From discrete complex to 1-D coordination polymer by subtle variation of ligand donor: structures and electrical conductivities

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ABSTRACT
A new coordination compound, [Cu(sphen)] (Hsphen = 2-sulfydryl-1,10-phenanthroline), as an analog of [Cu(ophen)] (Hophen = 1H-[1,10]phenanthroline-2-one), is synthesized and characterized by single-crystal X-ray diffraction. While [Cu(ophen)] is a planar discrete complex showing strong π−π stacking, [Cu(sphen)] is further connected by Cu–S bonds to form a one-dimensional coordination polymer. The bulk electrical conductivity of [Cu(sphen)] (5.0 × 10⁻³ S·cm⁻¹) is ~3 orders of magnitude higher than that of [Cu(ophen)] (3.9 × 10⁻⁶ S·cm⁻¹).

1. Introduction
Coordination polymers have attracted attention for their diversified applications in gas storage and separation [1–3], photoluminescence [4–6], chemical sensing [7–9], magnetism [10–13], electrical conductivity [14–20], etc., because of their designable and chemically modifiable framework structures. Relatively high electrical conductivity can be realized in coordination polymers featuring suitable metal–ligand connectivity and judiciously chosen metal ions and organic ligands [21]. For example, by replacing the phenol group of the ligands with thiophenol, the bulk electrical conductivities of both [Fe₂(DBSBC)] (H₂DBSBC = 2,5-disulfhydrylbenzene-1,4-dicarboxylic acid, σ = 5.8 × 10⁻⁷ S·cm⁻¹) and [Mn₂(DBSBC)] (σ = 1.2 × 10⁻¹² S·cm⁻¹) are about an order of magnitude higher than those of the DOBDC⁺⁻ (H₂DOBDC = 2,5-dihydroxyterephthalic acid) analogs (4.8 × 10⁻⁸ S·cm⁻¹ for [Fe₂(DOBDC)] and 3.0 × 10⁻¹³ S·cm⁻¹ for [Mn₂(DOBDC)]) [22]. In the isostructural metal–organic frameworks [M₂(TTFTB)] (M = Mn, Co, Zn, and Cd; H₄TTFTB = tetrathiafulvalene tetrabenzoic acid), the Cd compound, with the
largest cation radius and shortest S⋯S contact of 3.654(2) Å, showed the highest electrical conductivity (2.86 × 10⁻⁴ S·cm⁻¹), while the Mn, Co, and Zn compounds with longer S⋯S contacts of 3.693(1) to 3.773(3) Å showed electrical conductivities of 8.64 × 10⁻⁵ S·cm⁻¹ to 3.95 × 10⁻⁶ S·cm⁻¹, respectively [23]. Enhancing π–π stacking interactions offers another effective electron-transfer pathway to improve electrical conductivity. For example, [Ag(9,10-diphenylanthracene)(ClO₄)(C₆H₆)₂], with no aromatic stacking in the structure, is an insulator. While extending ligands to construct structures with shorter π–π distances, [Ag₂(benzol[a]pyrene)₃(C₆H₅CH₃)₂] (3.46 Å) and [Ag₄(coronene)₃(ClO₄)₄] (3.23 Å) exhibit good conductivities of 1.0 × 10⁻⁵ S·cm⁻¹ and 3.1 × 10⁻³ S·cm⁻¹ [24].

It has been reported that [Cu(ophen)] (1, Hophen = 1H-[1,10]phenanthrolin-2-one) is a binuclear planar molecule with a large π-conjugation system, which stacks to form a one-dimensional (1-D) chain. Here, we report that replacing the phenol group with thiophenol can produce a 1-D coordination polymer [Cu(sphen)] (2, Hsphen = 2-sulfydryl-1,10-phenanthroline) showing infinite –Cu–S– connections and slightly weaken π–π stacking interactions. The crystal structures, optical band gaps, and electrical conductivities of the two similar structures were compared in this work.

2. Experimental

2.1. General procedures

Hsphen was synthesized according to the literature procedure [25]. Other reagents and solvents were commercially available and used without purification. Powder X-ray diffraction (PXRD) patterns were recorded using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα) at room temperature. Fourier transform infrared (FTIR) spectra were obtained from KBr pellets on a Bruker TENSOR 27 FT-IR spectrometer from 400 to 4000 cm⁻¹. UV–Vis diffuse-reflectance spectra (DRS) were obtained from BaSO₄ powder on a Shimadzu UV-3600 UV–Vis–NIR spectrophotometer (200–800 nm). Electrical conductivity measurements were measured using a Keithley model 2400 sourcemeter under direct current using the two-probe method. Two gold wires were attached to both ends (i.e. along the a-axes as determined by an Oxford Gemini S Ultra CCD diffractometer using the axial photograph method) of the needle-shaped crystal specimens with fulmargin. The electrical conductivity of each compound was calculated by Ohm’s law on four different crystal specimens. All specimens were measured by sweeping the voltage over a wide range. The resistances of each specimen were obtained by linear fitting of the I-V curves. Besides, the electrical conductivities of compacted pellets were measured to be 3.2 × 10⁻⁷ S·cm⁻¹ for 1 and 1.6 × 10⁻⁴ S·cm⁻¹ for 2.

2.2. Synthesis

2.2.1. [Cu(ophen)] (1)

The sample of 1 was prepared according to reported procedures [26, 27]. A mixture of CuCl₂·2H₂O (17.0 mg, 0.1 mmol), Cu(CH₃COO)₂·H₂O (19.9 mg, 0.1 mmol), 1,10-phenanthroline (phen, 18.0 mg, 0.1 mmol), and water (6 mL) was stirred and adjusted to pH 10 with 2 M NaOH solution, then introduced in a 10 mL Teflon-lined stainless steel vessel and heated at 185 °C for 96 h, and then cooled to room temperature at 5 °C·h⁻¹. Dark-brown crystals were obtained by filtration, washed twice with water, and dried in air (yield: 45%).

2.2.2. [Cu(sphen)] (2)

A mixture of CuCl (9.9 mg, 0.1 mmol), Hsphen (21.2 mg, 0.1 mmol), N,N-dimethylacetamide (DMA, 8 mL), and acetone (1 mL) was introduced in a 10 mL Teflon-lined stainless steel vessel and heated at 160 °C for 96 h, and then cooled to room temperature at 5 °C·h⁻¹. Dark-brown crystals were obtained by filtration, washed twice with DMA, and dried in air (yield: 75%).
2.3. Single-crystal X-ray diffraction

Diffraction data were collected on an Oxford Gemini S Ultra CCD diffractometer with mirror-monochromated Cu Ka radiation. Absorption corrections were applied by using the multi-scan program CrysAlisPro. The structure was solved with the direct method and refined with a full-matrix least-squares with the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogens were generated geometrically. Crystal data as well as details of data collection and refinement are summarized in table 1.

3. Results and discussion

3.1. Syntheses and structures

Compound 1 was synthesized by solvothermal reaction of Cu(II) salt and phen in alkaline water, in which phen was in situ hydroxylated to form the ophen⁻ ligand by the help of metal ion [26, 27]. Considering that replacement of the oxygen donor in the ligand may improve electrical conductivity, we chose Hsphen to replace Hophen. Solvothermal reaction of CuCl and Hsphen in DMA/acetone at 160 °C afforded needle-shaped, dark-brown crystals of 2. PXRD confirmed the phase purity of 1 and suggested that 1 and 2 should have very similar structures (figure S1). FTIR spectra of 2 and Hsphen were compared (figure S2). Hsphen featured a stretching vibration at 3300 cm⁻¹ (strong and sharp) and in-plane bending vibrations at ~550 and ~1700 cm⁻¹ (strong and broad) of the S–H bond. These absorptions disappeared completely in 2, indicating that all thiol groups of Hsphen ligands participated in coordination with the Cu ions.

Single-crystal X-ray diffraction showed that 2 crystallizes in the space group P2₁/c (table 1), containing one Cu(I) and one sphen⁻ in the asymmetric unit. Similar with 1, each Cu(I) in 2 is chelated by two nitrogens from one sphen⁻ ligand [Cu–N 2.050(6) and 2.188(6) Å], and then two of such Cu(sphen) units couple by two equivalent Cu–S bonds [2.245(2) Å]. However, the Cu₂(sphen)₂ unit in 2 is stair-shaped rather than planar as for the discrete Cu₂(ophen)₂. Each Cu₂(sphen)₂ connects with two neighbors through additional Cu–S coordination bonds [2.373(2) Å] to furnish the tetrahedral coordination of Cu(I), forming a staircase-like 1-D chain running along the a-axis (figure 1). Inside the 1-D chain, there are strong offset π–π stacking interactions (face-to-face separation ca. 3.40 Å, shortest C⋯C 3.42 Å, C⋯N 3.39 Å, N⋯N 3.81 Å). These 1-D chains pack parallel to form the 3-D supramolecular structure.

Table 1. Crystallographic data and structure refinement results.

| Complex | 1 | 2 |
|---------|---|---|
| Formula | [Cu(ophen)] | [Cu(sphen)] |
| Formula weight | C₁₂H₇CuN₂O | C₁₂H₇CuN₂S |
| Temperature (K) | 180(2) | / |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P2₁/n | P2₁/c |
| a (Å) | 4.7747(4) | 3.8311(2) |
| b (Å) | 12.6876(11) | 19.2717(11) |
| c (Å) | 15.4457(14) | 12.8018(7) |
| β (°) | 95.316(1) | 94.004(5) |
| V (Å³) | 931.7(1) | 942.87(9) |
| Z | 4 | 4 |
| Dc (g·cm⁻³) | / | 1.936 |
| R₁ [I > 2σ(I)]¹ | / | 0.0646 |
| wR₂ [I > 2σ(I)]² | / | 0.1720 |
| R₁ (all data) | / | 0.0739 |
| wR₂ (all data) | / | 0.1776 |
| GOF | / | 1.060 |

¹R₁ = Σ||Fo| − |Fc||Σ|Fo|.
²wR₂ = [Σw(|Fo|²−|Fc|²)²/Σw(|Fo|²)]¹/².
with weak C–H⋯S hydrogen bonds (C⋯S 3.854 Å) as the strongest inter-chain interactions (figure 1). For comparison, the shortest Cu⋯O separation between adjacent Cu2(ophen)2 units in 1 is 3.412(2) Å, too long to be considered as a coordination bond. Probably because of the planar structure which facilitates π–π stacking, 1 exhibits slightly closer π–π stacking interactions (face-to-face separation ca. 3.38 Å, shortest C⋯C 3.39 Å, C⋯N 3.38 Å, N⋯N 3.42 Å) (table 2).

The UV–Vis DRS of 1, 2, and corresponding ligands were measured at room temperature. The absorbance spectra were transformed using the Kubelka–Munk Function [28, 29]

$$\alpha / S = (1 - R)^2 / 2R$$  \hspace{1cm} (1)

where \(R\) is the reflectance, \(\alpha\) is the absorption coefficient, and \(S\) is the scattering coefficient. As shown in figure 2, the band gaps of 1, 2, Hophen and Hsphen obtained by extrapolation of the linear portion of the absorption edges were estimated to be ca. 2.50, 1.61, 3.25, and 2.47 eV, respectively (figures 2 and S3), showing that the thiophenol ligand and corresponding metal complex have smaller band gaps and hence higher charge density than the phenol-based ones. Moreover, the band gap of 2 was close to that of Cu2S (1.2 eV) [30].

Table 2. Selected coordination bond lengths and close contacts of 1 and 2.

|          | 1            | 2            |
|----------|--------------|--------------|
| Cu1–N1   | 2.194(2) Å   | Cu1–N1       | 2.188(6) Å   |
| Cu1–N2   | 1.946(2) Å   | Cu1–N2       | 2.049(5) Å   |
| Cu1–O1   | 1.899(1) Å   | Cu1–S1       | 2.245(2) Å   |
| Cu1–O1B  | 3.412(2) Å   | Cu1–S1D      | 2.373(2) Å   |
| Cu1–Cu1A | 2.630(1) Å   | Cu1–Cu1A     | 2.894(2) Å   |
| O1⋯O1B   | 4.397(2) Å   | S1A⋯S1B      | 3.831(2) Å   |
| O1A⋯O1B  | 4.775(2) Å   | S1A⋯S1D      | 4.015(2) Å   |

1: \(A = -x, 2-y, -z\); \(B = 1-x, 2-y, -z\).
2: \(A = 1-x, 1-y, 2-z\); \(B = -x, 1-y, 2-z\); \(D = -1+x, y, z\).
3.2. Electrical conduction properties

In consideration of the similar supramolecular structures of \( \textbf{1} \) and \( \textbf{2} \) with very different metal-ligand connectivities, we studied their electrical conductivities by the two-probe method using single-crystal samples. The obtained average conductivities were \( 3.9 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1} \) for \( \textbf{1} \) and \( 5.0 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1} \) for \( \textbf{2} \) at room temperature. The conductivity of \( \textbf{2} \) is higher than typical values \( (10^{-9} \text{ to } 10^{-4} \text{ S}\cdot\text{cm}^{-1}) \) of cuprous coordination polymers [31–34], which can be explained by the infinite –Cu–S– chains and strong π–π stacking interactions. In contrast, the conductivity of \( \textbf{1} \) is lower than the typical values of cuprous coordination polymers. The difference between \( \textbf{1} \) and \( \textbf{2} \) is obviously larger than previous reports concerning isostructural complexes possessing phenolate and thiophenolate ligands, which can be explained by the fact that \( \textbf{1} \) is a discrete molecular complex, while \( \textbf{2} \) is a 1-D coordination polymer connected by infinite Cu–S chain. To further explore the conducting mechanisms of \( \textbf{1} \) and \( \textbf{2} \), their conductivities were measured at other temperatures. As shown in figure 3, from 243 K to 343 K, their conductivities increased from \( 9.4 \times 10^{-7} \text{ S}\cdot\text{cm}^{-1} \) to \( 5.4 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1} \) for \( \textbf{1} \) and from \( 3.0 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1} \) to \( 6.8 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1} \) for \( \textbf{2} \), showing a typical semiconducting behavior, following the Arrhenius law [35]:

\[
\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right)
\]

where \( E_a \) represents the activation energy and \( \sigma_0 \) is a pre-exponential factor. The \( E_a \) values of \( \textbf{1} \) and \( \textbf{2} \) were calculated as 146 and 84 meV, respectively (figure S4), which are similar with those of electrically conductive coordination polymers [36, 37].

Figure 3. Temperature-dependent electrical conductivities of single crystals of \( \textbf{1} \) and \( \textbf{2} \).
4. Conclusion

A new 1-D coordination polymer [Cu(sphen)] possessing infinite Cu–S chain has been synthesized and characterized. Although the structure of ophen– is similar to that of sphen–, the smaller radius of oxygen donor leads [Cu(ophen)] to be a discrete molecule. The bulk electrical conductivity of [Cu(sphen)] is ~3 orders of magnitude higher than that of [Cu(ophen)], which demonstrates that the contribution of the –Cu–S– chain to the electrical conductivity is more important than that of π–π stacking. This work provides an example for tailoring the structure and electrical conductivity of coordination polymers.

Supplementary material

The PDF file of figures of PXRD, FTIR, UV–Vis DRS, and Arrhenius plots of the temperature-dependent conductivities. Supplemental data for this article can be accessed via http://dx.doi.org/10.1080/00958972.2016.1190838. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center with CCDC number 1444347. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Disclosure statement

No potential conflict of interest was reported by the authors.

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