

Metal Phosphite Containing 24-Ring Channels with 10-Ring Windows

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The area of extra-large pore crystalline materials with more than 12 oxygen atoms spanning the circumference of a pore has been opened up with the preparation of aluminum phosphate VPI-5 in 1988.¹ A lot of these materials have been synthesized hydrothermally since then, accompanied by many efforts to understand the synthesis, energetics, and topology of extra-large-pore frameworks.^{2–4} The composition of these materials extends over silicates, phosphates, and germanium dioxide and has resulted in porous materials possessing unusual properties. Their applications have been broadened from traditional uses as catalysts and adsorbents to the new area, such as microelectronics, photoluminant phosphor, medical diagnosis, and so forth.⁵ It is remarkable that apart from a few silicate (e.g., UTD-1, CIT-5, ECR-34, SSZ-53, ITQ-33) and germanium dioxide (FDU-4, ASU-16) frameworks, most of the extra-large pore crystalline materials, especially 24-ring-containing structures, are composed of metal phosphate and usually have one-dimensional channel systems.⁶ Recently, a new change in the synthesis of phosphorus-based microporous materials focuses on the incorporating of pseudo-pyramidal hydrogen phosphite group HPO_3^{2-} in place of tetrahedral phosphate group PO_4^{3-} as the basic building units (BBU).^{7–9} Some metal phosphites with large or extra-large pores have been obtained.¹⁰ The present paper reports a novel porous crystalline $\text{Zn}_2\text{Al}_{0.57}\text{Cr}_{0.10}(\text{HPO}_3)_4[\text{C}_6\text{H}_{11}\text{NH}_3]_2(\text{H}_2\text{O})_4$ metal phosphite (denoted as Cr-NKU-24), which containing 24-ring channels formed from the coiling of a net with 10-ring windows.

Cr-NKU-24 was synthesized hydrothermally from a mixture of ZnO, CrCl_3 , pseudoboehmite, H_3PO_3 , H_2O , and cyclohexylamine (CHA) with a typical molar ratio being 0.4:0.4:0.8:1.5:1.0:100 ZnO/ CrCl_3 / Al_2O_3 / P_2O_3 /CHA/ H_2O . It can be obtained in a wide range of composition with ZnO from 0.25 to 0.50, P_2O_3 from 1.5 to 2.5, CHA from 0.30 to 1.20, and H_2O from 50 to 100. NKU-24 can be synthesized without the presence of CrCl_3 , and it is isostructural to Cr-NKU-24. Single crystal analysis revealed that the framework of Cr-NKU-24 consists of $\text{Zn}_2\text{Al}_{0.57}\text{Cr}_{0.10}(\text{HPO}_3)_4^-$ with $\text{C}_6\text{H}_{11}\text{NH}_3^+$ as the charge compensator. It crystallizes in the hexagonal,¹¹ space group $P6_3mc$ (No. 186) with $a = 15.269(2)$ Å, $c = 10.3336(3)$ Å, $V = 2086.91(80)$ Å³, $T = 293(2)$ K, $Z = 3$,

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(11) Crystal data for Cr-NKU-24: $\text{C}_6\text{H}_{40}\text{Al}_{0.57}\text{Cr}_{0.10}\text{NO}_{16}\text{P}_4\text{Zn}_2$, $M_r = 743.57$, hexagonal, space group $P6_3mc$ (No. 186), $a = 15.269(2)$ Å, $b = 15.269(2)$ Å, $c = 10.3336(3)$ Å, $\gamma = 120^\circ$, $V = 2086.8(8)$ Å³, $T = 293(2)$ K, $Z = 3$, $\mu = 2.080$ mm⁻¹, $\rho_{\text{calcd}} = 1.775$ g cm⁻³, a total of 10 509 reflections were measured, 1374 unique reflections ($R_{\text{int}} = 0.0409$). The final $wR(F^2_{\text{all data}})$ was 0.151, and $R(F_{\text{all data}})$ was 0.0565. Mo K α radiation, $\lambda = 0.71073$ Å, $1.54 \leq \theta \leq 26.37^\circ$. CCDC number 619171.

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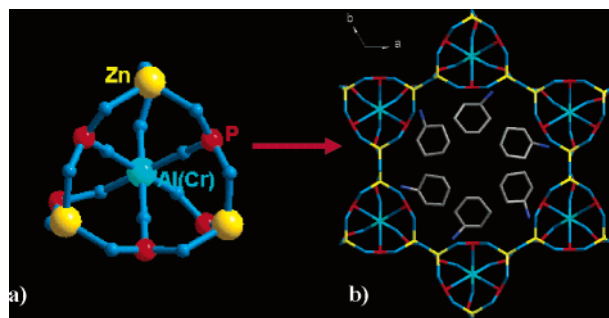


Figure 1. Building unit and 24-ring of Cr-NKU-24. (a) Building unit (color code: yellow, Zn; cyan, Al(Cr); red, P; blue, O; H atoms were omitted for clarity); (b) 24-ring constructed by six building units with CHA cations in the pore.

$\mu = 2.080 \text{ mm}^{-1}$, and $\rho_{\text{calcd}} = 1.775 \text{ g cm}^{-3}$. The occupancy value of Cr was determined from the fragment of thermal ellipsoid and its oxidation state along with the inductively coupled plasma (ICP) result (Supporting Information). The building unit of Cr-NKU-24 (Figure 1a) is built up of ZnO_4 tetrahedra, HPO_3^{2-} pseudo-pyramids, and $\text{Al}(\text{Cr})\text{O}_6$ octahedra with Al atoms partly substituted by Cr atoms. The presence of octahedral Cr^{3+} has been verified by the two typical bands at 444 and 630 nm in the diffuse reflectance UV–vis spectrum of Cr-NKU-24¹⁶ (Figure S5, Supporting Information). It contains one crystallographically Al(Cr) atom, one Zn atom, and two crystallographically distinct P atoms. In ZnO_4 tetrahedra, the bond lengths of Zn–O are in the range of 1.915(1)–1.955(1) Å. The P atom in the HPO_3^{2-} pseudo-pyramid shares three linkages to form P–O bonds with the bond lengths in the range of 1.476(1)–1.516(1) Å and leaves a terminal P–H bond. The existence of P–H bonds can also be confirmed by the characteristic band of phosphite anion in the IR spectrum [$\nu(\text{H–P}) = 2383 \text{ cm}^{-1}$,^{9b,c,10a} Figure S3, Supporting Information]. Three ZnO_4 tetrahedra and three HPO_3^{2-} pseudo-pyramids connect alternately forming the 6-ring of the building unit of Cr-NKU-24 (Figure 1a). The $\text{Al}(\text{Cr})\text{O}_6$ octahedron is located on the center of the 6-ring, with the Al(Cr)–O bond length ranging from 1.866(1) to 1.896(1) Å. Each $\text{Al}(\text{Cr})\text{O}_6$ octahedron links with three P and three Zn atoms in the 6-ring through Al(Cr)–O–P and Al(Cr)–O–P–O–Zn, respectively.

On the vertical plane of the *c*-axis, the building units link with each other through the free bonds of HPO_3^{2-} under the 6-ring and three ZnO_4 on the 6-ring of the unit with the strict alternation of ZnO_4 and HPO_3^{2-} . The 24-ring (Figure 1b, Figure 2) is constructed by the linkage of six building units and contains 12 ZnO_4 tetrahedra and 12 HPO_3^{2-} groups. On the other hand, two building units stack along the direction of *c*-axis through three P–O–Zn–O–P–O–Zn linkages to form a cluster structure of metal phosphite with three 10-ring windows (Figure 3b). A bunch of the clusters is formed in succession when the stacking continues extending along the *c*-axis direction. The main extra large channels of Cr-NKU-24 (Figure 2) can be depicted as the combination of six bunches of the clusters (Figure 3c). The wall of each 24-ring channel can be described as the coiling of a net composed of 10-rings (Figure 3a), which is just the 10-ring

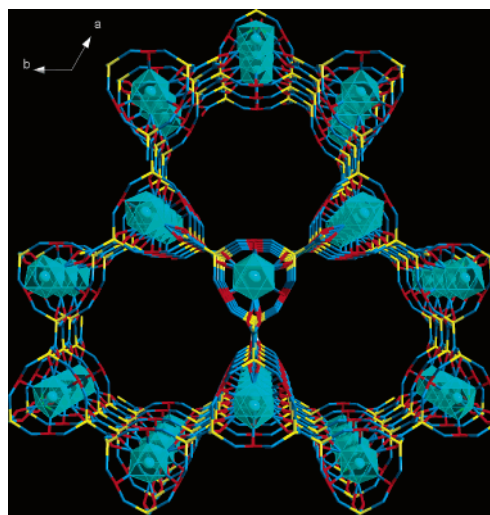


Figure 2. Relationship of the adjacent 24-ring channels in the structure of Cr-NKU-24. The organics present in the channel are omitted for clarity.

windows of the building clusters described above. As each bunch of the clusters is connected to the adjacent three 24-ring channels (Figure 3d), 10-ring window systems are formed among the adjacent 24-ring channels, which suitable size of molecules can go through (Figure 6S, Supporting Information).

The approximate diameters of the widest and narrowest cross sections are 16.26 Å and 13.44 Å, respectively, which is slightly larger than those of the 24-ring channels in FDU-46a (12.65 Å) and $\text{ZnHPO}_4\text{-CJ1}^{10a}$ (diameter 11 Å). The framework density of Cr-NKU-24 is 9.6 polyhedra per 1000 Å³. Compared with the values of ND-1 (12.1),^{6b} Cloverite (11.1),^{3b} NDHU-1 (10.1),^{6c} FDU-4 (11.1),^{6a} JDF-20 (11.2),^{3a} ASFe-1 (10.5),¹² $\text{N}(\text{CH}_3)_4\text{ZnH}_3(\text{PO}_4)_2$ (10.1),¹³ and $[\text{HN}(\text{CH}_2\text{-CH}_2)_3\text{NH}]\text{K}_{1.35}[\text{V}_5\text{O}_9(\text{PO}_4)_2] \cdot x\text{H}_2\text{O}$ (9.3),¹⁴ it is one of the lowest framework densities known for open-framework materials. There are six $\text{C}_6\text{H}_{11}\text{NH}_3^+$ cations residing in each 24-ring window. The alkyl groups of these cations extend into the hollow space of the 24-ring channel and their NH_3^+ groups to compensate the negative framework as well as to form H-bonds with the framework oxygen atoms (Figure 1b). The center space of the channels between the organic cations is empty, as in ND-1, with a distance of about 3.4 Å between the end carbon atoms of two CHA cations across the channels.

Cr-NKU-24 emits blue luminescence centered at 442 nm as excited by 252 nm wavelength. The emission and excitation spectra are shown in Figure 4. No emission from CHA was observed under 252 nm. The band intensity of Cr-NKU-24 is much stronger than that of NKU-24, for Cr is a well-known luminescence activator element.^{5c}

In summary, Cr-NKU-24 has a novel topological structure, which adds a new variety to the structure of extra large pore microporous materials. This work further suggests that the replacement of tetrahedral phosphate groups PO_4^{3-} by pyramidal phosphite units HPO_3^{2-} can reduce the M–O–P connectivity^{10a} and generate more-open interrupted framework structures to form extra-large microporous materials.

The experimental details are as follows. Cr-NKU-24 was synthesized hydrothermally from a mixture of ZnO, CrCl_3 ,

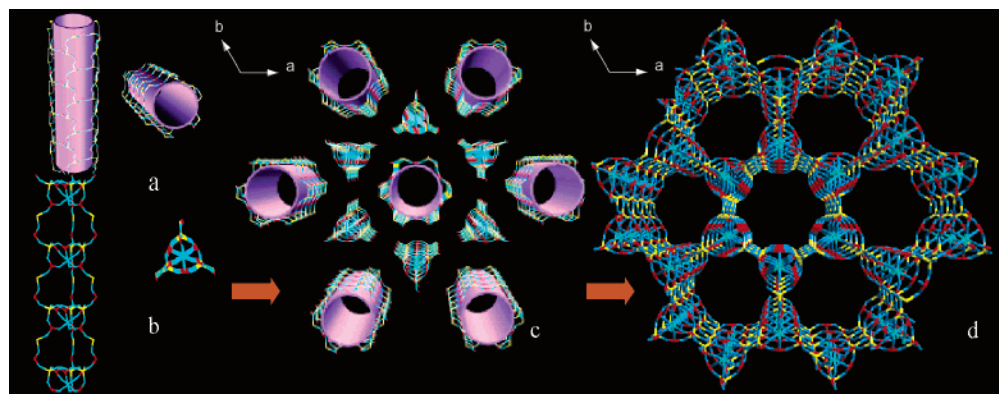


Figure 3. (a) Perspective view of a single 24-ring channel from different directions; the wall of 24-ring channel consists of 10-ring windows. (b) Perspective view of a bunch of building units from different directions, which exhibit a cluster structure. (c) Each channel is surrounded by six adjacent 24-ring channels. 24-Ring channels are linked each other through a bunch of cluster building units. (d) Three-dimensional open-framework structure of Cr-NKU-24 viewed along *c*-axis (color code: yellow, Zn; cyan, Al(Cr); red, P; blue, O; purple tube, 24-ring channel). Water and organic molecules are omitted.

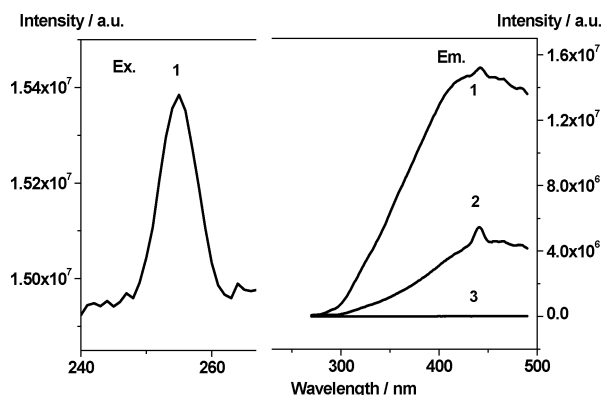


Figure 4. Excitation and emission spectra of (1) Cr-NKU-24 and (2) NKU-24 without Cr; (3) organic template CHA.

pseudoboehmite (water loss at 600 °C: 31.5 wt %), H_3PO_3 , H_2O , and CHA with a typical molar ratio of 0.4:0.4:0.8:1.5:1.0:100 $\text{ZnO/CrCl}_3/\text{Al}_2\text{O}_3/\text{P}_2\text{O}_3/\text{CHA/H}_2\text{O}$. The mixture was heated at 140 °C in Teflon lined stainless steel autoclaves for 55 h. After cooling, green prism-like crystals were filtered off from the mother liquor, then washed with distilled water and dried at room temperature.

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2500 X-ray diffractometer (Cu $\text{K}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$, $T = 25 \pm 2 \text{ }^\circ\text{C}$). The experimental X-ray powder diffraction patterns are in excellent agreement with the simulated ones on the basis of the single-crystal parameters, indicating phase purities and high degree of crystallinity (Figure S1, Supporting Information). Thermal analysis was performed on Netzsch STA 409 PC thermal analyzer at a heating rate of 10 °C/min in air. Element analysis was performed on an Elementar Varioel element analyzer. Its results showed Cr-NKU-24 with C, 18.84%; H, 4.97%; and N, 3.89%, which are in agreement with the calculated values: C, 19.37%; H, 5.38%; and N, 3.77%. ICP analysis was carried on T.T.A. ICP9000 (N+M) to confirm the metal ion and phosphorus contents. UV–

visible and solid-state photoluminescence (PL) studies were performed on powder samples at room temperature. The UV–vis spectra were measured on a JASCO V-570 spectrophotometer equipped with an integrating sphere attachment. PL spectra were measured on a Jobin Yvon Fluoro-Max-P spectro-fluorometer equipped with a Xe lamp (150 W) as the excitation light source.

The structure of Cr-NKU-24 was determined by single-crystal XRD using the Bruker 1000 SMART system. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXT-97.¹⁵ The positional parameters for Al, P, and O atoms were located by direct methods. The remaining non-hydrogen atoms were routinely located from Fourier difference maps during the course of the refinement. The C and N atoms in highly disordered CHA cations were positioned geometrically [$d(\text{N1}-\text{C4}) = 1.45 \text{ \AA}$; $d(\text{C}-\text{C}) = 1.52 \text{ \AA}$]. The P(2) atom was disordered over two positions with an equal occupancy to the P(2)'. All non-hydrogen atoms of the inorganic framework were refined anisotropically. The C and N positions in CHA cations are partially occupied. Their occupancy factors were refined from the fragment of thermal ellipsoid and to match that of thermal analysis and element analysis.

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Supporting Information Available: CIF file and ICP analysis details, crystal data and selected bond distances and angles for Cr-NKU-24, XRD patterns, perspective view of a single 24-ring viewed along the *b*-axis direction, Fourier transform infrared spectra, thermogravimetric curve, solid-state UV–vis spectra, and graphic showing 10-ring windows of Cr-NKU-24 along three directions (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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