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COMMUNICATION

Nitrogen-containing porous cerium trimetaphosphimate as a new efficient base catalyst†

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A new layer nitrogen-containing porous cerium trimetaphosphimate with pendant NH groups projecting into the channels has been synthesized and characterized. Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate is carried out with this complex as support in ethanol at 333 K. Experimental results indicate that it is an efficient base catalyst. The NH groups are incorporated into the host framework and provide the base sites for catalysis. This stable solid base catalyst can be reused without obvious loss of its activity for three cycles.

Crystalline metal silicates and phosphates have been widely use in the acid catalytic processes.[1] Their acid character comes from the metal centers and oxygens incorporate into the open frameworks. Recently, the industrial requirement of base solid catalyst has initiated research for zeolite and zeolite-like complexes with basic properties.[2] By comparison with liquid bases, basic zeolites and zeotypes show high efficiency for basic catalysis reactions and they simplify the separation process for organic preparations. In the past decades, various strategies have been developed for the exploration of new families of basic porous materials. Alkaline exchange is a common way to modify zeolite materials. However, their sensitivity to air or moisture for embedded alkaline complexes limits the routes for further applications.[3] Recently, a useful approach to prepare basic porous materials, decoration of the open framework with NH groups, has been reported.[4] According to the basis of the isoelectronic principle, the replacement of oxygen atoms by isoelectronic NH groups will not alter the charge of the fundamental building unit.[5] This introduction provides the basicity of the nitrogen sites in the open-framework materials. Extensive framework nitridation reactions have been carried out for silica and metal phosphates.[6] The treatments involve heating of zeolite analogues in a stream of ammonia gas at high temperature or doping NH species to reactive frameworks under mild reactions.[7] In many cases, this approach can easily induce structural collapse during the nitridation process at high temperature.[8] Hence, there is a great need for research and development of alternative NH doping techniques. As hundreds of metal phosphates have been prepared by the principle of crystal engineering,[1b] it is possible to build nitridate metal phosphates in a chimie douce approach. Until now, no structurally characterized nitridate zeolite or zeolite-like complexes have been reported. The position and ratio of NH groups in the open frameworks remain unknown. These factors prohibit further investigation of structural design and reaction mechanism for these species. Herein we report the first synthesis and structural characterization of nitrogen-containing cerium trimetaphosphimate $Ce(PO_2NH)_3 \cdot 5H_2O$ **1**, and its catalytic behavior in a Knoevenagel condensation reaction. In the structure of **1**, NH groups are embedded into the cavities and provide base sites for catalysis. The complex is reusable, and retains its activity and framework stability for the next catalytic cycles.

With the addition of $Na_3(PO_2NH)_3$ to a solution of $Ce(NO_3)_3 \cdot 6H_2O$ in a molar ratio of 1 : 2 under mild hydrothermal conditions, colorless crystals of a new nitrogen-containing cerium phosphate $Ce(PO_2NH)_3 \cdot 5H_2O$ **1** were obtained.[9] Single crystal data reveal that it has a layer structural motif.[10] Each cerium atom is surrounded by eight oxygen atoms with a distorted bicapped trigonal

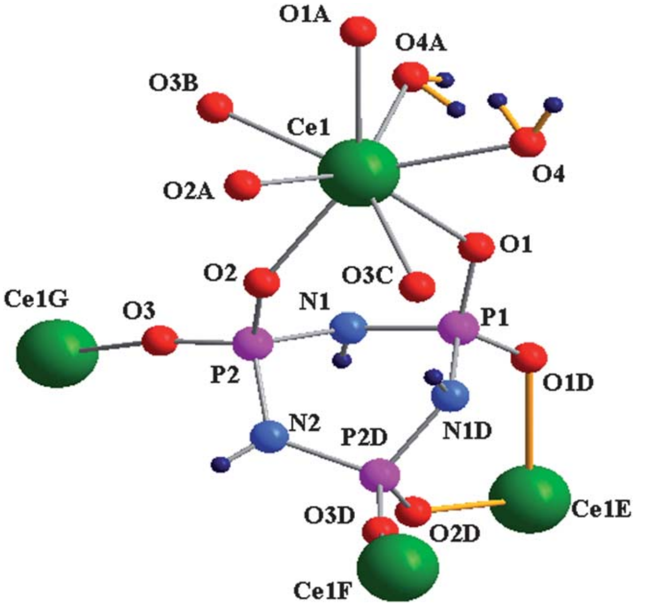

Fig. 1 The asymmetric unit of compound **1**, showing the atom-labeling scheme.

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prismatic coordination environment (Fig. 1). The Ce–O connections range from 2.418(3) Å to 2.571(3) Å, involving two coordination water molecules and six bidentate PO_2 groups of the trimetaphosphimate anions. The O–Ce–O bond angles vary from 70.58(10) to 81.79(19)°. These structural parameters are typical for eight-coordinate cerium in phosphate compounds.[11] The rings of the $(PO_2NH)_3^{3-}$ ligand exhibit a twist-boat conformation. All the bridging PON ligands engage in Ce–O linkages with vertex-sharing modes (P–O–Ce bond angle = 126.06(12)–155.49(19)°) (Fig. 2). The P–O bond distances range from 1.487(3) Å to 1.504(3) Å and the P–N distances fall between 1.662(3) to 1.681(3) Å. These geometrical parameters are in agreement with previous reports for related metal phosphates and metal phosphimates.[12] The connections between the CeO_8 bicapped trigonal prismatic polyhedra and P_2N_2 tetrahedra in the $(PO_2NH)_3^{3-}$ ligands result in a two-dimensional structural motif with three-membered and five-membered rings as subunits. The layer of the novel nitrogen-containing cerium trimetaphosphimate displays undulated micro-cavities due to the boat conformation of the bridging $(PO_2NH)_3^{3-}$ ligands. The pendant NH groups attach at the frame and point to the center of the cavities, providing base sites for the microporous material. Guest water molecules are located in the space between the layers and they form hydrogen bonds with the oxygen atoms of the host framework (O5···O4 = 2.76 Å, O6···O2 = 2.92 Å). BET measurements were determined by N_2 adsorption on a Micromeritics porosimeter. The sample was degassed at 100 °C for 12 h to remove the lattice water molecules. The results (average pore diameter: 0.57 nm, pore volume 0.1097 $cm^3\ g^{-1}$, surface area 291.43 $m^2\ g^{-1}$) indicate that it is a microporous phosphate material.

Thermogravimetric analysis (TGA) was performed on a polycrystalline sample of **1** (4.54 mg) from 25 °C to 800 °C. The diagram (Fig. 3) shows an obvious weight loss of 11.50% (50 °C–100 °C), corresponding to loss of three lattice water molecules per formula unit (anal. calcd 11.64%). Weight loss of 7.51% starts at 110–280 °C, attributed to loss of two coordinated molecules per formula unit (anal. calcd 7.75%). The XRD pattern shows no phase transition with the removal of lattice water molecules. After heating to 280 °C for 60 min, the XRD pattern indicates that the network collapses with the loss of coordinating water molecules and the sample begin to lose its crystallinity.

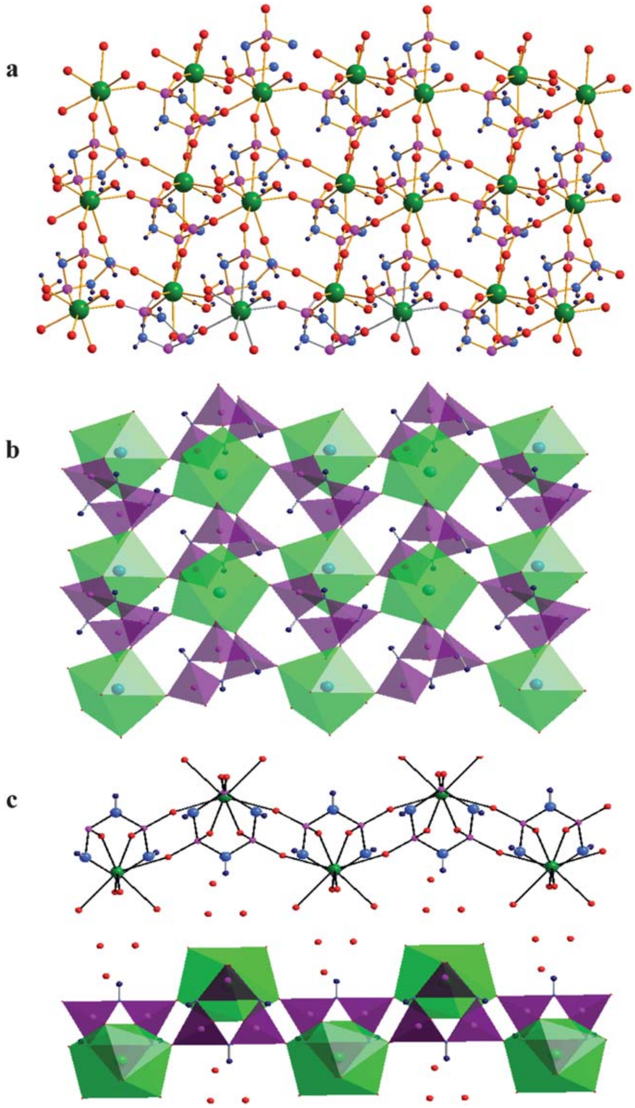


Fig. 2 (a) Layer structure of compound **1**. (b) Polyhedral view of the layer. (c) Packing diagram viewed along the [100] direction.

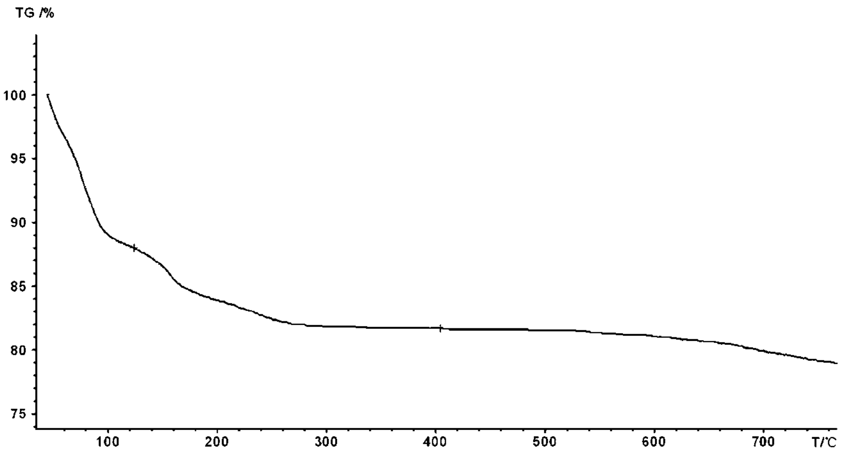
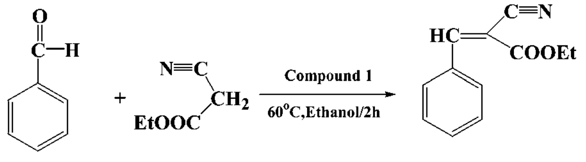


Fig. 3 The TGA diagram for compound **1**.



Scheme 1 Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate with compound **1** as catalytic support.

The basic catalysis performance of compound **1** was tested with the Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate in ethanol at 333 K (Scheme 1). In a batch experiment, Ce $(PO_2NH)_3\cdot 5H_2O$ was added to a solution of 20 mmol benzaldehyde and 20 mmol ethyl cyanoacetate in 5 ml of ethanol. The mixture was then stirred vigorously at 333 K for two hours. The solid material is a heterogeneous catalyst for this reaction. At the end of the reaction, it was removed by filtration, and solvent ethanol was taken away by vacuum distillation. Since the external and cavity active surface areas are important for the catalyst, there are two factors affecting the performance, as follows. a) The guest water molecules. From the single crystal data, it can be viewed that the lattice water molecules form hydrogen bonds with the framework. Their removal helps to release the base sites for the reaction. b) The amount of catalyst. The conversion of condensation product increases with increasing catalyst amount. The total surface area of the catalyst is increased and also more catalytic active sites are available. Fig. 4b shows that 0.75 mmol catalyst (pretreated for 2 h at 100 °C) gives yields of the condensation product up to 95%. The condensation product was analyzed by a GC-MS-QP2010 system equipped with a Zebron ZB-5ms capillary GC column (0.25 mm × 30 m; Phenomenex, Torrance, CA, USA) (gas chromatograph coupled to a mass spectrometer; carrier gas = helium; flow, 1 ml min^{-1}; oven, 40–400 °C; injector, 150 °C; detector, 250 °C). MS, FT-IR, ^1H NMR spectra and melting point of the condensation product indicate that it is ethyl (*E*)-α-cyanocinnamate. The peak at 2264 cm^{-1} is attributed to the $\nu(C{\equiv}N)$ stretch, while the peaks at 1747 cm^{-1} and 1601 cm^{-1} are assigned to the $\nu(C{=}O)$ and $\nu(C{=}C)$ stretch vibrations respectively. The data represent the characteristic bands of cyanocinnamate. The ^1H NMR ($CDCl_3$) spectrum was recorded on a Brucker Ultrashield 400 Plus (Fig. 4d): 1.306 (t, $J = 7.2$ Hz, 3H, ethyl), 4.301 (q, $J = 7.2$ Hz, 2H, ethyl), 7.275–7.4849 (m, 3H, *m*- and *p*-aromatic protons), 7.886–7.904 (m, 2H, *o*-aromatic protons), 8.157 (s, 1H, alkene proton). The product shows a melting point of 51 °C. These properties are comparable to the previously report for the (*E*) type of ethyl cyanocinnamate.[13] The base catalytic activity is related to the crystallinity of the solid during the reaction. The crystalline solid shows clearly higher activity than the amorphous solid (about 30%). With malononitrile as an active methylene compound, the condensation reaction shows a higher conversion

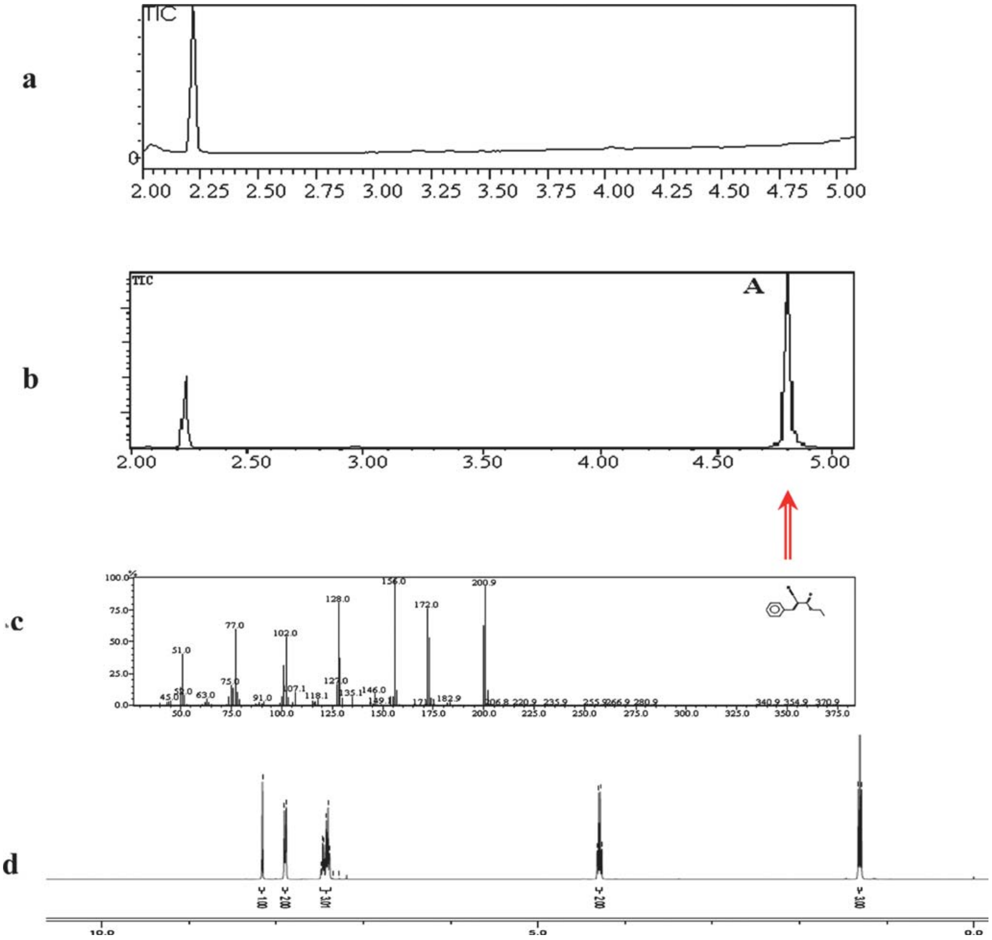


Fig. 4 GC-MS and ^{1}HNMR spectra of the condensation product: (a) blank (without catalyst); (b) with 0.75 mmol compound **1** (pretreated at 100 °C) as solid catalyst, catalytic yield 95%; (c) MS spectrum; (d) ^1H NMR spectrum.

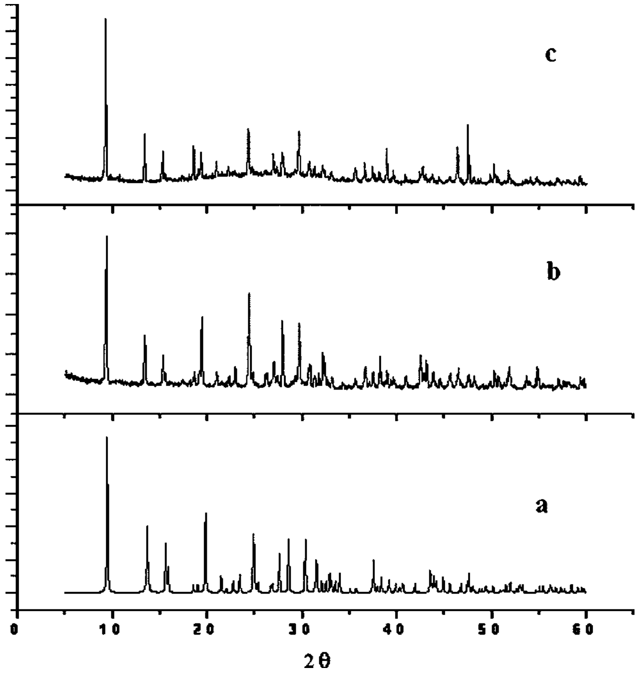


Fig. 5 PXRD patterns for compound **1**: (a) simulated from the single-crystal data; (b) sample before catalytic process; (c) sample after catalytic process.

than that of ethyl cyanoacetate. This indicates the existence of shape and size selectivity for the catalysis. The solid also show catalytic activity for other basic catalytic reactions, such as the trans-esterification reaction of ethyl acetate with methanol.

X-ray powder diffraction patterns for the thermal stability studies of **1** show phase purity of the bulk samples by comparison of the observed and simulated patterns (Fig. 5). Before and after the base catalytic process, no phase transition is observed for the XRD pattern indicating the stability of the $\mathrm{Ce(PO_2NH)_3 \cdot 5H_2O}$ framework structure. After washing with with $\mathrm{CH_2Cl_2}$, the base catalyst is reused without loss of its catalytic activity for the second and third runs.

In summary, the first rare-earth nitrogen-containing metal phosphate has been synthesized and characterized, demonstrating a new method to get nitrogen-containing crystalline zeolite-like microporous materials. With trimetaphosphimate as bridging ligand, the NH groups are introduced into the open framework and provide the basic sites for the catalyst. It shows activity for the Knoevenagel condensation reaction and retains the framework stability and activity for subsequent catalytic recycles. By analogy with the progress that has been made by rare-earth forms of metal phosphates, such as functional materials in catalysis, photonic device and trapping of radioactive elements,[14] it can be expected that this kind of open framework may find special applications in base-catalyzed reactions.

Acknowledgements

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9 A solution of $\mathrm{Na_3(PO_2NH)_3}$ (0.25mmol, 0.08g) was added dropwise to a solution of $\mathrm{Ce(NO_3)_3 \cdot 6H_2O}$ (0.5 mmol, 0.21 g) in 10 mL $\mathrm{H_2O}$ and stirred for 10 min at 25 °C. The solution was transferred to a 23 mL Teflon-lined steel autoclave and heated at 80 °C for 36 h. Colorless crystals of **1** were obtained with 56% yield. Anal. Found (calcd) for $\mathrm{H_{13}N_3O_{11}P_3Ce}$: H, 2.73(2.80); N, 9.17(9.05%).
10 Crystal data for **1**: $\mathrm{CeH_{13}N_3O_{11}P_3}$, M = 464.16, orthorhombic, $P2_12_12$, a = 7.3040(15) Å, b = 9.1675(18) Å; c = 9.5663(19) Å, V = 640.6(2) Å^3, Z = 2, μ(Mo-Kα) = 3.982 mm^{-1}, $\theta_{\max}$ = 24.95°, 4785 reflections measured, 1081 unique (R_{int} = 0.0412) and used to refine 110 parameters. $R1(2\sigma)$ = 0.0191.† CCDC reference number 794008.
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