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$[C_6N_4H_{24}]CoBe_6P_6O_{24}\cdot 3H_2O$: a novel 3-dimensional beryllophosphate zeolite-like structure encapsulating Co^{II} ions

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A novel cobalt beryllophosphate (CBP-CHA) with the chabazite framework topology has been hydrothermally synthesized by using a metal amine complex as a starting material. The structure was solved by single-crystal X-ray diffraction {crystal data for $[C_6N_4H_{24}]CoBe_6P_6O_{24}\cdot 3H_2O$: $M = 889.14$, rhombohedral, space group $R\bar{3}$, $a = 12.380(3)$, $b = 12.380(3)$, $c = 14.558(5)$ Å, $V = 1932.5(10)$ Å^3, $Z = 3$, $R_1 = 0.0878$, $R_w = 0.1929$}. The compound is unusual in that it is not only the first organically-templated $CoBePO_4$ phase, but it is also the first instance where Co^{II} ions are trapped in the double 6-ring (D6R) of the structure of CBP-CHA. A cobalt atom locates at the 3-fold axis in each D6R, chemically bonding to framework oxygen atoms and leading to contraction of the D6R. CBP-CHA has 3-dimensional 8-ring channels along the crystallographic [100] and [010] directions. The framework charges of CBP-CHA are balanced by both the protonated amines in the channel and Co^{II} ions trapped in the D6R.

1 Introduction

Microporous materials based on aluminosilicate have been applied as catalysts, sorbents and ion exchangers.[1] In the last few years, the interest in microporous and zeolite-analogous systems has focused primarily on aluminum phosphates[2] and substituted variants,[3–4] as well as on $GaPO_4$,[5–7] $ZnPO_4$,[8–11] $CoPO_4$[12–15] and $GaZnPO_4$.[16–17] In contrast, very little work has been carried out on beryllophosphates, perhaps in part due to the high toxicity of beryllium. From a structural point of view, beryllium is an ideal building block for zeolite structures because it is always tetrahedrally coordinated to oxygen atoms.[18]

Although a number of zeolite-analogue beryllophosphates have been reported, including ABW, ANA, CAN, EDI, FAU, LOS, RHO, BPH and SOD,[3,19] most of the materials were synthesized with alkali cations. Because negatively charged frameworks produced from divalent Be^{2+} need to balance with the cations, it is difficult to obtain pure beryllophosphate phases. By using the concentrated amine templating method, we have succeeded in preparing large pore (12-rings), organically-templated beryllophosphate molecular sieves with gmelinite topology.[18] Very recently, a 3-dimensional framework beryllophosphate containing 10- and 12-rings was prepared by using 1,3-diaminopropane cations as the template.[20]

Open-framework materials containing transition metals are of additional interest because of the possibility of their having useful magnetic and optical properties.[21–27] Magnetic channel structures could have many useful applications, including the separation of oxygen and nitrogen from air. $Mn_3(H_2O)$-$Ga(PO_4)_6$ is an example of magnetic gallophosphate encapsulating the trinuclear $Mn_3(H_2O)O_8$ cluster.[28] A cobalt(II) phosphate possessing a 12-membered magnetic channel has also been reported.[29]

In this paper, we describe the hydrothermal synthesis of a novel hydrated zeolite-like cobalt beryllophosphate (CBP-CHA), which is isotypic to the mineral chabazite and has a flexible framework. Co^{II} ions are encapsulated in the D6R units of the framework and play a structural role in stabilizing the units.

2 Experimental

2.1 Synthesis

CBP-CHA was synthesized hydrothermally under autogenous pressure. In a typical reaction mixture of the correct composition for the preparation of CBP-CHA, 0.75 g $CoCl_2\cdot 6H_2O$, 1.0 g 1,3-diaminopropane (1,3-DAP) and 10 g distilled water were mixed with stirring for 1 h, then 0.54 g $Be(OH)_2$ and 3.6 g 85% H_3PO_4 were added until the pH of the mixture was 2.1. After stirring at room temperature for 2 h, the resulting synthesis gel, of composition $CoCl_2\cdot 6H_2O$: 3 1,3-DAP : 4 BeO : 5 P_2O_5 : 170 H_2O, was heated at 160 °C for 3 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Transparent pink, cube-like crystals were obtained in 53% yield.

2.2 Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku D/Max-IIA diffractometer using Cu-Kα radiation ($\lambda = 1.5415$ Å). Scanning electron micrographs (SEM) were taken on a Hitachi S-520 electron microscope operating at 20 kV. The elemental analysis was performed on a Perkin-Elmer 2400 elemental analyzer. IR spectra (KBr pellets) were recorded on a Nicolet 360 FTIR spectrometer and thermogravimetric analysis/differential thermal analysis (TGA/DTA) was performed on a Perkin-Elmer TAC 7/DX analyzer in air with a heating rate of 10 °C min^{-1}, from 25 to 900 °C.

2.3 Crystal structure determination

A suitable single crystal of CBP-CHA was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Bruker SMART APEX CCD area detector equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. About 1.3 hemispheres of intensity data were collected at room temperature with a scan width of 0.30° in ω and an exposure time of 10 s per frame. Empirical absorption corrections were based on the equivalent reflections. The

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Table 1 Crystal data and structure refinement for CBP-CHA

	CBP-CHA
Formula	$[C_6N_4H_{24}]CoBe_6P_6O_{24}\cdot 3H_2O$
Formula weight	889.14
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	$R\bar{3}$
Unit cell dimensions	$a = 12.380(3)$ Å
	$b = 12.380(3)$ Å
	$c = 14.558(5)$ Å
Volume, Z	1932.5(10) Å^3, 3
Density (calculated)	2.292 Mg m^{-3}
Adsorption coefficient	1.170 mm^{-1}
$F(000)$	1353
Crystal size	0.25 × 0.20 × 0.20 mm
θ range for data collected	2.36–25.00°
Limiting indices	$-14 \leqslant h \leqslant 13$
	$-10 \leqslant k \leqslant 14$
	$-17 \leqslant l \leqslant 15$
Reflections collected	2781
Independent reflections	756 [R(int) = 0.0313]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data with $I > 2\sigma(I)$[a]/parameter	756/75
Goodness-of-fit on F^2	1.472
Final R indices [$I > 2\sigma(I)$][a]	$R1 = 0.0878$
	$wR2 = 0.1929$
R indices (all data)	$R1 = 0.0881$, $wR2 = 0.1931$
Largest diff. peak and hole	0.947 and −0.910e Å^{-3}

[a]Where $wR2 = [\Sigma[w(|F_O|^2 - |F_C|^2)^2]/\Sigma[w(|F_O|^2)^2]]^{1/2}$ and $R1 = \Sigma||F_O| - |F_C||/\Sigma|F_O|$.

structure was solved by direct methods followed by successive difference Fourier syntheses. All calculations were performed using SHELXTL and SHELXTL-97,[30] and final full-matrix refinements were against F^2. The crystallographic data for CBP-CHA are summarized in Table 1, positional coordinates are listed in Table 2, while selected bond distances and angles are given in Table 3.

CCDC reference number 169726. See http://www.rsc.org/suppdata/jm/b1/b106643a/ for crystallographic data in CIF or other electronic format.

3 Results and discussion

3.1 Synthesis and characterization

The reaction of Co^{II} ions with 1,3-DAP at room temperature yields the metal amine complex [Co (1,3-DAP)$_3$]$^{2+}$, used here as a starting material, which may be the key to preparing the CBP-CHA structure. Since the complex itself is unstable under hydrothermal conditions, it can act as an appropriate source of the amine and metal ions by slowly releasing them.[31] A very important factor in the synthesis is the selection of ligand.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 × 10^3) for CBP-CHA

	x	y	z	U(eq)[a]
Co(1)	0	10000	0	12(1)
Be(1)	2348(10)	10069(10)	934(7)	16(2)
P(1)	44(2)	7732(2)	967(2)	15(1)
O(1)	−739(5)	8374(5)	828(4)	15(1)
O(2)	1338(6)	8703(6)	1254(4)	20(2)
O(3)	−496(6)	6768(6)	1686(4)	22(2)
O(4)	61(6)	7136(6)	65(4)	22(2)
N(1)	9300(30)	4700(40)	9990(20)	71(11)
N(2)	7210(40)	4160(40)	10240(20)	63(9)
O(5)	2140(60)	7030(50)	2340(90)	580(100)

[a]U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond lengths [Å] and angles [°] for CBP-CHA[a]

Co(1)–O(1)#1	2.122(5)	O(1)#3–Co(1)–O(1)	90.9(2)
Co(1)–O(1)#2	2.122(5)	O(1)#1–Co(1)–O(1)#4	90.9(2)
Co(1)–O(1)#2	2.122(5)	O(1)#2–Co(1)–O(1)#4	89.1(2)
Co(1)–O(1)	2.122(5)	O(1)#3–Co(1)–O(1)#4	180.000
Co(1)–O(1)#4	2.122(5)	O(1)–Co(1)–O(1)#4	89.1(2)
Co(1)–O(1)#5	2.122(5)	O(1)#1–Co(1)–O(1)#5	90.9(2)
Be(1)–O(3)#6	1.560(11)	O(1)#2–Co(1)–O(1)#5	89.1(2)
Be(1)–O(2)	1.585(11)	O(1)#3–Co(1)–O(1)#5	89.1(2)
Be(1)–O(4)#4	1.624(11)	O(1)–Co(1)–O(1)#5	180.000
Be(1)–O(1)#2	1.660(11)	O(1)#4–Co(1)–O(1)#5	90.9(2)
P(1)–O(3)	1.473(6)	O(3)#6–Be(1)–O(2)	108.0(7)
P(1)–O(2)	1.505(6)	O(3)#6–Be(1)–O(4)#4	107.8(6)
P(1)–O(4)	1.512(6)	O(2)–Be(1)–O(4)#4	112.1(6)
P(1)–O(1)	1.546(5)	O(3)#6–Be(1)–O(1)#2	114.7(6)
O(1)–Be(1)#3	1.660(11)	O(2)–Be(1)–O(1)#2	107.5(6)
O(3)–Be(1)#7	1.560(11)	O(4)#4–Be(1)–O(1)#2	106.9(6)
O(4)–Be(1)#1	1.624(11)	P(1)–O(1)–Be(1)#3	124.1(5)
O(1)#1–Co(1)–O(1)#2	180.000	P(1)–O(1)–Co(1)	118.6(3)
O(1)#1–Co(1)–O(1)#3	89.1(2)	Be(1)#3–O(1)–Co(1)	113.5(4)
O(1)#2–Co(1)–O(1)#3	90.9(2)	P(1)–O(2)–Be(1)	136.5(5)
O(1)#1–Co(1)–O(1)	89.1(2)	P(1)–O(3)–Be(1)#7	175.4(6)
O(1)#2–Co(1)–O(1)	90.9(2)	P(1)–O(4)–Be(1)#1	124.0(5)

[a]Symmetry transformations used to generate equivalent atoms: #1 $y-1,-x+y,-z$;#2 $-y+1,x-y+2,z$; #3 $-x+y-1,-x+1,z$; #4 $x-y+1,x+1,-z$; #5 $-x,-y+2,-z$; #6 $y-1/3,-x+y+1/3,-z+1/3$; #7 $x-y+2/3,x+1/3,-z+1/3$; #8 $-x+2,-y+1,-z+2$; #9 $-y+1,x-y,z$; #10 $-x+y+1,-x+1,z$.

When ethylenediamine (en) is used, giving [Co(en)$_3$]$^{2+}$ as starting material instead of [Co (1,3-DAP)$_3$]$^{2+}$, a different type of beryllophosphate with gismondine topology [named $BePO_4$-GIS, $a = b = 12.7612(11)$ Å, space group $I2_13$][18] is formed; Using NH_4CNS as the ligand, another beryllophosphate with analcime topology [named $BePO_4$-ANA, $a = 12.7612(11)$ Å, space group $I2_13$] is obtained. The nature of the organic amine affects the synthesis products, and the synthesis conditions are summarized in Table 4.

The title compound, as well as $BePO_4$-GIS and $BePO_4$-ANA are synthesized under strongly acidic conditions (pH = 1–2), with a low crystallization temperature (140–160 °C) and a short crystallization period (24–72 h). If the pH is higher than 2 (for example 3.0), no solid product can be obtained. The crystallization temperature and time affect the size of the crystals. The optimum condition are at 145 °C for 48 h, the resulting crystals are single phase, transparent pink, cube-like with dimensions around 300 × 300 × 300 μm (Fig. 1). Fig. 2 shows the experimental X-ray powder diffraction pattern of CBP-CHA, which is in good agreement with the simulated X-ray diffraction pattern, showing a single phase CBP-CHA product. Chemical analysis of CBP-CHA gives C, H, N contents of 8.00, 3.36 and 6.12 wt% (calc. 8.10, 3.38 and 6.30 wt%), respectively, a C : H : N molar ratio of 1 : 5 : 0.67. Energy-dispersive X-ray analysis (EDX) gives the Co : P ratio as 14.51 : 85.49 (calc. 14.29 : 85.71). These results are in agreement with the formula of CBP-CHA found from the single-crystal analysis.

Table 4 Synthesis conditions and the resulting products

Sample	Ligand	pH	Temperature/ °C	Time/ days	Products
A[a]	1,3-DAP	2.1	160	3	CBP-CHA
B[a]	1,3-DAP	1.6	180	4	amorphous CBP-CHA
C[b]	en	2.3	160	3	$BePO_4$-GIS
D[c]	NH_4CNS	1.0	145	5	$BePO_4$-ANA

[a]Gel of composition: $CoCl_2\cdot 6H_2O$: 3 1,3-DAP : 4 BeO : 5 P_2O_5 : 170 H_2O. [b]Gel of composition: $MCl_2\cdot 6H_2O$: 3 en : 4 BeO : 5 P_2O_5 : 178.6 H_2O (M = Ni, Co). [c]Gel of composition: $CoCl_2\cdot 6H_2O$: 4 NH_4CNS : 4 BeO : 5 P_2O_5 : 185 H_2O.

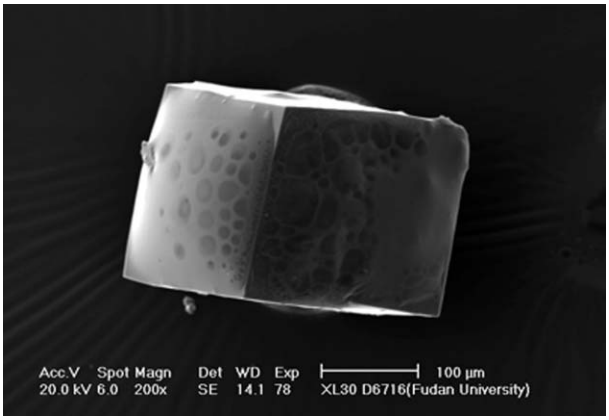

Fig. 1 SEM image showing the morphology and size of a single crystal of as-synthesized CBP-CHA (300 × 300 × 300 μm).

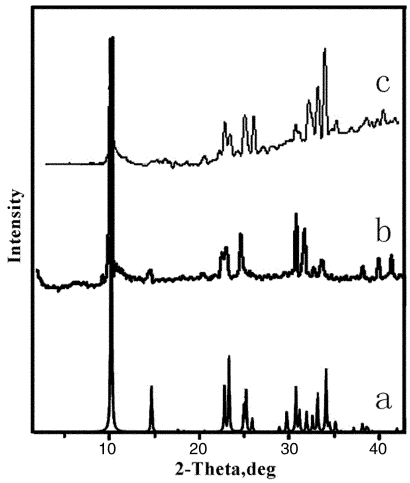

Fig. 2 X-Ray powder diffraction patterns of CBP-CHA: (a) simulated, (b) as-synthesized sample and (c) sample calcined at 400 °C in air for 2 h.

The IR spectrum of CBP-CHA shows broad bands at 992 and 1080 cm^{-1}, which are associated with the asymmetric stretching vibrations of PO_4 units. An absorbtion at 554 cm^{-1} appears as well, which is due to bending vibrations of phosphate groups. The broad bands observed at 3393 and 2933 cm^{-1} correspond to the combination and overlapping of the stretching vibrations of NH_2^+ and CH_2 groups. Sharp bands at 1649, 1534 and 1465 cm^{-1} are attributed to the N–H bending vibrations of the protonated amine.

After calcination at 400 °C in air, the intensity of the diffraction peaks reduced and the peaks shifted to slightly higher angles (Fig. 2), because of lattice contraction and partial framework collapse. TGA/DTA analysis of CBP-CHA shows that extra-framework species (organic amine and water molecules) are present. The weight loss of 5.2% before 350 °C corresponds to the release of three H_2O molecules (calc. 6.07%); there is a 3-step weight loss of 16.1% in the range 350–740 °C, which corresponds to the organic groups separating themselves from the framework. The total weight loss corresponds to the removal of the organic amine and water molecules from the structure (exp. 21.3%; calc. 23.17%).

3.2 Framework topology

Fig. 3 shows the asymmetric unit of CBP-CHA. The structure of CBP-CHA contains a beryllium and a phosphorous site. All of them are tetrahedrally coordinated, with Be–O distances ranging from 1.56 to 1.66 Å, P–O distances ranging from 1.47 to 1.55 Å, O–Be–O angles from 106.9 to 114.7° and O–P–O angles from107.6 to 111.4°, which are typical of values encountered in beryllophosphate. The cobalt atom locates at a special position with relative multiplicity of 1/6 in the structure of CBP-CHA, having octahedral coordination with respect to oxygen and average Co–O bond distances of 2.121 Å.

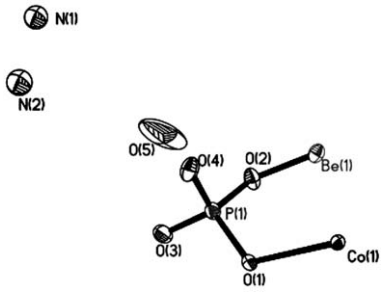

Fig. 3 Thermal ellipsoid plot (50% probability) and atomic labeling scheme for an asymmetric unit of CBP-CHA. Average bond distances: Be–O = 1.606(3), P–O = 1.510(3) and Co–O = 2.121(5) Å.

CBP-CHA has the same topological type of 3D framework as the zeolite chabazite. The framework of CBP-CHA is based on a network of strictly alternating BeO_4 and PO_4 tetrahedra in which all the vertices are shared. The organic molecules in the channels cannot be defined because of strong disorder. The secondary building unit (SBU) of CBP-CHA is D6R. By connecting these D6R units, a 3D network consisting of three types of channels with windows containing eight T-atoms (T = Be and P) is generated. Co^{II} ions are trapped in the center of the D6Rs (Fig. 4). Two sets of similar regular channels with dimensions of 3.8 × 3.8 Å run along the [100] and [001] directions (Fig. 5).

The structure can also be viewed as the stacks of 6-rings in the sequence AABBCC, which form [$8^6 6^2 4^{12}$] cages (Fig. 6). Different sequences of 6-rings lead to different topologies, *e.g.* AFT (AABBCCAACCBB) and gmelinite (GME) (AABB), We have also successfully synthesized a $BePO_4$-GME with the AABB 6-ring sequence.[18]

The beryllium atoms form Be–O–P bonds to four distinct phosphorous atom neighbors with an average distance of d_{av}(Be–O) = 1.606 Å and d_{av}(P–O) = 1.510 Å (Table 3). The mineral chabazite, $Ca_6[Al_{12}Si_{24}O_{72}]\cdot 40H_2O$ is trigonal ($R\bar{3}m$, a = 13.675, c = 14.767 Å, V = 2391.6 $Å^3$), the crystallographic symmetry of CBP-CHA is also trigonal but the space group is $R\bar{3}$ [a = 12.380(3), c = 14.558(5) Å, V = 1932.5(10) $Å^3$. The framework contraction is caused by beryllium and phosphorus atoms occupying the tetrahedral

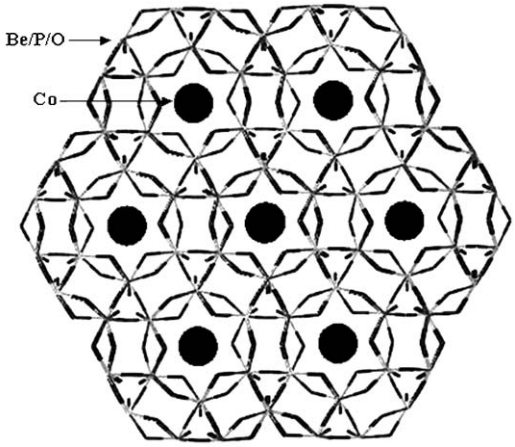

Fig. 4 The structure of CBP-CHA, based on a network of strictly alternating BeO_4 and PO_4 tetrahedra, viewed along the *c*-axis, showing the Co^{II} ions encapsulated in the cavities. The lines represents the beryllophosphate framework and the black circles denote Co^{II} ions.

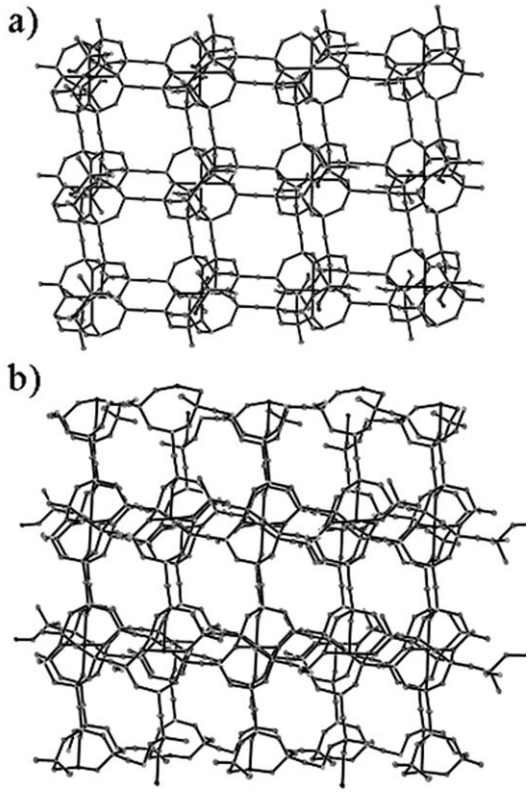

Fig. 5 The 8-ring channels along the crystallographic (a) [010] and (b) [100] directions in CBP-CHA. The extra-framework species have been omitted for clarity.

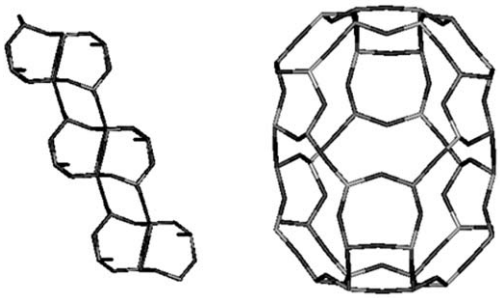

Fig. 6 (a) The AABBCC sequence of double 6-rings. (b) The $[8^6 6^2 4^{12}]$ cage of CBP-CHA. The extra-framework species, including Co atoms, were omitted for clarity.

site.[18] The negative framework charges of CBP-CHA ($[C_6N_4H_{24}]CoBe_6P_6O_{24}\cdot 3H_2O$) are balanced by both the protonated amines in the channels and Co^{II} ions trapped in the D6R. The framework tetrahedral atom density (the number of T-atoms in 1000 $Å^3$) for CBP-CHA is 18.

3.3 Location of Co^{II} and framework ordering

One interesting structural feature of CBP-CHA is that the Co^{II} ions are encapsulated in the center of the D6R (Fig. 7). Each Co atom lies on a 3-fold rotation axis and shares two oxygen atoms with adjacent Be and P atoms, forming –P–Co–Be– type 3-membered rings with an average Co–O bond distance of 2.121 Å and an average O–Co–O bond angle of 90°. The CHA structure is variable due to the considerable flexibility of framework.[32] As a result of the strong bonding force, the D6R units contract. Thus, the distortion of the framework eliminates the symmetric plane and reduces the symmetry to $R\bar{3}$.

The fact that fluorides can be trapped at the center of the D4R and favor the formation of novel framework structures (such as GaPO-LTA,[33] cloverite,[5] Mu-15,[34] and ULM-5 [6]) has been documented.[35] However, the structure encapsulating Co^{II} ions in the D6R is reported for the first time. Similar to the role of fluoride anions in stabilizing D4R units of the structure,[35] Co^{II} ions, by chemically bonding to the framework oxygen atoms, also aid formation of the D6R, so that a 3-dimensional framework is generated.

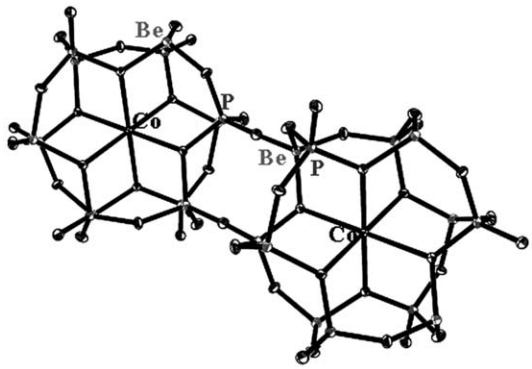

Fig. 7 View of the double 6-ring (D6R) encapsulating Co^{II} ions in the structure of CBP-CHA.

4 Conclusion

A novel cobalt beryllophosphate molecular sieve with a topology similar to that of the chabazite framework has been hydrothermally synthesized. The material provides the first instance of Co^{II} ions encapsulated in the channels of a molecular sieve. CBP-CHA provides an interesting example of the use of a metal amine complex in generating a novel beryllophosphate structure. The replacement of $[Co(1,3\text{-DAP})_3]^{2+}$ by other metal amine complexes, such as $[Co(en)_3]^{2+}$, $[Ni(en)_3]^{2+}$, $[Co(NH_4CNS)_3]^{2+}$, in the hydrothermal synthesis may result in some new porous structures. Further research on this theme is in progress.

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References

1 D. W. Breck, *Zeolite Molecular Sieve*, Wiley, New York, 1974.
2 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Carman and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
3 P. Feng, X. Bu and G. D. Stucky, *Nature*, 1997, **388**, 735.
4 M. Hartmann and L. Kevan, *Chem. Rev.*, 1999, **99**, 636.
5 M. Esteermamm, L. B. McCusker, C. Baerlocher, A. Merrouche and H. Kessler, *Nature*, 1991, **352**, 30.
6 T. Loiseau and G. Ferey, *J. Solid State Chem.*, 1994, **111**, 403.
7 A. M. Chippindale, *Microporous Mesoporous Mater.*, 1998, **21**, 271.
8 R. L. Bedard, (UOP Inc., USA), *US Pat.* 005302362, 1994.
9 W. T. A. Harrison, R. W. Broach, R. A. Bedard, T. E. Gier, X. Bu and G. D. Stucky, *Chem. Mater.*, 1996, **8**, 691.
10 W. T. Harrison and L. Hannooman, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 640.
11 S. B. Harmon and S. C. Sevov, *Chem. Mater.*, 1998, **10**, 3020.
12 J. Chen, R. Jones, S. Natarajan, M. B. Hursthouse and J. M. Thomas, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 639.
13 J. R. D. DeBord, R. C. Haushalter and J. Zubieta, *J. Solid State Chem.*, 1996, **125**, 270.
14 A. R. Cowley and A. M. Chippindate, *J. Chem. Soc., Dalton Trans.*, 1999, 2147.
15 C. N. R. Rao, S. Natarajan and S. Neeraj, *J. Am. Chem. Soc.*, 2000, **122**, 2810.

16 X. Bu, T. E. Gier, P. Feng and G. D. Stucky, *Mircoporous Mesoporous Mater.*, 1998, **20**, 371.
17 A. R. Cowley and A. M. Chippindale, *Microporous Mesoporous Mater.*, 1999, **28**, 163–172.
18 H. Zhang, M. Chen, Z. Shi, X. Bu, Y. Zhou, X. Xu and D. Zhao, *Chem. Mater.*, 2001, **13**, 2042.
19 X. Bu, T. E. Gier and G. D. Stucky, *Microporous. Mesoporous. Mater.*, 1998, **26**, 61.
20 T. William and A. Harrison, *Int. J. Inorg. Mater.*, 2001, **3**, 17.
21 M. Cavellec, D. Riou, C. Ninclaus, J. M. Greneche and G. Ferey, *Zeolites*, 1996, **17**, 250.
22 M. Riou-Cavellec, J. M. Greneche and G. Ferey, *J. Solid State Chem.*, 1999, **148**, 150.
23 K.-H. Lii, Y.-F. Huang, V. Zima, C.-Y. Huang, H.-M. Lin, Y.-C. Jiang, F.-L. Liao and S.-L. Wang, *Chem. Mater.*, 1998, **10**, 599.
24 A. Choudhury, S. Natarajan and C. N. R. Rao, *Chem. Commun.*, 1999, 1350.
25 P. Feng, X. Bu, S. H. Tolbert and G. D. Stucky, *J. Am. Chem. Soc*, 1997, **119**, 2497.
26 J. DeBord, R. D. Haushalter and R. C. Zubieta, *J. Solid State Chem.*, 1996, 125.
27 Y. Zhou, H. Zhu, Z. Chen, M. Chen, Y. Xu, H. Zhang and D. Zhao, *Angew. Chem., Int. Ed.*, 2001, **40**, 2166.
28 K.-F. Hsu and S.-L. Wang, *Inorg. Chem*, 2000, **39**, 1773.
29 A. Choudhury, S. Neeraj, S. Natarajan and C. N. R. Rao, *Angew. Chem., Int. Ed.*, 2000, **39**, 3091.
30 G. M. Sheldrick, SHELXTL, version 5.03, Software Package for Crystal Structure Determination, University of Göttingen, Geramany, 1994.
31 S. Natarajan, S. Neeraj, A. Choudhury and C. N. R. Rao, *Inorg. Chem.*, 2000, **39**, 1426.
32 J. L. Guth, H. Kessler, J. M. Higel, J. M. Lamblin, J. Patarin, A. Seive, J. M. Chezeau, R. Wey, M. L. Occelli and H. E. Robson, (eds.), in *Zeolite Synthesis*, ACS Symp.Ser. vol. 398, American Chemical Society, Washington, DC, 1989, p. 176.
33 A. Simmen, J. Patarin and Ch. Baerlocher, in *Proceedings of the 9th International Zeolite Conference, Montreal*, Butterworth-Heinemann, 1993, p. 433.
34 A. Matijasic, J-L. Paillaud and J. Patarin, *J. Mater. Chem.*, 2000, **10**, 1345.
35 M. Haouas, C. Gerardin, F. Taulelle, C. Estournes, T. Loiseau and G. Ferey, *Colloids Interfaces A*, 1999, **158**, 299.