

含农药配体的铜配合物的合成与介电性质

钱 坤 金杨波 李永绣*

(南昌大学稀土与微纳功能材料研究中心, 南昌 330047)

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Synthesis and Dielectric Properties of Copper(II) Coordination Compound with Organic Pesticide as Ligand

QIAN Kun JIN Yang-Bo LI Yong-Xiu*

(Research Center for Rare Earth & Micro/Nano Functional Materials, Nanchang University, Nanchang 330047)

Abstract: The hydrothermal treatment of 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol (CDTO) with $\text{Cu}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in the presence of methanol as solvent offers a molecular coordination compound $[\text{Cu}(\text{CDTO})_2(\text{OAc})_2]$ (**1**), whose dielectric physical properties has been investigated. Crystal data for **1**: Triclinic, $P\bar{1}$, $a=0.859\ 06(10)$ nm, $b=1.053\ 11(13)$ nm, $c=1.202\ 96(14)$ nm. $\alpha=111.540(2)^\circ$, $\beta=108.899(2)^\circ$, $\gamma=196.249(3)^\circ$. $V=0.925\ 09(19)$ nm³, $Z=1$, 3 579 unique data ($\theta_{\text{max}}=25.99^\circ$), $R=0.053\ 9$ (2 888 [$I \geq 2\sigma(I)$] reflections), $wR=0.154\ 1$ (all data), $\rho_{\text{max}}=0.55\ \text{e} \cdot \text{nm}^{-3}$. CCDC: 605591.

Key words: pesticide; crystal structure; dielectric permittivity; copper

During last three decades, much attention has been focused on the discovery, research and development of the dielectric properties of ceramics. And as a result, devices such as cell phone are now so common that many consumers are forgoing the hard-wired versions altogether. However, the discovery of unique ceramic materials that could be used as dielectric resonators and filters to store and transfer microwave communication signals is critical. Meanwhile, one has tried to find different dielectric material to apply in the corresponding fields. For example, the material with high dielectric constant and low dielectric loss were used in capacitance devices^[1], the compounds displaying high dielectric loss can be used in heating

resonator^[2], and the most interesting thing is that the ceramics with ultralow dielectric constant have found usage in the fabrication of high performance integrated circuits^[3,4]. To this end, the investigation about the dielectric properties of coordination compounds with organic ligands has been appeared more recently^[5]. Herein, we would like to report the synthesis and dielectric properties of the copper molecular coordination compound with a pesticide ligand.

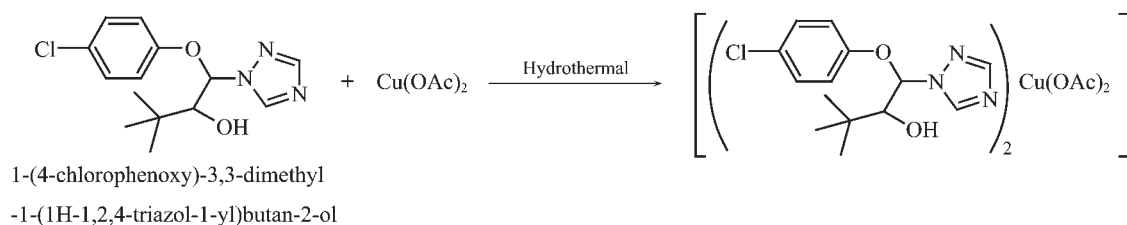
The organic ligand, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)butan-2-ol(CDTO), as a commercial product, was mixed together with $\text{Cu}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, and methanol at 70 °C under solvothermal conditions (Scheme 1). After several days, the reaction

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*通讯联系人。E-mail: yxli@ncu.edu.cn

第一作者: 钱 坤, 男, 25岁, 硕士; 研究方向: 配位化学, 稀土化学和材料。



Scheme 1

offered some blue block crystals $[\text{Cu}(\text{CDTO})_2(\text{OAc})_2]$ (**1**) with a yield of ca. 30.5% based on CDTO.

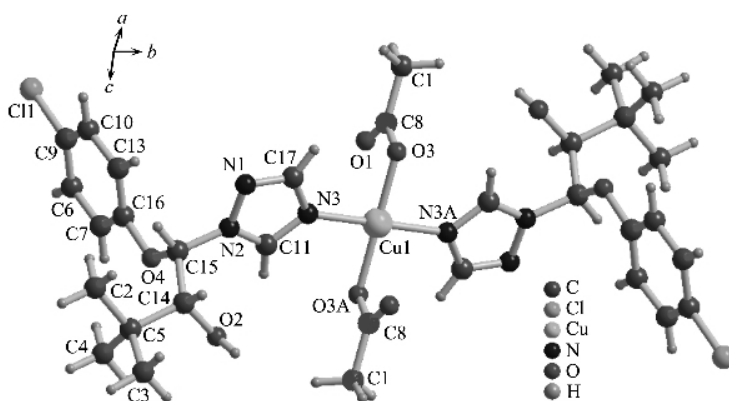
The IR spectrum of compound **1** shows two very strong peaks at 1579 and 1490 cm^{-1} (s), suggesting the presence of carboxylic acid group. In addition, a strong peak at 3415 cm^{-1} indicates there may be hydroxy group in **1**.

X-ray single crystal structure determination clearly reveals that the center atom Cu in compound **1** displays an approximately square plane coordination geometry in which acetate group and CDTO as monodentate ligands coordinate to the metal centers. However, another oxygen atom of carboxylate group and other two nitrogen atoms of triazole ring of CDTO fail to connect with other copper(II) center which results in the formation of discrete structure (Fig.1). Five atoms that involve four coordinated atoms (O3, O3A, N3 and N3A) and a metal center are almost in one plane. O3, O3A and Cu1 or N3, N3A and Cu1

are nearly in the same line and perpendicular to each other, that is the coordination mode of this compound defined as “*trans*”. The distances of Cu-N (0.199 3(3) nm) are shorter than those found in *trans*-bis(acetoxy)-N-(4-pyridyl)benzamidyl-copper(II)^[6] and bis(acetato-O)-bis (4-aminopyridine)-copper(II)^[7]. While the length of Cu-O (0.194 1 nm) bonds are comparable to those of two coordination compounds mentioned above. Finally, the distances of C-C, C-N, C-O and C-Cl are normal.

On the other hand, the hydroxyl groups of CDTO ligands and another uncoordinated oxygen atoms of acetate group come into being classic hydrogen bonds between two neighbouring molecules, and result in the formation of 1D chain as shown in Fig.2. At the same time, all of these chains packing together lead to the formation of 3D structure through the strong π - π stacking interactions.

The measurement of dielectric permittivity is



The coordination geometry of copper center can be best described as quadrilateral plane

Selected bond lengths (nm) and angles ($^\circ$):

Cu(1)-O(3) 0.194 1(2); Cu(1)-O(3)#1 0.194 1(2); Cu(1)-N(3)#1 0.199 3(3); Cu(1)-N(3) 0.199 3(3);
O(3)-Cu(1)-O(3)#1 180.000(1); O(3)-Cu(1)-N(3)#1 89.05(10); O(3)#1-Cu(1)-N(3)#1 90.95(10); O(3)-Cu(1)-N(3) 90.95(10);
O(3)#1-Cu(1)-N(3) 89.05(10); N(3)#1-Cu(1)-N(3) 180.000(1)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+2, -z+1$

Fig.1 Molecular structure of compound **1**

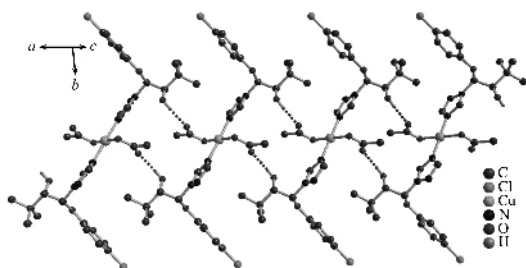


Fig.2 One dimensional chain view of compound **1** for the interaction of hydrogen bonds

conducted using automatic impedance HP4191A Analyzer with frequency of 100 Hz to 1 MHz. However, the relaxation process does not occur during the measurement of dielectric permittivity of this compound. The frequency dependence of the dielectric constant and dielectric loss of compound **1** at different temperature are depicted in Fig.4(a). It is easy to find that the dielectrics constant and dielectric loss almost have no changes with increasing frequency at 90.3 K, and the dielectric constant reaches the saturation at *ca.* 32 that is larger than those of normal organic compounds. Interestingly, the real part of permittivity decreases

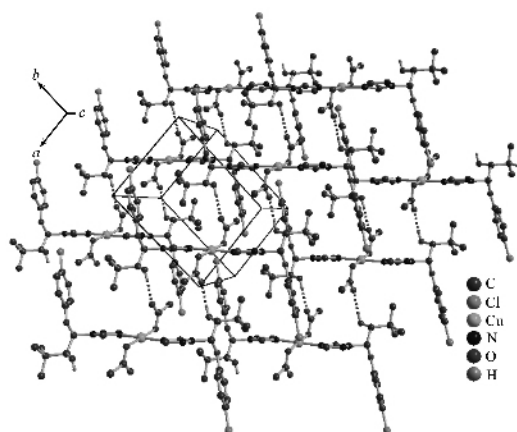
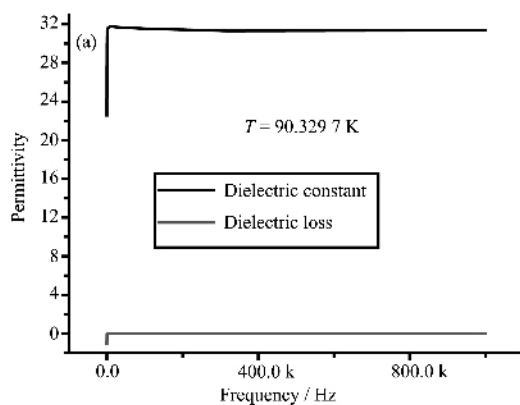


Fig.3 Packing view of coordination compound **1**

sharply at lowest frequency, and maintains 46.6 at 286.9 K as shown in Fig.4(b). Meanwhile, the dielectric loss remains basically unchanged with increasing frequency.

We have synthesized and characterized a new copper coordination compound with organic pesticide as ligand, and its dielectric property displays relatively high dielectric constant.

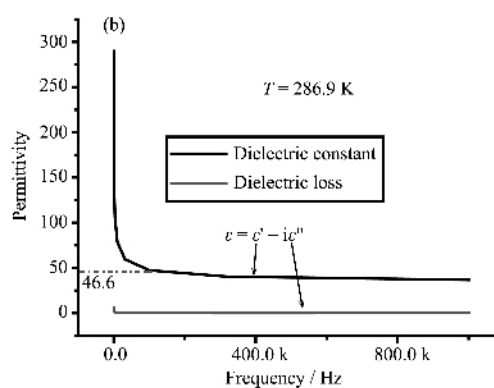


Fig.4 Frequency dependence of the real and imaginary parts of the dielectric response of compound **1** at different temperatures (ε is defined as $\varepsilon_1 - i\varepsilon_2$ where dielectric loss $\tan\delta = \varepsilon_2 / \varepsilon_1$)

Experiment

The mixture of $\text{Cu}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1 mmol) and CDTO (1.0 mmol) in 2 mL menthol and water solvent in a sealed tube were put in an oven at 70 °C. After two days, blue block crystals are obtained in 80% yield based on CDTO. Intensity data were collected at 293(2) K on a Bruker AXS SMART CCD. $\text{C}_{32}\text{H}_{42}\text{O}_8\text{Cl}_2\text{N}_6\text{Cu}$, $M = 773.16$, Triclinic, $P\bar{1}$, $a = 0.859\ 06\ (10)\ \text{nm}$, $b = 1.053\ 11(13)\ \text{nm}$, $c = 1.202\ 96(14)\ \text{nm}$. $\alpha = 111.540(2)^\circ$,

$\beta = 108.899(2)^\circ$, $\gamma = 196.249(3)^\circ$, $V = 0.925\ 09(19)\ \text{nm}^3$, $Z = 1$, 3 579 unique data ($\theta_{\text{max}} = 25.99^\circ$), $R = 0.053\ 9$ (2 888 [$I \geq 2\sigma(I)$] reflections), $wR = 0.154\ 1$ (all data), $\rho_{\text{max}} = 0.55\ \text{e} \cdot \text{nm}^{-3}$, water-H were not located. Programs used: SAINT, SADABS, SHELX-97, ORTEP.

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References:

- [1] (a)Vanderah T A. *Science*, **2002**,**298**:1182~1184
(b)Rijnders G, Blank D H V. *Nature*, **2005**,**433**:369~370
(c)Lee H N, Christen H M, Chrisholm M F, et al. *Nature*, **2005**,**433**:395~399
(d)Cava R J. *J. Mater. Chem.*, **2001**,**11**:54~62
- [2] (a)Marvan M, Jonscher A K, Fahnrich J. *J. Eur. Ceram. Soc.*, **2001**,**21**:1345~1348
(b)Mollà J, Gonzàlez M, Vila R, et al. *J. Appl. Phys.*, **1999**, **85**:1727~1730
- [3] Homes C C, Vogt T, Shapiro S M, et al. *Science*, **2001**,**293**: 673~676
- [4] (a)Zhang Q M, Bharti V, Zhao X. *Science*, **1998**,**280**:2101~ 2104
(b)Ang C, Yu Z. *Adv. Mater.*, **2004**,**16**:979
- (c)Takasu I, Izuoka A, Sugawara T, et al. *J. Phys. Chem. B*, **2004**,**108**:5527~5531
- (d)Akutagawa T, Takeda S, Hasegawa T, et al. *J. Am. Chem. Soc.*, **2004**,**126**:291~294
- (e)Horiuchi S, Kumai R, Okimoto Y, et al. *J. Am. Chem. Soc.*, **1999**,**121**:6757~6758
- (f)Terao H, Sugawara T, Kita Y, et al. *J. Am. Chem. Soc.*, **2001**,**123**:10468~10474
- [5] (a)Ye Q, Song Y M, Wang G X, et al. *J. Am. Chem. Soc.*, **2006**,**128**:6554~6555
(b)Okubo T, Kawajiri R, Mitani T, et al. *J. Am. Chem. Soc.*, **2005**,**127**:17598~17599
- [6] (a)Lah N, Koller J, Giester G, et al. *New J. Chem.*, **2002**,**26**: 933~938
(b)Xiong R G, You X Z, Abrahams B F, et al. *Angew. Chem. Int. Ed.*, **2001**,**40**:4422~4425
- [7] Noveron J C, Lah M S, Sesto R S D, et al. *J. Am. Chem. Soc.*, **2002**,**124**:6613~6625