 of $[Cu_2(\mu\text{-}L1)_4(L2)_2]$. The axial ligands L2 in the isolated binuclear complexes are most often neutral, since the anionic form, namely L2$^-$, easily forms bridges. Thus, the isolated *paddle-wheel* anions $[Cu_2(\mu\text{-}L1)_4(L2)_2]^{2-}$, meaning without *inter*-binuclear coordination bridges, are relatively rare.

A few such examples are reported in the literature, either with the carboxylato[12–15] or the chlorido[16,17] terminal axial anionic ligands L2$^-$. The copper(II) *paddle-wheel* type of complexes are known also to exhibit a strong antiferromagnetic interaction, and a magnitude of this interaction is particularly strong when the methanoates are the *intra*-binuclear bridging ligands L1$^-$.[18,19]

Herein, the structural and magnetic analysis of an ionic complex with the isolated binuclear complex anion in $(C_5H_6NO)_2[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]$ $(C_5H_6NO^+ =$ 4-hydroxypyridinium cation), is presented.

EXPERIMENTAL

X-ray Crystallography
The crystal data were collected on Nonius Kappa CCD diffractometer with graphite monochromated MoK_α radiation. The structure was solved by direct methods,[20] and the refinements were based on F^2 values and done by full-matrix least-squares[21] with all non-H atoms

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Table 1. Relevant crystal data and data collection summary for $C_{16}H_{18}Cu_2N_2O_{14}$ (**1**)

Relative molecular mass	589.40
Crystal system	orthorhombic
Space group	*Pbca*
a, *b*, *c* (in Å)	7.3353(1), 12.9434(2), 22.5076(3)
V / Å^3	2136.96(5)
Z	4
D_x / (g/cm^3)	1.832
μ / mm^{-1}	2.068
T / K	293(2)
Crystal colour, shape	green prism
Crystal dimensions / mm	0.15×0.15×0.18
$\theta_{min,max}$ / °	2.55, 27.48
R_{int}	0.0144
Refined parameters	171
Total, independent refl.	4553, 2451
Observed refl. [$I > 2\sigma(I)$]	2004
$R^{(a)}$ (observed)	0.0301
$wR_2^{(b)}$ (all data)	0.0868
$\Delta\rho_{min,max}$ / eÅ^{-3}	−0.596, 0.290

(a) $R = \sum \left|\left|F_o\right| - \left|F_c\right|\right| / \sum \left|F_o\right|$

(b) $wR_2 = \left\{ \sum \left[w(F_o^2 - F_c^2)^2 \right] / \sum \left[w(F_o^2)^2 \right] \right\}^{1/2}$

anisotropic. The hydrogen atoms on methanoates and nitrogen were refined freely, while the other hydrogen atoms were included in the model at geometrically calculated positions, and refined using a riding model. The figures were drawn using PLATON.[22] Details of the crystal data, data collection and refinement parameters are listed in Table 1. The selected bond lengths and angles are presented in Table 2. The crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center as supplementary material with the deposition numbers: CCDC 700959. Copies of the data can be obtained, free of charge *via* http://www.ccdc.cam.ac.uk/const/retrieving.html.

Physical Measurements

C,H,N analysis was performed with a Perkin-Elmer 2400 CHN Elemental Analyzer. Metal analysis was carried out electrogravimetrically with Pt electrodes. Vibrational spectrum of the solid sample was recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer, equipped with a Specac Golden Gate Diamond ATR as a sample support, using the reflectance technique (4000–600 cm^{-1}). Electronic spectrum was recorded as nujol mull with a Perkin-Elmer Lambda 19 UV/Vis/NIR spectrometer. X-band powder EPR spectra were recorded at two temperatures on a Bruker Elexsys E500 electron spin resonance spectrometer. The magnetic susceptibility data of powdered polycrystalline samples were measured with a Quantum Design SQUID MPMS-XL-5 magnetometer, equipped with a 5 T magnet. The data were investigated in the temperature interval 2–300 K in a magnetic field strength of $H = 1000$ Oe. The data were corrected for the experimentally determined contribution of the sample holder. Corrections for the diamagnetic response of the compound, due to closed atomic shells as estimated from the Pascal′s constants, were applied.[23] Powder XRD data were obtained with a PANalytical X′Pert PRO MPD diffractometer with CuK_α radiation.

Materials

All reagents were obtained commercially and were used without further purification.

Table 2. Selected bond lengths (in Å) and angles (in degrees) for **1**

Cu1···Cu1a	2.6398(5)	Cu1–O2	1.9676(17)	Cu1–O7	1.9781(15)
Cu1–O6	1.9549(16)	Cu1–O9	1.9840(17)	Cu1–O3	2.1531(15)
C12–O2a	1.245(3)	C11–O3	1.242(3)	C11–O5	1.243(3)
C12–O6	1.249(3)	C17–O7	1.253(3)	C17–O9a	1.244(3)
O6–Cu1–O2	168.24(7)	O6–Cu1–O7	89.46(8)	O2–Cu1–O7	89.27(7)
O6–Cu1–O9	89.79(8)	O2–Cu1–O9	89.16(7)	O7–Cu1–O9	168.67(7)
O6–Cu1–O3	96.90(7)	O7–Cu1–O3	98.81(6)	O2–Cu1–O3	94.85(7)
O9–Cu1–O3	92.51(7)				

H-bonding

D–H···A	D···A	D–H···A	D–H···A	D···A	D–H···A
N8–H1···O3$^{(a)}$	2.755(3)	160(3)	O4–H4···O5	2.489(2)	178

Symmetry operations: (a) 2–*x*, –½+*y*, ½–*z*

Bis(4-hydroxypyridinium) tetrakis(μ-methanoato-κO:$\kappa O'$) bis[(methanoato-κO)cuprate(II)] **1**: 4-hydroxypyridine (0.57 g, 6.0 mmol) was dissolved in a mixture of aceto-nitrile, methanol and methanoic acid (9/9/3 mL). $Cu_2(OH)_2CO_3$ was added to this solution (0.33 g, 1.5 mmol), and the mixture was heated and let boiling for 2 min. The resulting solution was cooled down to the room temperature and then left at 6 ºC for two days. The green crystalline product of **1** was filtered off and dried on air for half an hour. Average yield 70 %. *Anal.* Calcd for $C_{16}H_{18}Cu_2N_2O_{14}$: C 32.6, H 3.08, N 4.75, Cu 21.6 %. Found: C 33.2, H 3.14, N 4.89, Cu 21.2 %. IR ν_{max} 3100, 1629, 1613 $\nu_{as}(O_2C)$, 1505, 1417, 1389, 1374, 1349 $\nu_s(O_2C)$ cm^{-1}. UV/Vis λ_{max} 260, 380sh, 695 nm.

RESULTS AND DISCUSSION

Description of the Crystal Structure 1

A new ionic compound $(C_5H_6NO)_2[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]$ **1** was isolated from the acidified methanol/acetonitrile solution and is composed of a binuclear anionic *paddle-wheel* complex and two 4-hydroxypyridinium cations (Figure 1). The coordinated methanoato oxygen atoms occupy positions of a square-pyramid around the central copper(II) ion. All equatorial Cu–O bonds are within the range 1.9549(16)–1.9840(17) Å, while the axial ligand is as expected at a longer distance [Cu–O3 2.1531(15) Å]. The Cu–O bonds and Cu···Cu' *intra*-binuclear distances are within the expected range.[24] Though the axial methanoato ligands in **1** are not forming the *inter*-binuclear bridges (giving anionic complex moiety), both, the coordinated O3 and the non-coordinated O5 oxygen atoms are H-bonded with the 4-hydroxypyridinium cations, either to its nitrogen or oxygen atom [N8–H1···O3 2.755(3) Å, 160(3)°; O4–H4···O5 2.489(2) Å, 178°]. Due to these significantly strong H-bonds, only weak IR signals of ν(OH) and ν(NH) are found in the spectrum above 3000 cm^{-1}, the strongest among them at relatively low energy
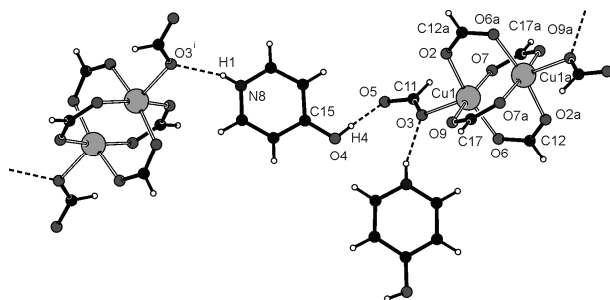
3100 cm^{-1}. The structure of **1** is additionally stabilized by the π-stacking of the cation pyridine rings that are almost co-planar (8.39°) [centroid···centroid distance 4.023(2) Å, mean *inter*-planar separation 3.769, 3.528 Å]. The anionic form of the *paddle-wheel* complex $[Cu_2(\mu\text{-}L1)_4(L2)_2]^{2-}$ is rarely found and is of two types, either with the carboxylato or the chlorido axial ligands $L2^-$.[12–17] Among them, only one example of the complex anion as in **1** is reported in $(C_3H_7N_2S)_2[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]$ $(C_3H_7N_2S^+$ = 2-amino-2-thiazolinium cation).[12] In this compound, similar stabilization *via* H-bonds is noticed as in **1**, practically giving pseudo-neutral molecules $\{(C_3H_7N_2S)_2[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]\}$. On the other hand, the ionic stabilization in **1** is extended to a 2D structure.

Magnetic and Spectroscopic Analysis

The molar magnetic susceptibility χ_M of the compound **1** gradually decreases upon lowering temperature from 300 to 100 K (Figure 2). This is characteristic for the antiferromagnetic (AFM) interaction of the *paddle-wheel* dicopper complexes. At temperatures below 90 K, χ_M increases, what can be attributed to small amounts of the mononuclear impurities (ρ) often found with Cu^{II} compounds of this type. Similar is found in the $\chi_M T$ versus T graph (inset in Figure 2) in the 90–300 K region. A constant, but very low $\chi_M T$ value below 90 K is in accordance with $S = 0$ ground state of this AFM coupled complex (no signal) and a small contribution of the paramagnetic species ($S = \frac{1}{2}$) in the sample. To estimate the magnitude of the AFM coupling 2J, the magnetic susceptibility data were fitted to the Bleaney-Bowers equation (Eq. (1)) for two interacting copper(II) ions using the Hamiltonian $H = -2J\, S_1 \cdot S_2$.[23] The least-squares fitting of the data leads to 2J = –500 cm^{-1}, g = 2.18 and ρ = 0.015. This is in agreement with the expected values for the methanoato bridging copper(II) *paddle-wheel* complexes.[18,19] The theoretical curve

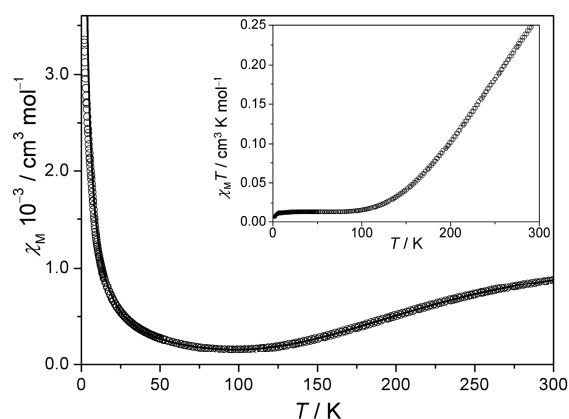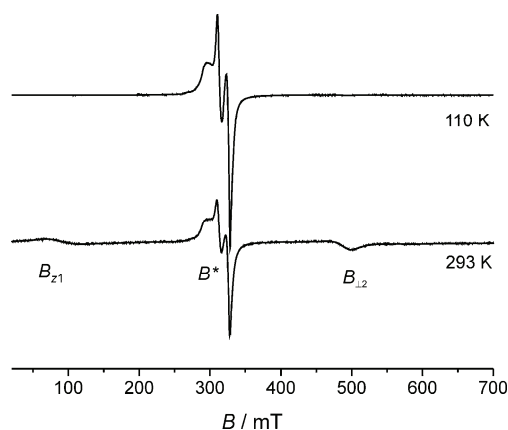

Figure 1. Dicopper(II) *paddle-wheel* complex anions and 4-hydroxypyridinium cations connected in the H-bonding network in $(C_5H_6NO)_2[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]$ **1**.

Figure 2. χ_M and $\chi_M \cdot T$ (inset) *vs.* T experimental (○) and fitted (solid line) curves for the compound **1**. Parameters are: 2J = –500 cm^{-1}, g = 2.18, ρ = 0.015.
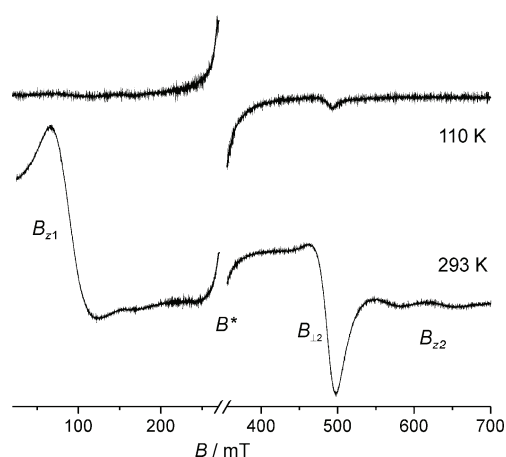
Figure 3. The EPR spectra of **1** at 293 K and 110 K.

using the above parameters is shown as a solid line in the Figure 2.

$$\chi_{\mathrm{M}} = \frac{2Ng^2\beta^2}{kT(3+e^{-2J/kT})}(1-\rho) + \frac{Ng^2\beta^2}{2kT}\rho \qquad (1)$$

The room temperature (293 K) X-band EPR spectrum of **1** shows signals typical for the $S = 1$ spin state of the dicopper(II) *paddle-wheel* complexes with the B_{z1} = 90.5 mT, $B_{\perp 2}$ = 487 mT and $B_{z2} \approx$ 600 mT (Figures 3, 4). Interestingly, two bands close to 600 mT appear (583, 656 mT), both in the B_{z2} expected region. The entire set of the $S = 1$ signals is of an unexpected low intensity and is accompanied by the dominant signal at 320 mT. This last signal remains in the 110 K spectrum of **1**, while the B_{z1}, $B_{\perp 2}$ and B_{z2} signals are hardly observed or can even not be seen in the low temperature spectrum (Figure 4). The origin of the 320 mT signal (B^*) is not clear-cut and two theories can be suggested. Either it is a result of rhombic mononuclear species of S = ½ spin state without a resolved hyper fine structure (a region, an impurity), or due to $S = 1$ spin system accompanying the others already mentioned (relative magnitude, only 1.5 % of mononuclear impurities suggested by the susceptibility data). The purity and stability of the compound was checked additionally by powder XRD data, and they do not differ from the results obtained upon the determined structure analysis of **1**.[25] Nevertheless, these results also can not exclude a presence of the non-crystalline decomposition products. Significantly higher magnitude of the antiferromagnetic interaction probably enables specific conditions revealing the observed EPR spectra, due to depopulation of the $S = 1$ state and $S = 0$ ground state filled already at temperatures above 100 K. On the other hand, the EPR observations may as well be related to the unusual anionic methanoato binuclear complex. Finally, the characteristic g and D values of **1** were not calculated due to not clear origin of the EPR signals. To engage at least some of the questions arose during this research, the

Figure 4. The EPR spectra of **1** as in Figure 3, but modified with a vertical direction stretching. By omission of the central spectral part to hide the H* signal (see Figure 3), the $S = 1$ signals are clearly seen in the high temperature spectrum, while they are poorly or not seen in the 110 K spectrum.

temperature dependant EPR spectra are planned to be recorded in the near future.

CONCLUSION

The anionic dicopper(II) *paddle-wheel* complex $[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]^{2-}$ forms with two 4 hydroxypyridinium cations a stable compound **1** in the acidic solution. A relatively rare anionic form of the copper(II) acetate hydrate type of compound $[Cu_2(\mu\text{-}L)_4L_2]^{2-}$ is obtained due to the non-bridging nature of the axial anionic ligands. The main role in a stabilization of this ionic compound is related to strong H-bonds between the axial anionic ligands and 4-hydroxypyridinium cations. A very strong antiferromagnetic coupling ($2J =$ 500 cm^{-1}) was determined by the susceptibility measurements, that is characteristic for this type of complexes in relation to the *intra*-binuclear bridging methanoato hydrogen atom. Such a magnitude of the magnetic interaction is closely related to the unusually low intensity of the $S = 1$ EPR signals B_{z1}, $B_{\perp 2}$ and B_{z2}, usually found for the room T spectra of the dicopper *paddle-wheel* complexes. Next to these signals, a much stronger signal is noticed at 320 mT that may be explained, either due to the mononuclear $S = $ ½ spin, or as an additional contribution of the binuclear $S = 1$ spin.

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SAŽETAK

Jak antiferomagnetizam u izoliranom anionskom dibakrovom(II) metanoato *paddle-wheel* kompleksu

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Sintetiziran je novi ionski spoj $(C_5H_6NO)_2[Cu_2(\mu\text{-}O_2CH)_4(O_2CH)_2]$, **1**, koji se sastoji od 4-hidroksipiridinij kationa i kompleksnog aniona. Anion je *paddle-wheel* (poput mlinskog kola) dibakrov(II) karboksilat sa četiri *sin,sin*-premošćujuća i dva aksijalna metanoato liganda. Određivanjem strukture rentgenskom difrakcijom **1** pokazalo se, da je molekulska struktura stabilizirana s dvjema H-vezama između kationa i aksijalnih *paddle-wheel* aniona (N–H···O 2,755(3), O–H···O 2,489(2) Å). Spoj pokazuje vrlo jaku ($2J$ = 500 cm^{-1}) *intra*-dinuklearnu antiferomagnetsku interakciju, primijećenu već kod sobne temperature, pripisanu metanoato *intra*-dinuklearnim mostovima. Tipični EPR S = 1 signali spinskog sustava dibakrovog *paddle-wheel* kompleksa pri 90 i 450–700 mT nađeni su u spektru pri sobnoj temperaturi, ali su slabo vidljivi u spektru pri 110 K. Ti signali su niskog intenziteta, popraćeni su prevladavajućim signalom pri 320 mT, i svi su usko povezani s vrlo jakom antiferomagnetskom interakcijom prisutnoj u **1**.