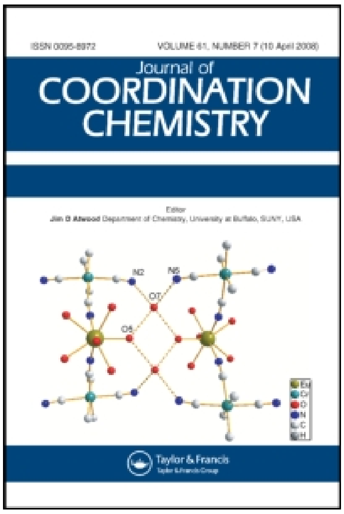

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Linear polymer of a copper(II) complex and its supramolecular selectivity

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The supramolecular framework $[Cu_2(TU)_4 \cdot (TAA)_4]_n$ (TU = thiourea; TAA = 2-(2-imino-4-oxo-5-thiazolidinylidene)acetic anion) has been synthesized by reaction of $CuCl_2 \cdot 2H_2O$ with meso-2,3-dibromosuccinic acid and thiourea. The one-dimensional supramolecular structure of the title complex is constructed through bridge-linkage of the S atoms on the thioureas between adjacent Cu(II) atoms, forming an infinite chain with lots of positive charges. Around the infinite chain, there are four groups of negatively charged hydrogen-bond tubes constructed by four TAA anions. The hydrogen-bond and ionic interactions between adjacent metal-organic polymeric chains and hydrogen-bond tubes form the three-dimensional supramolecular structure of the complex. Supramolecular selectivity from isomers of 2-(2-imino-4-oxo-5-thiazolidinylidene)acetic anion (TAA) has been studied by quantum calculation.

Keywords: Supramolecular selectivity; Crystal structure; Isomers; Polymers

1. Introduction

Metal-organic complexes with intriguing topologies have been studied for their versatile chemical and physical properties and potential applications in functional materials [1–11]. With the development of supramolecular chemistry, self-assembly has become an effective approach to construct functional complexes. Hydrogen bonds and π–π interactions provide for rational design of multidimensional metal-organic supramolecules [12–14] via self-assembly [15–20].

In this article, we synthesize a linear polymer of copper(II) with unique structure. Additionally, a very interesting property is its selectivity on the 2-(2-imino-4-oxo-5-thiazolidinylidene)acetic anion (TAA) because of the weak intermolecular interactions.

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2. Experimental

2.1. *General remarks*

Elemental analysis was performed with an Eager-200 element analyzer and IR spectra were obtained with a Shimadzu IR-470 spectrophotometer (4000–400 $\mathrm{cm^{-1}}$). Density was measured by using a pycnometer.

2.2. *Preparation*

About 0.55 g (2 mmol) of meso-2,3-dibromosuccinic acid ($C_4H_4O_4Br_2$) and 0.21 g (2 mmol) Na_2CO_3 were dissolved simultaneously in 10 mL of deionized water and the solution was refluxed for 5 min in order to complete the neutralization reaction. Then 10 mL of methanol solution containing about 0.31 g (4 mmol) thiourea was added and refluxed for 30 min. After the mixed solution changes from achromatous to yellow, 0.34 g (2 mmol) of $CuCl_2 \cdot 2H_2O$ deionized water solution was added into the mixed solution and refluxed for 1 h. Finally, the resulting liquid was filtered and slowly cooled to room temperature. After several days, well-formed, yellow, single crystals were obtained. The density measured is 1.82 $\mathrm{g\,cm^{-3}}$; the theoretical density is 1.82 $\mathrm{g\,cm^{-3}}$. $C_{12}H_{14}N_8S_4O_6Cu$ (%): Calcd C, 25.83, H, 2.53, N, 20.08; found: C, 25.88, H, 2.42, N, 20.09. IR (KBr): $\nu = 3438$, 3213, 1751, 1696, 1636, 1520, 981, 496 $\mathrm{cm^{-1}}$.

2.3. *Single-crystal structure determinations*

Crystallographic data for the title complex were collected at 293(2) K with a Bruker APEX area-detector diffractometer with Mo-Kα ($\lambda = 0.71073$ Å). Usual Lp and empirical adsorption corrections were applied [30]. The structures were solved by the Patterson method followed by Fourier syntheses and refinement by full-matrix least-squares against F^2 (SHELXL-97) [31]. H atom on the imino group was located in a difference Fourier map. All others were added by the theoretical method. The structure of $\{Cu_2[CS(NH_2)_2]_4 \cdot (C_5H_3N_2O_3S)_4\}_n$ is deposited as CCDC 256940 containing the supplementary crystallographic data for this article.

Crystal data. $C_{12}H_{14}N_8S_4O_6Cu$, Mw = 558.08, tetragonal, $P4_2/n$, $a = b = 19.6106(11)$ Å, $c = 5.2880(4)$ Å, $V = 2033.64(2)$ Å^3, $Z = 4$, $D_c = 1.82\ \mathrm{g\,cm^{-3}}$, $F(000) = 1132$, μ(Mo-Kα) $= 1.535\ \mathrm{mm^{-1}}$, $T = 293(2)$ K, $\theta = 1.5$–$27.5°$.

Data collection. Absorption correction: multi-scan, $R_{\mathrm{int}} = 0.0273$, $T_{\min} = 0.768$, $T_{\max} = 0.887$, $\theta_{\max} = 27.5°$, $h = -21 \rightarrow 25$, $k = -25 \rightarrow 25$, $l = -6 \rightarrow 6$.

Refinement. Refinement on F^2, $R[F^2 > 2\sigma(F^2)] = 0.047$, $wR(F^2) = 0.040$, $S = 1.126$, 2037 reflections $[I > 2\sigma(I)]$, $(\Delta/\sigma)_{\max} = 0.000$, 141 parameters, $\Delta\rho_{\max} = 0.575\ \mathrm{e\,Å^{-3}}$, $\Delta\rho_{\min} = -0.435\ \mathrm{e\,Å^{-3}}$.

3. Results and discussion

3.1. *Description of crystal structure*

The Cu(II) has tetrahedronal coordination (figure 1); the cell belongs to the tetragonal crystal system (figure 2). Selected bond lengths and angles for the title complex are presented in table 1.

Two sp^3 hybrid orbitals of Cu(II) bond with two sp^2 hybrid orbitals of S atoms on the thioureas to form the sp^2–sp^3 σ bonds, and the corresponding Cu–S bonds are 2.3644(7) Å. The other two sp^3 hybrid orbitals of Cu(II) bond the p orbital of two other S atoms on the thioureas to form p–sp^3 σ bonds, 2.3957(7) Å. Thus, there are two different thiourea molecules along each side of the *c*-axis because one group of thiourea molecules bond to Cu(II) from its lateral direction and the other group bond to Cu(II) from its obverse direction.

The S atoms on each thiourea bond to two neighboring Cu(II) ions with the p and sp^2 orbital; two neighboring Cu(II) ions are bridge-linked by two S atoms. The distance

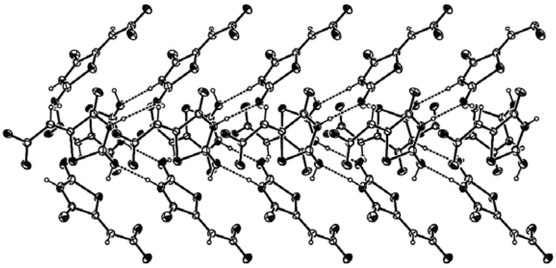


Figure 1. Linear chain structure of the title complex constructed through bridge-linkage of the S atoms on the thioureas between adjacent Cu(II) atoms.

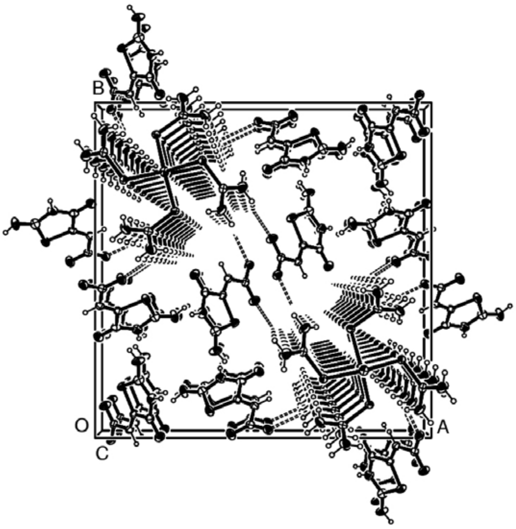


Figure 2. Cell structure of the title complex showing hydrogen bond interactions between the TAAs and thioureas.

Table 1. Selected bond lengths (Å) and angles (°) for the title complex.

Cu–S1	2.3957(7)	Cu–S1^a	2.3644(7)
S1^a–Cu–S1	107.962(8)	Cu–S1–Cu^d	67.479(17)
S1^a–Cu–S1^b	113.65(4)	C1–S1–Cu^d	115.50(10)
S1^c–Cu–S1	111.39(4)	C1–S1–Cu	101.35(11)

Symmetry code: a: $1/2+y$, $1-x$, $1/2+z$; b: $1-y$, $x-1/2$, $1/2+z$; c: $3/2-x$, $1/2-y$, z; d: $1-y$, $x-1/2$, $z-1/2$.

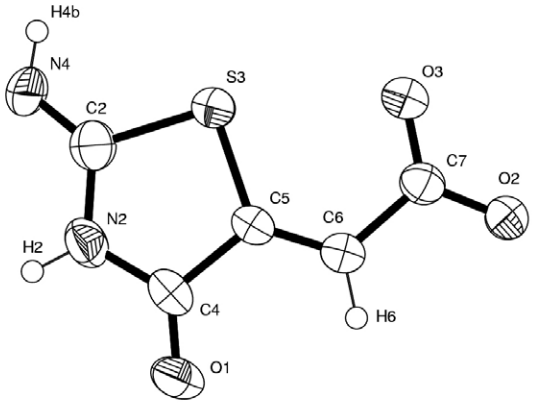


Figure 3. Structure of TAA anion in the title complex.

between neighboring Cu(II) ions is short at 2.6440(2) Å; this is the minimum in all similar structures [21–29]. All the Cu(II) ions along the *c*-axis are arranged on a line to form a linear chain structure (figure 1), but a metal bond can't exist in the title complex because the Cu(II)–Cu(II) length is out of the range for Cu–Cu metal bonds.

Along the linear chain structure, each four-atom group (Cu_2S_2) forms an approximate parallelogram and is vertical with the neighboring two Cu_2S_2 groups. The vertical structure elongates along the *c*-axis to form a linear polymer.

In order to keep the electric charge equilibrium, there are four columns of the arrangement of TAA anions (figure 3) around the linear chain structure. The dihedral angle between the mean plane of TAA anion and the mean plane of neighboring thiourea molecules is 5.59(21)°; there also exist many hydrogen bonds between the TAA anions and adjacent thiourea.

In summary, two TAA anions and two thiourea molecules at two linear chain structures form a hydrogen bond ring with 16 atoms (figure 2); in the same way, four TAA anions among four linear chain structures also form a hydrogen bond ring with 16 atoms (figure 4). All hydrogen bond rings along the same direction can be stacked into a hydrogen bond tube as shown in figure 5. The data of all hydrogen bonds are shown in table 2.

3.2. *Supramolecular selective recognition*

During synthesis of the title complex, the thioureas and the meso-2,3-dibromosuccinic acid can give two isomers of the 2-(2-imino-4-oxo-5-thiazolidinylidene)acetic anion (TAA) at first. The synthesis of TAA is shown in scheme 1.

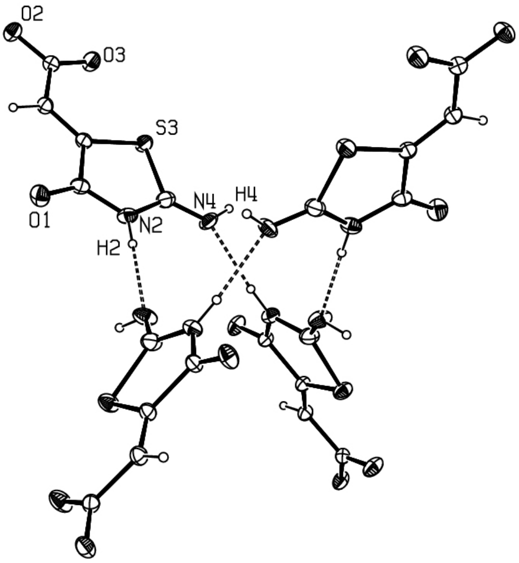


Figure 4. H-bond interaction between the TAAs.

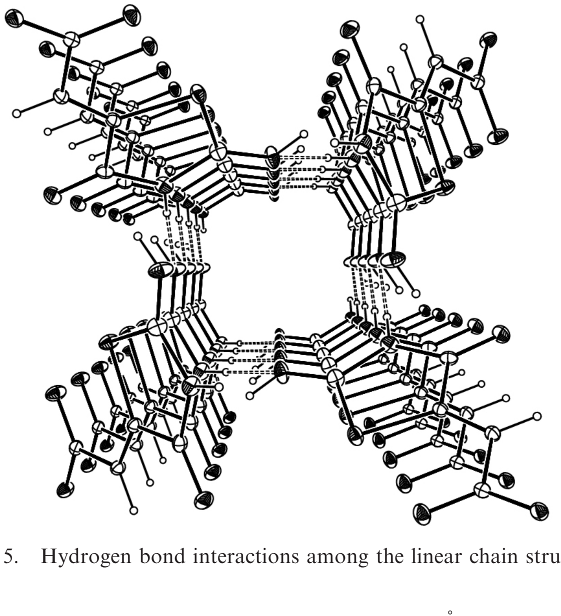
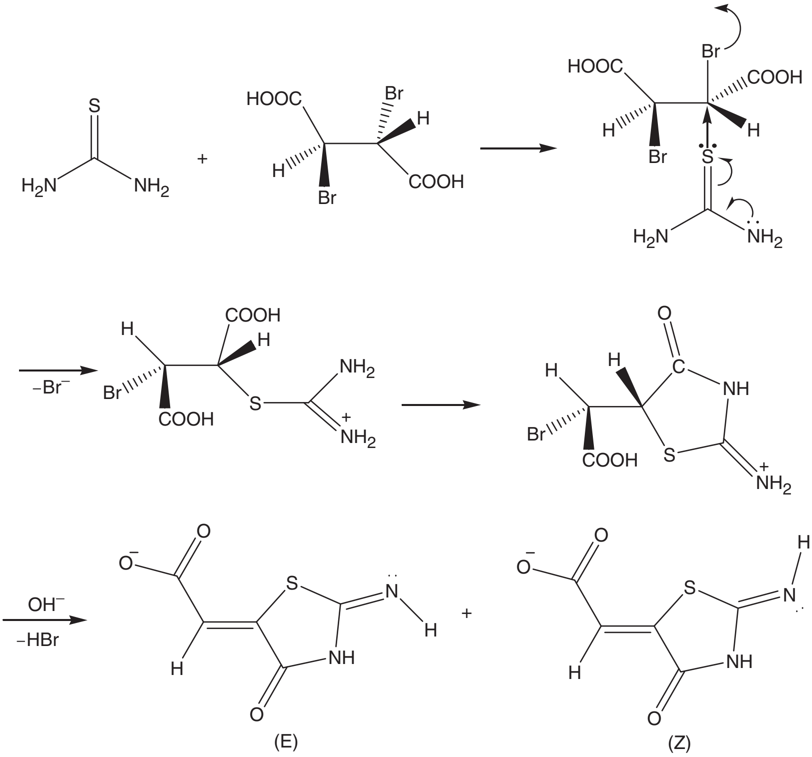


Figure 5. Hydrogen bond interactions among the linear chain structures.

Table 2. H-bonds in the title complex (Å, °).

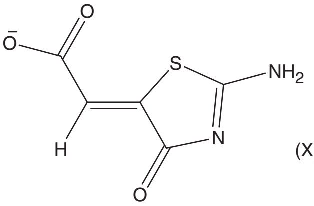
Donor–H ··· acceptor	D–H	H–A	D–A	∠D–H ··· A
N1–H1A ··· O3[a]	0.86	1.98	2.835(5)	176
N1–H1B ··· O1[b]	0.86	2.24	2.976(6)	144
N2–H2 ··· N4[c]	0.86	2.05	2.911(5)	175
N3–H3A ··· O2[d]	0.86	2.15	2.920(5)	150
N3–H3B ··· S1[e]	0.86	2.47	3.321(4)	171

Symmetry code: a: y, $1/2-x$, $1/2-z$; b: $1/2-x$, $1/2-y$, z; c: $1/2-y$, x, $3/2-z$; d: $-y$, $1/2+x$, $3/2+z$; e: $-1/2+y$, $1-x$, $1/2+z$.



Scheme 1. The synthesis mechanism of the TAA.

The Z and E isomers depend on the structure of the double bond C=N in TAA; both Z and E isomers can isomerize into the third isomer X:



(X)

The three isomers in the water have been examined theoretically on the PC computer by using the chemical software Gaussian94 at the level of the density functional theory (DFT): b3lyp/6–31 + G(d, p). The results show that the Self-Consistent Field (SCF) energy of the E, Z and X isomers are −925.92725, −925.92919 and −925.93220 a.u, respectively. The SCF energy of the Z isomer is 5.09 kJ mol^{-1} lower than the E isomer and the SCF energy of the X isomer is 7.90 kJ mol^{-1} lower than that of the Z isomer. Therefore the X isomer is the most stable, but the difference is so small that the three isomers can interconvert during the synthesis. The three isomers are a group of tautomers that interconvert at room temperature and couldn't affect crystallization because the interconversion is so fast.

The SCF energies of the TAA isomers don't determine which isomer exists in the title complex. Thus, the two kinds of hydrogen-bond ring structures making up the Z and

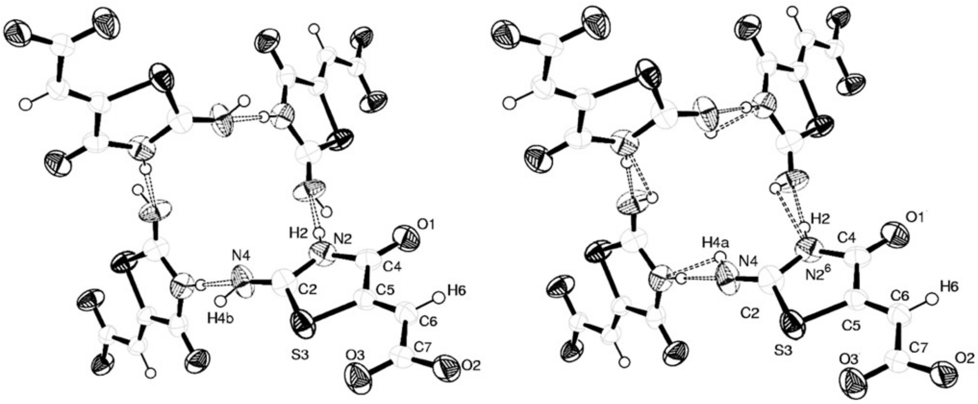


Figure 6. Hydrogen-bond ring structure made up of four Z (left) and E (right) isomer anions.

E isomers are investigated by quantum chemistry (see figure 6). The hydrogen-bond ring structure of the X isomer isn't chosen to be calculated because there aren't hydrogen bonds in its structure which would be unstable in the title complex.

The results show that the energy of the hydrogen-bond ring structure of Z isomers is 154.17 kJ mol^{-1} lower than that of the E isomer, indicating that the repulsion energy between adjacent hydrogen atoms (H2 and H4b) is larger than the formation energy of the hydrogen bond (N2–H2 $\cdots$ N4a (y, $1/2-x$, $3/2-z$)) in the E isomer. Therefore the hydrogen-bond ring structure of Z isomers is stable in the title complex.

In addition, the above crystal analysis shows that the two N2–H bonds outside of the thiazole ring in X isomers cannot form the H-bonds with other atoms, but the N1–H2 bond on the thiazole ring in Z or E isomers can form the H-bond with the N outside of the thiazole ring on the neighboring TAA anion. Hence the Z isomer is the only molecule in the complex. The existence of the isomer is chosen by the intermolecular weak interaction and HF energy of its own; that is, there is Z isomer in the crystal instead of E and X isomer.

The supramolecule has selected the isomer via its self-assembly.

Acknowledgements

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