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Article

$[Ph_3PCH_2Ph]_2[Zn_3(tp)_3Cl_2]$ and $Ni_3(tma)_2(H_2O)_8$: Two Unusual Claylike Frameworks of Metal–Polycarboxylate Coordination Polymers (tp = Terephthalate, tma = Trimesate)

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Two new compounds, $[Ph_3PCH_2Ph]_2[Zn_3(tp)_3Cl_2]$ (**1**) and $Ni_3(tma)_2(H_2O)_8$ (**2**) (tp = terephthalate, tma = trimesate), are metal–polycarboxylate coordination polymers prepared by similar hydrothermal synthesis techniques. X-ray single-crystal structural analysis shows that both compounds crystallize in the 2D claylike lamellar architectures, in which **1** possesses the interlayer $[Ph_3PCH_2Ph]^+$ exchangeable cation and has been confirmed by PXRD patterns. **1** ($C_{74}H_{56}Cl_2O_{12}P_2Zn_3$) belongs to monoclinic $P2_1/c$, $Z = 2$ ($a = 18.956(1)$ Å, $b = 10.2697(5)$ Å, $c = 17.067(1)$ Å, $\beta = 99.486(4)°$). **2** ($C_{18}H_{22}O_{20}Ni_3$) is attributed to triclinic $P\bar{1}$, $Z = 1$ ($a = 6.6643(8)$ Å, $b = 9.622(1)$ Å, $c = 10.089(1)$ Å, $\alpha = 112.675(2)°$, $\beta = 94.007(1)°$, $\gamma = 106.411(2)°$). Linear metal trinuclear clusters bridged by rigid linear tp ligands for **1** and trigonal tma ligands for **2** give rise to a novel 2D 6-linked (3,6) topological anionic network in **1** and an interesting 2D 3,6-linked molybdenite topological neutral network in **2**, respectively. Both compounds exhibit intense fluorescent emission bands at 410 nm ($\lambda_{exc} = 355$ nm) for **1** and 398 nm ($\lambda_{exc} = 300$ nm) for **2** in the solid state at room temperature.

Introduction

Supramolecular coordination polymeric solids have received much attention over the past decades, owing to not just their potential applications as functional materials but also their fascinating structural diversities of the architectures.[1,2] The design and synthesis of mineralominetic architectures of coordination polymers analogous to quartz, clays, and zeolites are still interesting topics in the coordination polymeric chemistry[3] because such architectures would be unprecedented not only their nanoscale channels or cavities but also offer novel functionality.[4] Many efforts have been devoted to the preparation of porous coordination frameworks

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(1) (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, 1995. (b) Robson, R. *Comprehensive Supramolecular Chemistry*; Pergamon: New York, 1996; Chapter 22, p 733. (c) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; ACS Publications: Washington, DC, 1992; Chapter 19, p 449. (d) Dai, J.-C.; Fu, Z.-Y.; Wu, X.-T. Supramolecular Coordination Polymers. In *Encyclopedia of Nanoscience and Nanotechnology*; Nalwa, H. S., Ed.; American Scientific Publishers: Valencia, CA, 2004; Vol. 10, p 247. (e) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* 1991, **113**, 3606. (f) Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 207. (g) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (h) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; O' Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319.

(2) (a) Byrn, M. P.; Curtis, C. J.; Hsiou, Y.; Khan, S. I.; Sawin, P. A.; Terzis, A.; Strouse, C. E. Solid-State Supramolecular Chemistry: Crystal Engineering. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Elsevier: Oxford, U.K., 1996; Vol. 6, p715. (b) Wurthner, F.; Sautter, A. *Chem. Commun*. **2000**, 445.

(3) (a) Desiraju, G. R. *Cryst. Eng., The Design of Organic Solids*; Elsevier: Amsterdam, 1989. (b) Plater, M. J.; Foreman, M. R. St. J.; Gelbrich, T.; Hursthouse, M. B. *J. Chem. Soc. Dalton Trans.* **2000**, 1995. (c) Zaworotko, M. J. *Chem. Soc. Rev*. **1994**, *23*, 283. (d) Robson, R.; Hoskins, B. F. *J. Am. Chem Soc.* **1990**, *112*, 1546. (e) Zaworotko, M. J. *Chem. Commun*. **2001**, 1. (f) Moulton, B.; Zaworotko, M. J. *Chem. Rev*. **2001**, *101*, 1629. (g) Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *Nature* **1995**, *374*, 792.

(4) (a) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev*. **2000**, *100*, 3483. (b) Evans, O. R.; Lin, W.-B. *Acc. Chem. Res*. **2002**, *35*, 511. (c) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schroder, M. *Coord. Chem. Rev*. **1999**, *183*, 117. (d) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed*. **1998**, *37*, 1461. (e) Braga, D. *J. Chem. Soc. Dalton Trans*. **2000**, 3705. (f) Robson, R. *J. Chem. Soc. Dalton Trans*. **2000**, 3735.

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related to zeolite-like types. Many very interesting examples of polymeric solids with 3D open-framework cavities have been reported, as in diamondoid,[5] primitive cubic (α-Po net),[6] honeycomblike,[6a,7] and other frameworks.[6a,7a,8] However, compared with the fascinating structural diversities of 3D porous polymeric solids, the 2D coordination polymeric frameworks are less abundant, of which the 2D claylike frameworks, in particular, have been rare so far. On the other hand, because of the steric limitation in the coordination geometry of metal centers, the fabrication of 2D polymeric frameworks by use of rigid multifunctional ligands often gives rise to the polymeric solids with lower linked networks, such as simple 2D 4-linked square grid (4,4),[6a,9] 2D 3-linked brick wall,[9a,10] herringbone,[11] and honeycomb (6,3) networks[12] or a bilayer framework.[7a,9l,13] There is still a challenge, to date, to construct the 2D polymeric frameworks containing the high-linked nodes by using rigid multifunctional ligand species, although several interesting cases of 2D polymeric frameworks with high-linked nodes up to 5-[14] and 6-linked[15] networks have been prepared by using flexible bridging ligands. One important structural characteristic in this area that has caught our attention is the role of metal multinuclear clusters in the coordination polymers. These clusters may give the possibility for serving as the flexible nodes in some way to bind the rigid tectonic ligand molecules. Recognizing the potential of this approach, we have embarked on a program aimed at using metal multinuclear clusters to prepare coordination polymeric solids with 2D high-linked topological networks and wish to get the 2D claylike polymeric frameworks related to anionic smectite or neutral kaolinite architectures. Our design strategy for the assembly of anionic smectite-like frameworks is the choice of various large bulky organic cations, such as organophosphonium or organoammonium, as interlayer counterions vs the use of small rigid polycarboxylate ligand molecules to construct the host anionic network with small grids for preventing disfavored guest enclathration and interpenetration phenomena. Here, we report two novel examples of 2D claylike supramolecular architectures formed by d-block transition metal−polycarboxylate coordination polymers, [Ph_3PCH_2Ph]$_2$[$Zn_3(tp)_3Cl_2$] (**1**) and $Ni_3(tma)_2(H_2O)_8$ (**2**) ([Ph_3PCH_2Ph] = benzyltriphenylphosphonium, tp = terephthalate, tma = trimesate), presenting an interesting 6-linked (3,6)

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(5) (a) Abrahams, B. F.; Hoskins, B. F.; Liu, J.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3045. (b) Lopez, S.; Kahraman, M.; Harmata, M.; Keller, S. W. *Inorg. Chem.* **1997**, *36*, 6138. (c) Blake, A. J.; Champness, N. R.; Khlobystov, A. N.; Lemenovskii, D. A.; Li, W.-S.; Schroder, M. *Chem. Commun.* **1997**, 1339. (d) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *Chem. Eur. J.* **2002**, *8*, 1520. (e) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *Chem. Commun.* **1994**, 1325. (f) Otieno, T.; Rettig, S. J.; Thompson, R. C.; Trotter, J. *Inorg. Chem.* **1993**, *32*, 1607. (g) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Chem. Commun.* **1994**, 2755. (h) Evans, O. R.; Xiong, R. G.; Wang, Z. Y.; Wong, G. K.; Lin, W. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 536. (i) Evans, O. R.; Wang, Z. Y.; Xiong, R. G.; Foxman, B. M.; Lin, W. B. *Inorg. Chem.* **1999**, *38*, 2969. (j) Hirsch, K. A.; Venkataraman, D.; Wilson, S. R.; Moore, J. S.; Lee, S. *Chem. Commun.* **1995**, 2199. (k) Chen, Z.-F.; Xiong, R.-G.; Abrahams, B. F.; You, X.-Z.; Che, C.-M. *J. Chem. Soc. Dalton Trans.* **2001**, 2453. (l) Evans, O. R.; Lin, W. B. *Chem. Mater* **2001**, *13*, 2705. (m) Reddy, D. S.; Dewa, T.; Endo, K.; Aoyama, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 4266. (n) Fu, Z.-Y.; Wu, X.-T.; Dai, J.-C.; Hu, S.-M.; Du, W.-X. *Eur. J. Inorg. Chem.* **2002**, 2730.

(6) (a) Dai, J.-C.; Wu, X.-T.; Hu, S.-M.; Fu, Z.-Y.; Zhang, J.-J.; Du, W.-X.; Zhang, H.-H.; Sun, R.-Q. *Eur. J. Inorg. Chem.* **2004**, 2096. (b) Tao, J.; Tong, M.-L.; Chen, X.-M. *J. Chem. Soc. Dalton Trans.* **2000**, 3669. (c) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127. (d) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (e) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.

(7) (a) Dai, J.-C.; Wu, X.-T.; Fu, Z.-Y.; Cui, C.-P.; Hu, S.-M.; Du, W.-X.; Wu, L.-M. Zhang, H.-H.; Sun, R.-Q. *Inorg. Chem.* **2002**, *41*, 1391. (b) Choi, H. J.; Lee, T. S.; Suh, M. P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1405.

(8) (a) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148. (b) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861. (c) Chen, B.; Eddaoudi, M.; Reineke, T. M.; Kampf, J. W.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 11559. (d) Chen, L.; Eddaoudi, M.; Hyde, S. T.; O’ Keeffe, M.; Yaghi, O. M. *Science* **2001**, *291*, 1021. (e) Dai, J.-C.; Wu, X.-T.; Fu, Z.-Y.; Hu, S.-M.; Du, W.-X.; Cui, C.-P.; Wu, L.-M.; Zhang, H.-H.; Sun, R.-Q. *Chem. Commun.* **2002**, 12. (f) Abrahams, B. F.; Batten, S. R.; Grannas, M. J.; Hamit, H.; Hoskins, B. F.; Robson, R. *Angew. Chem., Int. Ed.* **1999**, 38, 10, 1475. (g) Jiang, Y.-C.; Lai, Y.-C.; Wang, S.-L.; Lii, K.-H. *Inorg. Chem.* **2001**, *40*, 5320. (h) Liang, Y. C.; Cao, R.; Su, W. P.; Hong, M. C.; Zhang, W. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3304. (i) Fu, Z.-Y.; Hu, S.-M.; Dai, J.-C.; Zhang, J.-J.; Wu, X.-T. *Eur. J. Inorg. Chem.* **2003**, 2670.

(9) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Kondo, M.; Shimamura, M.; Noro, S.; Minakoshi, S.; Asami, A.; Seki, K.; Kitagawa, S. *Chem. Mater* **2000**, *12*, 1288. (c) Batten, S. R.; Hoskins, B. F.; Robson, R. *New J. Chem.* **1998**, *22*, 173. (d) Abrahams, B. F.; Hardie, M. J.; Hoskins, B. F.; Robson, R.; Sutherland, E. E. *Chem. Commun.* **1994**, 1049. (e) Groeneman, R. H.; MacGillivray, L. R.; Atwood, J. L. *Chem. Commun.* **1998**, 2735. (f) Aoyagi, M.; Biradha, K.; Fujita, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1369. (g) Hagrman, D.; Hammond, R. P.; Haushalter, R.; Zubieta, J. *Chem. Mater* **1998**, *10*, 2091. (h) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T. Y.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (i) MacGillivray, L. R.; Groeneman, R. H.; Atwood, J. L. *J. Am. Chem. Soc.* **1998**, *120*, 2676. (j) Park, S. H.; Kim, K. M.; Lee, S.; Jung, O. S. *Bull. Kor. Chem. Soc.* **1998**, *19*, 79. (k) Fu, Z.-Y.; Lin, P.; Du, W.-X.; Chen, L.; Cui, C.-P.; Zhang, W.-J.; Wu, X.-T. *Polyhedron* **2001**, *20*, 1925. (l) Dai, J.-C.; Hu, S.-M.; Wu, X.-T.; Fu, Z.-Y.; Du, W.-X.; Zhang, H.-H.; Sun, R.-Q. *New J. Chem.* **2003**, *23*, 914.

(10) (a) Fujita, M.; Kwon, Y. J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M. *New J. Chem.* **1998**, *22*, 1319. (c) Xia, S.-Q.; Hu, S.-M.; Dai, J.-C.; Wu, X.-T.; Fu, Z.-Y.; Zhang, J.-J.; Du, W.-X. *Polyhedron* **2004**, *23*, 1003.

(11) (a) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Dalton Trans.* **1999**, 1799. (b) Dong, Y. B.; Smith, M. D.; Layland, R. C.; Zur Loye, H. C. *Chem. Mater* **2000**, *12*, 1156. (c) Masse, R.; Nicoud, J. F.; Bagieu-Beucher, M.; Bourgogne, C. *Chem. Phys.* **1999**, *245*, 365. (d) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Schroder, M. *New J. Chem.* **1999**, *23*, 573. (e) Dong, Y. B.; Layland, R. C.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; Zur Loye, H. C. *Chem. Mater* **1999**, *11*, 1413.

(12) (a) Lee, E.; Kim, J.; Heo, J.; Whang, D.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 399. (b) Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* **1998**, *120*, 10622. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1088. (d) Sharma, C. V. K.; Zaworotko, M. J. *J. Chem. Soc. Chem. Commun.* **1996**, 2655.

(13) (a) Power, K. N.; Hennigar, T. L.; Zaworotko, M. *J. New J. Chem.* **1998**, *22*, 177. (b) Fu, Z.-Y.; Wu, X.-T.; Dai, J.-C.; Hu, S.-M.; Du, W.-X. *New J. Chem.* **2002**, *26*, 978. (c) Rujiwatra, A.; Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1999**, 2307. (d) Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739. (e) Kepert, C. J.; Rosseinsky, M. J. *Chem. Commun.* **1999**, 375. (f) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725. (g) Fu, Z.-Y.; Wu, X.-T.; Dai, J.-C.; Wu, L.-M.; Cui, C.-P.; Hu, S.-M. *Chem. Commun.* **2001**, 1856.

(14) Bu, X.-H.; Weng, W.; Li, J.-R.; Chen, W.; Zhang, R.-H. *Inorg. Chem.* **2002**, *41*, 413.

(15) (a) Bu, X.-H.; Chen, W.; Lu, S.-L.; Zhang, R.-H.; Liao, D.-Z.; Bu, W.-M.; Shionoya, M.; Brisse, F.; Ribas, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3201. (b) Li, J.-R.; Zhang, R.-H.; Bu, X.-H. *Cryst. Growth Des.* **2004**, *4*, 219. (c) Su, C.-Y.; Cai, Y.-P.; Chen, C.-L.; Kang, B.-S. *Inorg. Chem.* **2001**, *40*, 2210. (d) Lin, W.; Wang, Z.; Ma, L. *J. Am. Chem. Soc.* **1999**, *121*, 11249. (e) Long, D.-L.; Blake, A. J.; Champness, N. R.; Schroder, M. *Chem. Commun.* **2000**, 2273.

topological anionic network in **1** and 3,6-linked molybdenite topological neutral network in **2**, respectively.

Experimental Section

General Remarks. The title compounds were prepared from commercially purchased chemicals by typical hydrothermal reaction techniques in a Parr Teflon-lined reaction vessel under autogenous pressure heated in resistance furnaces. Infrared spectra were recorded on Nicolet Nexus 470 spectrometer using KBr pellets; elemental analyses were carried out with a Vario EL III elemental analyzer. Fluorescent data were collected on an Edinburgh FL-FS920 TCSPC system, and TGA (thermal gravimetric analysis) was performed with a heating rate of 10 °C·min^{-1} using a TA5200/MDSC2910 system. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV, 40 mA with Cu Kα ($\lambda = 1.5406$ Å) radiation with a scan speed of 2°·min^{-1} and a step size of 0.02° in 2θ. The pore volume analysis was accomplished with Platon software.[16]

$[Ph_3PCH_2Ph]_2[Zn_3(tp)_3Cl_2]$ (1). Compound **1** was first synthesized by the static reaction of zinc acetate dihydrate, H_2tp, $[Ph_3PCH_2Ph]$Cl, and water in a molar ratio of 3:4:2:556 under hydrothermal conditions at 200 °C for 4 days followed by annealing at a rate of ca. 3.5 °C·h^{-1} to give about 40% yield of **1** based on Zn as colorless prismlike crystals, which were collected by mechanical isolation and washed with water and absolute alcohol. Subsequently, a higher yield (~85% yield) of **1** was received from same approach but stoichometric ratio of 3:3:2:556. $C_{74}H_{56}Cl_2O_{12}P_2Zn_3$ (1466.14): Anal. Calcd (found): H, 3.85 (3.81); C, 60.62 (61.05); O, 13.09 (12.99); Cl, 4.84 (4.90). IR (KBr pellet, cm^{-1}): 3058 (m), 2940 (w), 2888 (m), 1600 (vs), 1502 (m), 1437 (s), 1371 (vs), 1143 (w), 1113 (s), 1029 (w), 996 (w), 883 (w), 824 (m), 788 (m), 746 (vs), 698(s), 584 (w), 505 (s), 450 (w) (see Supporting Information, Figure S1a).

$Ni_3(tma)_2(H_2O)_8$ (2). Compound **2** was first obtained as green block crystals in about 49% yield (based on Ni) from a similar hydrothermal reaction with a nickel acetate tetrahydrate/H_3tma/water molar ratio of 2.9:1:694 at 200 °C for 4 days that was then cooled at a rate of 3.5 °C·h^{-1} to room temperature. The same reaction using a stoichiometric ratio of 3:2:667 instead of the above 2.9:1:694 can raise the yield up to 86%. In additional, the isomeric $Ni_3(tma)_2(H_2O)_8$ (**2a**) (see Supporting Information, Tables S9−12) was prepared in about 9% yield in a similarly hydrothermal reaction with a nickel acetate tetrahydrate/H_3tma/$(C_2H_5)_4$NBr/water molar ratio of 4:1:1:694. $C_{18}H_{22}O_{20}Ni_3$ (734.49): Anal. Calcd (found): H, 3.02 (3.30); C, 29.44 (28.55); O, 43.57 (43.96). IR (KBr pellet, cm^{-1}): 3566 (w, sh), 3442 (vs, br), 3170 (m, br), 2110 (m), 1614 (vs), 1551 (vs), 1520 (s), 1477 (m), 1437 (vs), 1371 (vs), 1207 (w), 1147 (m), 1109 (m), 1057 (vw), 947 (w), 926 (m), 881 (w), 847 (w), 816 (w), 800 (vw), 762 (s), 721 (vs), 571 (w), 548 (w), 534 (vw, sh), 459 (m) (Figure S1b).

Structure Determinations. Data collections for **1** and **2** were, respectively, performed on a Rigaku Mercury CCD diffractometer and a Siemens Smart CCD area-detector diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Empirical absorption corrections were applied for all of the data sets that were made with the Multiscan program[17] for **1** and the SADABS program[18] for **2**. The structure was solved by direct methods using SHELXS-97[19] and refined by full-matrix least-squares techniques using SHELXL-97.[20] All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Final refinements converged at R1 = 0.0367 for **1** and 0.0538 for **2**. Some crystallographic data are summarized in Table 1, and the selected bond lengths and bond angles of the two compounds are listed in Table 2. More details on crystallographic information, as well as refinement data and anisotropic displacement parameters, are in the Supporting Information.

Table 1. Some Crystal, Data Collection, and Structure Refinement Parameters for **1** and **2**

compound	**1**	**2**
empirical formula	$C_{74}H_{56}Cl_2O_{12}P_2Zn_3$	$C_{18}H_{22}O_{20}Ni_3$
fw	1466.14	734.49
cryst syst	monoclinic	triclinic
space group, Z	$P2_1/c$ (No. 14), 2	$P\bar{1}$ (No. 2), 1
a/Å	18.956(1)	6.6643(8)
b/Å	10.2697(5)	9.622(1)
c/Å	17.067(1)	10.089(1)
V/Å^3	3277.0(3)	560.8(1)
α/°		112.675(2)
β/°	99.486(4)	94.007(1)
γ/°		106.411(2)
μ/mm^{-1}	1.284	2.600
ρ_{calcd}/g·cm^3	1.486	2.175
λ(Mo Kα)/Å	0.71073	0.71073
T/K	293(2)	293(2)
collected reflns	23 924	2852
independent reflns	7467	1908
observed reflns	6739 (>2$\sigma(I)$)	1410 (>2$\sigma(I)$)
R_{int}	0.0258	0.0347
R1[a]	0.0367 (for obs.)	0.0538 (for obs.)
wR2[b]	0.0854 (for obs.)	0.1364(for obs.)

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = \{\sum w[(F_o^2 - F_c^2)^2]/\sum w[(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3]$.

Results and Discussion

Synthesis and Characterization. Two claylike supramolecular coordination polymers are formulated as $[Ph_3PCH_2Ph]_2[Zn_3(tp)_3Cl_2]$ (**1**) and $Ni_3(tma)_2(H_2O)_8$ (**2**); either are obtained in similar hydrothermal synthesis conditions, based upon the elemental analysis data. The synthetic reproducibility for both compounds is very nice. The yield for either **1** or **2** can be raised up to ~85% or 86% when the repeated synthesis is done with stoichiometric ratio of the reactants. Change in both the reaction temperature (160 °C) and the stoichiometric ratio for **1** will yield a new 4-linked square grid (4,4) lamellar framework $[Ph_3PCH_2Ph][Zn(tp)Cl]$—another 2D claylike anionic species with the same interlayer $[Ph_3PCH_2Ph]^+$ cation.[21] Attempts failed to prepare an anionic framework polymeric architecture analogous to compound **2** but having interlayer $(C_2H_5)_4N^+$ cations. Both compounds are very stable in air at ambient temperature, and **2** is almost insoluble in common solvents such as water, alcohol, acetonitrile, chloroform, acetone, and toluene. TGA suggests that the decomposition of compound **1** occurs at about 250 °C, finishing at ca. 450 °C with a decline stage up to 900 °C, and the final thermal decomposition product at 900 °C

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(16) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2003.

(17) Rigaku, *CrystalClear*, Version 1.3; Rigaku Corporation: Tokyo, 2000.

(18) Blessing, R. H. *Acta. Crystallogr.* **1995**, *A51*, 33.

(19) Sheldrick, G. M. *SHELXS-97*, *Program for X-ray Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

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

(21) Yang, G.-D.; Dai, J.-C. Unpublished research.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

	1[a]		
Zn(1)−Cl	2.2802(7)	Zn(2)−O(1b)	2.133(2)
Zn(1)−O(4a)	1.964(2)	Zn(2)−O(5b)	2.052(2)
Zn(1)−O(6)	1.975(2)	Zn(2)−O(5)	2.052(2)
Zn(1)−O(2)	1.980(2)	Zn(2f)−O(3)	2.083(2)
Zn(1e)−O(4)	1.964(2)	Zn(2)−O(3c)	2.083(2)
Zn(2)−O(1)	2.133(2)	Zn(2)−O(3a)	2.083(2)
O(4a)−Zn(1)−O(6)	117.70(8)	O(4a)−Zn(1)−Cl	104.76(6)
O(4a)−Zn(1)−O(2)	109.02(8)	O(6)−Zn(1)−Cl	102.82(6)
O(6)−Zn(1)−O(2)	119.88(8)	O(2)−Zn(1)−Cl	99.42(6)
O(5b)−Zn(2)−O(5)	180.00(9)	O(3c)−Zn(2)−O(1b)	94.77(7)
O(5b)−Zn(2)−O(3c)	91.94(7)	O(3a)−Zn(2)−O(1b)	85.23(7)
O(5)−Zn(2)−O(3c)	88.06(7)	O(5b)−Zn(2)−O(1)	85.77(7)
O(5b)−Zn(2)−O(3a)	88.06(7)	O(5)−Zn(2)−O(1)	94.23(7)
O(5)−Zn(2)−O(3a)	91.94(7)	O(3c)−Zn(2)−O(1)	85.23(7)
O(3c)−Zn(2)−O(3a)	180.0	O(3a)−Zn(2)−O(1)	94.77(7)
O(5b)−Zn(2)−O(1b)	94.23(7)	O(1b)−Zn(2)−O(1)	180.000(1)
O(5)−Zn(2)−O(1b)	85.77(7)		
	2[b]		
Ni(1)−O(1)	2.043(5)	Ni(2f)−O(5)	2.119(4)
Ni(1)−O(9)	2.061(5)	Ni(2)−O(2)	2.029(4)
Ni(1)−O(10)	2.062(4)	Ni(2)−O(2b)	2.029(4)
Ni(1)−O(8)	2.079(6)	Ni(2)−O(10b)	2.064(4)
Ni(1)−O(4a)	2.080(5)	Ni(2)−O(10)	2.064(4)
Ni(1)−O(7)	2.086(5)	Ni(2)−O(5c)	2.119(4)
Ni(1e)−O(4)	2.080(5)	Ni(2)−O(5d)	2.119(4)
O(1)−Ni(1)−O(9)	87.7(2)	O(10)−Ni(2)−O(5d)	88.3(2)
O(1)−Ni(1)−O(10)	95.3(2)	O(5c)−Ni(2)−O(5d)	180.0(2)
O(9)−Ni(1)−O(10)	175.3(2)	O(2)−Ni(2)−O(2b)	180.0(2)
O(1)−Ni(1)−O(8)	91.5(2)	O(2)−Ni(2)−O(10b)	89.3(2)
O(9)−Ni(1)−O(8)	90.9(2)	O(2b)−Ni(2)−O(10b)	90.8(2)
O(10)−Ni(1)−O(8)	92.6(2)	O(2)−Ni(2)−O(10)	90.8(2)
O(1)−Ni(1)−O(4a)	96.6(2)	O(2b)−Ni(2)−O(10)	89.3(2)
O(9)−Ni(1)−O(4a)	88.0(2)	O(10b)−Ni(2)−O(10)	180.0(3)
O(10)−Ni(1)−O(4a)	88.1(2)	O(2)−Ni(2)−O(5c)	87.3(2)
O(8)−Ni(1)−O(4a)	171.8(2)	O(2b)−Ni(2)−O(5c)	92.7(2)
O(1)−Ni(1)−O(7)	171.0(2)	O(10b)−Ni(2)−O(5c)	88.3(2)
O(9)−Ni(1)−O(7)	86.3(2)	O(10)−Ni(2)−O(5c)	91.7(2)
O(10)−Ni(1)−O(7)	91.1(2)	O(2)−Ni(2)−O(5d)	92.7(2)
O(8)−Ni(1)−O(7)	82.0(3)	O(2b)−Ni(2)−O(5d)	87.3(2)
O(4a)−Ni(1)−O(7)	89.9(2)	O(10b)−Ni(2)−O(5e)	91.7(2)

[a] Key: (a) $x, -y + 1/2, z - 1/2$; (b) $-x + 1, -y + 1, -z + 1$; (c) $-x + 1, y + 1/2, -z + 3/2$; (d) $-x + 1, -y + 2, -z + 1$; (e) $x, -y + 1/2, z + 1/2$; (f) $-x + 1, y - 1/2, -z + 3/2$. [b] Key: (a) $x - 1, y - 1, z$; (b) $-x, -y, -z$; (c) $-x, -y, -z - 1$; (d) $x, y, z + 1$; (e) $x + 1, y + 1, z$; (f) $x, y, z - 1$.

is ZnO (found 16.2%, calcd 16.7%; Figure S2a, Supporting Information). The TGA trace for **2** shows two weight-loss stages, the first starts at 127 °C up to 208 °C, giving a weight loss of about 19.5%, corresponding to the loss of eight aqua ligands (calcd, 19.6%), following by a stage until 428.8 °C. Complete decomposition of **2** was finished at ca. 468.5 °C (Figure S2b). This is consistent with the structure of **2** and suggests that the framework of **2** have thermal stability similarly to compound **1**. The IR spectra of both compounds show that the characteristic bands of the carboxylate groups in the usual region at 1371−1437 cm^{-1} for the symmertric vibration and 1614−1551 cm^{-1} for the asymmertric vibration. The bands at 3058, 1502, 1437 cm^{-1}, as well as bands at 1113, 996, 2888, 2940 cm^{-1} for **1** confirm the presence of [Ph_3PCH_2Ph]$^+$ cation. The splitting of $\nu_{s(COO)}$ at 1437 and 1371 cm^{-1} and $\nu_{as(COO)}$ at 1614 and 1551 cm^{-1} for **2** reflects that the carboxylate groups of tma ligand have a variety of coordination fashions. Moreover, the absence of the expected bands at 1690−1730 cm^{-1} attributed to the protonated carboxylate groups for either indicate the full deprotonation of H_2tp and H_3tma on the reactions with metal ions, while the broad bands at 3566 and 3442 cm^{-1} for **2** suggests that the presence of coordinated water molecules. These are consistent with the structures of both compounds.

Structure. X-ray single-crystal analysis reveals that the crystal structure of **1** is a 2D claylike lamellar architecture. As shown in Figure 1, there are three zinc centers (Zn1, Zn1b, and Zn2) in the building unit of **1**, in which both Zn1 and Zn2 centers are crystallographic independently while Zn1b is an equivalent atom related to Zn1 center from the monoclinic $P2_1/c$ symmetric operation. The 4-coordinated Zn1 center lies in a little distorted tetrahedral coordination sphere [tetrahedral angle within 99.42(6)−119.88(8)°], bonding to a μ_t-Cl ligand and to three oxygen donors (O2, O6, and O4a) of three bridging bidentate carboxylate groups that are from three separated tp ligands. Generally, the tetrahedral coordinated geometry associated with a rigid linear ligands will result in diamondoid motif. However, the present tetrahedrally coordinated Zn1 center is linked to three rigid linear tp ligands and a terminal μ_t-Cl ligand, thus generating an approximately C_3-symmetric tripodlike subunit where the μ_t-Cl ligand lies on the ∼3-fold axis. Note that these three tp ligands are also bridged to the Zn2 center, so as to prevent

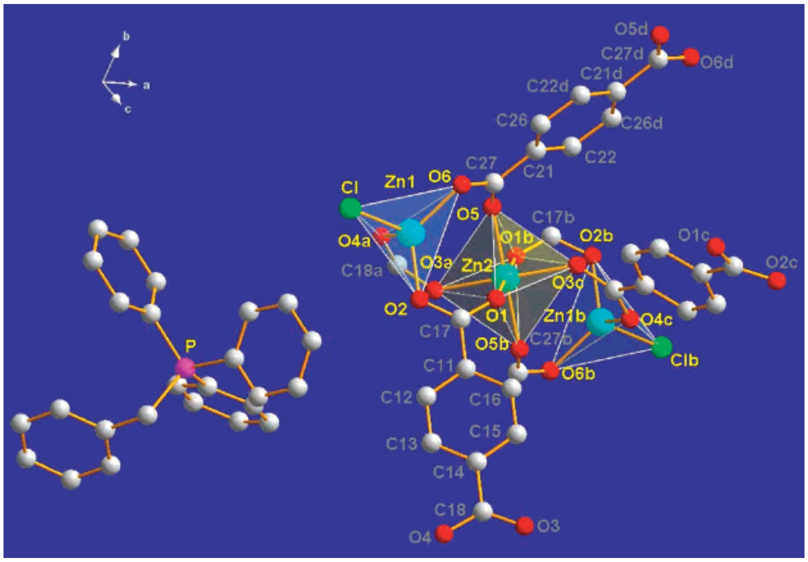

Figure 1. View of **1** depicting the coordination environment around the Zn1 and Zn2 centers, the hydrogen atoms are omitted for clarity: (a) $x, -y + 1/2, z - 1/2$; (b) $-x + 1, -y + 1, -z + 1$; (c) $-x + 1, y + 1/2, -z + 3/2$; (d) $-x + 1, -y + 2, -z + 1$.

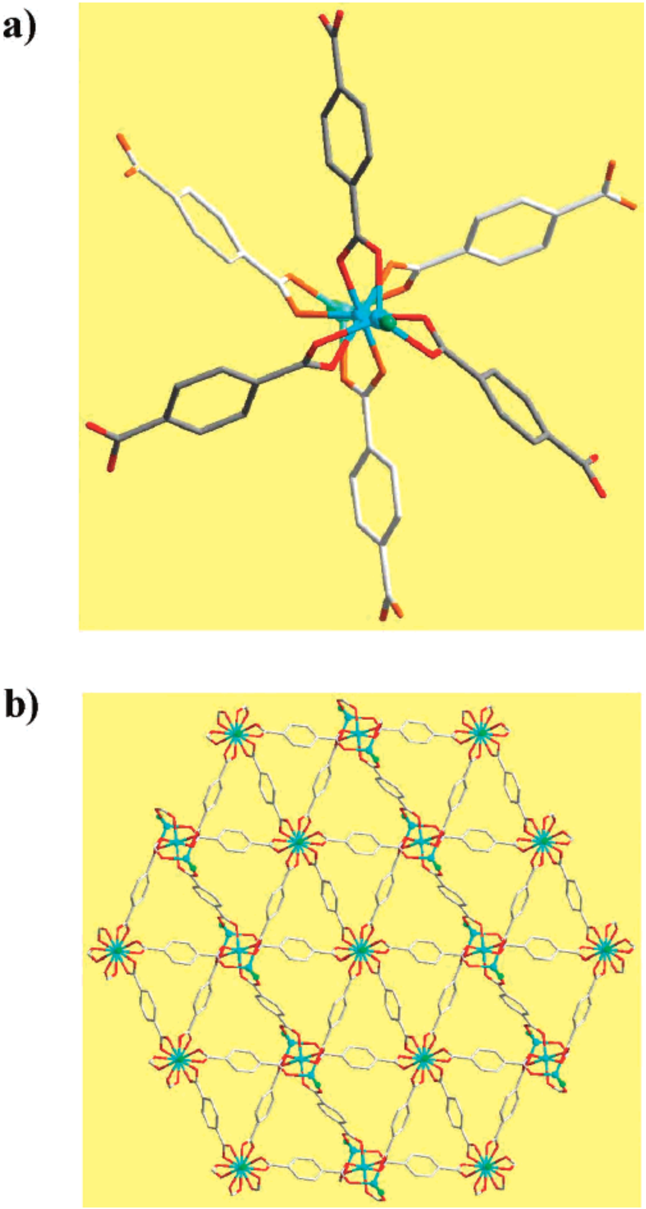

Figure 2. (a) View showing a 6-linked node with S_6 symmetry down the *a* axis in **1** assembled by C_3-symmetric Zn−tp tripods; the lighter colored tripod is related to the darker via the crystallographic S_6-symmetric operation. (b) 2D (3,6) topology network in **1**.

this tripod from extending to yield a well-known 3-linked (6,3) network. The Zn2 center lies in an octahedral coordinated environment, completed by six oxygen donors (O1, O1b, O3a, O3c, O5, and O5b) of six different bridging bidentate carboxylate groups of six separated tp ligands, of which three tp ligands (Figure 2a, darker colored) belong to above Zn1 tripod, and the rest of the three tp molecules (Figure 2a, lighter colored) are actually another tripod related to Zn1b center followed by the crystallographic S_6-symmetric operation. As a result, these three zinc center are therefore bridged to construct a linear trinuclear $\{Zn_3O_{12}Cl_2\}$ cluster through six different bis-bidentate tp ligands, the distance of center Zn2 to two other zinc atoms separation [Zn2⋯Zn1(Zn1b)] is 3.5461(2) Å and the angle of (Zn1⋯Zn2⋯Zn1b) is 180°. On the other hand, each tp ligand is linked to four different zinc centers through two bridging bidentate carboxylate groups. In additional, a large bulky guest $[Ph_3PCH_2Ph]^+$ cation is in an isolated form and not linked to the building unit. In such a way, the trinuclear $\{Zn_3O_{12}Cl_2\}$ clusters as the 6-linked nodes are interconnected through tp tectons to yield a 2D anionic framework with regular trigonal grids, an average 10.12 Å (9.96−10.27 Å) of grid lines (cluster⋯cluster separations) and an ~60° [58.964(1)° and 62.072(1)°] of grid angles (cluster⋯cluster⋯cluster angles), the topology belonged to novel 2D (3,6) (Schläfli symbol $3^6.4^6.5^3$) network (Figure 2b) and is, to our knowledge, still very rare so far in coordination polymer chemistry.[15b−e] Only a few examples of polymeric solids related to such a 2D (3,6) network topology were reported, of which three containing flexible linear ligands[15b−d] and one formed by flexible $\pi-\pi$ stacking interactions.[15e] Obviously in these limited examples,[15b−e] the flexity seems to be the key for fabrication of such a 2D 6-linked (3,6) network because these flexible ligands or $\pi-\pi$ stacking are available for adopting a up-and-down linkage fashion bridging two six-coordinated metal ions stretch out to generate such a topology. However, it is important to note that compound **1**, completely different from those reported cases, is directly fabricated by the assembly of rigid linear tp tectons with metal centers. The flexity in the present case was provided by linear trinuclear $\{Zn_3O_{12}Cl_2\}$ clusters rather than tp molecules. The linear trinuclear $\{Zn_3O_{12}Cl_2\}$ clusters here play an important role to serve as the flexible node available for fitting the trans−trans bridge connection of rigid tp ligands, also clearly for preventing disfavor interpenetrating network.[1g,h] These 2D (3,6) network sheets in **1** are stacked in a "face-to-face" fashion along the view of the *a* axis, an almost perfect eclipsed array. Thus, the whole crystal structure of **1** is an interesting smectite-like lamellar architecture with ~11.65 Å of layered dimension (sheet thickness) vs ~8.48 Å interlayer spacings, which are occupied by interlayer guests—$[Ph_3PCH_2Ph]^+$ counter cations (Figure 3). The effective cavities in **1**, after the removal of the interlayer cations, will have a quite large volume of 2140.3 Å^3, which reaches 65.3% of the unit cell volume (3277.0 Å^3).

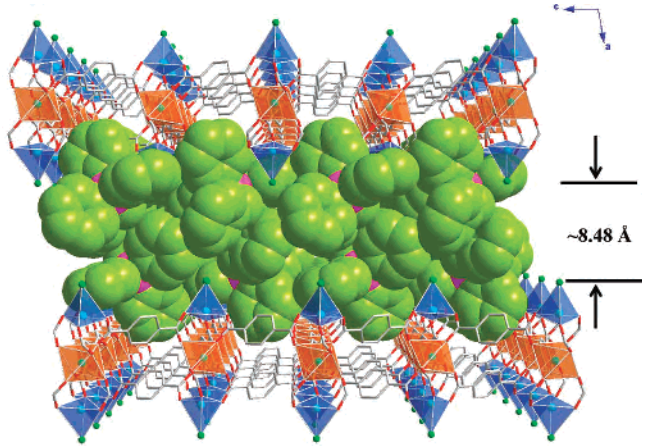

Figure 3. 2D smectite-like lamellar architecture in **1**, ~8.48 Å interlayer spacings are occupied by interlayer $[Ph_3PCH_2Ph]^+$ cations.

The structure of **2** also presents a 2D claylike lamellar architecture. The local coordination environment around the

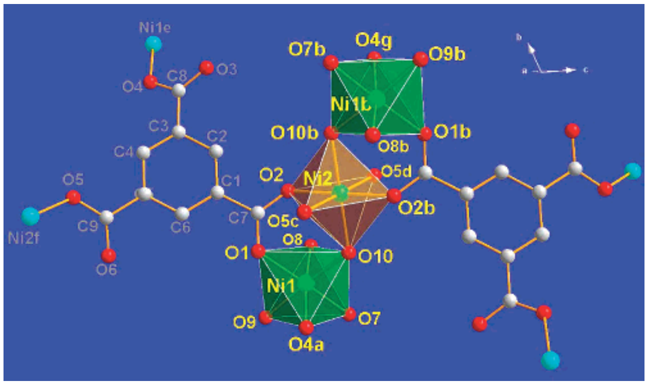

Figure 4. Coordination environment around the Ni1 and Ni2 centers in **2**; the hydrogen atoms are omitted for clarity: (a) $x - 1, y - 1, z$; (b) $-x, -y, -z$; (c) $-x, -y, -z - 1$; (d) $x, y, z + 1$; (e) $x + 1, y + 1, z$; (f) $x, y, z - 1$.

nickel centers in **2** is given in Figure 4. It also contains a linear trinuclear metal cluster that is constructed by two crystallographically independent six-coordinated nickel centers (Ni1, Ni2), one tma, and four aqua molecules (μ_t-O7, μ_t-O8, μ_t-O9, and μ_2-O10). In this structure, each tma ligand has two different coordination fashions—two unidentate carboxylate groups and one bridging bidentate carboxylate group—in which the bidentate group bridges to two nickel centers (e.g., Ni1 and Ni2) while two unidentate groups, respectively, bond to two other different nickel centers (e.g., Ni1e, Ni2f). On the other hand, the Ni1 center lies in a distorted octahedral coordination sphere and is coordinated by three μ_t-aqua molecules (O7, O8, and O9) and a μ_2-aqua ligand (O10), as well as two oxygen donors, respectively, belonging to a bridging bidentate carboxylate group (O1) and a unidentate carboxylate group (O4a) from two separated tma ligands, the angles of O−Ni1−O are in the range 82.0(3)−175.3(2)°. The other six-coordinated nickel center (Ni2) also lies in a distorted octahedral coordination geometry, being coordinated by two μ_2-aqua molecules (O10, O10b) as the apexes and four oxygen donors (O2, O2b, O5c, O5d) in the equator, in which two oxygen atoms (O2, O2b) come from two different bidentate carboxylate groups of two separate tma ligands, while the other two oxygen donors (O5c, O5d) belong to two different unidentate carboxylate groups of two different tma molecules. These two nickel centers (Ni1, Ni2), as well as Ni1b, an equivalent atom related to the Ni1 center, are bridged to construct a linear trinuclear $\{Ni_3O_{16}\}$ cluster by sharing two octahedral corners (O10, O10b) having an Ni1•••Ni2 separation of 3.61 Å. Thus, each tma molecule as a 3-linked node bridges three trinuclear $\{Ni_3O_{16}\}$ clusters, whereas each trinuclear $\{Ni_3O_{16}\}$ cluster served as a 6-linked node connects to six separate tma ligands. In this way, the trinuclear $\{Ni_3O_{16}\}$ clusters are interconnected through tma tectons to give rise to a remarkable 2D 3,6-linked network (Figure 5a), another interesting claylike lamellar neutral framework with 10.08 Å of layered dimension. On topological view, this 2D 3,6-linked claylike structure can be attributed to a prototypical molybdenite-[22] or berndtite-type[23] network (Figure 5b) and is, to our knowledge, still limited in coordination polymer chemistry to date.[24] Neither interpenetrating nor encapsulated guest molecules are found. The neighboring sheets are stacked in a tongue-and-groove model (Figure 6), resulting in the smart packing of whole crystal structure of **2** that gives substantial stuffy grid channels and small interlayer spacing.

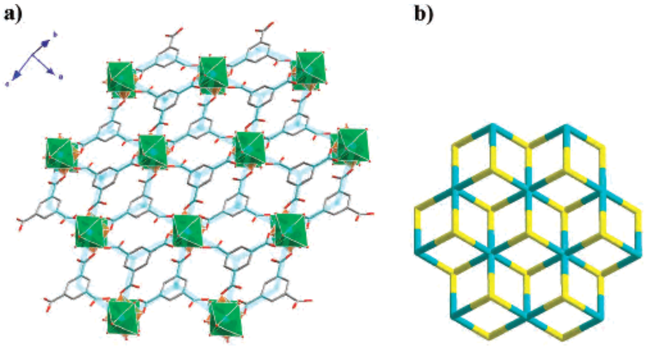

Figure 5. (a) View of the 2D 3,6-linked network in **2**. (b) Schematic diagram showing 2D 3,6-linked molybdenite topological network based upon **2**.

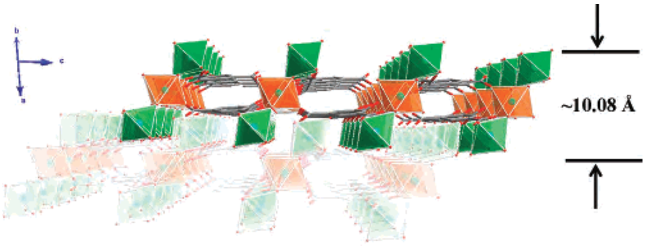

Figure 6. View of 2D kaolinite-like lamellar architecture in **2** showing smart tongue-and-groove stacking of the neighboring sheets.

Properties. Similar to natural smectite clays, compound **1** possesses interlayer $[Ph_3PCH_2Ph]^+$ counter cations. An interesting question arises. Does the compound **1** have the ability to exchange cations from an aqueous solution? To study the ionic exchange property, the polycrystalline sample of **1** was immersed in a saturated NH_4Cl solution and stirred at 30 °C for 70 min under ultrasonic conditions (59 kHz). The mixture was then separated by filtration and was air-dried for PXRD data collection. The experimental results are presented in Figure 7. As shown in Figure 7, exchanged solid of **1** has a completely different PXRD pattern (Figure 7, green) far away the original crystals (Figure 7, blue) almost consistent with the calculated pattern for removal guest $[Ph_3PCH_2Ph]^+$ (Figure 7, pink), showing that all of the $[Ph_3PCH_2Ph]^+$ cations are displaced by the NH_4^+ cations. In addition, exchanged by other inorganic cation species are also found (Figure S3, Supporting Information). These confirm the assumption that the interlayer $[Ph_3PCH_2Ph]^+$ cation in **1** is exchangeable. In particular, the cation-exchange activity for **1** is important that means this solid material will be an attractive candidate for use as catalysts, templates in the

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(22) Bell, R. E.; Herfert, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 3351.

(23) Al-Alamy, F. A. S.; Balchin, A. A.;White, M. *J. Mater. Sci*. **1977**, **12**, 2037.

(24) (a) Batten, S. R.; Jensen, P.; Kepert, C. J.; Kurmoo, M.; Moubaraki, B.; Murray, K. S.; Price, D. J. *J. Chem. Soc. Dalton Trans*. **1999**, 2987. (b) Manson, J. L.; Arif, A. M.; Miller, J. S. *J. Mater Chem*. **1999**, *9*, 979.

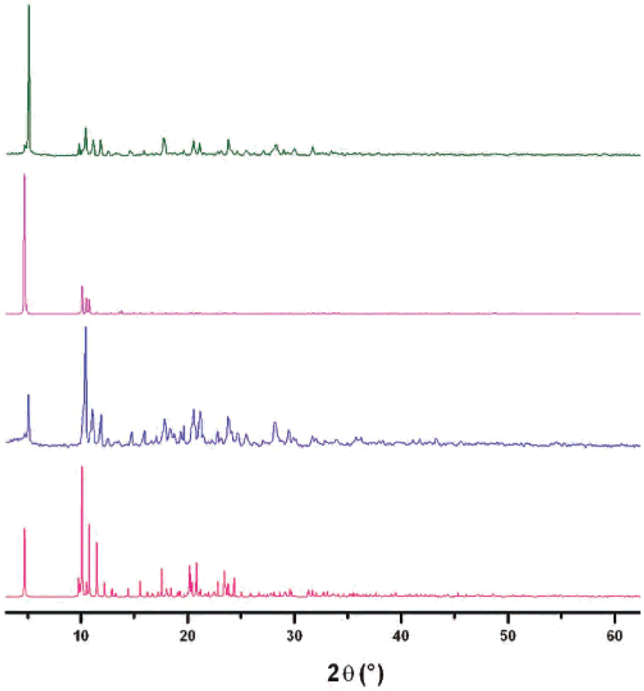

Figure 7. X-ray diffraction patterns of **1** for polycrystalline sample collected after NH_4^+ ionic exchange (green), the simulation (pink) based on the single-crystal structure of **1** after removal of guest $[Ph_3PCH_2Ph]^+$ cation, as-synthesized polycrystalline sample (blue), and calculated from single-crystal data (red).

synthesis, a host matrix of composites, or ion storage because the positively charged molecules can be easy and convenient introduced or intercalated into its interlayer galleries.

Figure S4 (Supporting Information) gives the emission spectra of **1** and **2** in the solid state at ambient temperature. The intense fluorescent emissions occurred in the same range for two different metal centers at 410 nm ($\lambda_{exc} = 355$ nm) for **1** and 398 nm ($\lambda_{exc} = 300$ nm) for **2** are observed, which can be assigned to the ligand-to-metal charge transfer (LMCT) bands. Also, **1** exhibits a quenching of the fluorescence with $\tau = 1.34$ ns (Figure S5). These fluorescent behaviors associated with the similar thermal stabilities for **1** and **2** can be imputed to both compounds having closely trinuclear clusters that metal centers with similar coordinated environments. Similar cases have been also observed in the polymers $\{[Cd(pydc)(bpp)]{\cdot}0.5\ H_2O\}_n$ and $\{[M(pydc)(H_2O)(bpe)_{0.5}]{\cdot}0.5H_2O\}_n$ (M = Co, Mn; pydc = 3,4-pyridinedicarboxylate; bpp = 1,3-bis(4-pyridyl)propane; bpe = 1,2-bis(4-pyridyl) ethane).[8i] In additional, due to difference of d-electronic transitions between two different metal centers, easier for the d^8 Ni^{2+} ion than for the d^{10} Zn^{2+} ion, a weak emission peak at 485 nm for **2**, assigned to MLCT, has been also observed.

Conclusion

In summary, two supramolecular coordination polymers, exhibiting novel claylike architectures, have been synthesized and characterized. This work demonstrates that 2D networks with high-linked nodes are not just limited to coordination polymers of the flexible ligand species. The rigid linear and even trigonal tectonic multifunctional ligands also can be used to construct 2D 6-linked polymeric networks of d-block transition metals. The linear metal trinuclear clusters clearly play an important role in generation either compound **1** or **2**, for them not only to serve as a common 6-linked node but also to provide partial flexility for dissolving the rigorous demands of connection of rigid linear or trigonal ligands and therefore reinforce the framework stabilities.[1h] The ionic exchange activity, fluorescence character, thermal stability, and insolubility in common polar and nonpolar solvents of these kinds of compounds may be useful in application as potential catalysts, ion storage, or photoactive materials.

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Supporting Information Available: X-ray crystallographic files in CIF format, additional crystallographic information for **1**, **2**, and **2a**, IR spectra, TGA traces, and emission spectra for both **1** and **2**, and powder patterns that illustrate the ionic exchange activity of **1**, and fluorescent quenching plot of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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