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Role of spacers and substituents in the self-assembly process: Syntheses and characterization of two novel thiocyanatocuprates polymers

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ABSTRACT

Two novel cation-induced complexes, {(Phen-dq) $[Cu_2(SCN)_4]\}_n$ (**1**) and {(Phen-dzp) $[Cu_2(SCN)_4]\}_n$ (**2**) [Phen-dq = $(C_{14}H_{12}N_2)^{2+}$, 5,6-dihydropyrazino[1, 2, 3, 4-*lmn*]-1, 10-phenanthrolinium, Phen-dzp = $(C_{15}H_{14}N_2)^{2+}$, 6,7-dihydro-5*H*-[1, 4]diazepino[1, 2, 3, 4-*lmn*][1,10]phenanthroline-4, 8-diium], have been synthesized via the self-assembly reaction in solution. The compound **1** possesses a two-dimensional supramolecular network linked by bridging thiocyanate groups. Complex **2** is also a two-dimensional polymeric architecture with the organic cation Phen-dzp trapped in it. Each Cu(I) atom is coordinated by two N atoms and two S atoms from four NCS groups to form a $Cu_2(NCS)_2$ rectangular dimer unit. In these two compounds, thanks to the difference from organic cations, the simple modification from Phen-dq to Phen-dzp leads to distinct structures between **1** and **2**, and these "planar" cations are effective guests to manipulate the aggregate structure of thiocyanatocuprates.

The constructions and characterizations of supramolecular materials with novel properties represent new directions in solid-state chemistry [1–3]. This is due to fundamental interest in self-assembly processes, supramolecular chemistry and perhaps, most significantly, crystal engineering, topological diversity and potential applications in the fields including superconductors, catalysis, magnetic materials, optical materials, luminescent materials, solution adsorption or separation, and so on [4–8]. The supramolecular compounds, especially the coordination polymers directed by organic cations, have gradually become one of the most active exploring areas of the chemical engineering and molecular science [9]. Generally, the polymers have distinctive cavities or channels in network, so they possess different kinds of novel properties. Thereby, we try to explore the laws of self-assembly and mechanism in M (IB, IIB)-X supramolecular polymers. Among the numerous families of hybrid functional materials, the polymeric frameworks of halogenocuprates(I) are important, but there are fewer examples of thiocyanatocuprates extended structures [10]. In the recent studies, the use of 1,ω-bis(pyridinium)alkane cation-templated synthesis in the construction of polymeric thiocyanate frameworks has been reported [11,12]. The reason why we selected NCS^- group was that it exhibits various bonding modes, such as terminal (*t*-) mode, end-on μ_2-bridging mode, end-to-end μ_2-bridging mode and 1,1,3-μ_3-bridging mode [13]. In this article, we reported the synthesis, crystal structure and fluorescent properties of two novel thiocyanatocuprates(I) coordination polymers: {(Phen-dq) $[Cu_2(SCN)_4]\}_n$ (**1**) and {(Phen-dzp) $[Cu_2(SCN)_4]\}_n$ (**2**) induced by organic cation Phen-dq [14] and Phen-dzq [15] (Scheme 1), which represent a new advancement in this direction.[1]

The X-ray single-crystal structure analysis [16][2] reveals that complex **1** crystallizes in the monoclinic system with space group *P*2(1)/c. The structure of the compound **1** is made up of organic Phen-dq cations trapped in the infinite 2D inorganic $[Cu_2(SCN)_4]_n$ nets. The

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[1] *Synthesis of {(Phen-dq)* $[Cu_2(SCN)_4]_n$ *(**1**) and {(Phen-dzp)* $[Cu_2(SCN)_4]_n$ *(**2**).* The Phen-dq and Phen-dzp were prepared as the bromide salt by direct alkylation of 1,10-phenanthroline monohydrate with 1, 2-dibromoalkane and 1, 3-dibromoalkane. Other chemicals were obtained from commercial sources and used as received without further purification. The title complex **1** was prepared: A methanol solution of Phen-dq·2Br (0.388 g, 1 mmol) was added to a stirring colorless solution of CuNCS (0.121 g, 1.0 mmol) dissolved in 10 mL of DMF/H_2O (volume ratio of 4:1) in the presence of excess KNCS (0.498 g, 5.0 mmol). The solution was then filtered and slowly evaporated in a vial at room temperature. Dark crystals of **1** suitable for X-ray analysis were obtained after 7 days in about 41% yield. The product is not soluble in common solvents. Anal. Calcd for $C_9H_6CuN_3S_2$: C, 38.08; H, 2.13; N, 14.80. Found: C, 38.05; H, 2.25; N, 14.88%. Compound **2** was obtained as green crystals by a similar reaction procedure. Yield: 51.7%. The product is not soluble in common solvents. Anal. Calcd for $C_{19}H_{14}Cu_2N_6S_4$: C, 39.22; H, 2.43; N, 14.41. Found: C, 39.23; H, 2.45; N, 14.48%.

[2] *X-ray structure determination.* Crystallographic data for the title compounds were collected at 291(2)K on a Bruker APEX-II area-detector diffractometer with Mo–Ka radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using SADABS. The structure was solved with direct methods and refined with full-matrix least-squares techniques on F^2 using the SHELXTL program package [14]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restrains. Crystal data for the compound **1**: monoclinic, *P*2(1)/n, a = 8.8380(14) Å, b = 10.7982(17) Å, c = 11.6389(18) Å, $\alpha = 90°$, $\beta = 112.31°$, $\gamma = 90°$, V = 1027.6(3) Å^3, Z = 4, *F*(000) = 568, GOF = 1.265, $R_1 = 0.0656$, $wR_2 = 0.1521$; crystal data for the compound **2**: monoclinic, *P*2(1)/c, a = 17.805(8) Å, b = 10.352(5) Å, c = 11.709(5) Å, $\alpha = 90°$, $\beta = 91.735(8)°$, $\gamma = 90°$, V = 2157.0(18) Å^3, Z = 4, *F*(000) = 1100, GOF = 2.559, $R_1 = 0.1576$, $wR_2 = 0.4004$.

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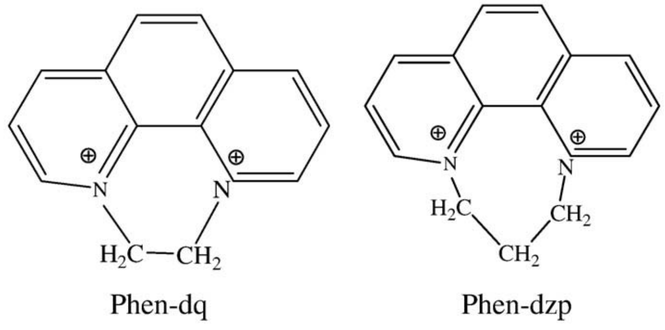

Scheme 1. Phen-dq and Phen-dzp.

unit structure is shown in Fig. 1. In the polymeric structure, copper atoms are in distorted tetrahedral sites, covalently coordinated to two N atoms and two S atoms from distinguished NCS$^-$ groups with the bond angles ranging from 52.0 (2) to 121.6 (3)°.The Cu–N distances vary from 1.946 (6) to 1.960 (5) Å, comparable with those found in the pyridinium analogue (1.93–1.95 Å) and $[(CuBr)_3(C_{10}H_7N_3)]$ (2.004 (2) Å) [17]. Each inorganic polymeric net is composed of large hexagonal rings, which is formed by sharing four μ-N, S NCS$^-$ groups and two $[Cu_2(NCS)_2]$ rectangular units and further binds with six adjacent hexagonal rings. In these hexagonal rings there exist three types of opposite furthest Cu–Cu dimensions: 15.58, 11.64 and 9.63 Å. However, the Cu···Cu separations through the single μ-NCS bridge have one distance of 6.06 Å; the Cu–Cu distance in the $[Cu_2(NCS)_2]$ rectangular unit is 5.27 Å. Topologically, the network can be identified as a 2D (6,3) net (Fig. 2), where two bridging NSC$^-$ anions in the $[Cu_2(NCS)_2]$ rectangular units only act as a connector, slightly different from the regular one, $\{(bpe)[Cu_2(NCS)_4]\}_n$ [12]. In the solid state, the Phen-dq dications are located in large cavities among the sheets (Fig. 3) in the polymer with no unusually short contacts to it, as evidenced by their considerable flexibility for maneuvering. In consequence, dication geometries are imprecise as well as being somewhat uncertain in their assignment.

Complex **2** is also a two-dimensional polymeric architecture with the organic cation Phen-dzp trapped in it. The polymeric anion comprises two different types of crystallographically independent copper atoms Cu1 and Cu2 linked by thiocyanate groups. Both copper atoms are four-coordinate and are in distorted tetrahedral geometry. Cu1 has an environment of two nitrogen atom [Cu1–N, 1.935 (15) and 1.998 (14) Å] and two sulfur atoms [Cu1–S, 2.294 (4) and 2.651 (5) Å], Cu2 is coordinated by two sulfur atoms [Cu2–S, 2.288 (5) and 2.664 (5) Å] and two nitrogen atoms [Cu2–N, 1.920 (15) and 1.980 (10) Å]. In the distorted tetrahedron of copper atom, the bond angles range from 96.9 (5) to 129.1 (4)°. They compare well with those found in its pyridinium analogue $\{[pyH^+][Cu_2(SCN)_3^-]\}_n$ (103.7 (1)–122.1 (4)°) [18]. This coordinate mode forms a $Cu_2(NCS)_2$ rectangular dimer unit, and the separation of the adjacent Cu(I)···Cu(I) is 5.344 Å. In the polymeric structure, SCN$^-$ as a multidentate ligand exhibits its various bonding modes such as terminal SCN$^-$ group with Cu–N (t-SCN$^-$), end-to-end bridging mode μ_2-N, S SCN$^-$ and 1,1,3-μ_3-bridging mode μ_3-S,S,N SCN$^-$.

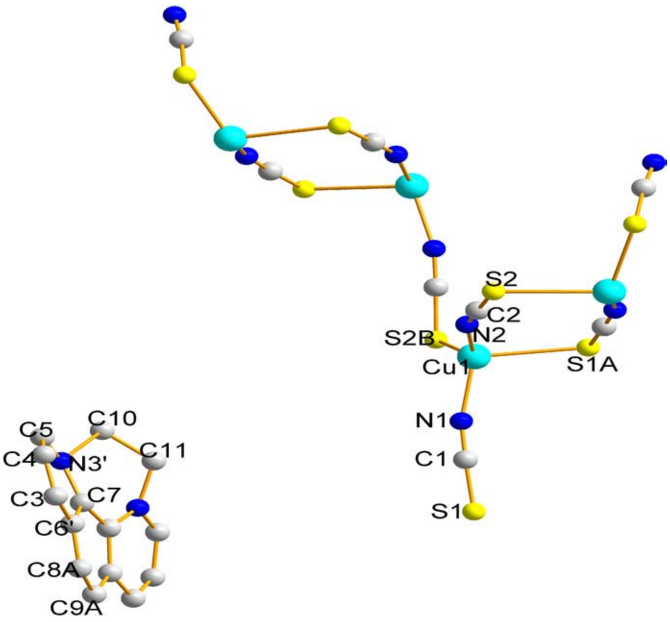

Fig. 1. A drawing of the copper (I) coordination environment in the compound **1**.

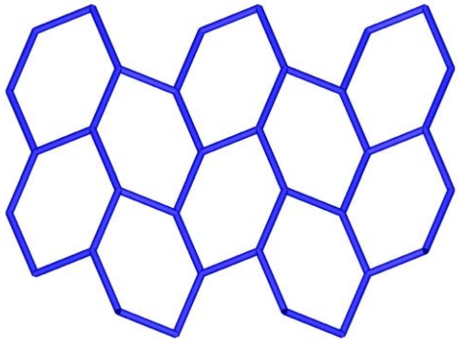

Fig. 2. View of the coordination environment of the Cu center in the compound (**1**) along c-direction, showing the (6,3) topology.

Each inorganic polymeric planar net is composed of large hexagonal rings formed by sharing four NCS$^-$ and two $[Cu_2(NCS)_2]$ rectangular units with six adjacent hexagonal rings. In these hexagonal rings there also exist three types of opposite furthest Cu–Cu dimensions: 12.84, 11.71 and 8.60 Å. Correspondingly the Cu···Cu separations through the μ-NCS single bridge have two distances of 6.11 and 6.01 Å; the Cu–Cu distance in the $[Cu_2(NCS)_2]$ rectangular unit is 5.34 Å. Topologically, in **2** the network can be identified as a regular 2D (6,3) net (Fig. 4); whereas in **1** the (6,3) ring displays two kinds of pack modes, indicative of distinctive difference with that in **2**. This 2D infinite space packing was realized through weak C–H···S bond and C–H···N bond interactions, as is shown in Fig. 5. In both two compounds, the Phen-dq and Phen-dzp portions, acting as anti-anti-anti-anti configuration, interlude irregularly in the two-dimensional network of the inorganic polymeric part. The two compounds have lower dimension structures than the 3D structure $\{(bppt)[Cu_2(NCS)_4]\}_n$ [17]. All this boils down to the cation size effect between "linear" and "planar" cations. There have been reported inorganic $(CuNCS)_n$ networks perforated with N-containing dications [12,17], but **1** and **2** can be regarded as the first representative examples of polymeric framework from 1,10-phenanthroline derivatives dication.

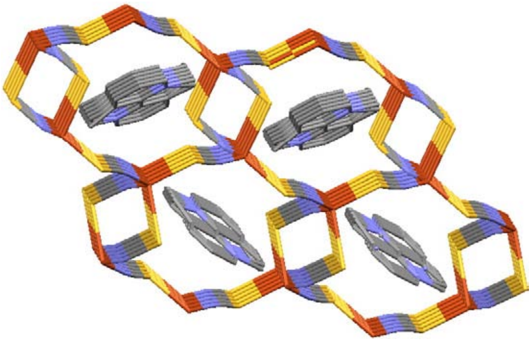

Fig. 3. The supramolecular architecture of complex **1** in the ac plane.