

Two Ethylenediamine-Templated Zeolite-Type Structures in Zinc Arsenate and Cobalt Phosphate Systems

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Hydrothermal syntheses and X-ray crystal structures of two zeolite-type structures encapsulating protonated ethylenediamine and consisting of three-dimensional 8-ring channels are presented. UCSB-3 and ACP-3 are isostructural and have zeolite-type topologies. The framework consists of cross-linked bifurcated hexagonal-square (bhs) chains, similar to that found in the zeolite-type structure, AlPO₄-D. Alternatively, like a number of zeolite structures such as ABW, gismondine, merlinoite, and phillipsite, the framework can be considered as superimposed 4.8² nets. UCSB-3 is the only amine-templated arsenate with a zeolite-type topology. Crystal data for (H₃NCH₂CH₂NH₃)_{0.5}·ZnAsO₄ (UCSB-3): *M* = 235.35, space group *P*4₂/*n*, *a* = 10.7598(1) Å, *c* = 9.1015(1) Å, *V* = 1053.71(2) Å³, *Z* = 8, *D*_c = 2.967 g cm⁻³, *MoK*α, *λ* = 0.71073 Å, *μ* = 10.815 mm⁻¹, *2θ*_{max} = 56.26°, *R*(*F*) = 2.67% for 84 parameters and 1262 reflections with *I* > 2σ(*I*). Crystal data for (H₃NCH₂CH₂NH₃)_{0.5(1-x)}·Al_xCo_{1-x}PO₄ (*x* ≈ 0.15, ACP-3): space group *P*4₂/*n*, *a* = 10.4236(1) Å, *c* = 8.9487(1) Å, *V* = 972.29(2) Å³, *Z* = 8, *MoK*α, *2θ*_{max} = 56.52°, *R*(*F*) = 3.59% for 92 parameters and 1108 reflections with *I* > 2σ(*I*). © 1998 Academic Press

INTRODUCTION

Zeolites have been extensively studied because of their utility in commercial processes such as catalysis and gas separation (1). Since 1980s, there has been an intense search for materials with new framework topologies or compositions with the expectation that such materials could lead to new applications (2). Remarkable success has been achieved in aluminophosphate and substituted aluminophosphate systems (3). More recently, a number of hydrated alkali zinco- (or beryll-) phosphates and arsenates have been reported to have framework structures isotypic to those of zeolites. These include Na₆(H₂O)₈(ZnPO₄)₆ (sodalite), (Na,TMA)₉₆M₉₆P₉₆O₁₉₂ (*M* = Be or Zn, zeolite X), Li₄M₄P₄O₁₆·4H₂O (*M* = Be or Zn, zeolite ABW), and Li₂₄Be₂₄P₂₄O₉₆·40H₂O (zeolite rho) (4, 5).

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The use of organic amines in divalent metal phosphate and arsenate systems (MPO₄⁻¹ or MAsO₄⁻¹, *M* = Zn²⁺, Be²⁺, Co²⁺, ...) has led to the synthesis of a variety of novel structures (6–11). However, unlike the above hydrated structures, none of the amine-templated framework structures in zinc, beryllium, or cobalt phosphate and arsenate systems discovered so far is a zeolite analog (12). In fact, a very common feature found in these amine-templated zinc, beryllium, or cobalt phosphates and arsenates is the framework interruption that can occur on either *T*²⁺ (Zn, Be, or Co) or *T*⁵⁺ (P or As) sites. In reporting two sodalite-related zincophosphates (7), we showed that their framework interruptions can be understood from the charge matching between the framework and the guest molecule.

In a systematic search for zeolite-type structures in zinc, beryllium, and cobalt phosphate or arsenate systems, in addition to the syntheses of hydrated zeolite analogs mentioned above (5), we also found an ethylenediamine-templated zinc arsenate open framework structure. However, due to the twinning and the associated pseudosymmetry, the structural characterization has not been satisfactory until now. Here we report the crystal structure of this amine-templated zinc arsenate. It is the only zeolite-type zinc arsenate with an amine as the structure-directing agent. We also report here an isostructural ethylenediamine-templated aluminium cobalt phosphate open framework structure. Two closely related compounds with different compositions are DAF-2 (a cobalt phosphate) (13) and DAF-3 (a zinc phosphate) (14).

EXPERIMENTAL

Hydrothermal Syntheses

UCSB-3. To a polypropylene bottle (60 mL) was added 3.30 g of ethylenediamine, 10 mL H₂O, and 7.71 g of 2 M Zn(NO₃)₂. An initial gel precipitate dissolved completely, and heat was evolved on shaking the mixture. A total of 4.74 g of 4 M H₃AsO₄ were then added, giving an initial gel which again dissolved completely on shaking. Standing at 4°C overnight gave no crystals, and 1.70 g of the arsenic acid

solution was added to lower the pH from about 10 to 9.5, giving a dilute sol on shaking. After standing a day at 70°C, small crystals could be seen growing, and after 4 days the solids were recovered by standard filtration and drying techniques. The product (1.06 g) was separated by sonication and decantation.

ACP-3. $\text{CoCO}_3 \cdot x\text{H}_2\text{O}$ (13.22 g) was mixed with 108.23 g of distilled water and 26.78 g of 85% H_3PO_4 . In a separate beaker, aluminium isopropoxide (10.06 g) was mixed with 85% H_3PO_4 (10.32 g) and ethylene glycol (52.28 g), followed by stirring at room temperature for 24 h. A portion of the ethylene glycol solution (23.41 g) was mixed with the above Co^{2+} -containing aqueous solution, and the mixture was stirred for 20 min. To 29.83 g of the above mixture was added quinuclidine (1.05 g), piperazine (3.08 g), and ethylenediamine (0.60 mL). The mixture was then heated at 180°C for 4 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Blue prismatic crystals were obtained together with some blue needle-like crystals. The needle-like phase is an analog of a mineral zeolite (merlinoite) and has already been reported (15). The prismatic phase also has a zeolite-type structure and is reported here.

Elemental analysis. Quantitative elemental analysis of the phosphate (ACP-3) was carried out on a Cameca SX-50 electron probe microanalyzer equipped with five wavelength dispersive (WD) X-ray spectrometers and one energy dispersive (ED) X-ray spectrometer. The instrument was controlled by a Sun workstation, and the analyses for Al, Co, and P were simultaneously performed on three WD spectrometers. The observed data in mass percent and relative atomic numbers in parenthesis are 1.797 (3.89) Al, 29.78 (29.51) Co, and 17.07 (32.17) P. Assuming 0.15 for x in the formula (Table 1), the calculated values in mass percent are 2.31 Al, 28.54 Co, and 17.65 P. The energy dispersive spectrum showed a small, distinct peak for Al, confirming the substitution of Al for Co.

Single crystal X-ray crystallography. Crystals were glued to thin glass fibers with epoxy resin and mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source ($\text{MoK}\alpha$) operating at 50 kV and 40 mA. A full sphere of intensity data was collected in 2082 frames with ω scans (width of 0.30° and exposure time of 30 s per frame). The empirical absorption corrections were based on the equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. The structures were solved by direct methods followed by successive difference Fourier methods. All calculations were performed using SHELXTL running on Silicon Graphics Indy 5000. Final full-matrix refinements were against F^2 and included secondary extinction correction and anisotropic thermal parameters for

TABLE 1
A Summary of Crystal Data and Refinement Results

Name	UCSB-3	ACP-3
Formula	$(\text{EDA}^c)_{0.5}(\text{ZnAsO}_4)$	$(\text{EDA}^c)_{0.5(1-x)}(\text{Al}_x\text{Co}_{1-x}\text{PO}_4)$ ($x \approx 0.15$)
Habit	Square plate	Prism
Color	Clear	Blue
Size (μm^3)	$0.20 \times 0.20 \times 0.12$	$0.13 \times 0.067 \times 0.067$
a (Å)	10.7598(1)	10.4236(1)
c (Å)	9.1015(1)	8.9487(1)
V (Å ³)	1053.71(2)	972.29(2)
Z	8	8
Space group	$P4_2/n$ (No. 86)	$P4_2/n$
$2\theta_{\text{max}}$ (deg)	56.26	56.52
Unique data	1287	1199
Parameters	84	92
$R(F)^a$ (%)	2.67	3.59
$R_w(F^2)^b$ (%)	7.03	7.84
GOF	1.14	1.15

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$, with $F_o > 4.0\sigma(F)$.

^b $R_w(F^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, with $F_o > 4.0\sigma(F)$; $w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, where $P = (F_o^2 + 2F_c^2)/3$; $A = 0.0417$, $B = 1.5057$ for UCSB-3, and $A = 0.0364$, $B = 1.2228$ for ACP-3.

^c EDA = $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3$.

non-hydrogen atoms. Two hydrogen atoms on the nitrogen atom of ACP-3 were located from the difference map and refined isotropically. Other hydrogen atoms were not included. The crystallographic results are summarized in Table 1, while atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively.

The crystal structures for both crystals were solved and refined from twinned crystals with an equal volume ratio between the two domains [the refined values are 49.0(2)% vs 51.0(2)% for UCSB-3 and 48.2(2)% vs 51.8(2)% for ACP-3]. The twofold twin axis is along the crystallographic [110] direction. The concentration of Al at Co sites is not significant enough to affect the structural refinement which assumes an occupancy of 1 for Co at framework metal atom sites. Due to the incorporation of Al^{3+} , some sites for ethylenediamine may be vacant or some ethylenediamine molecules may not fully diprotonated.

RESULTS AND DISCUSSION

Description of Framework Connectivity

Since ACP-3 and UCSB-3 are isostructural and structurally related to zeolites, they are discussed together below using some of the terms commonly used for describing the zeolite framework topology. The asymmetric unit is $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)_{0.5}(\text{ZnAsO}_4)$ or $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)_{0.5(1-x)}(\text{Al}_x\text{Co}_{1-x}\text{PO}_4)$, and all atoms are on the general positions of space group $P4_2/n$. The framework consists of strictly alternating ZnO_4 (or CoO_4 and AlO_4) and AsO_4

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	$U(\text{eq})^a$
UCSB-3				
As(1)	6130(1)	4086(1)	1987(1)	15(1)
Zn(1)	6283(1)	3930(1)	8350(1)	17(1)
O(1)	5007(4)	5050(4)	2579(4)	46(1)
O(2)	6643(4)	4519(4)	325(3)	30(1)
O(3)	7242(3)	4287(5)	3246(4)	45(1)
O(4)	5585(6)	2632(4)	2020(4)	60(2)
N(1)	3757(4)	3737(4)	4936(4)	25(1)
C(1)	2829(9)	2843(9)	4325(10)	22(2)
C(2)	2757(9)	2870(10)	5611(10)	23(2)
ACP-3				
P(1)	6101(1)	4066(1)	2016(1)	15(1)
Co(1)	6285(1)	3904(1)	8400(1)	18(1)
O(1)	5040(4)	5001(4)	2465(4)	37(1)
O(2)	6602(3)	4374(3)	456(3)	28(1)
O(3)	7159(3)	4263(5)	3171(4)	42(1)
O(4)	5573(4)	2711(3)	2116(4)	45(1)
N(1)	3793(4)	3740(5)	4948(7)	30(1)
C(1)	2846(10)	2815(10)	4339(13)	34(3)
C(2)	2781(10)	2880(10)	5626(12)	30(2)
H(1)	4195(66)	3929(72)	4262(83)	65(24)
H(2)	4208(68)	3616(72)	5506(79)	58(26)

^a $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor. The positions of C(1) and C(2) in both UCSB-3 and ACP-3 are 50% occupied.

(or PO_4) tetrahedral units forming 4-, 6-, and 8-rings. The secondary building unit (SBU) of these two structures is the single 4-ring with apices pointing up and down alternatively (denoted) as UDUD (16).

These UDUD single 4-rings belong to one of the four types of 4-rings classified previously (17), and they form infinite chains along the crystallographic c axis. Along the chain, each pair of 4-rings are joined so that two 6-rings having four common T-atoms are created (Fig. 1). This type of chain has been classified as a bifurcated hexagonal-square chain (bhs) (18) and is also called a narsarsukite chain. A twofold axis (at coordinates $\frac{1}{4}\frac{3}{4}z$) passes through the centers of all 4-ring units along the chain.

Each bhs chain is joined directly to two other bhs chains to form a sheet (Fig. 2). The formation of such a sheet leads to the creation of 4-rings of a new type between bhs chains in addition to the creation of 8-rings (Fig. 2). These sheets are stacked along the $[110]$ direction to form a three dimensional framework with 8-ring channels. The three-dimensional framework can be alternatively described as constructed from the same sheets which are oriented parallel to the (-110) plane and are stacked along the $[-110]$ direction, creating 8-ring channels in the $[-110]$ direction.

When viewed down the c axis, the three-dimensional framework can be described as either cross-linked bhs chains or stacked 4.8^2 nets (18). Chains are arranged into a square pattern, encircling the third type of 8-ring channels (Fig. 3). The connectivity patterns between these chains along two mutually perpendicular directions ($[110]$ and $[-110]$) are identical. When using superimposed layers of the 4.8^2 type nets to describe the framework structure of the title compounds, we should note that in each 4.8^2 sheet, one free corner of each tetrahedral atom can point up (U) or down (D) from the layer. For each 8-ring in the title compounds, tetrahedral atoms in the ring can be described as UUUUUDD.

Four structures were theoretically developed from UDUD rings several decades ago (19). None of these structures was found in natural or synthetic compounds at that time. For each 8-ring in these four theoretical structures, tetrahedral atoms in the ring can be described as UUD-DUDD (Type 1), UDUDUDUD (Type 2), UUDUD-DUD (Type 3), and UUDUDUDD (Type 4), respectively. Thus, the title compounds have the same framework topology as the Type 1 structure.

Comparison with Known Zeolite Structures

The above description of the framework topology based on 4.8^2 nets can be compared to several known zeolite

TABLE 3
Selected Bond lengths (\AA) and Angles (deg)

UCSB-3			
As(1)–O(4)	1.671(4)	As(1)–O(3)	1.671(3)
As(1)–O(2)	1.677(3)	As(1)–O(1)	1.681(3)
Zn(1)–O(1)	1.961(3)	Zn(1)–O(3)	1.920(4)
Zn(1)–O(2)	1.945(3)	Zn(1)–O(4)	1.960(4)
N(1)–C(1)	1.494(11)	N(1)–C(2)	1.551(10)
C(1)–C(2)	1.535(12)		
O(4)–As(1)–O(3)	111.1(3)	O(4)–As(1)–O(2)	113.1(2)
O(3)–As(1)–O(2)	110.3(2)	O(4)–As(1)–O(1)	108.7(3)
O(3)–As(1)–O(1)	102.4(2)	O(2)–As(1)–O(1)	110.7(2)
O(3)–Zn(1)–O(2)	114.7(2)	O(3)–Zn(1)–O(4)	117.2(3)
O(2)–Zn(1)–O(4)	109.7(2)	O(3)–Zn(1)–O(1)	106.4(3)
O(2)–Zn(1)–O(1)	110.9(2)	O(4)–Zn(1)–O(1)	96.3(2)
ACP-3			
P(1)–O(4)	1.518(4)	P(1)–O(2)	1.525(3)
P(1)–O(3)	1.526(3)	P(1)–O(1)	1.528(3)
Co(1)–O(3)	1.917(3)	Co(1)–O(2)	1.933(3)
Co(1)–O(1)	1.951(3)	Co(1)–O(4)	1.956(4)
N(1)–C(1)	1.484(11)	N(1)–C(2)	1.511(11)
C(1)–C(2)	1.510(12)		
O(4)–P(1)–O(3)	112.0(2)	O(4)–P(1)–O(2)	110.3(2)
O(2)–P(1)–O(3)	110.1(2)	O(4)–P(1)–O(1)	108.4(3)
O(2)–P(1)–O(1)	110.7(2)	O(3)–P(1)–O(1)	105.0(2)
O(3)–Co(1)–O(2)	113.2(2)	O(3)–Co(1)–O(1)	107.6(2)
O(2)–Co(1)–O(1)	110.5(2)	O(3)–Co(1)–O(4)	115.4(2)
O(2)–Co(1)–O(4)	111.0(2)	O(1)–Co(1)–O(4)	98.2(2)

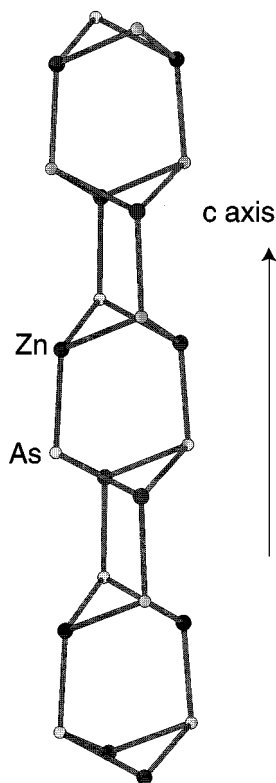


FIG. 1. A bifurcated hexagonal-square chain (bhs) in UCSB-3.

structures also constructed from 4.8^2 nets (18). For each 8-ring in the gismondine structure, four adjacent corners are directed upward while the other four corners are directed downward (UUUDDDDD). In phillipsite, six adjacent corners are up and the other two are down. Merlinoite has double 8-rings, in addition to the UUDDUUDD configuration. Note that for the title compounds, the UUDDUUDD configuration does not uniquely define a framework topology. Another zeolite type structure (ACP-1) with a different framework topology can also be considered as constructed from 4.8^2 nets with the UUDDUUDD configuration for each 8-ring (15). ACP-1 does not have 4-ring chains, however, because it consists of only double 4-ring units.

There are only two crystallographically unique tetrahedral atoms in the title compounds. They have the same T -atom loop configuration (two 4-rings sharing a corner, Type B2) (20). This type of loop configuration has been observed in 23 other zeolite structure types, including the well-known sodalite (16). However, only three of these known zeolites types (ANA, LAU, and SOD) consist of tetrahedral atoms with only this type of loop configuration. None of these three structures consists of bhs chains. Thus the framework topology reported here is different from any zeolite structure types tabulated thus far (16).

The bhs chain is not very common among zeolite structure types (18). Another zeolite structure type with bhs chains is APD found in $\text{AlPO}_4\text{-D}$ with the orthorhombic symmetry (16). The connectivity between bhs chains in $\text{AlPO}_4\text{-D}$ is different from that found in the title compounds. One notable difference is that in $\text{AlPO}_4\text{-D}$, 6-rings are created when two bhs chains are joined together. In comparison, all 6-rings in the title compounds exist in the bhs chains. The bhs chain was also identified in a nonzeolite, banalsite, $\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ (21).

To have a zeolite-like framework topology, a strict alternation of ZnO_4 or CoO_4 tetrahedra with AsO_4 or PO_4 is required. However, since either Zn or Co can adopt other coordinations, such as trigonal bipyramidal or octahedral, the crystallization of nontetrahedral Zn or Co compounds is often a competing process to the formation of tetrahedral frameworks and can even prevent the formation of tetrahedral compounds. Even if Zn or Co take tetrahedral coordination, the bridging oxygen atoms are often coordinated between two metal atoms and one P (or As) atom or there is a framework interruption on T^{2+} or T^{5+} sites. Thus, there is a limited number of pure T^{2+}/T^{5+} zeolite analogs or zeolite-like structures. UCSB-3 represents the first successful synthesis of an amine-templated zeolite-type arsenate structure in the T^{2+}/T^{5+} system.

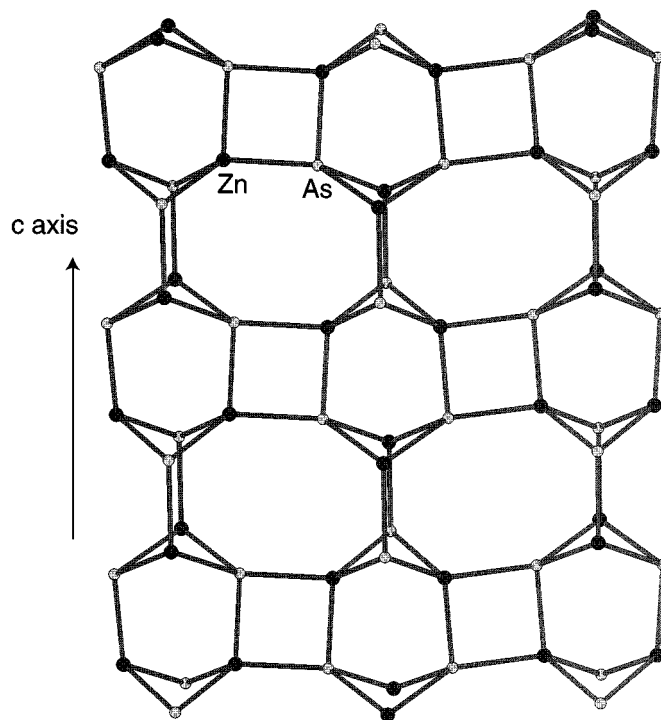


FIG. 2. A two-dimensional sheet viewed down the crystallographic $[110]$ direction.

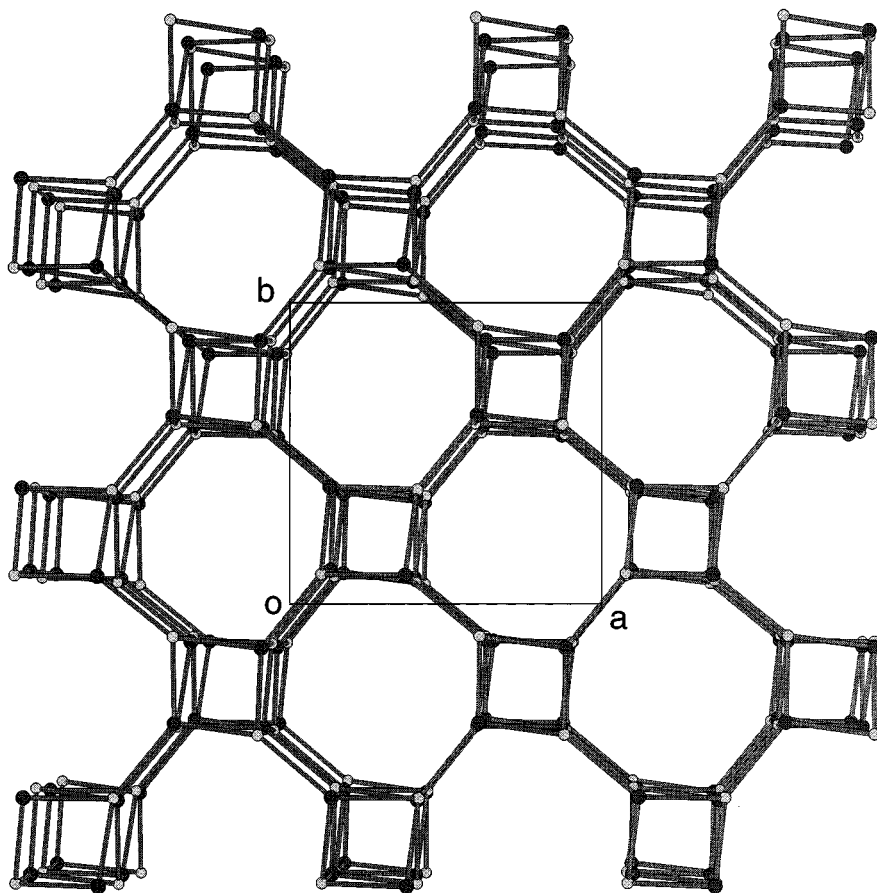


FIG. 3. Eight-ring channels viewed down the crystallographic c axis in UCSB-3.

Description of Extra Framework Species

The diprotonated ethylenediamine molecules are located on twofold axes at the center of 8-ring channels. They are not completely disordered, as is the case in some other amine-containing molecular sieves. Two nitrogen atoms are ordered, whereas two carbon atoms have two possible locations as illustrated in Fig. 4. The same twofold axis ($\frac{1}{4}\frac{1}{4}z$) along the c axis passes through ethylenediamine molecules in both orientations. These six atomic sites approximately form a plane which is parallel to the Miller planes (110) or (-110). The ordering of the nitrogen atoms is probably due to the formation of N-H...O-type hydrogen bonds between guest molecules and oxygen atoms of the host framework. The three shortest contacts in UCSB-3 are 2.90, 2.91, and 2.93 Å for N1---O1, N1---O3, and N1---O2, respectively.

In a related compound, DAF-2, the crystal structure was described in a fourfold supercell with a lower crystallographic symmetry and there was no disorder associated with ethylenediamine molecules (13). Data collections with a two-dimensional CCD detector on two title compounds

covered the full reciprocal space, and no super reflections were detected. Thus the difference in the orientation of ethylenediamine and the incorporation of Al^{3+} onto Co^{2+} sites in ACP-3 may be responsible for the different crystal structures between the title compounds and DAF-2.

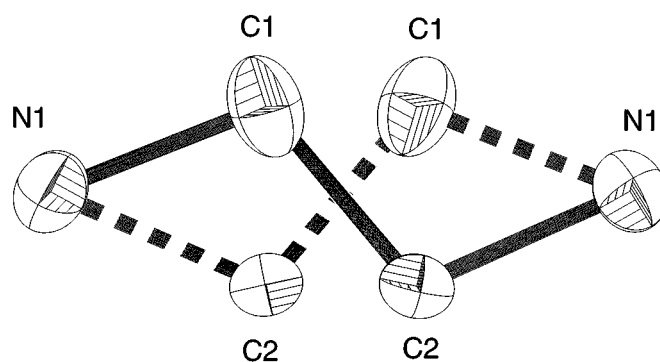


FIG. 4. Two orientations of diprotonated ethylenediamine molecules (50% ORTEP drawing) in ACP-3.

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