

Synthesis, Characterization and Quantum Chemical Studies on a Novel Cobalt(II) 1,2,3,4-Tetra-(4-pyridyl)-thiophene Coordination Polymer

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The rational design and assembly of coordination polymers have received increasing attention and been developing rapidly in recent years.¹ Being easily and efficiently constructed from relatively simple subunits, these complexes exhibit fine-tuning structural diversity and potential applications in the development of optical, electronic, and magnetic devices.²⁻⁴

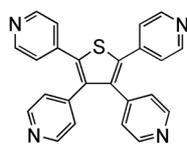
It is well known that some weak interactions usually affect the structures of coordination polymers, such as hydrogen bonding and π - π stacking interactions.^{5,6} Moreover, they can further link low-dimensional entities into high-dimensional supramolecular networks.^{7,8} So, the most feasible strategy used to design and construct coordination polymers is to select suitable poly-functional ligands that enable the control on the structural motifs.⁹ Some tetratopic pyridyl-bridging ligands are of the recent surge of research interest, for example, 1,4-dihydroxy-1,2,4,5-tetra-(4-pyridyl)-cyclohexane, 1,2,4,5-tetra-(4-pyridyl)-benzene and 1,2,3,4-tetra-(4-pyridyl)-cyclobutane.¹⁰⁻¹⁴ Compared with the linear 4,4'-bipyridine and 4,4'-bipyridine-like N,N'-donor ligands,¹⁵ these tetradentate ligands induce unique structural topologies and exhibit interesting physical properties in many complexes.¹⁰⁻¹⁴ In this field, however, the rigid symmetric ligand 1,2,3,4-tetra-(4-pyridyl)-thiophene (TPT, Scheme 1) is less explored in the self-assembly of coordination polymers.¹⁶ This ligand also possesses four potential coordinating N-donor atoms. Therefore, it can coordinate to metal centers with diverse modes.

For investigating the coordination chemistry of TPT and preparing novel materials with interesting structural topologies and excellent physical properties, we have recently been engaged in the research of polymeric complexes with this tetratopic pyridyl-bridging ligand.¹⁷ The aim of this work is to carry out a systematic investigation on the structural characterization of the $[\text{Co}(\text{TPT})_2(\text{NCS})_2]_n \cdot 2n\text{H}_2\text{O}$ (**1**) polymeric complex by using

experimental and theoretical methods. The IR spectrum, electronic transition property, thermal stability, and second-order nonlinear optical (NLO) property have also been studied.

The X-ray diffraction study reveals that complex **1** crystallizes in the *P2* space group and features a 2-D supermolecular network formed by the hydrogen bonding interactions between the water molecules and 1-D double-stranded chains. As far as we know, the coordination polymers with this chiral space group are relatively rare.¹⁸ As depicted in Figure 1, the Co1 exhibits a slightly distorted octahedral coordination sphere. The basal plane is defined by four pyridyl nitrogen atoms, while the apical positions are occupied by two nitrogen atoms from two NCS⁻ anions. And the metal ion Co1 locates in the center of the basal plane. The distances between the metal atom and different types of nitrogen atoms in the CoN₆ range from 2.078(3) to 2.2099(15) Å, which are comparable to the reported values. The degrees of distortion from an ideal octahedral geometry are reflected from *cisoid* angles [86.74 - 94.61°] and *transoid* angles [174.4 - 175.7°].

From Figure 2, one can observe that the Co(II) atoms are first connected by V-shape bridge of the two coordinated pyridines of the TPT ligand to form 1-D ladderlike network along the *b* axis. The nearest distance between two Co(II) centers is 9.7508 Å. Besides, these 1-D chains are further connected by the strong intermolecular hydrogen bonding interaction between uncoordinated pyridine nitrogen atom and free water molecule (O2-H2C...N4 2.725(2) Å) to form a 2-D supermolecular net-



TPT

Scheme 1

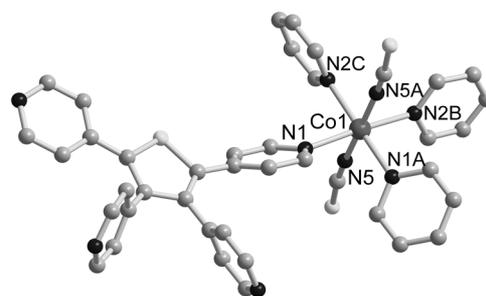


Figure 1. Molecular structure of the complex **1** (Symmetry codes are listed in Table 1).

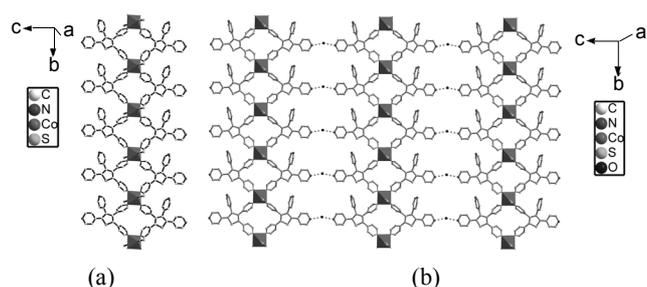


Figure 2. (a) Perspective view of 1-D chain of **1** connected by the TPT ligand; (b) Perspective view of 2-D supermolecular network formed by strong H-bonded interactions.

Table 1. Selected geometric parameters by X-ray single crystal diffraction and B3LYP/LANL2DZ calculation for the title complex^a

Parameter	Experimental	Calculated	Error ^b
Bond lengths (Å)			
Co1-N1	2.2099(15)	2.208	-0.002
Co1-N2	2.194(3)	2.222	0.028
Co1-N5	2.078(3)	2.111	0.033
N1-C5	1.390	1.359	-0.031
N5-C25	1.179(5)	1.201	0.022
C1-C2	1.376(7)	1.388	0.012
C2-C3	1.461(9)	1.459	-0.002
C3-C4	1.407(9)	1.389	-0.019
C5-C6	1.390	1.401	0.011
C6-C7	1.390	1.416	0.026
C1-C7	1.436(7)	1.475	0.039
C1-S1	1.723(7)	1.808	0.085
C4-S1	1.719(6)	1.808	0.089
Bond angles (°)			
N1-Co1-N1A	89.10(12)	89.11	0.01
N1-Co1-N2B	89.24(8)	91.42	2.18
N1-Co1-N5	89.42(14)	89.13	-0.29
N1A-Co1-N2B	175.70	179.44	3.74
N1A-Co1-N2C	89.24(6)	91.07	1.83
N1A-Co1-N5A	89.42(14)	89.94	0.52
N2B-Co1-N5	89.36(17)	89.33	-0.03
N2B-Co1-N5A	86.74(15)	90.26	3.52
N2C-Co1-N5A	89.36(17)	90.18	0.82
Torsion angles (°)			
N1-Co1-N1A-N5	89.35	89.12	-0.23
N1-Co1-N1A-N5A	-94.62	-89.65	4.97
N1-Co1-N2B-N5	-89.43	-89.11	0.32
N2B-Co1-N2C-N1A	176.15	179.80	3.65
N2B-Co1-N2C-N5	-89.18	-89.30	-0.12
N2B-Co1-N2C-N5A	86.72	90.26	3.54
C5-N1-Co1-N2C	-74.70	-76.31	-1.61
C25-N5-Co1-N1	-76.76	-80.10	-3.34
C25-N5-Co1-N1A	12.28	9.00	-3.28
C25-N5-Co1-N2C	-78.65	-79.92	-1.27

^aSymmetry codes: A: -x, y, 2-z; B: -x, 1+y, 2-z; C: x, 1+y, z. ^bError = calculated value - experimental value.

work.

The optimized geometry of **1** has been obtained at B3LYP/LANL2DZ level of theory and listed in Table 1. As seen in Table 1, most of the predicted geometric parameters are slightly

larger than those experimentally determined. This is most likely due to the fact that the experimental data describe complex **1** in the solid state, whereas the calculated data correspond to the compound in the gas phase. Comparing the theoretical results with the experimental ones, it can be found that the largest difference in bond lengths occurs at the Co1-N5 bond with the discrepancy of 0.033 Å. Considering the bond angles, the largest deviation between the experimental and theoretical values is 3.74° corresponding to the angle N1A-Co1-N2B. On the other hand, the changes of the torsion angles are larger than those of bond angles with the largest error of 4.97°. In general, these deviations are reasonable which occur mainly due to the hydrogen bonds existed in the experimental structure while the calculation only based on the related mononuclear skeleton [Co(TPT)(pyridyl)₃(NCS)₂]. Therefore, we can draw a conclusion that the optimized geometry closely resembles the crystal structure of **1** and B3LYP/LANL2DZ level can provide satisfying calculational precision for the system studied here.

The IR spectrum of the title compound shows broad peaks in high energy bands ranging from 3580 to 3200 cm⁻¹ due to the existence of free water molecules involved in hydrogen bonds system. In the middle energy range, the typical IR absorption of CN is observed at 2081 cm⁻¹ as a singlet peak. It means that the IR band of NCS groups is occurring in only one coordination metal sphere. On the low energy side of the spectrum, a series of bands are observed, 1598 (s) ν_{C=N}, 1543 (w), 1410 (s) ν_{C-S}. In this case, the X-ray diffraction analysis was allowed to assign unambiguous binding mode of the thiocyanate group.

To better understand the nature of the electronic transition property of the title complex, time-dependent density functional theory calculations and molecular orbital analyses were carried out to investigate the electron transitions in the photoluminescent process.¹⁹ According to our calculations, the lowest-energy absorption maximum for the complex **1** should be attributed to the S₀-S₄ transition (wavelength: 484.93 nm; oscillator strength: 0.07), as the oscillator strength of the S₀-S₁ transition (wavelength: 545.89 nm) is only 0.02. Here, the S₀-S₁ transition is associated with transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), while the dominant S₀-S₄ transition is associated with the transition from HOMO-1 to LUMO+1. As shown in Figure 3, the orbital HOMO-1 is thiocyanate-based and LUMO+1 is a mixture of TPT/polypyridyl π* along with metal-based orbital, so the luminescent emission of **1** is a mixed ligand-to-ligand charge transfer (LLCT) and ligand-to-metal charge transfer (LMCT) character.

Thermogravimetric analysis (TGA) for complex **1** was performed, as depicted in Figure 4. It can be noted that the first weight loss of 3.36% occurs below 60 °C (calcd 3.61%), which corresponds to the loss of two free water molecules per formula. Subsequently, a plateau region is observed ranging from 60 to 337 °C. Then, consecutive decomposition takes place in the temperature range of 337 - 462 °C attributed to the total destruction of the framework. Clearly, we can conclude that the framework of complex **1** are very stable in a higher temperature region (~ca. 340 °C) and worthy of further investigation as a candidate of thermally stable material.

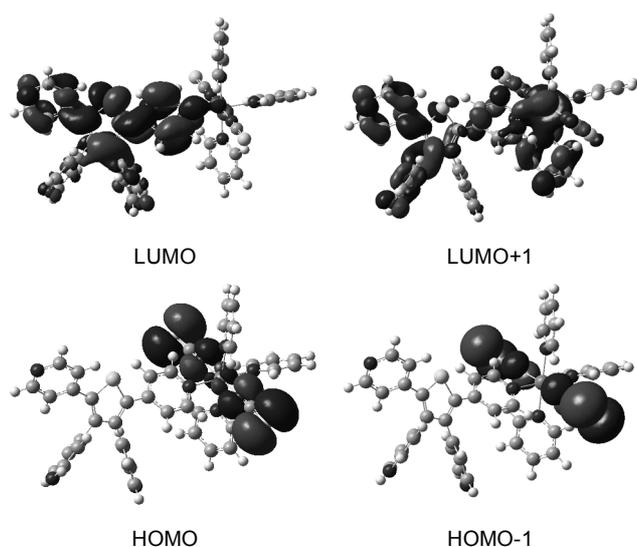


Figure 3. Contour plots of the relevant molecular orbitals (from HOMO-1 to LUMO+1) in the electronic transitions of the title compound.

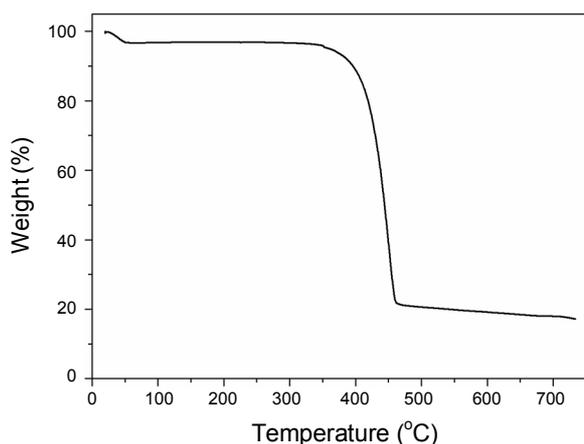


Figure 4. TGA curve of the title complex.

The chiral network is itself noncentrosymmetric, so the bulk is an acentric material that might have potential applications as NLO-active materials.²⁰ Preliminary experimental results show that the complex **1** displays modest powder SHG efficiency, which is approximately 0.5 time that of urea. This confirms that it crystallizes in a polar space group and agrees with the structural analysis and it has potential application as the second-order NLO material.

In summary, a novel coordination polymer constructed from an interesting versatile tetradentate ligand TPT has been successfully isolated and structurally characterized. It exhibits a 1-D ladderlike network and is further connected by strong hydrogen bonding interactions to form a 2-D supramolecular network. The TPT ligand exhibits a novel coordination mode compared to the previously reported coordination polymers assembled from TPT. The skeleton of **1** is thermally stable up to a higher temperature of 337 °C after losing the guest water molecules. In addition, complex **1** displays modest powder SHG efficiency and would be a good candidate for hybrid

organic-inorganic NLO-active materials.

Experimental Section

Materials and instruments. All analytical reagents were purchased from commercial sources and used without further purification. 1,2,3,4-Tetra-(4-pyridyl)-thiophene was synthesized according to the reported work.¹⁷ C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The IR spectrum was recorded using KBr discs on a Bruker Vector 22 spectrophotometer in the 4000 - 400 cm^{-1} region. Thermogravimetric analysis was performed on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 10 °C/min between ambient temperature and 700 °C. The NLO intensity was approximately estimated by measuring a powder sample of 80 - 150 μm diameter in the form of a pellet relative to urea. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate a second-harmonic-generation (SHG) signal from powder samples.

Computational details. The hybrid density functional theory (DFT) B3LYP (Becke's three parameter nonlocal exchange functional along with the Lee-Yang-Parr correlation functional)²¹ was employed to study the complex **1**. "Double- ξ " quality basis set LANL2DZ, which uses Dunning D95V basis set on first row atoms and Los Alamos ECP plus DZ on Na-Bi, was employed as the basis set. The related mononuclear skeleton $[\text{Co}(\text{TPT})(\text{pyridyl})_3(\text{NCS})_2]$ with experimental geometry was used to calculate and evaluate the structural and electronic properties of the complex **1**. All the calculations have been performed with the Gaussian 03 software package²¹ on a Pentium IV computer using the default convergence criteria.

Preparation of $[\text{Co}(\text{TPT})_2(\text{NCS})_2]_n \cdot 2n\text{H}_2\text{O}$ (1**).** A solution of TPT (0.1 mmol) in ethanol (4 mL) was layered over an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) mixed with NH_4NCS (0.2 mmol). Pink single crystals of **1** suitable for X-ray diffraction analysis were obtained by slow interlayer diffusion. The resulting crystals were filtered, and washed with water and ethanol. Yield: 37% (based on Co^{2+}). Anal. Calcd for $\text{C}_{50}\text{H}_{36}\text{CoN}_{10}\text{O}_2\text{S}_4$: C 60.29, H 3.64, N 14.06. Found: C 60.07, H 3.85, N 13.89%.

Crystal structure analysis. $\text{C}_{50}\text{H}_{36}\text{CoN}_{10}\text{O}_2\text{S}_4$, $M = 996.06$, Monoclinic, $P2_1$, $a = 9.2912(15)$, $b = 9.7508(16)$, $c = 12.792(2)$ Å, $\beta = 96.845(3)$, $V = 1150.7(3)$ Å³, $Z = 1$, $D_c = 1.437$ g cm^{-3} , $F(000) = 513$, $R_{\text{int}} = 0.0344$, $S = 1.050$, $R_1 = 0.0560$, and $wR_2 = 0.1156$. X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω -scan technique. Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively. The Flack x parameter (absolute structure parameter) is calculated to be 0.08(3). Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 702868.

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