A Novel Coordination Polymer Incorporating a Dimeric Silver Unit: Increasing Structural Dimensionality through Ag–Ag and Ag–Hetero Atom Interactions

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A novel complex assembly $[Ag_2(tdpd)]_n$ (H_2tdpd = 1,4,5,6-tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile) was synthesized and characteraized. $[Ag_2(tdpd)]_n$ consists of dinuclear modules with Ag–Ag interactions. The dimmer modules are connected each other by additional but effective Ag–hetero atom interactions forming a three-dimensional structure.

Polynuclear metal complexes and solid-state extended lattices, particularly those of coinage metal(I) ions with d^{10} electronic configuration, have attracted much attention in view of their intriguing structural diversity and the d^{10}–d^{10} interaction between two closed shell cations. By taking advantage of Ag–Ag interaction that promotes the aggregation of silver(I) centers into various polyhedra, various kinds of cage and cluster compounds are obtained.[1] On the other hand, weak dative interactions, that is, Ag–hetero atom interactions are used to increase the dimensionality of the assemblies and influence the supramolecular structure although the interactions are not controllable and the bond formation is subjected to serendipity.[2] In these contexts, if the Ag–Ag interaction is used to assemble molecular components in the weak bonding-based structural motifs, the solid may be a new type of inorganic–organic assembly. This idea extends our interest to design weak bonding interaction-based higher dimensional suprastructures of metal complexes by crystal engineering. To construct a novel silver(I) coordination polymer, 1,4,5,6-tetrahydro-5,6-dioxo-2,3-pyrazinedicarbonitrile (H_2-tdpd) is chosen to connect metal centers. Deprotonation of this molecule yields $tdpd^{2-}$ dianion with potentially over six coordination or hydrogen-bonding sites, and thus the excellent bridging capabilities allow the formation of polymeric frameworks displaying a wide variety of geometries.[3] In this communication, we will report a novel three-dimensional silver(I) polymer, $[Ag_2(tdpd)]_n$ (**1**), which is constructed from ladder-like chains.

1 was obtained by the following method: an aqueous solution (10 mL) of silver perchlorate (2×10^{-5} mol) was transferred to a glass tube, then an aqueous solution (10 mL) of H_2tdpd (1×10^{-5} mol) was poured into the tube without mixing the two solutions. Yellow plate crystals began to form at ambient temperature in a week; yield 90%.[4] Anal. Found: C, 19.05; N, 14.75%. Calcd for $Ag_2C_6N_4O_2$: C, 19.18; N, 14.91%. An ORTEP drawing of the structure around the silver atoms in **1** with the atom-numbering scheme is shown in Figure 1a. Compound **1** consists of two nonequivalent silver ions and a $tdpd^{2-}$ dianion forming a dimeric building unit $[Ag_2(tdpd)]$ in a crystal. The presence of multipoint recognition patterns between tdpd and Ag in $[Ag_2(tdpd)]$ is of interest. The $tdpd^{2-}$ dianions are attached to eight silver centers by six hetero atoms using coordination-bonding interaction, Ag–Ag interaction and Ag–hetero atom contact (vide infra). The Ag–Ag separation (3.088(1) Å) in the dimeric units of **1** is significantly shorter than twice the van der Waals radii of silver (3.44 Å). A fragment Ag–N–C–O–Ag is similar to that found in the ligand-supported dinuclear Ag complex.[5] In the presence of the anionic ligand, the metal–metal separation becomes shorter to produce the argentophilic attraction. Therefore, Ag(1) and Ag(2) assume distorted planar and square pyramidal coordination geometry, respectively. The dimeric building units are connected each other by the coordination bonding interactions (Ag(1)–O(1); 2.211(5) Å, Ag(1)–N(2′); 2.227(6) Å, Ag(2)–N(1); 2.190(6) Å, Ag(2)–O(2′);

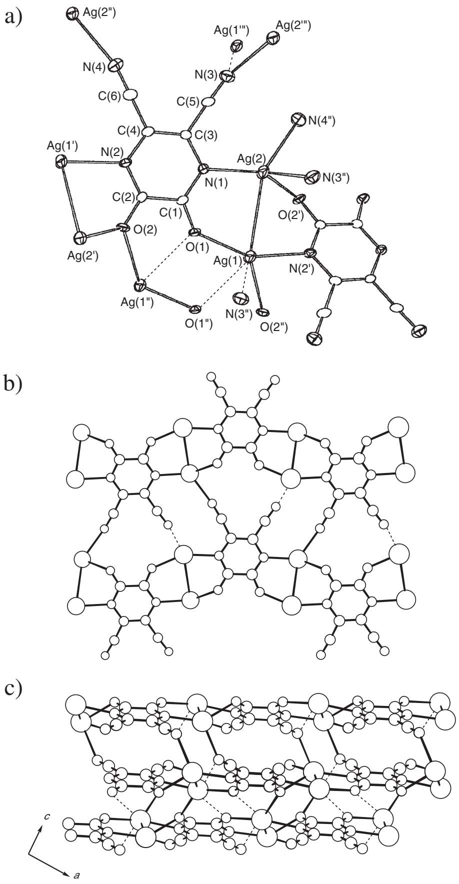

Figure 1. (a) ORTEP drawing of **1** with labelling scheme and thermal ellipsoids at the 50% probability level for Ag, O, N, and C atoms. (b) Part of the 2-D structure of **1**. (c) Assembled structure of **1**.

2.299(5) Å) forming a ladder-like "tape" motif extending to the diagonal between the *a* and *c* axes. The cyano groups of the tdpd^{2-} dianions project forward to the both sides of the tape motif alternatively to interact to the adjacent tape motifs. Figure 1b shows a corrugated sheet structure of **1**, constructed from the tape motifs bridged by interchain coordination interactions between the Ag(2) ion and the nitrogen atom of the cyano group (Ag(2)–N(4′): 2.401(6) Å) Interestingly, another Ag–N contact,[2] which may support the sheet, is found (Ag(1)–N(3′); 2.728(5) Å). Furthermore, the sheet is connected by two types of coordination-bonding interactions (Ag(2)–N(3″); 2.485(6) Å, Ag(1)–O(2″); 2.589(5) Å) and an additional Ag–O contact (Ag(1)–O(1′); 2.800(5) Å)[2] forming a three-dimensional structure (Figure 1c). There are two types of inter-sheet distances due to the packing sequence. The sheet possesses two sides: "oxygen-rich" (OR) and "nitrogen-rich" (NR) sides, and then, the stacking sequence becomes ···OR–NR···NR–OR···OR–NR···.

Figure 2a shows a Raman spectrum (50–200 cm^{-1}) for **1**. The vibrational mode of interest in this work is a Ag–Ag stretching vibration $\nu(\mathrm{Ag_2})$. On the basis of the frequency range (33–114 cm^{-1}) where this mode should appear $\nu(\mathrm{Ag_2})$ is assigned at 72.5 cm^{-1} and the force constant $F(\mathrm{Ag_2}) = \mu(2\pi c\nu(\mathrm{Ag_2}))^2$ (μ = reduced mass) estimated from the $\nu(\mathrm{Ag_2})$ value assuming a pure Ag_2 stretching mode is 0.18 mdyn·Å^{-1}. There is a linear correlation between the Ag_2 bond distance and $\ln F(\mathrm{Ag_2})$ ($r(\mathrm{Ag_2}) = -0.284 \ln F(\mathrm{Ag_2}) + 2.53$), and the obtained value fits close to the line of the correlation.[6] This supports the assignment of the Raman band to the Ag–Ag stretching vibration. Figure 2b shows the electronic absorption spectra of **1** and tdpd^{2-} dianion at room temperature. One absorption shoulder is observed at 237 nm for **1** while no absorption shoulder is found for tdpd^{2-} dianion. This absorption would not arise from intraligand transition and can be assigned to a spin-allowed ($4d_{\sigma^*} \rightarrow 5p_{\sigma}$) transition originating from Ag(I)–Ag(I) interactions in the ground and excited states.[6] Moreover, the complex displays intense solid-state photoluminescence with emission maximum at 610 nm upon excitation at 237 nm (Figure 2c). This emission may be assigned to a metal to ligand charge-transfer (MLCT) transition (Figure 2d).[6] These results also support the presence of Ag(I)–Ag(I) interaction in the solid state.

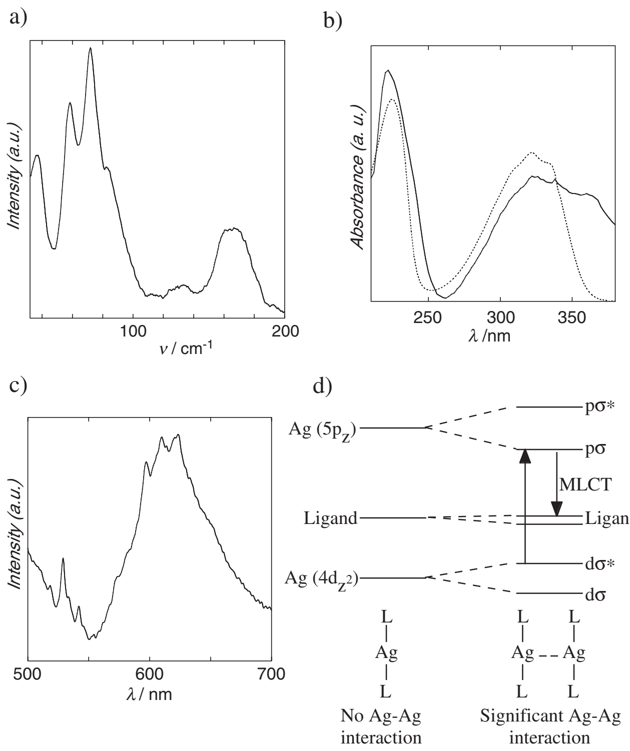

Figure 2. (a) Raman spectrum of **1**. (b) Absorption spectra of **1** in KBr (solid line) and ethanol solution of H_2tdpd with excess of triethylamine (broken line). (c) Emission spectrum of **1** in solid state. (d) Schematic representation of the orbital splittings expected with Ag–Ag interactions.

In conclusion, the present work demonstrates that the ligating property of tdpd^{2-} dianion leads to the formation of the disilver unit with Ag–Ag interaction for infinite coordination networks. By the choice of suitable coordination sites of tdpd^{2-}, novel metal-assembled complexes with unique topologies will be constructed. Moreover, weak bonding interactions are effective tools for the control of dimensionality and supramolecular topology.

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4 Crystal data for **1**: $Ag_2C_6N_4O_2$, fw = 375.83; pale yellow, monoclinic, space group $P2_1/n$, $a = 12.381(4)$, $b = 8.029(2)$, $c = 7.370(3)$ Å, $\beta = 95.67(3)^\circ$, $V = 726.1(4)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 3.438$ gcm^{-3}, $\mu(\mathrm{Mo\,K\alpha}) = 53.46$ cm^{-1}, $R = 0.058$ ($I > 2\sigma(I)$), $wR_2 = 0.151$ (all data). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (CCDC 229192).

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