Formation of a Novel Polymeric Cadmium(II) Complex Bridged by Sulfur and Thiocyanato Ions

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The title complex, $\{[N(CH_3)_4]_2[Cd(SCN)_2S]\}_n$, was prepared by self-assembling from the reaction of a methanol/water (volume ratio, 1/1) solution containing cadmium(II) thiocyanate with equivalent amount of tetramethylammonium thiocyanate. The result of single X-ray determination for the complex reveals that a novel polymeric cadmium(II) complex bridged by sulfur and thiocyanato ions was obtained, which formed a two-dimensional (2D) structure.

Recently, there are much attention in the field of research on formation of self-assembled coordination polymers because of their tunability and many potential applications.[1–3] The synthesis of low dimensional organic-inorganic hybrid materials with useful physical properties presents an attractive new direction in solid state chemistry.[4,5] This can be accomplished by incorporating certain organic moieties with low-dimensional inorganic networks. The synthetic approach is based on self-assembly of the functional components into well-defined crystalline materials, which allows important structure-property relationships to be established.[6,7]

The nonlinear optical (NLO) system of metal complexes gives a new dimension of study and introduces many new variables in the development of chemistry and photonics technology.[8–11] The discovery of the thiocyanato complexes of cadmium(II) as new NLO materials, in which the metal atoms are bridged linearly by thiocyanate (SCN) ions, has already been reported.[12–15] Furthermore, on the basis of polymeric cadmium thiocyanate anions and certain counter organic cations,[5,7,12,14–17] the new series of coordination compounds may be described as inorganic polymers with organic spacers (IPOS), a class of hybrid materials combining the advantageous properties of inorganic, organic, and polymeric materials.[18–20] From this expectation, we have synthesized the title complex, $\{[N(CH_3)_4]_2[Cd(SCN)_2S]\}_n$ (**1**), which forms an infinite two-dimensional (2D) layered structure constructed by self-assembling. The crystal structure was determined by the single-crystal X-ray diffraction method.

In this context, complex (**1**) represents our first successful attempt in utilizing a sandwich cations (tetramethylammonium) as a spacer/controller in influencing the arrangement and alignment of the infinite anionic layers. In this layered inorganic lattices, cadmium(II) atoms are bridged by thiocyanate and sulfur ions forming a new type of polymeric 2D-structure. To the best of our knowledge, such a kind of structure, in which inorganic polymeric layers were linked with organic spacers by mutual electrostatic interaction, was attractive and widely studied. So it was thought to be reasonably interesting to study this new kind of configuration and clarify the peculiar structure.

Complex (**1**), $\{[N(CH_3)_4]_2[Cd(SCN)_2S]\}_n$, was prepared in a methanol/water (volume ratio, 1/1) solution containing the cadmium(II) thiocyanate and equivalent amount of tetramethylammonium thiocyanate.[21] This mixture was stirred under reflux for 20 h and then, the colorless solution was cooled and filtered. The filtrate was left standing for several days at ambient temperature and precipitated crystals suitable for X-ray structural analysis[22] were obtained from slow evaporation (Yield: 65%; Anal. Calcd for (**1**): C, 29.34; H, 5.87; N, 13.69%. Found: C, 29.18; H, 5.62; N, 13.83%).

In our experiments, an usual synthesis method results in a novel complex of an unusual structure containing sulfur ions probably due to the decomposition of cadmium(II) thiocyanate in the hot solution.[13b] In the peculiarly interesting structure of (**1**), a new type of 2D polymeric layer structure contains cadmium atoms bridged by thiocyanate (SCN) ions and sulfur ions in a zig-zag way (Figure 1). Tetramethylammonium cations are not bridged but isolated from the polymeric anions, only mutual electrostatic interaction between them (Figure 2).

Atom labeling and principle structural features of polymeric $\{[N(CH_3)_4]_2[Cd(SCN)_2S]\}_n$ reveal that the major anionic layers in the crystal structure have unique polymeric form and respective types of bridging modes. The respective cadmium(II) atoms are 2N4S-hexa-coordinated, building up slightly distorted octahedral geometries. Neighboring cadmium atoms are either bridged by two SCN (μ-1,3-NCS) ions or bridged by two sulfur

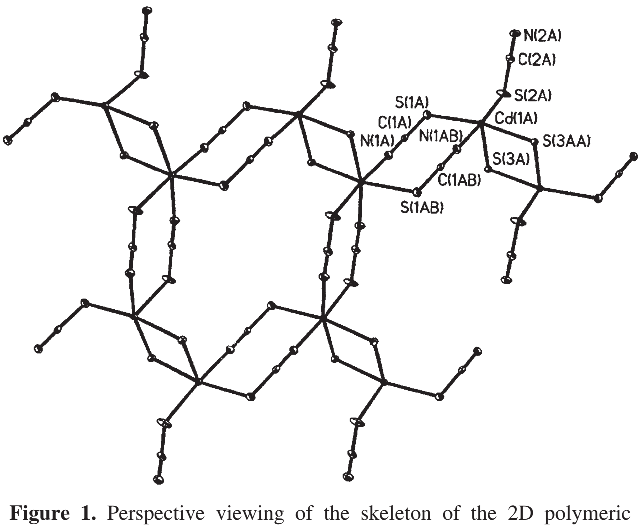

Figure 1. Perspective viewing of the skeleton of the 2D polymeric anion of (**1**).

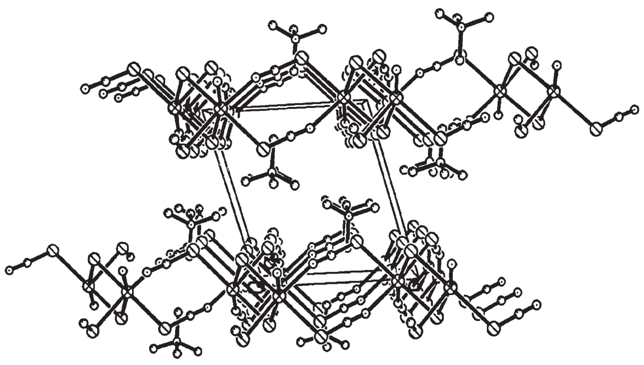

Figure 2. Crystal packing drawing of (**1**). Hydrogen atoms are omitted for clarity.

ions (μ_2-S) on the same side, not in cases of the other thiocyanatocadmate(II) complexes.[14,23,24] The coordinated modes in the structure can be successfully explained by the hard and soft acids and bases (HSAB) concept.[25]

Both of thiocyanate and sulfur ions are doubly bridged donors resulting in the formation of the anionic polymeric layers. The observed Cd–S bond length of the bridging SCN [Cd(1)–S(1): 2.726(2) Å, Cd(1)–S(2): 2.738(2) Å] is longer than that of the bridging S [Cd(1)–S(3): 2.6569, Cd(1)#3–S(3): 2.6041 Å] revealing that there are some difference between the coordinated Cd–S bonds in the novel bridged crystal structure. The bond length of Cd–S(μ_2-S) is shorter than that of Cd–S(1,3-SCN) indicating that the sulfur ion (μ_2-S) coordinates to cadmium(II) atom more easily. However, the respective Cd–S bond lengths as well as Cd–N bond lengths are a little different from each other and that, all of them are shorter than the respective sums of Shannon's ionic radii: 2.79 and 2.41 Å.[26] Additionally, the values of bond lengths of (**1**) are not much different from the respective values of lewis base adducts of the cadmium(II) thiocyanate, which have the same type of doubly bridged SCN ions in their linearly polymeric structures.[14,27]

The photoluminescence behavior[28] of (**1**) in solid state was carried out at room temperature revealing that the complex with such specific molecular structure exhibited a strong fluorescent emission band at ca. 423 nm (Excitation: 336 nm), which is shorter compared with the emission of $Cd(SCN)_2$ at ca. 450 nm and that of CdS particles from 500 nm to 700 nm.[29] In addition, thermogravimetric analysis (TGA) of the crystalline sample showed no chemical decomposition below 299 °C exhibiting high thermal stability. Further heating of it resulted in the formation of CdS at 425 °C, as indicated by the total weight loss of 66.1% (Calcd 65.7%) of the sample.

In conclusion, the present study shows that such a novel 2D polymeric structure as that in this article can be assembled from small component molecules by the rational design of suitable ligands and metal ions. It is mutual electrostatic interactions, existing between the 2D polymeric layer anions and the isolated cations, that effectively constructs a stable multilayered organic-inorganic hybrid structure. This result leads to a close packed arrangement favoring the formation of a highly ordered material. The condensed coordination polymer may be an excellent candidate as advanced materials for the light-emitter applications owing to its strong fluorescence emission and reasonable thermal stability. Further studies on related properties are currently under investigation.

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22 Crystal data for (**1**): $CdC_{10}H_{24}N_4S_3$ $M_w = 408.92$, triclinic, $P\bar{1}$, $a = 8.2238(3)$ Å, $b = 8.9636(2)$ Å, $c = 9.0804(3)$ Å, $\alpha = 107.718(1)°$, $\beta = 101.396(1)°$, $\gamma = 99.230(1)°$, $V = 607.36(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.831$ g cm^{-3}, Mo Kα, $T = 183(2)$ K, A total of 3704 reflections were measured. $R = 0.0677$, and $wR_2 = 0.1750$ for 2292 observed reflections with $I > 2\sigma(I)$. Min. and Max. resd. dens. are −2.77(7) and 2.59(5) e.A^{-3}, respectively.

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28 The photoluminescence spectra of (**1**) in solid state were measured with a Perkin Elmer LS50B spectrofluorimeter. Strong emission at approximately 423 nm (Excitation: 336 nm) was observed which can be assigned to the $\pi^* \rightarrow \pi$ transition of the thiocyanate moiety.

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