

三氮唑配合物 $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{C}_4\text{H}_8\text{N}_4)_2] \cdot 2\text{CH}_3\text{CN}$ 的合成及晶体结构

刘家成 庄金钟* 游效曾

(南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)

$\text{Cu}(\text{CH}_3\text{COO})_2$ 和 4-氨基-3, 5-二甲基-1, 2, 4-三氮唑反应制得标题化合物的单晶 $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{C}_4\text{H}_8\text{N}_4)_2] \cdot 2\text{CH}_3\text{CN}$ 。晶体属三斜晶系, 空间群, $a = 8.266(2)$, $b = 8.585(2)$, $c = 10.741(2)$ Å $\alpha = 75.58(3)$, $\beta = 88.46(3)$, $\gamma = 86.35(3)^\circ$, $V = 736.7(3)$ Å³, $Z = 1$, $D_c = 1.509 \text{ g} \cdot \text{cm}^{-3}$, $F(000) = 346$, $\mu = 1.502 \text{ mm}^{-1}$ 。X-射线衍射结构分析表明, $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{C}_4\text{H}_8\text{N}_4)_2$ 单元是中心对称的双核配合物, 两个铜原子间距为 2.698 Å。每个金属原子被围成四方锥的配位结构, 四个乙酸根配体中最近的四个氧原子处在底面上 [$\text{Cu}-\text{O} = 1.965(3) \sim 1.986(3)$ Å], 一个 4-氨基-3, 5-二甲基-1, 2, 4-三氮唑配体位于顶点位置 $\text{Cu}-\text{N} = 2.172$ Å。

关键词: 双核铜配合物 4-氨基-3, 5-二甲基-1, 2, 4-三氮唑 乙酸桥 晶体结构
分类号: O614.121 O626.26

Synthesis and Crystal Structure of a Triazole Complex $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{C}_4\text{H}_8\text{N}_4)_2] \cdot 2\text{CH}_3\text{CN}$

LIU JiaCheng ZHUANG JinZhong* YOU XiaoZeng

(Coordination Chemistry Institute and State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093)

Single crystals of the new title compound $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{C}_4\text{H}_8\text{N}_4)_2] \cdot 2\text{CH}_3\text{CN}$ are obtained from the reaction of $\text{Cu}(\text{CH}_3\text{COO})_2$ and 4-aminor-3, 5-dimethyl-1, 2, 4-triazole. It crystallizes in the triclinic space group $P1$, with $a = 8.266(2)$, $b = 8.585(2)$, $c = 10.741(2)$ Å $\alpha = 75.58(3)$, $\beta = 88.46(3)$, $\gamma = 86.35(3)^\circ$, $V = 736.7(3)$ Å³, $Z = 1$, $D_c = 1.509 \text{ g} \cdot \text{cm}^{-3}$, $F(000) = 346$, $\mu = 1.502 \text{ mm}^{-1}$. X-ray crystal structure analysis revealed that $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{C}_4\text{H}_8\text{N}_4)_2$ unit is a crystallographically centrosymmetric binuclear complex, with Cu atoms distance $\text{Cu}(1)-\text{Cu}(1A)$ of 2.698 Å. Each metal atom is coordinated in a square pyramidal environment by four nearest oxygen atoms from four acetate ligands [$\text{Cu}-\text{O} = 1.965(3) \sim 1.986(3)$ Å] on the basal plane, and one 4-aminor-3, 5-dimethyl-1, 2, 4-triazole ligand at the apical position with $\text{Cu}-\text{N} = 2.172$ Å。

收稿日期: 1999-03-08。收修改稿日期: 1999-04-02。

国家自然科学基金资助项目(NO. 29631040)。

* 通讯联系人。

第一作者: 刘家成, 男, 36岁, 理学博士; 研究方向: 多核配合物的合成与结构。

Keywords: dicopper complex 4-amino-3,5-dimethyl-1,2,4-triazole acetato bridges
crystal structure

0 Introduction

Coordination compound with 1,2,4-triazole (Rtrz) as a ligand have interesting features, not only because of the different modes of coordination, but also because of very interesting magnetic properties. The triazole rings substituted on the 4-position act as monodentate and 1,2-bridging modes. For the copper(II) complex containing triple N1,N2-1,2,4-triazole bridges or second small bridging anions, the linear trinuclear compound $[\text{Cu}_3(\text{metrz})_6(\text{H}_2\text{O})_4](\text{CF}_3\text{SO}_3)_6(\text{H}_2\text{O})_4$ (metrz = 3-methyl-4-ethyl-1,2,4-triazole)^[11], and $[\text{Cu}_3(\text{H}_2\text{ahmt})_6\text{Cl}_4]\text{Cl}_2$ (H₂ahmt = 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole)^[12], the linear chain compound $[\text{Cu}(\text{hyetrz})_3](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (hyetrz = 4-(2-hydroxyethyl)-1,2,4-triazole)^[13], and $[\text{Cu}(4\text{-H-1,2,4-triazole})\text{Cl}]_\infty$ ^[14] have been structurally characterized. Recently, in the course of our study of metal complexes containing 4-amino-3,5-dimethyl-1,2,4-triazole (abbreviated admtrz) and anions as bridging ligands, we isolated the title complex $[\text{Cu}(\text{admtrz})(\text{CH}_3\text{COO})_2]_2 \cdot 2\text{CH}_3\text{CN}$ and report here its preparation and structure.

1 Experimental

1.1 Synthesis

To admtrz (90 mg, 0.8 mmol) dissolved in absolute ethanol (10 mL) was added $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ (80 mg, 0.4 mmol) in ethanol (25 mL) with stirring overnight at room temperature. The light green precipitate was collected by filtration, washed with ethanol and ether, and dried in vacuo over P_4O_{10} . Crystals of the title compound were obtained by very slow cooling the hot saturated anhydrous acetonitrile solution of above product for several days, which are very unstable and sensitive to moisture. Yield: 90% anal. calcd. for $\text{C}_{20}\text{H}_{34}\text{Cu}_2\text{N}_{10}\text{O}_8$. C, 35.87; H, 5.12; N, 20.92%. Found: C, 35.68; H, 5.31; N, 20.80%.

1.2 Crystallographic Data Collection and Structure Determination

A light blue crystal with dimensions 0.59 mm × 0.59 mm × 0.18 mm of the title compound was selected and sealed in a Lindeman capillary containing the mother liquor. Intensity data were collected at 293(2) K on an Enraf-Nonius CAD-4 diffractometer operating in the ω -2 θ scan mode with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation, reflections up to $2\theta = 50^\circ$ were measured. Of the 2836 reflections measured, 2581 unique reflections were used for structure refinements. Index ranges $h = -9 \rightarrow 9$, $k = 0 \rightarrow 10$, $l = -11 \rightarrow 12$.

The structure was solved by direct method and refined on F^2 by full-matrix least-square methods using SHELXTL 5.0^[51]. All the non-hydrogen atoms were refined anisotropically. H atoms were placed in their calculated position (C-H, 0.96 and N-H, 0.90 Å) assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure factors calculations. All computations were carried out on a PC-586 computer.

using the SHELXTL-PC^[15] Program Package. The final $R_1 = 0.0395$, $wR_2 = 0.1071$ [$I > 2\sigma(I)$], $w = 1 / [\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2) / 3$, and $S = 1.056$. In the final difference map, residual densities $\Delta\rho$ are 0.931 and $-0.319\text{ e} \cdot \text{\AA}^{-3}$, respectively. The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1, selected bond distances and angles in Table 2.

Table 1 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters($\text{\AA}^2 \times 10^3$) for [Cu₂(CH₃COO)₄(C₆H₈N₄)₂] · 2CH₃CN

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Cu(1)	5197(1)	5447(1)	8712(1)	49(1)	C(2)	7102(6)	607(5)	10098(5)	69(1)
O(1)	6167(5)	3217(4)	9016(3)	70(1)	C(3)	7711(4)	6114(4)	10268(4)	53(1)
O(2)	5886(4)	2503(4)	11135(3)	68(1)	C(4)	9291(5)	6802(6)	10445(5)	68(1)
O(3)	7275(4)	6188(4)	9142(3)	64(1)	C(5)	8048(5)	4341(6)	6363(5)	65(1)
O(4)	6946(4)	5486(5)	11253(3)	69(1)	C(6)	6739(5)	5592(5)	5951(4)	53(1)
N(1)	5574(7)	6042(4)	6642(3)	56(1)	C(7)	5288(5)	7550(5)	4705(4)	60(1)
N(2)	4630(5)	7306(5)	5863(4)	64(1)	C(8)	4734(7)	8806(7)	3557(5)	79(1)
N(3)	6580(4)	6505(4)	4717(3)	55(1)	C(9)	9527(8)	709(7)	13204(7)	93(2)
N(4)	7657(5)	6337(5)	3720(4)	69(1)	C(10)	9542(10)	2363(8)	13252(7)	104(2)
C(1)	6339(4)	2239(5)	10089(4)	56(1)	N(5)	9534(10)	-580(7)	13073(8)	137(3)

*U*_{eq} is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 2 Selected Bond Distances and Angles in Cu₂(CH₃COO)₄(C₆H₈N₄)₂] · 2CH₃CN

bond	distance/ \AA	bond	distance/ \AA	bond	distance/ \AA
Cu(1) – O(1)	1.981(3)	Cu(1) – O(3)	1.976(3)	Cu(1) – O(2A)	1.965(3)
Cu(1) – O(4A)	1.986(3)	Cu(1) – N(1)	2.172(4)	N(1) – N(2)	1.401(5)
C(1) – O(1)	1.251(5)	C(3) – O(3)	1.257(5)	C(1) – O(2)	1.243(5)
C(3) – O(4)	1.238(5)	C(1) – C(2)	1.498(5)	C(3) – C(4)	1.503(6)
angle	($^\circ$)	angle	($^\circ$)	angle	($^\circ$)
O(1) – Cu(1) – O(2A)	165.9(2)	O(3) – Cu(1) – O(4A)	165.8(2)	N(1) – Cu(1) – O(1)	95.5(1)
N(1) – Cu(1) – O(2A)	98.6(2)	N(1) – Cu(1) – O(3)	96.6(1)	N(1) – Cu(1) – O(4A)	87.1(2)
O(1) – Cu(1) – O(3)	90.1(2)	O(1) – Cu(1) – O(4A)	87.1(2)	O(3) – Cu(1) – O(2A)	89.4(2)
O(2A) – Cu(1) – O(4A)	89.9(2)	Cu(1) – N(1) – N(2)	119.5(3)	Cu(1) – N(1) – C(6)	130.5(3)
Cu(1) – O(1) – C(1)	125.7(3)	Cu(1) – O(3) – C(3)	124.1(3)	O(1) – C(1) – O(2)	125.2(4)
O(3) – C(3) – O(4)	124.7(4)				

2 Results and discussion

The structure of the [Cu(admtrz) (CH₃COO)₂]₂ unit of the title compound (Fig. 1) is quite similar to that of [Cu(CH₂ClCO₂)₂ (2-M epy)]₂^[61], and [Cu₂(C₆H₅COO)₄(DENA)₂]^[71] (DENA = N, N-Diethylnicotinamide). The dimeric complex, [Cu(admtrz) (CH₃COO)₂]₂ has a center of symmetry and two Cu^{II} atoms surrounded by four acetate groups and two admtrz ligands. The admtrz ligands are coordinated to Cu atoms through the triazole N atoms in monodentate way. The acetate groups act as bridging ligands. This is a rare example of a polycopper(II) complex with triazole ligands only in monodentate rather than 1, 2-bridging forms coordination. The Cu(1) ... Cu(1A) distance [2.6978(11) Å] is longer than those found in the complexes [Cu₂(CH₃COO)₄(H₂O)₂]^[81] (2.64 Å) and [Cu₂(CH₃COO)₄(py)₂]^[191] (2.63 Å). The bridging network forms two planes P1 [Cu(1), O(1), C(1), O(2), Cu(1A), O(1A), C(1A) and O(2A)] and P2 [Cu(1), O(3), C(3), O(4), Cu(1A), O(3A), C(3A) and O(4A)], the dihedral angle being 90.9°.

Each copper(II) is bound to four oxygen atoms lying in a plane with 1.976(8) Å of average Cu-O bond length and 89.1(4)° of average O-Cu-O bond angle. A square-pyramidal coordination environment around each Cu atom is completed by the N atom of a admtrz ligand at 2.172(4) Å from Cu atom. The copper atom is 0.24 Å out of the basal plane towards the coordinating nitrogen atom of the triazole ring. The plane through all non-hydrogen atoms of admtrz forms 81.7° dihedral angle with the basal plane.

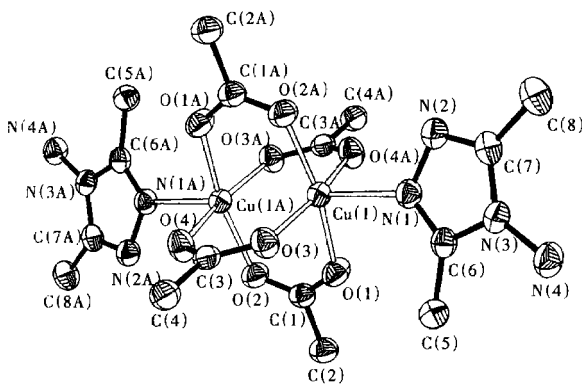


Fig. 1 Crystal structure of $[\text{Cu}(\text{admtrz})(\text{CH}_3\text{COO})_2]_2$

References

- [1] Vreugdenhil W., Haasnoot J. G., Reedijk J., Wood J. S. *Inorg. Chim. Acta*, **1990**, 167, 109.
- [2] van Koningsbruggen P. J., van Hal J. W., de Graaff R. A. G., Haasnoot J. G., Reedijk J. *J. Chem. Soc., Dalton Trans.*, **1993**, 2163.
- [3] Garcia Y., van Koningsbruggen P. J., Braric G., Guionneau P., Chasseau D., Cascrano G. L., Moscovici J., Lambert K., Michalowicz A., Kahn O. *Inorg. Chem.*, **1997**, **36**, 6357.
- [4] Jarvis J. A. *Acta Crystallogr.*, **1962**, **15**, 964.
- [5] Siemens, *SHELXTL (Version 5.0)*, Siemens Industrial Automation, Inc, Analytical Instrumentation, USA, 1995.
- [6] Davey G., Stephens F. S. *J. Chem. Soc A*, **1970**, 2803.
- [7] Hökelek T. *Acta Cryst.*, **1995**, **C51**, 2020.
- [8] van Niekerk J. N., Schoening F. R. L. *Acta Cryst.* **1953**, **6**, 227.
- [9] Barclay G. A., Kennard C. H. L. *J. C. S.* **1961**, 5244.