

Coordination polymers based on square planar Co(II) node and linear spacer: solvent-dependent pseudo-polymorphism and an unprecedented interpenetrating structure containing both 2D and 3D topological isomers†

Dong Mok Shin,^a In Su Lee,^b Young Keun Chung*^a and Myoung Soo Lah^c

^a School of Chemistry, the Center for Molecular Catalysis, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea. E-mail: ykchung@plaza.snu.ac.kr

^b Advanced Materials Research Institute, LG Chemical Ltd., Research Park, Taejeon, 305-380, Korea

^c Department of Applied Chemistry and Chemistry, College of Science and Technology, Han Yang University, Ansan 425-170, Korea

Received (in Cambridge, UK) 23rd October 2002, Accepted 14th March 2003

First published as an Advance Article on the web 2nd April 2003

Reaction of Co(NCS)₂ with 1-methyl-1'-(4-pyridyl)-2-(4-pyrimidyl)ethylene (mppe) in different solvents yields two kinds of novel coordination polymer structures of [Co(mppe)₂(NCS)₂]_n: one of them shows an unprecedented interpenetrating structure with both 2D and 3D topological isomers.

The construction of new coordination polymer networks through the rational combination of organic ligands 'spacers' and metal 'nodes' is an area of intense current interest.¹ In past years, a large number of coordination polymers have been engineered using ditopic rigid ligands such as 4,4'-bipyridine and square planar, tetrahedral or octahedral metal centers and their networks have been shown to be strictly limited by the stoichiometry.² For example, self-assembly of 4,4'-bipyridyl ligand and a square planar metal complex with a 1:2 ratio generally leads to 2D sheets with square grids.³ While examples of 2D grids have been widely encountered, a few of the 3D frames such as cubic NbO (6⁴8²), tetragonal CdSO₄ (6⁵8), or 'dense net' (7⁵9) topology have hitherto been reported. Moreover, to the best of our knowledge, no example has been reported of a structure containing both topologically different 2D and 3D isomers. We herein report two pseudo-isomeric coordination polymer architectures of [Co(mppe)₂(NCS)₂]_n (**1**) and [[Co(mppe)₂(NCS)₂]₂·2[Co(mppe)₂(NCS)₂]]·5CH₃OH]_n (**2**), which were selectively obtained by the assembly of 1-methyl-1'-(4-pyridyl)-2-(4-pyrimidyl)ethylene (mppe)⁴ and Co(NCS)₂ in a different reaction medium. **1** shows an inclined interpenetrating 2D grid structure. Moreover, very intriguingly, **2** exhibits an unprecedented crystal structure in which 2D and 3D isomeric networks with the same composition are mutually interpenetrating.

When an aqueous solution of Co(NCS)₂ was layered onto a solution of mppe in methanol and stood for several days, scarlet single crystals of **1** suitable for an X-ray analysis were grown on the interface of the two solutions.†§ The X-ray structural analysis of **1** reveals the formation of an interpenetrating 2-dimensional framework structure with a rectangular grid. Each cobalt center is in a compressed octahedral environment surrounded by two pyridines and two pyrimidines occupying equatorial sites and two SCN ligands occupying axial sites (Figure 1). The cobalt centers are linked by four mppe ligands and play the role of square planar nodes in the network. Thus, in this manner, a 2D framework sheets with 13.57 × 13.57 Å squares are formed (Figure 2a). Each 2D sheet is inclined and interpenetrated with further sheets lying along the square diagonal and, thus, its cavities are self-filled (Figure 2b).

Orange crystals of **2** were grown by layering a solution of Co(NCS)₂ in methanol onto a solution of mppe dissolved in

nitromethane.¶§ The structural determination of a single crystal disclosed that **2** had a more complex and interesting structure consisting of mutually interpenetrating 3D and 2D framework networks. The structure contains two crystallographically distinct cobalt centers, Co(1) and Co(2), and each of them acts as a square planar connecting node for 3D and 2D networks, respectively. There are no significant differences between the cobalt centers and both of them are located on an almost identical coordination environment to that found in **1**. The Co(1) nodes connect with two equivalent neighbors and two other neighbors with a 90° twist angle, such that a 3D open channel network belonging to the CdSO₄ topological type is generated

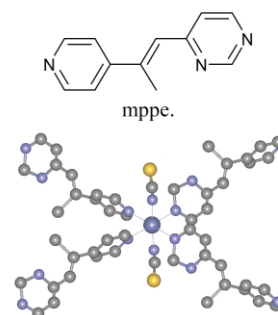
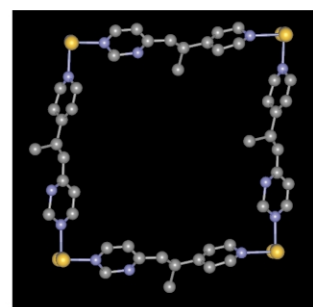
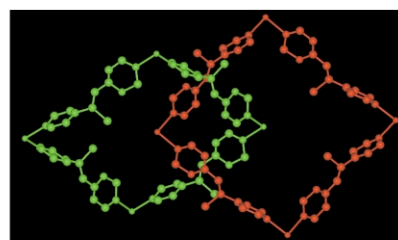


Fig. 1 Coordination environment around Co atom in **1**.



(a)



(b)

Fig. 2 (a) A 2D framework sheet containing 13.57 × 13.57 Å square. (b) Inclined interpenetration of two sheets. SCNs are omitted for clarity.

† Electronic supplementary information (ESI) available: synthesis of mppe, discussion and additional figures. See <http://www.rsc.org/suppdata/cc/b2/b210320f/>

as depicted in Figure 3. There exist two independent 3D nets in the crystal. Co(2) lies on a site with 2-fold imposed symmetry so that the structure of the 2D network possessing Co(2) nodes is very similar to that of the square grid sheet found in **1**. Two independent 3D nets and 2D nets interpenetrate in a slightly intricate manner as shown in Figure 4. Interpenetration phenomena involving 3D and 2D networks are quite rare.⁵ The sole known example is found in the crystal of $\{[\text{Cu}_2(\text{IN})_4 \cdot 3(\text{H}_2\text{O})] \cdot [\text{Cu}_2(\text{IN})_4 \cdot 2\text{H}_2\text{O}]\} \cdot 3\text{H}_2\text{O}$ (IN: isonicotinate).⁶ In the crystal, 2D and 3D nets have different chemical compositions. In contrast, the two types of networks in **2** are topological isomers and have an identical chemical composition. In spite of this interpenetration, a close-packed structure does not result; rather, it is porous such that solvent molecules occupy 21.5% out of its total volume.⁷ The crystal of **2** turns blue upon removal of solvate molecules.

The cause of the solvent-dependent pseudo-polymorphism phenomenon found between **1** and **2** is not clear at this stage.⁸ However, it can be reasoned that the solvent molecules involved play a crucial role in templating the porous structure of **2** over the closed packed structure found in **1**. Recently, Fujita,⁹ Stang,¹⁰ and Zaworotko¹¹ reported some relevant results, wherein the framework interpenetration is engineered by exploiting noncovalently bound organic guests.

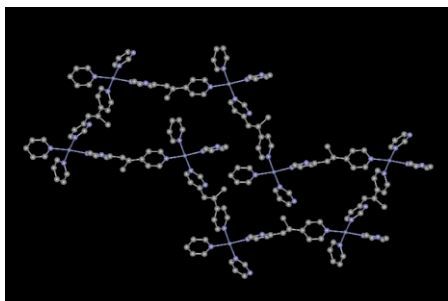


Fig. 3 A 3D open framework of **2** with a CdSO_4 topological type. Only pyridyl and pyrimidyl rings of mppe are presented and SCNs are omitted for clarity.

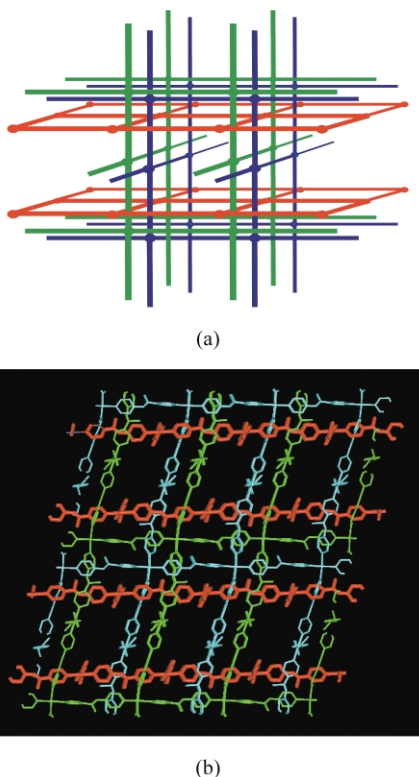


Fig. 4 A 3D interpenetration structure of **2**. (a) Schematic representation. (b) Two independent 3D structures (green, cyan) and 2D sheets (red).

In summary, we have demonstrated the solvent dependent pseudo-polymorphism of 2D and 3D coordination polymer constructed using a square planar Co(II) node and a linear mppe spacer. We have also demonstrated the first example of an interpenetrating coordination polymer structure involving both 2D and 3D topological isomers.

This work was supported by grant No. RO1-1999-000-0041-0 of the Korea Science and Engineering Foundation (KOSEF) and KOSEF through the Center for Molecular Catalysis. DMS thanks the Ministry of Education for the Brain Korea 21 Fellowship.

Notes and references

‡ 0.03 g (0.15 mmol) of mppe in MeOH was layered onto a solution of 0.015 g (0.086 mmol) of $\text{Co}(\text{NCS})_2$ in H_2O . The resulting solution was stood for several days to give 0.03 g (0.053 mmol) of **1** (70%). Single crystals suitable for X-ray analysis were grown on the interface of the two solutions. Elemental Analysis of **1**· H_2O (calc) H:3.98(4.12) C:53.40(53.14) N:19.21(19.08) S:10.49(10.89)%

§ Single crystal X-ray data of **1** were collected on a SMART CCD diffractometer at 173K and of **2** on an Enraf-Nonius CCD diffractometer at room temperature using graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS-97), and refined against all F^2 data (SHELXS-97). All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were treated as idealized contributions. The electron density contribution of the disordered solvent molecules was added to the calculated F^2 values via back-Fourier transformation. This calculation was performed with the routine CALC SQUEEZE as implemented in the PLATON package. Crystal data for **1**: $\text{C}_{26}\text{H}_{22}\text{CoN}_8\text{S}_2$ (173K). $M = 569.57$, orthorhombic, space group $P2_12_12$, $a = 16.4121(12)$, $b = 19.4406(15)$, $c = 9.3903(7) \text{ \AA}$, $V = 2996.1(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc.}} = 1.263 \text{ g cm}^{-3}$, absorption coefficient = 0.740 mm^{-1} , total reflections collected 18409, unique 7029 ($R_{\text{int}} = 0.0248$), GOF = 0.985, $R_1 = 0.0735$, $R_w = 0.2148$ ($I > 2\sigma(I)$). **2**: $\text{C}_{78}\text{H}_{66}\text{Co}_3\text{N}_{24}\text{S}_6 \cdot 5(\text{CH}_4\text{O})$ (293 K). $M = 1868.91$, monoclinic, space group $C2/c$, $a = 19.965(1)$, $b = 18.731(1)$, $c = 27.203(1) \text{ \AA}$, $\beta = 119.879(3)^\circ$, $V = 9547.9(6) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc.}} = 1.300 \text{ g cm}^{-3}$, absorption coefficient = 0.706 mm^{-1} , total reflections collected 15236, unique 8685 ($R_{\text{int}} = 0.079$), GOF = 1.011, $R_1 = 0.1088$, $R_w = 0.3022$ ($I > 2\sigma(I)$). CCDC 195591 and 195592. See <http://www.rsc.org/suppdata/cc/b2/b210320f/> for crystallographic data in .cif or other electronic format.

¶ 0.015 g (0.086 mmol) of $\text{Co}(\text{NCS})_2$ in MeOH was layered onto a solution of 0.03 g (0.15 mmol) of mppe in nitromethane. The resulting solution was stood for several days to give 0.026 g (0.046 mmol) of **2** (61%). Single crystals suitable for X-ray analysis were grown on the interface of the two solutions. Elemental Analysis of **2**· $3\text{CH}_3\text{OH}$ (calc) H:4.00(4.36) C:53.68(53.90) N:19.00(18.64) S:10.30(10.64)%

- (a) J. A. R. Navarro and B. Lippert, *Coord. Chem. Rev.*, 2001, **222**, 219; (b) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (c) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483.
- (a) M. J. Zaworotko, *Chem. Commun.*, 2001, 1; (b) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638; (c) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby and M. Schroder, *Coord. Chem. Rev.*, 1999, **183**, 117.
- (a) K. Uemura, S. Kitagawa, M. Kondo, K. Fukui, R. Kitaura, H.-C. Chang and T. Mizutani, *Chem. Eur. J.*, 2002, **8**, 3587; (b) N. G. Pschirer, D. M. Ciurtin, M. D. Smith and U. H. F. Bunz and H.-C. zur Loye, *Angew. Chem. Int. Ed.*, 2002, **41**, 583; (c) K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem., Int. Ed.*, 2000, **39**, 3843; (d) M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
- See the Supporting Information†.
- (a) S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1460; (b) S. A. Barnett, A. J. Blake, N. R. Champness and C. Wilson, *Chem. Commun.*, 2002, 1640.
- J. Y. Lu and A. M. Babb, *Chem. Commun.*, 2001, 821.
- A. L. Spek (2002) *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.
- More discussion, see the Supporting Information†.
- K. Biradha and M. Fujita, *J. Chem. Soc., Dalton Trans.*, 2000, 1.
- F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 11982.
- (a) K. Biradha, A. Mondal, B. Moulton and M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.*, 2000, 3837; (b) K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward and M. J. Zaworotko, *Chem. Commun.*, 1999, 1327.