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Novel hybrid hetero-sandwich architectures *via* stoichiometric control of host–guest self-organization†

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Received (in Columbia, MO, USA) 31st October 2003, Accepted 5th January 2004
First published as an Advance Article on the web 18th February 2004

Thiocyanate cadmium and methylviologen hybrid host–guest compounds give two novel multiple sandwich architectures with regular or irregular grids of the anionic layer in the structures as effected by the molar ratios of starting ingredients, and show evidence of charge-transfer to the organic dications.

Conceptually, the multiple expression of molecular information consisting of a set of pre-programmed instructions has just started to emerge as a theme in self-organized metallosupramolecular architectures.[1,2] For the final products, the structures and functions should be reasonably predictable and tunable, because such information is pre-coded initially in the starting ingredients. Organic–inorganic hybrid materials fabricated by host–guest approaches, such as cadmium thiocyanate inorganic hosts with organic species as guests, can be one such set of examples.[3–8] As yet, little attention has been paid to the studies of compounds with an anionic cadmium thiocyanate host with cationic guest.[5–8] To the best of our knowledge, most of the these frameworks are 1-D structures while 2-D or 3-D anionic frameworks are rather rare,[5–8] and 3-D structures have not, as yet, been identified. To date, there are only three previous examples of 2-D anionic cadmium thiocyanate layered structures ($[RbCd(NCS)_3]$, $[(12C4)_2Cd][Cd_2(NCS)_6]$ and $[(12C4)_2Cd][Cd_3(NCS)_8]$).[5,6] The organic species, cationic methylviologen ($[MV]^{2+}$ = *N*,*N*′-dimethyl-4,4′-bipyridinium), has an adjustable torsional angle between two bipyridinium rings. Therefore, it is quite reasonable to predict that $[MV]^{2+}$ will play a role as an anisotropic steric "template" in the formation of the anionic framework of higher dimensions, since the shape, size, and charge of the guest have considerable effect on the arrangement of the host framework structure. Additionally, $[MV]^{2+}$ has been used in applications and research areas related to biology, photochemistry, and electrochemistry, owing to its interesting electron-accepting nature.[9,10]

Our aim is to fabricate unique organic–inorganic hybrid compounds, both as novel host–guest structures for purposes of learning about design principles, and for developing physical properties of materials. Herein, we report two novel hetero-sandwich compounds, $[MV][Cd(NCS)_2(NCS)_{4/2}]$ **1** and $[MV]_3[Cd_7(NCS)_{40/2}(H_2O)_2]$ **2**, with cadmium thiocyanate and $[MV]^{2+}$ as the inorganic and organic building blocks, respectively. The synthesis of **1** and **2** was affected by taking molar ratios of 9:1:1.5 and 9:3:1.5 for KSCN, $3CdSO_4{\cdot}8H_2O$ and $[MV]Cl_2{\cdot}2H_2O$, thus producing yellow crystals **1** and colorless crystals **2**, respectively. The single-crystal X-ray structure determinations§ reveal that the building blocks of the coordination polymer for **1** assemble into a 2-D regular grid, and for **2** into an irregular network while $[MV]^{2+}$ arrays are arranged in quasi-layers between networks (Fig. 1)

In **1**, each Cd^{2+} ion is linked by four single-mode NCS^- bridges along the *b*- and *c*-axis to form a regular grid framework (Fig. 1(a)), and by two N-coordinated terminal NCS^- ligands pointing up/down out of the *bc*-plane. Along the *b*- or *c*-axis, each chain consists

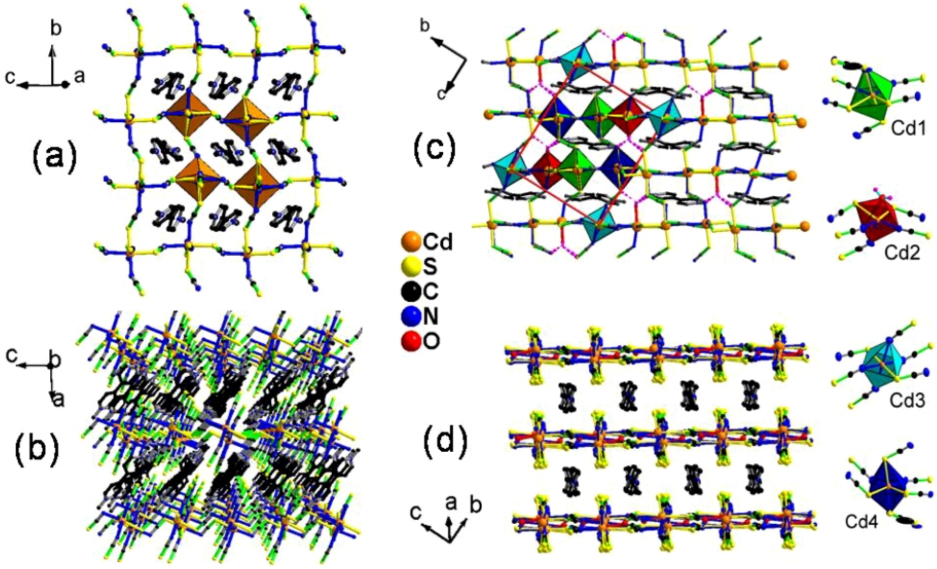

Fig. 1 Perspective view of the stacking of the infinite 2-D inorganic layer and organic host array for **1** (a) and **2** (c), including building unit indications of the cadmium octahedra in **2**, and a view along layers for demonstrations of hybrid hetero-sandwich architectures of **1** (b) and **2** (d).

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† Electronic supplementary information (ESI) available: chemical preparations, crystal data and details of determinations, the structure of compound $[MV](NCS)_2$, IR spectra for compounds **1**, **2** and methylviologen dichloride and EPR spectra for compounds **1** and **2**. Table S1: Crystallographic data for $[MV](NCS)_2$. See http://www.rsc.org/suppdata/cc/b3/b313846a/

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DOI: 10.1039/b313846a

of unique $\cdots$N–C–S–Cd–N–C–S$\cdots$ or $\cdots$S–C–N–Cd–S–C–N$\cdots$ moieties with average Cd$\cdots$Cd distances of ~ 6.77 Å. The extended 2-D network is thereby composed of alternating chains in these two directions. The $[MV]^{2+}$ species with two twisted rings at a dihedral angle of 23.1° reclines in the interlayer space of the inorganic frameworks and the overlap of the two layers resembles a checkerboard when viewed from the direction shown (Fig. 1(a)). The long axes of all viologen molecules are parallel to each other and mitered into the inorganic layers with a bevel of ~ 51.8° (Fig. 1(b)). The inorganic layer is connected to organic species *via* hydrogen bonds of CH$\cdots$N or CH$\cdots$S, which stabilizes the hetero-sandwich structure and extends to a 3-D supramolecular structure.

The inorganic framework of **2** reveals an unprecedented pattern from a view of the *bc*-plane (Fig. 1(c)), in which each Cd^{2+} ion is linked by a single-mode NCS^- bridge in longitude and is knitted by double-mode asymmetrical bridges in latitude. It is noteworthy that the single linkage longitudinal strand is not infinite, but strings only seven latitudinal twines; at two breakpoints, each single strand is terminated by water coordinating to the Cd^{2+} ions. Alternatively, the linkage from H_2O at the breakpoint is completed by intralayer hydrogen bonding OH$\cdots$N (1.956 Å) and OH$\cdots$S (2.389 Å) to the next string in each layer. An irregular grid is thereby formed as compared to the regular one in **1**. Another obvious novelty is the coexistence of four varieties of Cd^{2+} coordinating units in one unit cell of **2**. The distorted octahedral units show *cis*-$[Cd1N_2S_4]$, $[Cd2N_3S_2O]$, *trans*-$[Cd3N_4S_2]$ and *fac*-$[Cd4N_3S_3]$ linked by eleven independent thiocyanate ligands. Therefore, the nature of the inorganic polymer can be described by the more appropriate formula of $\{[Cd1(NCS)_{6/2}]_2[Cd2(NCS)_{5/2}(H_2O)]_2[Cd3(NCS)_{6/2}]$-$[Cd4(NCS)_{6/2}]_2{}^{6-}\}_n$. It is helpful to note that the NCS^- ligands between the *cis*-$[Cd1N_2S_4]$ and *fac*-$[Cd4N_3S_3]$ are disordered, switching over from Cd1–NCS–Cd4 to Cd1–SCN–Cd4. Thus, the *cis*-$[Cd1N_2S_4]$ and *fac*-$[Cd4N_3S_3]$ change to *fac*-$[Cd1'N_3S_3]$ and *cis*-$[Cd4'N_2S_4]$, respectively. To the best of our knowledge, such 2-D motifs have not been reported previously. The organic layer consists of three species of $[MV]^{2+}$, including a coplanar $[MV]^{2+}$ and two twisted $[MV]^{2+}$ species (dihedral angle 39.22°). Unlike **1**, the long-axes of all $[MV]^{2+}$ molecules are not only parallel to each other but also are parallel to the direction of the inorganic layer, forming a significantly shorter interlayer separation (~ 8.3 Å) than that in **1** (~ 11.7 Å).

In a view parallel to the layer, the inorganic layer displays a beautiful recurrent knotted cord-like appearance linked by single NCS^- bridges. All $[MV]^{2+}$ lie in the middle channel of the rectangle formed by four adjacent knots from two adjacent inorganic layers to demonstrate the hetero-sandwich structure (Fig. 1(d)). A combination of weaker van der Waals and electrostatic forces must be responsible for the interactions between layers as no hydrogen bonds are found between the inorganic layer and $[MV]^{2+}$. Significant evidence comes from the fact that sulfur atoms in the double NCS^- bridges are out-of plane and are situated on top of piled up knotted ions on both sides of the inorganic layer as a partial charge assembled to constrain/restrain the $[MV]^{2+}$ ranks. The arrangement of charges of the cationic groups and the anionic polymer optimizes both dimensional and symmetric effects. In fact, this apparent interplay or correlations between host and guest could be established in the analysis of the crystal structure. However, the symmetric $[MV]^{2+}$ molecule and the 2-D assembly of the inorganic host that define a symmetry center in structures **1** and **2** imply that second-order harmonic effects will be absent.

Accordingly, the observation of two motifs of the hetero-sandwiched structures, which are obtained from the same chemical reagents in aqueous solution but with different ratios, contributes to the discussion on the nature of the assembly of the $[Cd(NCS)_m]_n$ frameworks. Generally, the product ratios m of the $[Cd(NCS)_m]$ polymer is three or less as a consequence of the six types of coordination of the Cd^{2+} and the bi- or multi-dentate coordination of NCS^-. With a $9NCS^-:Cd^{2+}$ molar ratio, **1** was prepared in the form of $[MV][Cd(NCS)_4]$, which is the second example of the $[Cd(NCS)_4]$ framework after $[Me_4N]_2[Cd(NCS)_4]$.[5,8*b*] However, the 2-D grid network in **1** is obviously different from the 1-D chain in $[Me_4N]_2[Cd(NCS)_4]$ although both have two terminating NCS^-. The dimensional difference in **1** and $[Me_4N]_2[Cd(NCS)_4]$ can be explained by the templating effect of the organic species used. Planar $[MV]^{2+}$ may be responsible for the formation of 2-D $[Cd(NCS)_4]_n$, while globular $[Me_4N]^+$ does so for 1-D $[Cd(NCS)_4]_n$. Similarly, a remarkable 2-D structure of **2** is formed even with the lower ratio of $3NCS^-:Cd^{2+}$. In this case, the thiocyanate reagent can not adequately replace H_2O of $[Cd(OH_2)_6]^{2+}$ from $CdSO_4$ hydrate so as to assemble solid $[Cd(NCS)_3]_n$ polymers as a small fraction of NCS^- may react with $[MV]^{2+}$ to form $[MV](NCS)_2$. Consequently, a certain number of H_2O molecules residing in the host framework of **2** produce the unexpected network with $m = 20/7$, slightly less than the ratio of 3 in the initial reagent.

In summary, two novel 2-D hetero-sandwich compounds **1** and **2** have been designed and synthesized, using the dication $[MV]^{2+}$ as the organic guest. From these structures, the multiple self-organization processes can be encoded in stoichiometric relationships. Such multiple information from molecular structures might be distinguished by studies of charge-transfer (CT) behaviour from the inorganic host to the guest, which have been verified by IR, EPR and solid-state ^1H, ^{13}C as well as ^{113}Cd NMR spectroscopies. More detailed studies are now in progress.

We gratefully acknowledge financial support of this work by the National Natural Science Foundation of China (grant No. G20001004, 19835050).

Notes and references

§ *Crystal data*: for **1**, $C_{16}H_{14}N_6S_4Cd$, $M = 530.97$, monoclinic, space group $P2_1/c$ (no. 14), $a = 11.728(1)$, $b = 13.294(1)$, $c = 13.240(1)$ Å, $\beta = 93.79(1)°$, $U = 2059.9(2)$ Å^3, $T = 173$ K, $Z = 4$, μ(Mo-Kα) = 1.479 mm^{-1}, 17230 reflections measured, 3620 unique ($R_{int} = 0.043$), the final $wR(F^2)$ was 0.128 (all data). For **2**: $C_{56}H_{46}N_{26}O_2S_{20}Cd$, $M = 2543.19$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.4079(8)$, $b = 12.7469(10)$, $c = 15.7543(10)$ Å, $\alpha = 86.74(1)$, $\beta = 71.98(1)$, $\gamma = 84.51(1)°$, $U = 2167.67(30)$ Å^3, $T = 210$ K, $Z = 1$, μ(Mo-Kα) = 2.221 mm^{-1}, 37635 reflections measured, 9553 unique ($R_{int} = 0.025$), the final $wR(F^2)$ was 0.068 (all data). CCDC 201155 and 201156. See http://www.rsc.org/suppdata/cc/b3/b313846a/ for crystallographic data in CIF or other electronic format.

1 J.-M. Lehn, *Science*, 2002, **295**, 2400.

2 (*a*) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022; (*b*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*c*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417.

3 (*a*) C. R. Kagan, D. B. Mitzi and C. D. Dimitrakopoulos, *Science*, 1999, **286**, 945; (*b*) D. B. Mitzi, *Prog. Inorg. Chem.*, 1994, **48**, 1.

4 (*a*) P. G. Lacroix, R. Clement, K. Nakatani, J. Zyss and I. Ledoux, *Science*, 1994, **263**, 685; (*b*) T. Vossmeyer, G. Reck, L. Katsikas, E. T. K. Haupt, B. Schulz and H. Weller, *Science*, 1995, **267**, 1476.

5 H. Zhang, X. Wang, K. Zhang and B. K. Toe, *Coord. Chem. Rev.*, 1999, **183**, 157, and references therein.

6 (*a*) V. G. Thiele and D. Z. Messer, *Z. Anorg. Allg. Chem.*, 1980, **646**, 225; (*b*) R. Gronbaek and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 1889.

7 J. Pickard and S. Dechert, *Z. Anorg. Allg. Chem.*, 1999, **625**, 153.

8 (*a*) M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 424; (*b*) Y. Kuniyasu, Y. Suzuki, M. Taniguchi and A. Ouchi, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 179; (*c*) W. Z. Chen, F. H Liu and X. Z. You, *J. Solid State Chem.*, 2002, **167**, 119.

9 (*a*) *Photoinduced Electron Transfer*, ed. M. A. Fox and M. A. Chanon, Elsevier, Amsterdam, The Netherlands, 1988; (*b*) P. M. S. Monk, *The Viologens: Physicochemical Properties, Synthesis and Applications of the Salts of 4,4-Bipyridine*, John Wiley & Sons, New York, 1998.

10 (*a*) Z. J. Tang and A. M. Guloy, *J. Am. Chem. Soc.*, 1999, **121**, 452; (*b*) H. Yoshikawa, S. Nishikiori, K. Suwinska, R. Luboradzki and J. Lipkowski, *Chem. Commun.*, 2001, 1398; (*c*) A. Bose, P. He, C. Liu, B. D. Ellman, R. J. Twieg and S. P. Huang, *J. Am. Chem. Soc.*, 2002, **124**, 4.