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Two-Dimensional Coordination Polymer with a Non-interpenetrated (4,4) Net Showing Anion Exchange and Structural Transformation in Single-Crystal-to-Single-Crystal Fashion

Arshad Aijaz, Prem Lama, and Parimal K. Bharadwaj*

Chemistry Department, Indian Institute of Technology Kanpur, 208016, India

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A new non-interpenetrated two-dimensional (2D) rectangular-grid coordination polymer, $\{[Co(L)_2(H_2O)_2]\cdot(BF_4)_2\cdot 4DMF\}_n$ (**1**), has been synthesized using a new rod-like ligand, 3,5-bis(4-imidazol-1-ylphenyl)-[1,2,4]triazol-4-ylamine (**L**). Weakly H-bonded BF_4^- anions present within the voids can be exchanged by ClO_4^- and NO_3^- anions to generate $\{[Co(L)_2(H_2O)_2]\cdot(ClO_4)_2\cdot 2DMF\cdot 2H_2O\}_n$ (**2**) and $\{[Co(L)_2(H_2O)_2]\cdot(NO_3)_2\cdot 2DMF\cdot 2H_2O\}_n$ (**3**) in single-crystal-to-single-crystal (SC-SC) manner. In the case of exchange by Cl^- ion, the crystallinity is not maintained, and so it is proven by IR spectroscopy, PXRD, and elemental analysis. In addition, **3** shows an interesting structural transformation (2D → 1D) with bond rupture/formation leading to the formation of a new coordination polymer, $\{[Co(L)_2(H_2O)_2]\cdot(NO_3)_2\cdot 2DMF\cdot H_2O\}_n$, (**5**), again in SC-SC fashion.

Introduction

In the past decades, generation of coordination polymers has gained considerable interest because of their variety of topological architectures and diverse fascinating functionalities for potential applications.[1] The systematic tunable organic linkers and the coordination tendencies of metal ions are two key components for the formation of desired functional coordination polymers.[2] Under suitable reaction conditions, the prescribed architectures of these polymers comprising periodically decorated functionalities can be generated, which might act as promising candidates for special applications.[3] Among the numerous coordination polymers that have been documented,[4] the square-grid topology stands

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*To whom correspondence should be addressed. Tel: (+91)-512-2597304. Fax: (+91)-512-2597436. E-mail: pkb@iitk.ac.in.

(1) (a) Lee, J. Y.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. B. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450. (b) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330. (c) Zacher, D.; Shekhah, O.; Woell, C.; Fischer, R. A. *Chem. Soc. Rev.* **2009**, *38*, 1418. (d) Kuppler, R. J.; Timmons, D. J.; Fang, Q.-R.; Li, J.-R.; Makal, T. A.; Young, M. D.; Yuan, D.; Zhao, D.; Zhuang, W.; Zhou, H.-C. *Coord. Chem. Rev.* **2009**, *253*, 3042. (e) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502. (f) Wang, M.; Xie, M.-H.; Wu, C.-D.; Wang, Y.-G. *Chem. Commun.* **2009**, 2396. (g) Kurmoo, M. *Chem. Soc. Rev.* **2009**, *38*, 1353. (h) Horike, S.; Dinca, M.; Tamaki, K.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 5854. (i) Vittal, J. J. *Coord. Chem. Rev.* **2007**, *251*, 1781. (j) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (k) Pan, L.; Olson, D. H.; Ciemnolonski, L. R.; Heddy, R.; Li, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 616.

(2) (a) Perry, J. J., IV; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400. (b) Biradha, K.; Ramanan, A.; Vittal, J. J. *Cryst. Growth Des.* **2009**, *9*, 2969. (c) Aakeroy, C. B.; Champness, N. R.; Janiak, C. *CrystEngComm* **2010**, *12*, 22. (d) Prakash, M. J.; Lah, M. S. *Chem. Commun.* **2009**, *23*, 3326. (e) Natarajan, S.; Mahata, P. *Chem. Soc. Rev.* **2009**, *38*, 2304. (f) Britt, D.; Furukawa, H.; Wang, B.; Glover, T. G.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 20637. (g) Zhu, X.; Zhao, J.-W.; Li, B.-L.; Song, Y.; Zhang, Y.-M.; Zhang, Y. *Inorg. Chem.* **2010**, *49*, 1266. (h) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176. (i) Lopez, N.; Zhao, H.; Prosvirin, A. V.; Chouai, A.; Shatruk, M.; Dunbar, K. R. *Chem. Commun.* **2007**, *44*, 4611. (j) Lloyd, G. O.; Atwood, J. L.; Barbour, L. J. *Chem. Commun.* **2005**, *44*, 1845. (k) Harrison, R. G.; Fox, O. D.; Meng, M. O.; Dalley, N. K.; Barbour, L. J. *Inorg. Chem.* **2002**, *41*, 838. (l) Chen, Z.; Xiang, S.; Zhao, D.; Chen, B. *Cryst. Growth Des.* **2009**, *9*, 5293.

(3) (a) Rowsell, J. L. C.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4670. (b) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (c) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477. (d) Willans, C. E.; French, S.; Barbour, L. J.; Gertenbach, J.-A.; Junk, P. C.; Lloyd, G. O.; Steed, J. W. *Dalton Trans.* **2009**, *33*, 6480. (e) Sumida, K.; Hill, M. R.; Horike, S.; Dailly, A.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 15120. (f) Klein, N.; Senkovska, I.; Gedrich, K.; Stoeck, U.; Henschel, A.; Mueller, U.; Kaskel, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 9954. (g) An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2010**, *132*, 38. (h) Hurd, J. A.; Vaidhyanathan, R.; Thangadurai, V.; Ratcliffe, C. I.; Moudrakovski, I. L.; Shimizu, G. K. H. *Nat. Chem.* **2009**, *1*, 705. (i) Navarro, J. A. R.; Barea, E.; Rodriguez-Dieguez, A.; Salas, J. M.; Ania, C. O.; Parra, J. B.; Masciocchi, N.; Galli, S.; Sironi, A. *J. Am. Chem. Soc.* **2008**, *130*, 3978. (j) Chun, H.; Seo, J. *Inorg. Chem.* **2009**, *48*, 9980.

(4) (a) Jiang, D.; Urakawa, A.; Yulikov, M.; Mallat, T.; Jeschke, G.; Baiker, A. *Chem.—Eur. J.* **2009**, *15*, 12255. (b) Reger, D. L.; Horger, J.; Smith, M. D.; Long, G. J. *Chem. Commun.* **2009**, *41*, 6219. (c) Ingleson, M. J.; Heck, R.; Gould, J. A.; Rosseinsky, M. J. *Inorg. Chem.* **2009**, *48*, 9986. (d) Cheon, Y. E.; Park, J.; Suh, M. P. *Chem. Commun.* **2009**, *36*, 5436. (e) Hong, S.; Oh, M.; Park, M.; Yoon, J. W.; Chang, J.-S.; Lah, M. S. *Chem. Commun.* **2009**, *36*, 5397. (f) Wang, M.-S.; Guo, S.-P.; Li, Y.; Cai, L.-Z.; Zou, J.-P.; Xu, G.; Zhou, W.-W.; Zheng, F.-K.; Guo, G.-C. *J. Am. Chem. Soc.* **2009**, *131*, 13572. (g) Vaidhyanathan, R.; Iremonger, S. S.; Dawson, K. W.; Shimizu, G. K. H. *Chem. Commun.* **2009**, *35*, 5230. (h) Nouar, F.; Eubank, J. F.; Bousquet, T.; Wojtas, L.; Zaworotko, M. J.; Eddaoudi, M. *J. Am. Chem. Soc.* **2008**, *130*, 1833. (i) Zhang, J.-Y.; Cheng, A.-L.; Yue, Q.; Sun, W.-W.; Gao, E.-Q. *Chem. Commun.* **2008**, *7*, 847. (j) Ouellette, W.; Prosvirin, A. V.; Whitenack, K.; Dunbar, K. R.; Zubieta, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2140. (k) Guo, Z.; Li, G.; Zhou, L.; Su, S.; Lei, Y.; Dang, S.; Zhang, H. *Inorg. Chem.* **2009**, *48*, 8069.

out as an important class not only because of the desirable applications associated with such frameworks but also because the formation of this structure type is often highly predictable.[5] It is well known that long N,N′-type ligands can lead to square-grid structures containing large cavities when they are reacted with metals capable of adopting octahedral or square-planar coordination geometries.[6] Furthermore, it is generally accepted that longer ligands often favor interpenetrating square-grid structures.[7] However, interpenetration can often be avoided by suitable organic linkers and controlling the reaction conditions.[8]

As an important property of coordination polymers, anion exchange has attracted increasing attention in recent years because it makes such polymers potentially attractive as anion exchange materials.[9] The anions trapped in the cavity, which is weakly H-bonded, can be exchanged with different anions. From the reported studies, neutral N-donor ligands have been found to be most useful building blocks for the construction of coordination polymers that are able to show anion exchange properties. In most of the reported cases, anion exchange was proven by IR spectroscopy and PXRD patterns,[9,10] as crystallinity is not maintained in such cases.[11] Tzeng and co-workers[11a] recently reported a coordination polymer based on an amide-functionalized tripodal ligand capable of anion exchange in single-crystal-to-single-crystal (SC-SC) fashion. Cohen and co-workers[11b] have also reported an interesting example of anion exchange in SC-SC fashion. However, it should be noted here that to absolutely confirm a SC-SC anion exchange process, microscopic studies of crystal morphology is important.[12]

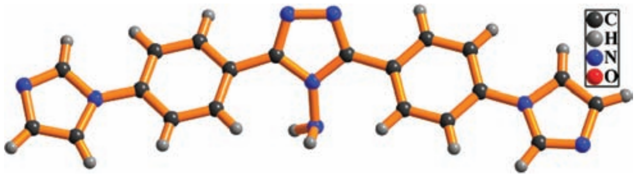

Figure 1. Molecular structure of ligand **L**.

Herein, we report a non-interpenetrated square-grid coordination polymer, $\{[\mathrm{Co(L)_2(H_2O)_2}]\cdot(\mathrm{BF_4})_2\cdot 4\mathrm{DMF}\}_n$ (**1**), with a new N,N′-type ligand (Figure 1), 3,5-bis(4-imidazol-1-ylphenyl)-[1,2,4]triazol-4-ylamine (**L**), capable of anion exchange in a SC-SC manner.

An important feature of **L** is the presence of an amino group at the center that might be expected to act as a donor in H-bonding interactions. The pores containing amino groups as functional units in the channels are particularly attractive for guest uptake and ion exchange studies, thus making such coordination polymers potentially attractive as molecular-based functional materials.[13] Also, the transformation of a two-dimensional (2D) framework into a one-dimensional (1D) structure, as described herein, is rather unusual.

Experimental Section

Materials and Methods. 4-Fluorobenzonitrile and metal salts were purchased from Aldrich and used as received. 4-Imidazol-1-ylbenzonitrile was synthesized following a reported procedure as a white powder.[14] All solvents, imidazole, hydrazine hydrate,

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(5) (a) Wang, Z.; Kravtsov, V. Ch.; Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 2877. (b) Yang, J.; Ma, J.-F.; Liu, Y.-Y.; Batten, S. R. *CrystEngComm* **2009**, *11*, 151. (c) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676. (d) Gao, Q.; Jiang, F.-L.; Wu, M.-Y.; Huang, Y.-G.; Wei, W.; Hong, M.-C. *Cryst. Growth Des.* **2010**, *10*, 184. (e) Ma, S.; Sun, D.; Forster, P. M.; Yuan, D.; Zhuang, W.; Chen, Y.-S.; Parise, J. B.; Zhou, H.-C. *Inorg. Chem.* **2009**, *48*, 4616. (f) Cao, X.-Y.; Lin, Q.-P.; Qin, Y.-Y.; Zhang, J.; Li, Z.-J.; Cheng, J.-K.; Yao, Y.-G. *Cryst. Growth Des.* **2009**, *9*, 20.

(6) (a) Wu, C.-D.; Ma, L.; Lin, W. *Inorg. Chem.* **2008**, *47*, 11446. (b) McManus, G. J.; Perry, J. J.; Perry, M.; Wagner, B. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 9094. (c) Chen, B.; Fronczek, F. R.; Maverick, A. W. *Chem. Commun.* **2003**, *17*, 2166. (d) Gurunatha, K. L.; Maji, T. K. *Inorg. Chem.* **2009**, *48*, 10886. (e) Biradha, K.; Hongo, Y.; Fujita, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3843.

(7) (a) Zhuang, C.-F.; Zhang, J.; Wang, Q.; Chu, Z.-H.; Fenske, D.; Su, C.-Y. *Chem.—Eur. J.* **2009**, *15*, 7578. (b) Dong, Y.-B.; Wang, P.; Huang, R.-Q.; Smith, M. D. *Inorg. Chem.* **2004**, *43*, 4727. (c) Biradha, K.; Fujita, M. *Chem. Commun.* **2002**, 1866. (d) Su, C.-Y.; Goforth, A. M.; Smith, M. D.; zur Loye, H.-C. *Chem. Commun.* **2004**, 2158. (e) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murrar, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762.

(8) (a) Chen, C.-L.; Goforth, A. M.; Smith, M. D.; Su, C.-Y.; zur Loye, H.-C. *Inorg. Chem.* **2005**, *44*, 8762. (b) May, L. J.; Shimizu, G. K. H. *Chem. Commun.* **2005**, *10*, 1270. (c) Tsai, C.-C.; Luo, T.-T.; Yin, J.-F.; Lin, H.-C.; Lu, K.-L. *Inorg. Chem.* **2009**, *48*, 8650. (d) Sbircea, L.; Sharma, N. D.; Clegg, W.; Harrington, R. W.; Horton, P. N.; Hursthouse, M. B.; Apperley, D. C.; Boyd, D. R.; James, S. L. *Chem. Commun.* **2008**, *43*, 5538. (e) Ohmura, T.; Usuki, A.; Fukumori, K.; Ohta, T.; Ito, M.; Tatsumi, K. *Inorg. Chem.* **2006**, *45*, 7988. (f) Zhang, J.-J.; Wojtas, L.; Larsen, R. W.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2009**, *131*, 17040. (g) Pschirer, N. G.; Ciurtin, D. M.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. *Angew. Chem., Int. Ed.* **2002**, *41*, 583.

(9) (a) Ma, J.-X.; Huang, X.-F.; Song, Y.; Song, X.-Q.; Liu, W.-S. *Inorg. Chem.* **2009**, *48*, 6326. (b) Xu, G.-C.; Hua, Q.; Okamura, T.; Bai, Z.-S.; Ding, Y.-J.; Huang, Y.-Q.; Liu, G.-X.; Sun, W.-Y.; Ueyama, N. *CrystEngComm* **2009**, *11*, 261. (c) Xu, G.-C.; Ding, Y.-J.; Okamura, T.; Huang, Y.-Q.; Bai, Z.-S.; Hua, Qing; Liu, G.-X.; Sun, W.-Y.; Ueyama, N. *Cryst. Growth Des.* **2009**, *9*, 395. (d) Xu, G.-C.; Ding, Y.-J.; Okamura, T.; Huang, Y.-Q.; Liu, G.-X.; Sun, W.-Y.; Ueyama, N. *CrystEngComm* **2008**, *10*, 1052. (e) Custelcean, R.; Moyer, B. A. *Eur. J. Inorg. Chem.* **2007**, *10*, 1321. (f) Du, M.; Zhao, X.-J.; Guo, J.-H.; Batten, S. R. *Chem. Commun.* **2005**, *38*, 4836. (g) Yang, G.; Raptis, R. G. *Chem. Commun.* **2004**, *18*, 2058. (h) Lee, E.; Kim, J.; Heo, J.; Whang, D.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 399. (i) Zhao, W.; Fan, J.; Song, Y.; Kawaguchi, H.; Okamura, T.; Sun, W.-Y.; Ueyama, N. *Dalton Trans.* **2005**, *8*, 1509. (j) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10402. (k) Maji, T. K.; Matsuda, R.; Kitagawa, S. *Nat. Mater.* **2007**, *6*, 142.

(10) (a) Fan, J.; Sun, W.-Y.; Okamura, T.; Zheng, Y.-Q.; Sui, B.; Tang, W.-X.; Ueyama, N. *Cryst. Growth Des.* **2004**, *4*, 579. (b) Du, M.; Guo, Y.-M.; Chen, S.-T.; Bu, X.-H.; Batten, S. R.; Ribas, J.; Kitagawa, S. *Inorg. Chem.* **2004**, *43*, 1287. (c) Hamilton, B. H.; Kelly, K. A.; Wagler, T. A.; Espe, M. P.; Ziegler, C. J. *Inorg. Chem.* **2004**, *43*, 50. (d) Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568. (e) Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Chae, H. K.; Jang, H. G.; Hong, J. *Inorg. Chem.* **2001**, *40*, 2105. (f) Min, K. S.; Suh, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 6834. (g) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (h) Vyasamudri, S. Y.; Maji, T. K. *Chem. Phys. Lett.* **2009**, *473*, 312. (i) Zhang, J.-J.; Zhao, Y.; Gamboa, S. A.; Munoz, M.; Lachgar, A. *Eur. J. Inorg. Chem.* **2008**, *19*, 2982. (j) Sarkar, M; Biradha, K. *Cryst. Growth Des.* **2007**, *7*, 1318. (k) Shu, M.; Tu, C.; Xu, W.; Jin, H.; Sun, J. *Cryst. Growth Des.* **2006**, *6*, 1890.

(11) (a) Tzeng, B.-C.; Chiu, T.-H.; Chen, B.-S.; Lee, G.-H. *Chem.—Eur. J.* **2008**, *14*, 5237. (b) Halper, S. R.; Do, L.; Stork, J. R.; Cohen, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 15255. (c) Michaelides, A.; Skoulika, S. *Cryst. Growth Des.* **2009**, *9*, 2039.

(12) (a) Cui, X.; Khlobystov, A. N.; Chen, X.; Marsh, D. H.; Blake, A. J.; Lewis, W.; Champness, N. R.; Roberts, C. J.; Schroeder, M. *Chem.—Eur. J.* **2009**, *15*, 8861. (b) Thompson, C.; Champness, N. R.; Khlobystov, A. N.; Roberts, C. J.; Schroder, M.; Tendler, S. J. B.; Wilkinson, M. J. *J. Microsc.* **2004**, *214*, 261. (c) Khlobystov, A. N.; Champness, N. R.; Roberts, C. J.; Tendler, S. J. B.; Thompson, C.; Schroeder, M. *CrystEngComm* **2002**, *4*, 426. (d) Yang, H.; Li, L.; Wu, J.; Hou, H.; Xiao, B; Fan, Y. *Chem.—Eur. J.* **2009**, *15*, 4049.

(13) (a) Seo, J.; Matsuda, R.; Sakamoto, H.; Bonneau, C.; Kitagawa, S. *J. Am. Chem. Soc.* **2009**, *131*, 12792. (b) Lin, X.; Jia, J.; Zhao, X.; Thomas, K. M.; Blake, A. J.; Walker, G. S.; Champness, N. R.; Hubberstey, P.; Schroeder, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7358. (c) Kosal, M. E.; Chou, J.-H.; Wilson, S. R.; Suslick, K. S. *Nat. Mater.* **2002**, *1*, 118. (d) Kitagawa, S.; Matsuda, R. *Coord. Chem. Rev.* **2007**, *251*, 2490. (e) Kitagawa, S.; Noro, S.; Nakamura, T. *Chem. Commun.* **2006**, *7*, 701. (f) Cairns, A. J.; Perman, J. A.; Wojtas, L.; Kravtsov, V. C.; Alkordi, M. H.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 1560.

(14) Zhu, L.; Guo, P.; Li, G.; Lan, J.; Xie, R.; You, J. *J. Org. Chem.* **2007**, *72*, 8535.

and K_2CO_3 were procured from S. D. Fine Chemicals, India. All solvents were purified prior to use.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer model 1320 spectrometer (KBr disk, 400–4000 cm^{-1}). ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA500 FT (500 and 125 MHz, respectively) instrument in DMSO-d_6 with Me_4Si as the internal standard. ESI mass spectra were recorded on a Waters Q-TOF Premier mass spectrometer. X-ray powder patterns (Cu Kα radiation at a scan rate of 3° deg/min, 293 K) were acquired on a Siefert ISODEBYEFLEX-2002 spectrometer, while thermogravimetric analysis (TGA) was obtained by a Mettler Toledo instrument (heating rate of 5 °C/min). Microanalyses for the compounds were obtained using a CE-440 elemental analyzer (Exeter Analytical Inc.). Adsorption isotherms were measured in a Micromeritics Tristar 3000 volumetric instrument under continuous adsorption conditions. Prior to measurement, samples were heated at 180 °C for 4 h and outgassed to 10^{-3} Torr using a Micromeritics Flowprep.

Synthesis of 3,5-Bis(4-imidazol-1-ylphenyl)-[1,2,4]triazol-4-ylamine (L). This ligand was synthesized via condensation of 4-imidazol-1-ylbenzonitrile with hydrazine under solvothermal conditions. A mixture of 4-imidazol-1-ylbenzonitrile (0.6 mmol) and $N_2H_4 \cdot H_2O$ (0.2 mL) in 1 mL of EtOH was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 130 °C for three days and then allowed to cool to room temperature. Rectangular colorless crystals of **L** were collected in 84% yield and were recrystallized with a mixture of DMF and MeOH (1:5). IR (cm^{-1}): 3310(m), 3122(m), 1642(w), 1609(m), 1538(m), 1493(s), 1302(s), 1107(m), 1057(s), 960(m), 910(m), 838(s), 758(w), 737(m), 695(w), 654(m). ^{1}H NMR, δ (ppm): 8.35 (s, 2H), 8.13 (d, 4H), 7.83 (s, 2H), 7.82 (d, 4H), 7.12 (s, 2H), 2.46 (s, 2H). ^{1}H NMR, δ (ppm): 118.47, 120.62, 125.80, 130.34, 130.62, 136.10, 138.16, 154.24. ESI-MS: *m*/*z* (80%) 369.1580 [M + 1]$^+$.

Synthesis of $\{[Co(L)_2(H_2O)_2]\cdot(BF_4)_2\cdot 4DMF\}_n$ (1). In a typical procedure, $Co(BF_4)_2\cdot 6H_2O$ (0.50 mmol) was added slowly into a boiling DMF/EtOH solution (1:6 v/v) of **L** (0.25 mmol) with constant stirring over a period of 30 min. Then, the solution was left to stir for 6 h and allowed to cool to room temperature to afford a pink-colored precipitate. The precipitate was collected by filtration and dried in air. This pink solid was dissolved in hot DMF (5 mL), and 0.5 mL of water was added, whereupon the color of the solution changed to pale pink. After stirring for 2 h at room temperature, the solution was filtered and the filtrate left at RT for crystallization. After one month, rectangular pink-colored crystals of **1** appeared at the bottom of the conical flask suitable for X-ray crystallography. Yield: 35%. Anal. Calcd for $C_{52}H_{64}N_{20}O_6B_2F_8Co$: C, 48.12; H, 4.97; N, 21.58. Found: C, 48.55; H, 4.81; N, 21.78. IR (cm^{-1}): 3380(br), 3139(w), 2926(w), 1658(s), 1504(s), 1386(w), 1308(m), 1247(m), 1189(m), 1067(s), 963(w), 934(w), 828(m), 740(m), 691(w), 657(m).

Synthesis of the Anion-Exchanged Products $\{[Co(L)_2(H_2O)_2]\cdot(ClO_4)_2\cdot 2DMF\cdot 2H_2O\}_n$ (2) and $\{[Co(L)_2(H_2O)_2]\cdot(NO_3)_2\cdot 2DMF\cdot 2H_2O\}_n$ (3). Freshly prepared crystals of **1** were immersed in a 0.05 M aqueous solution of NaX (X = ClO_4^- or NO_3^-) for one week at room temperature to obtain **2** and **3**. In each case, the crystallinity was maintained (*vide infra*). Compound **3** can also be prepared by adopting a procedure similar to that of **1** using $Co(NO_3)_2\cdot 6H_2O$ instead of $Co(BF_4)_2\cdot 6H_2O$ albeit in significantly low yield (15%). Anal. Calcd for $C_{46}H_{54}N_{18}O_{14}Cl_2Co$ (**2**): C, 45.55; H, 4.48; N, 20.78. Found: C, 45.69; H, 4.56; N, 20.18%. IR (cm^{-1}): 3107(s), 2924(s), 1603(m), 1565(s), 1454(m), 1391(s), 1254(m), 1212(m), 1110(s), 1078(m), 852(m), 778(m), 722(s), 698(m). Anal. Calcd for $C_{46}H_{54}N_{20}O_{12}Co$ (**3**): C, 48.55; H, 4.78; N, 24.61. Found: C, 48.73; H, 4.63; N, 24.38. IR (cm^{-1}): 3126(br), 1648(m), 1614(m), 1503(s), 1383(s), 1308(m), 1116(m), 1065(m), 962(m), 932(w), 838(m), 741(m), 656(m), 618(w).

Synthesis of $\{[Co(L)_2(H_2O)_2]\cdot(Cl)_2\cdot 4DMF\cdot 3H_2O\}_n$ (4). This complex was synthesized adopting a procedure similar to that for **2** and **3**. Freshly prepared crystals of **1** were immersed in a 0.05 M aqueous solution of NaCl (5 mL) at room temperature for one week to obtain **4**. The sample was collected by filtration and dried in air. Anal. Calcd for $C_{52}H_{70}N_{20}O_9Cl_2Co$: C, 50.00; H, 5.64; N, 22.42. Found: C, 50.73; H, 5.83; N, 22.18. IR (cm^{-1}): 3384(br), 1613(m), 1503(s), 1303(m), 1266(m), 1114(m), 1165(m), 961(m), 930(w), 841(m), 738(m), 657(m).

Synthesis of $\{[Co(L)_2(H_2O)_2]\cdot(NO_3)_2\cdot 2DMF\cdot H_2O\}_n$ (5). Freshly prepared crystals of **3** were immersed in 0.10 M formaldehyde solution in chloroform (5 mL) at room temperature for 5 days to obtain crystals of **5**. Anal. Calcd for $C_{46}H_{56}N_{20}O_{11}Co$: C, 47.79; H, 4.88; N, 24.23. Found: C, 47.21; H, 4.59; N, 24.17.

X-ray Structural Studies. Single-crystal X-ray data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Linear absorption coefficients, scattering factors for the atoms, and the anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. Data integration and reduction were processed with SAINT[15] software. An empirical absorption correction was applied to the collected reflections with SADABS[16] using XPREP.[17] The structure was solved by the direct method using SHELXTL and refined on F^2 by full-matrix least-squares techniques using the SHELXL-97[18] program package. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were either located in successive difference Fourier maps or added at calculated positions. The H atoms were treated as riding atoms using SHELXL default parameters. The crystal and refinement data are collected in Table 1, while selected bond angles and distances are given in Table S1 (Supporting Information).

Results and Discussion

The new ligand 3,5-bis(4-imidazol-1-ylphenyl)-[1,2,4]triazol-4-ylamine (**L**) was readily prepared in 84% yield via condensation of hydrazine hydrate with 4-imidazol-1-ylbenzonitrile under solvothermal conditions. It is known that organonitriles are active for the addition reactions of nucleophiles, electrophiles, or asymmetric dipolar cycloadditions to the C–N triple bonds,[19] offering attractive potential routes for the creation of new bonds under solvothermal conditions. Chen et al.[19c] have given the possible mechanism for the synthesis of 1,2,4-triazoles from organonitriles and hydrazine in the absence/presence of metal ions, which involve amidrazone as the key intermediate. The single-crystal structure of **L** showed that it is a nonplanar rod-like linker with terminal imidazoles at transoid configuration. The terminal imidazolyl N···N separation in **L** is 17.176 Å, which is significantly long for the formation of large grid coordination polymers. In the crystal structure of **L**, two water molecules are also hydrogen-bonded with the amino group (N4···OW1 2.955, N4···OW2 2.832 Å).

Single-crystal X-ray analysis of **1** reveals that it forms a characteristic grid structure of (4, 4) net topology. In this complex, **L** adopts a distorted cis-configuration in which all

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(15) *SAINT+*, 6.02 ed.; Bruker AXS: Madison, WI, 1999.

(16) Sheldrick, G. M. *SADABS: Empirical Absorption Correction Program*; University of Göttingen: Göttingen, Germany, 1997.

(17) *XPREP*, 5.1 ed.; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(18) Sheldrick, G. M. *SHELXL-97: Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(19) (a) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299. (b) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771. (c) Cheng, L.; Zhang, W.-X.; Ye, B.-H.; Lin, J.-B.; Chen, X.-M. *Inorg. Chem.* **2007**, *46*, 1135.

Table 1. Crystal and Structure Refinement Data

	L	**1**	**2**	**3**	**5**
molecular formula	C20 H20 N8 O2	C52 H64 B2 Co F8 N20 O6	C46 H54 Cl2 Co N18 O14	C46 H54 Co N20 O12	C46 H52 Co N20 O11
fw	404.44	1297.78	1212.90	1138.02	1120.01
temperature, K	100(2)	100(2)	100(2)	100(2)	100(2)
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\overline{1}$	$P21/c$	$P21/c$	$P21/c$	$C2/c$
a, Å	7.457(3)	14.304(4)	13.894(4)	13.913(2)	21.267(5)
b, Å	9.653(3)	11.686(5)	11.540(2)	11.039(3)	7.840(4)
c, Å	14.449(4)	18.483(3)	17.899(2)	17.712(2)	29.455(5)
α, deg	93.340(4)	90.00	90.00	90.00	90.00
β, deg	94.198(3)	103.608(5)	110.321(4)	112.450(3)	98.405(6)
γ, deg	109.955(5)	90.000	90.00	90.00	90.00
U, Å^3	971.2(7)	3002.8(16)	2691.3(11)	2514.1(8)	4858(4)
Z	2	2	2	2	4
ρ_{calc} Mg/m^3	1.38	1.44	1.49	1.50	1.53
μ, mm^{-1}	0.096	0.377	0.499	0.426	0.438
F(000)	423.9	1345.6	1253.7	1185.7	2331.3
reflns collected	5106	14 209	13 300	12 619	11 984
indep reflns	3377	4992	4716	4409	4278
GOF	1.037	0.997	1.055	1.036	1.065
final R_{in} [$I > 2\sigma(I)$]	R1 = 0.0500	R1 = 0.0561	R1 = 0.0863	R1 = 0.0567	R1 = 0.0596
	wR2 = 0.1231	wR2 = 0.1369	wR2 = 0.2261	wR2 = 0.1405	wR2 = 0.1451
R_{in} all data, F^2 refinement	R1 = 0.0618	R1 = 0.0754	R1 = 0.1083	R1 = 0.0852	R1 = 0.0729
	wR2 = 0.1374	wR2 = 0.1521	wR2 = 0.2521	wR2 = 0.1614	wR2 = 0.1572

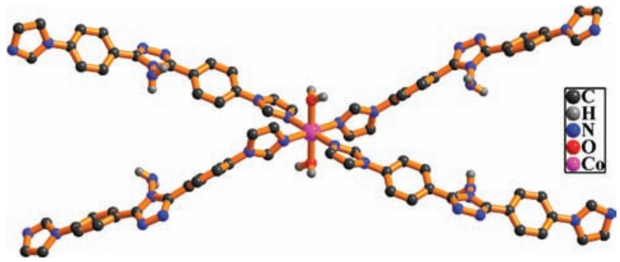

Figure 2. Coordination environment around the cobalt(II) atom in **1** (lattice anion and solvent molecules are omitted for clarity).

five aromatic rings are in different planes. The asymmetric unit contains one Co(II) ion (half-occupancy), one **L**, one coordinated water molecule, one noncoordinated BF_4^- anion, and two free DMF solvent molecules. The metal ion adopts a distorted octahedral geometry coordinated to four N atoms from four different ligands in the equatorial positions (Co−N, 2.134−2.156 Å) and two O atoms from two water molecules in the axial positions (Co−O, 2.108 Å) (Figure 2).

The grid of this (4,4) network is described by a 72-membered Co_4L_4 macrocyclic ring with a rectangular grid size of 33.5 × 7.7 Å^2 considering the van der Waals radius of Co(II). In this structure, the network is cationic, which is compensated by BF_4^- anions in the voids (Figure 3). Besides, DMF guest molecules also occupy available void spaces in the structure. The free amino group in the wall of the framework is involved in H-bonding with the fluorides of the trapped BF_4^- anions (F1···N8 = 2.883, F2···N8 = 2.967 Å). The DMF molecules present in the void are also involved in H-bonding interactions with metal-bound water hydrogens (O1···OW1 = 2.734 Å).

Even though ligand **L** is quite long, no interpenetration takes place due to the presence of the rigid triazole moiety in the middle, which provides greater steric bulk. These 2D rectangular grids are stacked over one another in an ---ABCABC--- fashion to generate a 3D coordination polymer with rectangular channels observed along the crystallographic *a*-axis (Figures 4 and 5). Strong $\pi\cdots\pi$ interactions among the 2D layers stabilize the overall 3D structure.

The IR spectrum shows a strong peak at 1067 cm^{-1} corresponding[20] to a free BF_4^- anion (Figure S2). The bands around 1504 and 1189 cm^{-1} in the IR spectrum are assigned[20] to the imidazole ring stretching vibrations. A broad peak at 3380 cm^{-1} indicates[20] the coordinated water molecules in **1**. Thermogravimetric analysis shows a two-step weight loss corresponding to four DMF solvent molecules (22.5%) at 160 °C followed by two coordinated water molecules at 310 °C (2.8%) (found: 22.9% and 3.1%), while the framework is stable up to 420 °C (Figure S1). The solvent-accessible volume in **1**, calculated with the PLATON program,[21] is found to be 37.9% of the total unit cell volume.

To examine permanent porosity and storage capability, the adsorption properties of desolvated **1** have been studied with N_2 gas at 77 K. The adsorption measurement leads to the conclusion that no nitrogen molecules (kinetic diameter ~3.64 Å) diffuse into the pores at all. This may be attributed to the small pore size due to the presence of anions in the cavities and the partial amorphous nature of desolvated **1**. This is also corroborated by the PXRD studies, which indicate this nature of the desolvated framework (Figure S9).

As revealed by the crystal structure of **1**, the BF_4^- anions are only loosely bonded to the framework through hydrogen bonds. Since this complex is insoluble in common organic solvents including water and the anion is loosely bound, it is probed for possible exchange of the anion. A suitable crystal of **1** is dipped in an aqueous solution of $NaClO_4$, and the BF_4^- anions are exchanged by ClO_4^- anions to generate $\{[Co(L)_2(H_2O)_2]\cdot(ClO_4)_2\cdot 2DMF\cdot 2H_2O\}_n$ (**2**) in one week, keeping a crystallinity suitable for single-crystal X-ray analysis. The morphology of the crystal remains unchanged as

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(20) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed.; Wiley & Sons: New York, 1997.

(21) Spek, A. L. *PLATON*, Version 1.62; University of Utrecht, 1999.

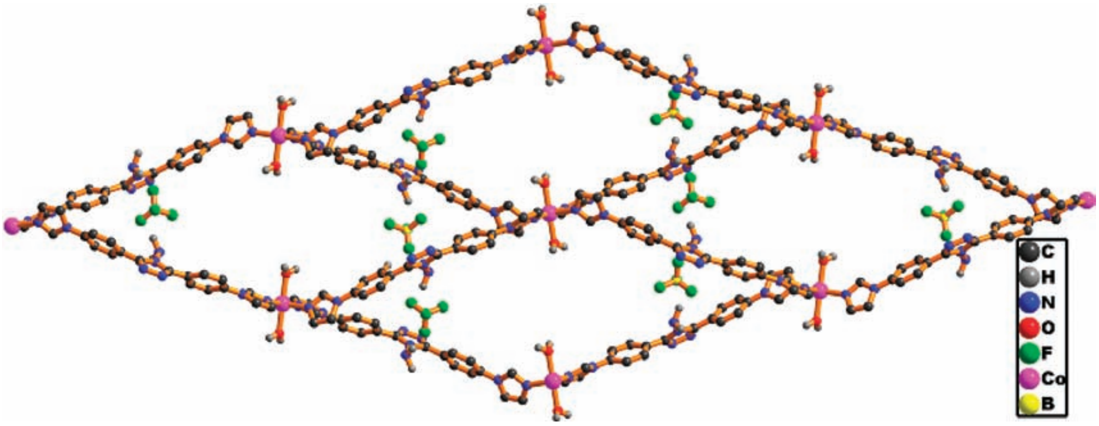

Figure 3. Schematic view of the trapped BF_4^- anions in the 2D rectangular-grid structure of **1**.

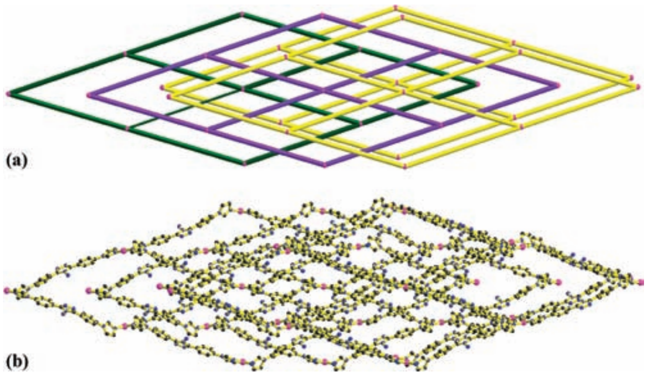

Figure 4. Schematic representation (a) and view (b) of the ABCABC stacking of rectangular-grid layers of **1**.

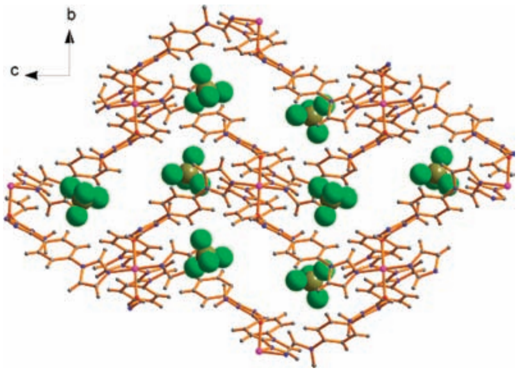

Figure 5. Crystal packing of the 2D layers in **1** viewed down the *a*-axis (solvent molecules are omitted for clarity.

viewed under a microscope (Figure S10). When the crystal is taken out of the solution after 3 days and its structure determined, no anion exchange is found to have taken place. X-ray analysis of **2** reveals complete anion exchange with the same (4,4) net topology as the parent structure. The ClO_4^- anions occupy the positions of the displaced BF_4^- anions in the crystal lattice (Figure 6). One of the two DMF molecules in the asymmetric unit is also replaced by a water molecule. The O atoms of the ClO_4^- anions form hydrogen bonds with the free amino group as in **1** (O2$\cdots$N7 and O3$\cdots$N7 = 3.010 Å). Complex **2** does not show any stretching vibration at 1067 cm^{-1} due to BF_4^- anions (as observed in **1**) in its IR spectrum. Instead, an intense broad band appears around 1110 to 1080 cm^{-1} due to ClO_4^- anions. To investigate the reversibility of the anion exchange process, the exchanged crystal (**2**) is dipped in an aqueous solution of $NaBF_4$ to regenerate **1**. But it turns opaque and diffracts weakly, so that no structural information can be obtained. However, the elemental analysis, IR spectrum, and the PXRD pattern of the sample prepared by keeping crystals of **2** in $NaBF_4$ for 7 days are identical to those of **1** (Supporting Information).

When a crystal of **1** is dipped in an aqueous solution of $NaNO_3$, it generates $\{[Co(L)_2(H_2O)_2]\cdot(NO_3)_2\cdot 2DMF\cdot 2H_2O\}_n$ (**3**), keeping the crystallinity and morphology intact (Figure S11). The structure of **3** reveals complete exchange of BF_4^- with the NO_3^- anion, keeping the same (4,4) net topology of the parent structure (**1**). Like in **2**, one of the two DMF molecules in the asymmetric unit is replaced by a water molecule. However, the NO_3^- anions are somewhat displaced with respect to the BF_4^- positions in **1** and form hydrogen bonds with trapped water molecules (O$\cdots$OW2 = 2.905 Å). In the IR spectrum of **3**, the stretching vibrations due to BF_4^- disappear while new peaks in the region 1305−1380 cm^{-1} appear, attributable[20] to NO_3^- anions. To investigate the reversibility of the anion exchange process, the exchanged crystal (**3**) is dipped in an aqueous solution of $NaBF_4$ to regenerate **1**. Like the previous case, the crystal turns opaque and does not diffract, although the elemental analysis, PXRD pattern, and IR spectrum of this sample prepared by keeping crystals of **3** in $NaBF_4$ for 7 days are identical to those of **1** (Supporting Information). It is also observed that freshly prepared crystals of **1** turn opaque and lose crystallinity when dipped in deionized water or in aqueous $NaClO_4$/$NaNO_3$ for more than 10 days. Also, crystals of **1** in the mother liquor become opaque after 15 days. When exposed to air at RT, the crystals do not survive for more than two days. Crystals of **1** do not survive in aqueous NaCl solution for more than 3 days at RT, although BF_4^- anions are replaced by Cl^- ions. Data collected on a crystal after dipping it for 3 days in aqueous solution to obtain **4** afford an approximate structure.[22] Although the structure is highly disordered, it shows the absence of BF_4^- anions and the presence of Cl^- in its place. Both elemental analysis and IR spectral studies indicate the absence of BF_4^- anions. The PXRD patterns of the exchanged solid (**4**) are very similar to that of **1**, suggesting the framework to be intact upon anion exchange (Figure S9). To

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(22) Unit cell parameters for **4**: a = 12.272(5) Å, b = 36.985(5) Å, c = 13.339(6) Å, β = 96.865(5)°, U = 6011(4).

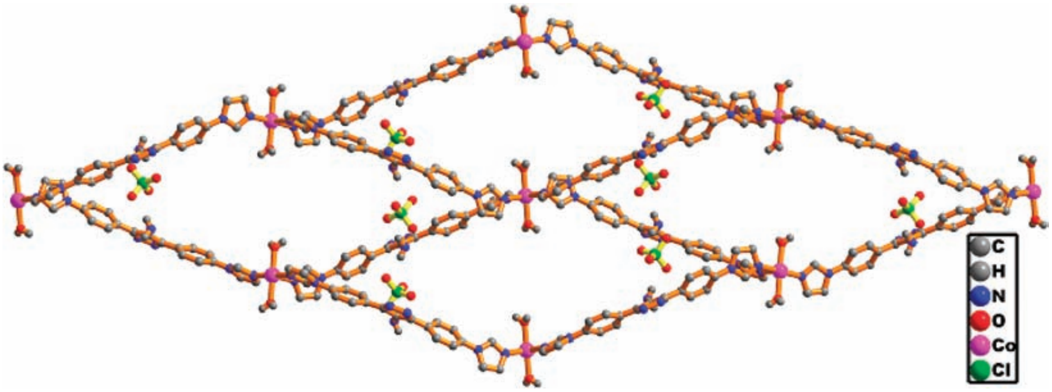

Figure 6. Trapped ClO_4^- anions in the 2D rectangular-grid structure of **2**.

investigate the reversibility of the anion exchange process, the exchanged crystal (**3**) is dipped in an aqueous solution of $NaBF_4$ to regenerate **1**. The elemental analysis, PXRD pattern, and IR spectrum of this sample prepared by keeping crystals of **4** in $NaBF_4$ for 7 days are identical to those of **1** (Supporting Information). There are very few examples reported where anion exchange is occurring in a SC-SC fashion, and the results obtained here are still unprecedented to the best of our knowledge.

It should be noted that anion exchange is a size and shape recognition process. The voids in which the anions located should be large enough to allow the original anions to exit and new anions to enter. These anion exchanges were found to be selective; only the substitutions of BF_4^- by ClO_4^-, NO_3^-, or Cl^- were achieved, whereas attempted anion exchange of BF_4^- with PF_6^-, BPh_4^-, or organic anions such as $C_6H_5COO^-$ proved unsuccessful. Also, the Cl^- ion, being smaller in size compared to other ions studied, can replace BF_4^- at a much faster rate (within 3 days). This demonstrates that the exchange process depends on the size of the anions. The diameters of BF_4^-, ClO_4^-, NO_3^-, PF_6^-, and BPh_4^- are calculated to be approximately 3.4, 3.8, 3.2, 3.5, and 8.7 Å, respectively, and thus it would seem that the anion exchange is closely related to the size of the cavities in **1** (ca. $\sim 4.2 \times 4.8$ Å^2 by considering the van der Waals radii) compared to the sizes of the various anions. The reason for nonexchange with PF_6^- could be associated with the geometry of this anion.

Interestingly, in an attempt of postsynthetic modification,[23] a crystal of **3** is dipped in 0.1 M formaldehyde in $CHCl_3$. After 5 days, the crystal is taken out and its structure determined as $\{[Co(L)_2(H_2O)_2]\cdot(NO_3)_2\cdot 2DMF\cdot H_2O\}_n$ (**5**). The morphology of the crystal remains unchanged (Figure S12). Single-crystal X-ray analysis reveals that **5** is a one-dimensional chain extending along the *b*-axis. The coordination mode of the metal ion remains the same as in **3**. However, the Co_4L_4 macrocyclic units in **3** are replaced by Co_2L_2 macrocyclic rings in **5**. The distance between two cobalt centers is 19.384 Å, while the NO_3^- anion is H-bonded with the triazole amino group ($O\cdots\cdot N = 2.938$ Å). This change from **3** to **5** is found to be irreversible. Due to the presence of four Ar−C single bonds in the ligand, it is expected to exhibit significant configurational flexibility that enables it to connect metal centers in different manners and leads to a great variety of structures. On comparing the configuration of **L** in **3** and **5**, none of the four rings are in the same plane in either structure. Also, large changes in torsion angle between imidazole and aromatic benzene plane are observed: 43.20° and 33.08° for **3**; 38.17° and 0.79° for **5**. Interestingly, the structures of both **3** and **5** look quite similar when viewed along the crystallographic *b*-axis (Figure 7). All attempts of this structural transformation with other compounds remained unsuccessful, and in each case the crystallinity is lost completely.

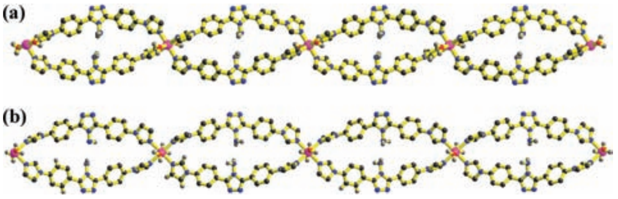

Figure 7. View of the (a) single two dimensional sheet along the *b*-axis in **3** and (b) 1D chain of **5** along the *b*-axis.

Again, the possibility of dissolution of **1** in successive solutions followed by crystallization or renucleation at the surface and growth of the new phase is excluded by the photographs taken (see Supporting Information) of the as-synthesized suitable-sized crystal of **1** and when it transforms to **2**, **3**, or **5**, which shows no change in size, morphology, and transparency. In addition, the insolubility of **1** in water is checked by NMR spectra taken after crystals of **1** are dipped in D_2O for 7 days, which shows no peak corresponding to the organic moiety of polymer **1**.

Conclusions

We have synthesized a coordination polymer having (4,4) net non-interpenetrating topology with a new long ligand. This polymer exhibits anion exchange capability in a SC-SC manner. The uncoordinated BF_4^- anions can be easily exchanged with ClO_4^- and NO_3^- anions, keeping the crystallinity. In the case of exchange with Cl^- the crystallinity is lost, although IR spectroscopic and elemental analysis show exchange has taken place. Also, an interesting structural transformation (2D → 1D) has been identified that involves Co−N bond cleavage and new Co−N bond formation again in a SC-SC fashion. We can expect that using a longer ligand having electron-rich moieties as substituents may also prevent interpenetration and create porous materials with large voids. These results suggest that this fascinating system may

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[23] (a) Wang, Z.; Cohen, S. M. *Chem. Soc. Rev.* **2009**, *38*, 1315. (b) Song, Y.-F.; Cronin, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 4635.

have significant potential for application as new molecular-based functional materials.

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Supporting Information Available: Selected bond angles and distances for all compounds, IR, TGA, NMR, ESI-MS, and X-ray powder diffraction patterns, and photographs of crystals. This information is available free of charge via the Internet at http://pubs.acs.org.