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研究简报

邻苯二甲酸单乙酯铜配合物的晶体结构与强反铁磁性

贾丽慧[1,2] 刘祖黎*[,1,3] 刘 蔚[1] 谷云飞[1] 姚凯伦[1]
([1]华中科技大学物理系,武汉 430074)
([2]武汉工程大学化工与制药学院,武汉 430074)
([3]南京大学配位化学国家重点实验室,南京 210093)

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Crystal Structure and Magnetic Property of a Strong Antiferromagnetic Copper(Ⅱ) Complex with Mono-ethyl Phthalate

JIA Li-Hui[1,2] LIU Zu-Li*[,1,3] LIU Wei[1] GU Yun-Fei[1] YAO Kai-Lun[1]
([1]*Department of Physics, Huazhong University of Science and Technology, Wuhan* 430074)
([2]*School of Chemical engineering and Pharmacy, Wuhan Institute of Chemical and Technology, Wuhan* 430074)
([3]*State Key Laboratory of Coordination Chemistry Institute, Nanjing University, Nanjing* 210093)

Abstract: A hydrated tetra-carboxylato-bridged dinuclear copper(Ⅱ) complex $[Cu_2(mEP)_2(H_2O)_2]_2$ (**1**) (mEp is mono-ethyl phthalate or 1,2-benzenedicarboxylate monoethyl ester) has been prepared and characterized by X-ray diffraction single crystal structure analysis and magnetic measurements. This dinuclear complex adopts dimeric paddle-wheel cage structure and the coordination model around each copper(Ⅱ) atom is square-pyramidal with four oxygen atoms of the carboxylate groups from four different mono-ethyl phthalate ligands and one oxygen atom of water as apical position. The magnetic data for **1** exhibited strong intramolecular antiferromagnetic interaction between the two paramagnetic metal ions with $2J=-315.18$ cm^{-1}. Comparing with other related complexes in structure and magnetic propertity, the main factor which determines the strong antiferromagnetic interaction in the dimeric copper(Ⅱ) carboxylates is the electronic structure of the bridging O-C-O moiety. CCDC: 624561.

Key words: mono-ethyl phthalate; tetra-carboxylato-bridged dinuclear copper(Ⅱ); strong antiferromagnetic interaction; magnetostructural correlation

Copper (Ⅱ) carboxylates have been extensively studied from different points of view because the carboxylato anions exhibit different bonding models influencing their properties. Especially binuclear copper(Ⅱ) carboxylates are useful models to design and study the magnetic-exchange interactions and most of them are also biologically active substances, metal-ion-drugs, and models for protein-metal binding sites[1~6]. Recently, phthalate monoesters as the derivative of phthalic acid monoethylation has been frequently investigated in analytical science , environment science and biological science mainly because it is present in our environment and in human body as a bioactive phthalate metabolite[7~10]. So far very little has been pub-

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*通讯联系人。E-mail:jialihui715@gmail.com;zlliu@mail.hust.edu.cn
第一作者:贾丽慧,女,36 岁,副教授,研究方向:分子基磁性材料的设计合成及磁性研究。

lished that describes the transition metal coordination complexes of phthalate monoesters. In this work, we report the synthesis, crystal structure and magnetic property of a binuclear copper(Ⅱ) complex with monoethyl phthalate ligand. To our knowledge, it is the first transition metal coordination complex of phthalate monoesters. Obviously the study is very important to investigate the metabolism of bioactive phthalate monoesters in biosystem.

1 Experimental

1.1 Material required and instrumentation

All chemicals were reagent grade and were used as commercially obtained. Elemental analyses were performed with a Vario EL Ⅲ CHNOS Elemental Analyzer. IR spectra were recorded on a Perkin-Elmer System FTIR 2000 spectrophotometer in the form of KBr pellets. The magnetic measurement was carried out on a polycrystalline sample with a Quantum Design MPMS-7 SQUID magnetometer in a field of 1T Diamagnetic corretions were made with Pascal′ s constants for all constituent atoms.

1.2 Synthesis of the compound $[Cu_2(mEP)_2(H_2O)_2]_2$ (1)

An ethanolic solution (20 mL) of *o*-phthalic acid (1 mmol) was mixed with copper chloride dihydrate (1 mmol) and an ethanolic solution (10 mL) of sodium dicyanamide (1.33 mmol) with continuous stirring. The reaction mixture was allowed to crystallize at room temperature for three weeks to yield dark blue quadrate crystal suitable for X-ray diffraction. Elemental analysis calculated for $C_{40}H_{40}Cu_2O_{18}$ (%): C, 51.29; H, 4.27. found: C, 51.36; H, 4.31. IR (KBr): 598.00, 782.54, 1 316.39, 1 403.67, 1 560.72, 3 069.60, 3 379.75 cm^{-1}.

1.3 Crystal structure determination

A single crystal with dimensions of 0.10 mm × 0.10 mm × 0.04 mm was selected and mounted on a Bruker SMART CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 07 nm) for the data collection. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXS-97 and SHELXL-97 programs [11,12]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added theoretically and refined with riding model and fixed isotropic thermal parameters. Detailed data collection and refinement of the complex are summarized in Table 1, and the selected bond distances and angles are listed in Table2.

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Table 1 Crystallographic data for complex 1

Empirical formula	$C_{40}H_{40}Cu_2O_{18}$	D_{calc} / ($Mg\cdot m^{-3}$)	1.542
Formula weight	935.8	Absorption coefficient / mm^{-1}	1.134
Temperature / K	292(2)	F(000)	482
Crystal system	Triclinic	θ range/ (°)	2.28~26.00
Space group	$P\bar{1}$	Index ranges	$-12 \leqslant h \leqslant 10, -13 \leqslant k \leqslant 13, -12 \leqslant l \leqslant 13$
a / nm	0.106 1(5)	Reflections collected	4 377
b / nm	0.106 2(5)	Independent reflections (R_{int})	3 281 (0.125 8)
c / nm	0.108 8(6)	Refinement method	Full-matrix least-squares on F^2
α / (°)	71.6(5)	Data / restraints / parameters	3 281 / 0 / 274
β / (°)	88.90(6)	Goodness-of-fit on F^2	0.939
γ / (°)	61.30(3)	Final R indices [$I>2\sigma(I)$]	R_1=0.105 7, wR_2=0.242 0
Volume / nm^3	1.008(9)	R indices (all data)	R_1=0.217 0, wR_2=0.294 6
Z	1	Largest diff. peak and hole / ($e\cdot nm^{-3}$)	1 096 and −1 054

[a] $R=\sum||F_o|^2-|F_c|^2|/\sum|F_o|^2$; [b] $wR=\{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2 Selected bond lengths (nm) and bond angles (°) for complex 1

Cu(1)-O(3)	0.192 1(15)	Cu(1)-O(4)#1	0.192 2(18)	Cu(1)-O(5)	0.194 9(15)
Cu(1)-O(9)	0.196 3(14)	Cu(1)-O(8)	0.210 6(13)	Cu(1)-Cu(1)#1	0.264 7(13)
O(3)-Cu(1)-O(4)#1	90.00(7)	O(3)-Cu(1)-O(5)	87.10(7)	O(4)#1-Cu(1)-O(5)	168.1(4)

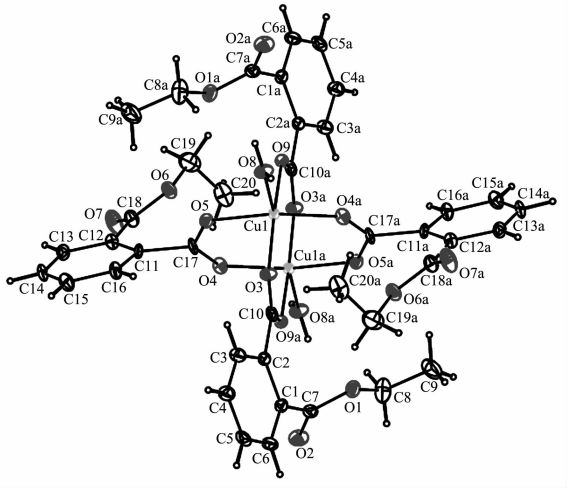
Continued Table 2

O(3)-Cu(1)-O(9)	167.7(4)	O(4)#1-Cu(1)-O(9)	89.10(6)	O(5)-Cu(1)-O(9)	91.30(6)
O(3)-Cu(1)-O(8)	95.10(5)	O(4)#1-Cu(1)-O(8)	94.50(7)	O(5)-Cu(1)-O(8)	97.20(7)
O(9)-Cu(1)-O(8)	97.20(6)	O(3)-Cu(1)-Cu(1)#1	83.70(5)	O(4)#1-Cu(1)-Cu(1)#1	84.20(7)
O(5)-Cu(1)-Cu(1)#1	84.10(7)	O(9)-Cu(1)-Cu(1)#1	84.00(5)	O(8)-Cu(1)-Cu(1)#1	178.2(3)
Cu(1)-O(8)-H(8D)	121.4	Cu(1)-O(8)-H(8E)	127.7	H(8D)-O(8)-H(8E)	110.6
C(10)#1-O(9)-Cu(1)	121.4(9)	O(3)-C(10)-O(9)#1	126.2(15)	O(3)-C(10)-C(2)	118.4(15)
O(9)#1-C(10)-C(2)	115.4(13)	O(2)-C(7)-O(1)	124.3(18)	O(4)-C(17)-O(5)	125.5(11)

2　Results and discussion

2.1　Crystal structure

The crystal structure of complex **1** is showen in Fig.1. Each Cu(Ⅱ) atoms is pentacoordinated with one oxygen atom of the coordinated water molecular assuming apical position and with four oxygen atoms of four different mono-methyl phthalate anions assuming the basal positions in tetragonal pyramidal arrangement. A dimmer results from the fact that the carboxyl groups of the four mono-ethyl phthalate anions function as bridging groups in a syn-syn arrangement, the other four oxygen atoms of them forming the base of the second tetragonal pyramid. Obviously the dimeric paddle-wheel cage structural units in previous reports appeared in this case[3,13~18].



mEp is mono-ethyl phthalate

Fig.1　Molecular structure of the complex $[Cu_2(mEP)_2(H_2O)_2]_2$ (**1**)

The mean length of the Cu-O (carbox) bond in **1**, 0.193 9 nm, shorter than the corresponding length in reported complexes[16~19]. The Cu-O (H_2O) bond distance, 0.210 6 nm, is also much shorter. According to the trend reported in the literature [20~21], a lengthening of the Cu-Cu distance is accompanied by a shortening of the Cu-O(H_2O) bond and also the Cu-Cu-O (carbon) angles are well correlated with the M-M distances. This case is just observed in the title complex. The result above is seen from the comparison in Table 3. As seen above, the values of mean bond parameters are similar among various dinuclear copper (Ⅱ) carboxylate complexes, except small variations resulting from bonding ability, steric requirements of different carboxylates and packing factors. Comparing to *o*-phthalic acid, phthalate monoesters seem easier to form dinuclear carboxyl-bridged copper complexes due to the steric effect of esterified carboxyl substituents.

Table 3　Comparison of the main mean distances (nm) and angles (°) and magnetic data for Copper(Ⅱ) dimeric carboxylates

compd	Cu-Cu	Cu-O^- (carbox)	Cu-O^- (H_2O)	Cu-Cu-O^- (carbox)$^-$	φ bend / (°)	$-2J$ / cm^{-1}	ref.
1	0.261 4(2)	0.196 9	0.216 1(2)	84.4		300	[16]
2	0.620(1)	0.196 8	0.213 1(4)	84.3	12.0	250	[18]
3	0.262 4(7)	0.199	0.217(2)	84.3	7.3	280	[19]
4	0.264 7(5)	0.193 9	0.210 6(13)	84.0	1.66	315	this work

1: $[Cu(CH_3COO)_2(H_2O)]_2$; 2: $[Cu(2,6\text{-}MeO_2C_6H_3COO)_2(H_2O)]_2$; 3: $[Cu(2\text{-}Br\text{-}C_6H_4COO)_2(H_2O)]_2$;
4: $[Cu_2(mEP)_2(H_2O)_2]_2 \cdot 2H_2O$ (**1**) (mEp is mono-ethyl phthalate).

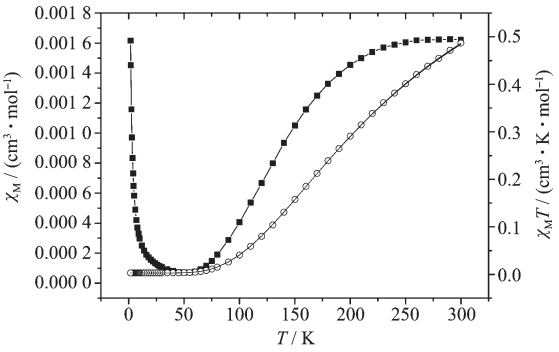
2.2　Magnetic property study

The magnetic behavior of **1** was investigated using a superconducting quantum interference device (SQUID) detector in the temperature range 2 ~300 K

within an applied magnetic field of 2 000 Oe. The variation of the reciprocal of $\chi_M T$ and χ_M vs T is presented in Fig.2. The room-temperature value of $\chi_M T$ is equal to 0.486 8 emu·K·mol^{-1}, while it drops down to 0.002 9 emu·K·mol^{-1} at temperatures below 4 K. The value of $\chi_M T$ keeps decrease steadily on lowering the temperature which indicates existence of strong antiferromagnetic couplings between the copper(Ⅱ) centers. The magnetic susceptibility data were best fitted to the modified Bleaney-Bowers equation for S=1/2 dimers under a $-2JS_1S_2$ spin Hamiltonian[22]:

$$\chi_M=\frac{2Ng^2\beta^2}{kT}\cdot\frac{1}{3+e^{-2J/kT}}\cdot(1-\rho)+\rho\cdot\frac{Ng^2\beta^2}{2kT}$$

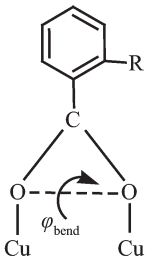
where ρ is the percent of monomeric impurity and other symbols have their usual meanings. The best fitting parameters obtained from this simulation are g=2.209, $-2J$=315 cm^{-1}, ρ=0.32% with the agreement factor $R=\sum[(\chi_M)_{obs}-(\chi_M)_{calc}]^2/\sum[(\chi_M)_{obs}]^2=3.036\times10^{-11}$.



Solid line represents the best fit to the modified Bleaney-Bowers expression

Fig.2 Plot of χ_M (left scale) and $\chi_M T$ (right scal) vs temperature T for the title complex

Comparing with other related complexes in structure and magnetic propertity, the main factor which determines the strong antiferromagnetic interaction in the dimeric copper(Ⅱ) carboxylates is the electronic structure of the bridging O-C-O moiety. This electronic structure of the bridging O-C-O moiety is reflected through the bending angle of the O-C-O moiety relative to the Cu–O⋯O–Cu plane, φ_{bend}. As illustrated in Scheme 1, the unpaired electrons in the $d_{x^2-y^2}$ orbital of the Cu Ⅱ cations interact with each other through the molecular orbitals of the bridging ligands. The spin superexchange interaction of the binuclear Cu Ⅱ complex can be understood in terms of the natural (non-orthogonalized) magnetic orbitals[23~25]. The natural magnetic orbital (NMO) of the Cu atom in the cage structure is mainly the $d_{x^2-y^2}$ orbital and has tails on the bridges. The spin superexchange interaction increases along with the overlap integral of two non-orthogonalized $d_{x^2-y^2}$ orbitals of the Cu Ⅱ atoms. When the Cu-O-C-O-Cu bridge bends, the overlap between the $d_{x^2-y^2}$ orbital of the Cu Ⅱ cations and the $2p_x$ orbital of the benzoate oxygen atoms in the symmetric HOMO decreases and the tails of the tails of the NMO on the bridge decrease. Consequently, the spin super-exchange interaction is suppressed by the smaller overlap of the NMO′s in the bent bridges (φ_{bend}) compared with that in the coplanar bridges.



Scheme 1 Electronic structure of the bridging O-C-O moiety

In the title complex the bending angle of the bridge is 1.66(2)°,smaller than those of [Cu(2,6-MeO_2-$C_6H_3COO)_2(H_2O)]_2$ (12.0(2)°) and [Cu(2-Br-$C_6H_4COO)_2$ $(H_2O)]_2$ (7.3(2)°). Thus the value of $-2J$ is higher in the title complex. This indicates that the overlap between the $d_{x^2-y^2}$ orbitals of the Cu Ⅱ atoms decrease with an opening the bending angle of Cu-O-C-O-Cu and the spin super-exchange interaction is suppressed. Finally, Our result show that the higher magnitude of magnetic coupling |2J| is more sensitive to the electronic structure of the bridging O-C-O moiety comparing to other related complexes(see Table 3).

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