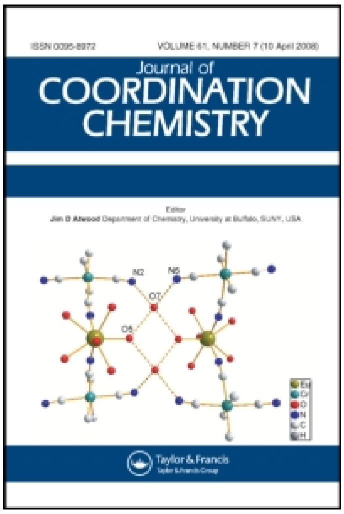

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Three Ag(I) and Cu(II) complexes of 4-pyridin-4-yl-(1,3) dithiol-2-one

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Three Ag(I) and Cu(II) complexes of 4-pyridin-4-yl-(1,3) dithiol-2-one

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Single crystals of Ag(I) and Cu(II) complexes with 4-pyridin-4-yl-(1,3) dithiol-2-one (PYDO), $[Ag(PYDO)_2]ClO_4$, $[Ag(PYDO)_2(NO_3)]$, and $[Cu(PYDO)_2(NO_3)_2]$ have been prepared and characterized. PYDO displays excellent coordination to Cu(II) and Ag(I). The 1,3-dithiol five-member ring is an electron donor that enhances the coordination ability of the py group. HOMO-1 σ coordination and d–π electron back-donating from metal to ligand (LUMO) are suggested based on the calculation. Weak interactions and secondary bonds from the anion to cation play an important role in the molecular assembly.

Keywords: Metal complex; Crystal structure; Molecular orbit; Coordination bond

1. Introduction

Bifunctional molecules featuring a TTF (tetrathiafulvalene) unit with a pyridine, TTF-py, have been explored and a series of new TTF compounds with transition metal centers have been synthesized [1–3]. Only a few structures of TTF-py, in which pyridine directly links to the TTF without a spacer, have been explored (figure 1a) [3]. 4-Pyridin-4-yl-(1,3) dithiol-2-one (PYDO) (figure 1b) is an intermediate for synthesis of this type of TTF derivative [4] and also a donor–acceptor ligand. Selecting PYDO as the ligand to prepare single crystal with transition metals and study their coordination mode will help to understand the solid state chemistry of TTF-py-M materials.

We report herein the preparation of three new metal compounds $[Ag(PYDO)_2]ClO_4$, $[Ag(PYDO)_2(NO_3)]$, and $[Cu(PYDO)_2(NO_3)_2]$. Crystal structures and the coordination of the complexes are discussed.

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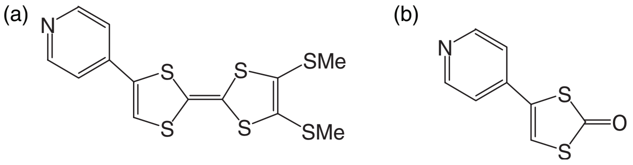

Figure 1. (a) TTF derivative with directly linked pyridyl; (b) 4-pyridin-4-yl-(1,3) dithiol-2-one (PYDO).

2. Experimental

2.1. *Reagents and instruments*

The ligand 4-pyridin-4-yl-(1,3) dithiol-2-one (PYDO) was synthesized as described in the literature [4]. Elemental analyses of C, H, and N were performed using an EA 1110 elemental analyzer. IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-3150 spectrometer.

2.2. *Synthesis of [Ag(PYDO)$_2$]ClO$_4$*

To a solution of PYDO (4.0 mg, 0.02 mmol) in dichloromethane (2 mL) was added a solution of $AgClO_4$ (4.1 mg, 0.01 mmol) in acetonitrile (2 mL). The mixture was stirred for 30 min at room temperature, and turning to a yellow solution. The mixture was filtered and enclosed in a glass tube and then layered with ethyl ether. Yellow single crystals were obtained on the interface after 4 days (yield: 35.2%). IR (KBr, cm^{-1}): 3449(s), 1636(vs), 1597(m), 1412(m), 1250(w), 1114(s), 1080(m), 872(w), 794(w), and 686(m). Anal. Calcd for $C_{16}H_{10}AgClN_2O_6S_4$: C, 32.15; H, 1.69; N, 4.69%. Found: C, 32.59; H, 2.01; N, 4.33%.

2.3. *Synthesis of [Ag(PYDO)$_2$(NO$_3$)]*

[Ag(PYDO)$_2$]NO$_3$ (**2**) was prepared by a similar method used for the synthesis of **1** except that $AgClO_4$ was replaced by $AgNO_3$. Yellow single crystals were obtained on the interface after 5 days (yield: 28.6%). IR (KBr, cm^{-1}): 3008(m), 2959(m), 2342(s), 1652(s), 1592(m), 1558(m), 1384(vs), 794(w), 687(m), and 668(m). Anal. Calcd for $C_{16}H_{10}AgN_3O_5S_4$: C, 34.36; H, 1.80; N, 7.52%. Found: C, 34.19; H, 1.94; N, 7.34%.

2.4. *Synthesis of [Cu(PYDO)$_2$(NO$_3$)$_2$]*

[Cu(PYDO)$_2$](NO$_3$)$_2$ (**3**) was prepared by a similar method used for synthesis of **1**. Blue single crystals were obtained on the interface after 7 days (yield: 76.1%). IR (KBr, cm^{-1}): 3419(s), 1713(m), 1643(s), 1613(s), 1551(m), 1481(m), 1288(m), 1011(w), 872(w), 787(w), 702(w), and 556(w). Anal. Calcd for $C_{16}H_{10}CuN_4O_8S_4$: C, 33.28; H, 1.75; N, 9.71%. Found: C, 33.47; H, 2.03; N, 9.32%.

2.5. *X-ray structure determination*

All measurements were carried out on the Rigaku Mercury CCD diffractometer at 293 K using ω-scan methods with graphite monochromated Mo-Kα radiation

Table 1. Crystallographic data and details for **1**, **2** and **3**.

Formula	$C_{16}H_{10}AgN_2O_6S_4Cl$	$C_{16}H_{10}Ag\ N_3O_5S_4$	$C_{16}H_{10}CuN_4O_8S_4$
Formula weight ($g\,mol^{-1}$)	597.86	560.38	578.06
Color, habit	Yellow, Block	Yellow, Block	Blue, Block
Dimensions (mm^3)	0.50 × 0.20 × 0.04	0.76 × 0.23 × 0.10	0.60 × 0.50 × 0.20
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Ibca	Ibca	$P2_1/c$
Unit cell dimensions (Å, °)			
a	10.526(3)	10.328(3)	8.1879(19)
b	12.698(4)	12.681(3)	14.007(3)
c	30.491(8)	30.223(8)	9.220(2)
β	90	90	92.373(5)
V(Å^3)	4075(2)	3958.4(18)	1056.5(4)
T(K)	293(2)	293(2)	293(2)
Z	8	8	2
D_{Calcd} ($g\,cm^{-3}$)	1.949	1.881	1.817
μ(mm^{-1})	1.569	1.475	1.483
F(000)	2368	2224	582
Unique reflections (total)	1873	1824	1927
Reflections (gt)	1604	1676	1776
$R_1(I > 2\sigma I)$	0.0797	0.0814	0.0360
wR_2 (all)	0.2085	0.2571	0.0897
Goodness-of-fit	1.197	1.215	1.084

Table 2. Selected bond lengths (Å), bond angles (°), torsion angles (°) and important weak interactions (Å).

	1	**2**	**3**
Ag(1)–N(1)	2.130(7)	2.127(7)	
Cu(1)–N(1)			1.975(2)
O(1)–C(7)	1.205(10)	1.218(12)	1.204(3)
C(7) ··· C(7)	3.266(11)		
C(7) ··· O(1)	3.160(10)		
Ag(1)–O(4)		2.663(20)	
O(1) ··· O(2)			2.951(3)
N(1)–Ag(1)–N(1)	176.2(4)	173.0(4)	
O(4)–Ag(1)–O(4)		109.9(6)	
O(2) ··· Ag(1) ··· O(2)	87.73(27)		
O(2)–Cu(1)–O(3)			54.49(8)
N(1)–Cu(1)–N(1)			180.00(15)
C(4)–C(3)–C(6)–C(8)	4.9(11)	–5.8(11)	19.7(4)

($\lambda = 0.71073$ Å). An absorption correction was applied using a multi-scan correction method. The structures of **1**, **2**, and **3** were solved by direct methods using SHELX97 [5] and refined by full-matrix least-squares (SHELXL97) [5]. All non-hydrogen atoms were located with successive difference Fourier syntheses and refined anisotropically, while H atoms were positioned geometrically and allowed to ride on their parent atoms. The final cycle of full-matrix least-squares refinement on F^2 converged with unweighted and weighted agreement factors of R_1 and wR_2. Due to the disorder of ClO_4^- in **1** and NO_3^- in **2**, the values for **1** and **2** are somewhat large. A summary of the experimental details and selected refinement results for **1**–**3** is given in table 1. Selected bond lengths, bond angles, torsion angles, and important weak interactions are given in table 2.

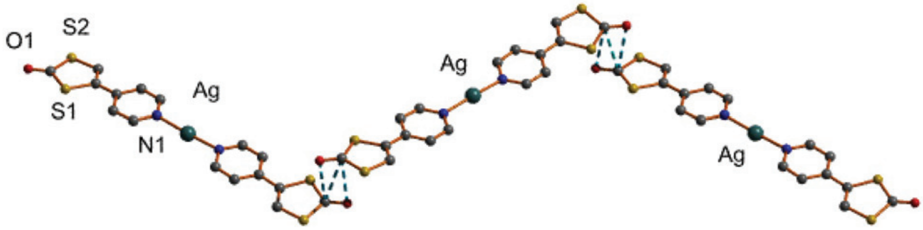

Figure 2. Crystal structure of **1** showing the C···O (3.160(10) Å) and C···C (3.266(11) Å) assembled 1-D zigzag chain; the hydrogen atoms and the perchlorate are omitted for clarity.

3. Results and discussion

3.1. *Crystal structure of 1*

The crystal structure of **1** is shown in figure 2. Compound **1** crystallizes in orthorhombic with space group Ibca and consists of $[Ag(PYDO)_2]^+$ and ClO_4^-. The ligand is coordinated to silver(I) by nitrogen of pyridine in a nearly linear geometry with the Ag1–N1 bond distance of 2.130(7) Å and the N(2)–Ag(1)–N(1) angle of 176.2(4)°. The ligands are approximately coplanar, since the dihedral angle between least-squares planes of the dithiol-one moiety and the pyridyl group is 5.2(2)°.

The distance between the nearest O of ClO_4^- and Ag^+ is 2.895(11) Å (somewhat longer than the Van der Waals sum of 2.740 Å), so the interaction between them is very weak, but does affect the N–Ag–N angle. There are important C···C (3.266(11) Å) and C···O (3.160(10) Å) short interactions between the C=O groups of the neighboring molecules, which assemble to a 1-D zigzag chain (figure 2). The chains are further connected to form a network *via* weak C–H···O interactions (figure 3).

3.2. *Crystal structure of 2*

Compound **2** crystallizes in orthorhombic with the same space group (Ibca) as **1**. There is a considerable degree of isostructurality between structures **1** and **2**. The Ag atom is also coordinated by two N atoms of the pyridine groups in a nearly linear geometry (figure 4). Bond distance of Ag(1)–N(1) is 2.127(7) Å, comparable to those of **1**. In addition, the distance between the nearest O atom of NO_3^- and the Ag is 2.663(20) Å (shorter than the Van der Waals sum of 2.740 Å), indicating the existence of a secondary bond of Ag with NO_3^-. Therefore, Ag(I) can be considered as an anamorphic tetrahedral geometrical configuration with N(2)–Ag(1)–N(1) angle of 173.0(4)°. By the Ag–NO_3–Ag weak bonding the compound shows an 1-D structure (figure 5) in which the anions are disordered. The separation of overlapped py planes is about 3.60 Å, showing very weak $\pi\cdots\pi$ interaction. The dihedral angle between least-squares planes of the dithiol and the pyridyl is 5.8(2)°, similar to **1**.

3.3. *Crystal structure of 3*

$[Cu(PYDO)_2(NO_3)_2]$ crystallizes in monoclinic with space group $P2_1/c$. The Cu lies on an octahedral coordination center comprised of four oxygens from two NO_3^- and two

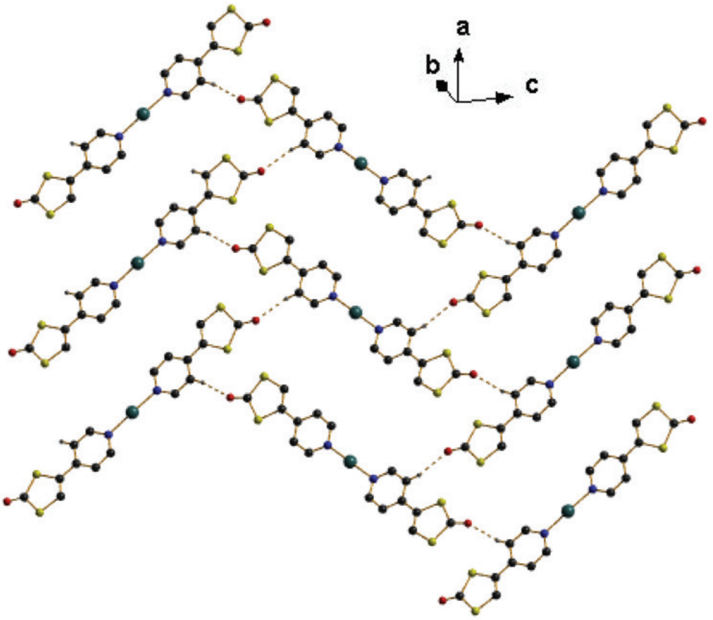

Figure 3. The 2-D cation's packing showing the weak C–H···O hydrogen bond interactions.

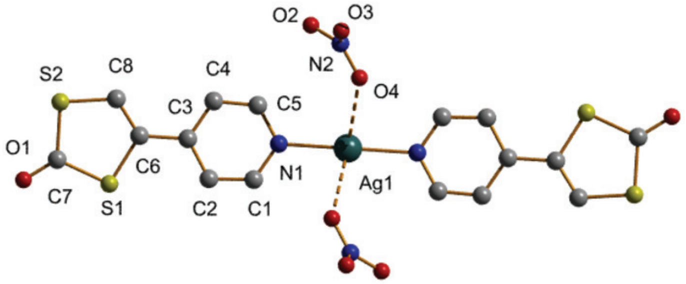

Figure 4. Crystal structure of **2**; the hydrogen atoms and the disordered oxygens in nitrate are omitted for clarity.

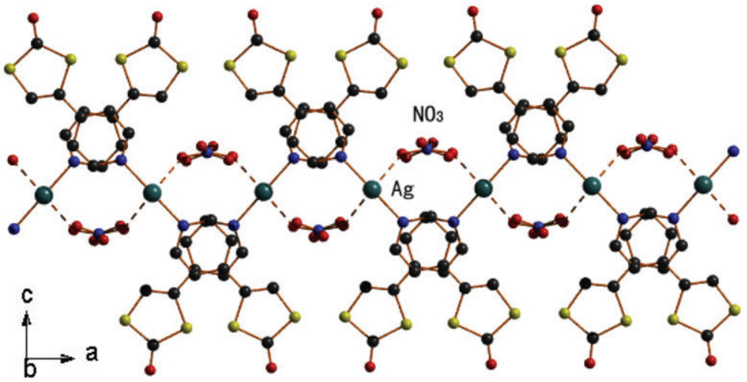

Figure 5. Secondary Ag–O (nitrate) coordination assembled in a 1-D double chain.

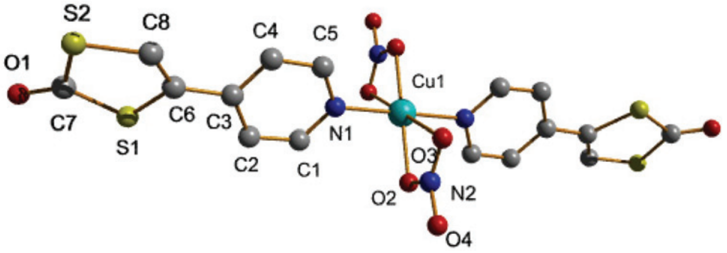

Figure 6. Crystal structure of **3**; the hydrogen atoms are omitted for clarity.

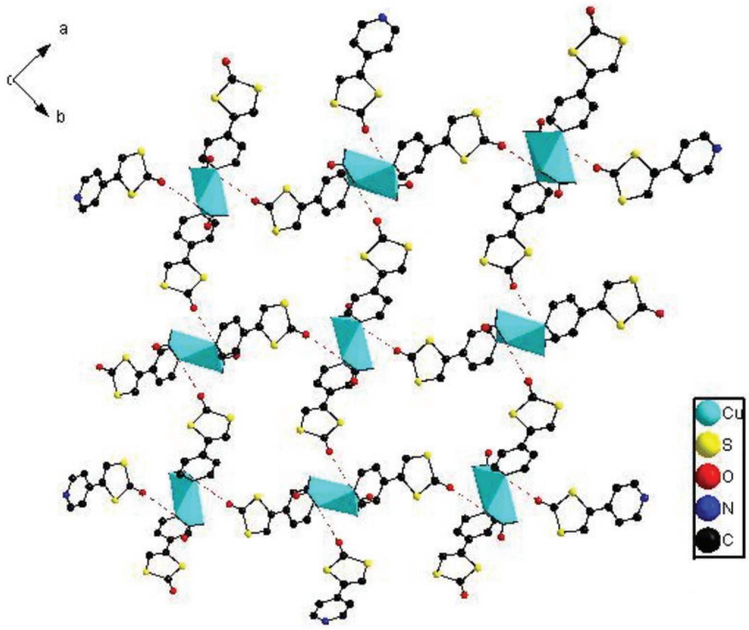

Figure 7. The O· · ·O weak interaction assembled in a 2-D network.

nitrogens of two PYDO ligands with Cu–O bond lengths in the range 1.991–2.578 Å and Cu–N distance of 1.975 Å (figure 6). The O(one)···O(nitrate) contacts (2.951 Å) play an important role in the crystal structure. A 2-D network is constructed through these contacts (figure 7). The dihedral angle between least-squares planes of the dithiol-one moiety and the pyridyl group is 23.4(6)°.

3.4. *The nature of the M–N(py) bond*

To understand the nature of the N–M bond, molecular orbital population of HOMOs and LUMOs for PYDO were calculated using Gaussian 03 with the B3LYP functional and the 6-31G** basis set [6] (Supplementary material). The HOMO orbital shows a π symmetry mode, while the HOMO-1 orbital is a σ type symmetry in py so that the contribution from N(py) to metal ions in these complexes is mainly attributed to the

HOMO-1. The calculated result shows the electron population of HOMO-1 enhances the σ donation from py to metal ion. The LUMO shows π symmetry, matching the symmetry of d orbital of Ag or Cu. Therefore, the d-LUMO overlap occurs with electron back-donation from metal to ligand. The following conclusions can be drawn: (1) the N–M coordination bond is strong with more than single bond order and (2) the ΔE of the LUMO–HOMO is not significantly affected due to non-bonding properties of the HOMO. UV-Vis spectra of the ligand and the complexes confirm the explanation. The HOMO → LUMO excitation was calculated at 4.16 eV (298 nm, $f = 0.1127$), in good agreement with the position of the lowest band observed experimentally (Supplementary material). There is not a significant shift of this band when the metal ion is coordinated, in accord with calculation.

4. Conclusion

Single crystals of three Ag(I) and Cu(II) complexes with 4-pyridin-4-yl-(1,3) dithiol-2-one (PYDO) have been prepared and characterized. The ligand displays excellent coordination ability to Cu(II) and Ag(I). The 1,3-dithiol five-member ring is an electron donor enhancing coordination of the py group. The σ coordination and d–π electron back-donation from metal to ligand are suggested for these compounds. Weak interactions and secondary bonds from anion to cation play an important role in the crystal structure.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 696278–696280. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033, or E-mail: deposit@ccdc.cam.ac.uk

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