An organically templated open-framework cobalt germanate

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Abstract

An open-framework cobalt germanate of the formula, $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$ has been prepared under solvo/hydrothermal conditions in the presence of ethylenediamine. The germanate is constructed by Ge_9O_{18} clusters and contains eight- and ten-membered channels. Besides connecting two Co sites, the amine also acts as a bis-chelating agent and protrudes into the eight-membered channel.

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1. Introduction

Germanate-based zeolite structures containing Ge_8O_{20} have attracted much attention [1]. The Ge–O–Ge angles in these compounds are around $130°$ in place of the $145°$ Al–O–Si angle in the aluminosilicates. Various zeolitic open germanates have been reported by several workers including Xu et al. [2], Stucky et al. [3], Dadachov et al. [4], Zhao et al. [5], Yaghi et al. [6] and Puebla et al. [7]. Several layered open germanates have also been reported, typical examples being a zinc germanate by Parise et al. [8], a copper germanate by Monge et al. [9], $K_2ZrGe_2O_7$ by Clearfield et al. [10] and $K_3Nb_5GeO_{16} \cdot 2H_2O$ by Stucky et al. [11]. Stucky et al. [12] have recently reported an open-framework zinc germanate of the type $[Ge_9O_{18}Zn_2(OH)_4] \cdot 3(NH_2CH_2CH_2NH_2)$ by molecular templating route while Yaghi et al. [13] have described a four-connected microporous material of the composition ZrO_6F_2 $(H_2DAB) \cdot H_2O$ containing a high proportion of 3-rings. Jacobson et al. [14,15] have synthesized organically templated open-framework niobium germanates with low framework density and ion-exchange properties. Puebla et al. [16] have obtained germanates containing transitional metal complexes with potential uses in catalysis. We have synthesized an organically templated cobalt germanate of the formula $[Co_2(NH_2(CH_2)_2$

$NH_2)_3][Ge_9O_{18}(OH)_4]$, **I**, under solvo/hydrothermal conditions. While the structure of **I** is analogous to that of the zinc germanate of Stucky et al. [12], it has certain novel features, a noteworthy one being the presence of the cobalt amine complex in the eight-membered channel.

2. Experimental

The cobalt germanate, $[Co_2(NH_2(CH_2)_2NH_2)_3]$ $[Ge_9O_{18}(OH)_4]$, **I**, was synthesized by employing solvo/hydrothermal route using ethylenediamine (en)/water mixture. In a typical synthesis, 0.109 g of germanium dioxide and 0.238 g of cobalt chloride were dissolved in 2.0 ml en and 1.0 ml water. 0.258 g of piperazine (PIP) was then added and the mixture stirred continuously for 1 h. Finally, 0.1 ml of HF (48%, w/w aqueous solution) was added and the resulting dark brown solution homogenized for 30 min. The final mixture with the composition $GeO_2:CoCl_2 \cdot 6H_2O:30en:55H_2O:3PIP:2.7$ HF with an initial pH greater than 11, was sealed in a teflon-lined Parr autoclave and heated at $180°$ for 10 days. The autoclave was then allowed to cool for a period of 4 h. The pH of the supernatant solution was around 9. The resulting product, containing pink-coloured rod-shaped crystals suitable for single-crystal X-ray diffraction (XRD), was filtered and washed thoroughly with deionized water. The yield was $\sim 55\%$ with respect to Ge. The role of PIP is probably to fine

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tune the pH of the medium which helps to form monophasic material. Without the addition of PIP in the reaction mixture, a colourless impurity phase also appears along with **I**. Qualitative analysis indicated the absence of F in the product. Synthesis carried out without HF also yields **I** in powder form. So the role of HF could be just a mineralizer.

The powder XRD pattern of the powdered single crystals of **I** indicated that the product was a new material. The pattern was consistent with the structure determined by single-crystal XRD. A least-squares fit [17] of the powder XRD (Cu$K\alpha$) lines, using the $h\,k\,l$ indices garnered from single-crystal X-ray data, gave the following cell: $a = 14.022(3)$, $b = 12.972(3)$, $c = 14.665(1)$ Å, which is in good agreement with that determined by single-crystal XRD. Powder XRD data for **I**, $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$, are listed in Table 1. EDAX analysis indicated that the ratio of Co:Ge is 2:9. Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere in the range from $25°$ to $1000°C$.

A suitable single crystal ($0.08 \times 0.08 \times 0.20$ mm^3) of the title compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected at room temperature in 1321 frames with ω scans (width of $0.30°$ and exposure time of 20 s per frame). The final unit cell constants were determined by a least-squares fit of 1931 reflections in the range $3° < 2\theta < 46.5°$. Pertinent experimental details for the structure determinations are presented in Table 2.

The structure was solved by direct methods using SHELXS-86 [18] and difference Fourier syntheses. The hydrogen positions for bridging hydroxide (O8) and terminal hydroxyl (O11) were initially located in the difference Fourier maps and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. The hydrogen atoms for the bonded amine molecules were not put for the final refinement because of disorder in one of the carbon, C1 (SOF of C1 and C1A are 0.30 and 0.70, respectively) and nitrogen, N3 (SOF of N3 and N3A are 0.70 and 0.30, respectively) sites. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms (except the

Table 1
X-ray powder data for $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$

h	k	l	$2\theta_{obs}$	$\Delta(2\theta)^a$	d_{cal}	$\Delta(d)^b$	$I_{rel}{}^c$
1	1	1	11.099	0.004	7.987	−0.003	100.00
0	0	2	12.108	0.021	7.332	−0.013	56.45
2	0	0	12.634	−0.005	7.013	0.003	71.39
1	0	2	13.597	−0.047	6.498	0.022	11.89
0	2	0	13.678	0.009	6.486	−0.005	66.51
2	1	1	15.612	0.011	5.686	−0.004	19.78
1	2	1	16.245	0.004	5.463	−0.001	39.02
0	2	2	18.284	0.006	4.858	−0.002	7.20
2	2	1	19.601	−0.017	4.529	0.004	6.86
1	1	3	20.423	−0.015	4.349	0.003	12.30
2	2	2	22.268	−0.009	3.993	0.002	46.50
1	3	1	22.393	0.023	3.977	−0.004	22.21
1	3	2	24.772	0.023	3.6	−0.004	17.24
2	3	2	27.112	−0.013	3.289	0.002	19.75
3	1	3	27.29	−0.002	3.27	0	23.78
2	0	4	27.493	0.025	3.249	−0.003	28.28
4	0	2	28.246	0.019	3.163	−0.002	13.71
3	2	3	29.816	−0.017	2.996	0.002	9.74
2	4	0	30.376	−0.007	2.943	0.001	10.08
2	2	4	30.801	0.005	2.905	−0.001	25.27
4	2	2	31.476	−0.006	2.843	0.001	27.35
3	3	3	33.662	−0.018	2.662	0.002	42.43
5	2	1	35.387	−0.026	2.536	0.002	5.49
1	5	1	35.732	−0.009	2.513	0.001	18.04
0	0	6	36.816	0.028	2.444	−0.002	18.77
4	2	4	38.142	−0.002	2.36	0	15.40
6	0	0	38.56	0.031	2.338	−0.002	10.37
3	3	5	41.955	0.001	2.154	0	5.96
0	0	8	49.731	−0.024	1.833	0.001	8.67
6	3	4	50.955	0.023	1.793	0	5.91

^{a} $2\theta_{obs}$−$2\theta_{calc}$.
^{b} d_{obs}−d_{calc}.
^{c} $100 \times I/I_{max}$.

Table 2
Crystal data and structure refinement parameters for $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$, **I**

Emperical formula	$Co_2Ge_9O_{22}N_6C_6H_{28}$
Space group	*Pbca*
T (K)	293
a (Å)	14.039(3)
b (Å)	12.987(2)
c (Å)	14.705(4)
α (deg)	90.0
β (deg)	90.0
γ (deg)	90.0
Volume (Å^3)	2681.1(11)
Z	8
Formula mass	1307.52
ρ_{calc} (g cm^{-3})	3.239
λ (Mo$K\alpha$) Å	0.71073
μ (mm^{-1})	11.243
θ range (deg)	1.55–23.28
Total data collected	10451
Index ranges	$-14 \leqslant h \leqslant 15, -11 \leqslant k \leqslant 14, -11 \leqslant l \leqslant 16$
Unique data	1930
Observed data ($\sigma > 2\sigma(I)$)	1557
Refinement method	Full-matrix least-squares on $|F^2|$
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0510$, w$R_2 = 0.1524$
R indices (all data)	$R_1 = 0.0666$, w$R_2 = 0.1640^a$
Goodness of fit (S)	1.039
No. of variables	204
Largest difference map peak and hole e Å^{-3}	1.060 and −2.652

^{a} $W = 1/[\sigma^2(F_o)^2 + (0.0894P)^2 + 98.2020P]$ where $P = [F_o^2 + 2F_c^2]/3$.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$, **I**

	x	y	z	U (eq)^a
Ge(1)	5236(1)	1758(1)	6446(1)	9(1)
Ge(2)	6668(1)	1602(1)	4875(1)	9(1)
Ge(3)	5049(1)	2210(1)	3518(1)	10(1)
Ge(4)	3706(1)	2333(1)	4994(1)	10(1)
Ge(5)	5000	0	5000	8(1)
Co(1)	3703(2)	3931(2)	6584(2)	45(1)
O(1)	5031(6)	465(7)	6220(6)	10(2)
O(2)	5341(7)	1868(7)	7606(6)	14(2)
O(3)	6311(6)	2155(7)	5926(6)	14(2)
O(4)	4302(6)	2569(7)	6071(6)	12(2)
O(5)	7900(6)	1567(7)	4721(6)	12(2)
O(6)	6293(6)	317(7)	4861(6)	11(2)
O(7)	6231(6)	2286(8)	3930(6)	17(2)
O(8)	4724(7)	1184(7)	2787(6)	16(2)
O(9)	4113(7)	2972(7)	3975(6)	18(2)
O(10)	4693(6)	1365(6)	4637(6)	9(2)
O(11)	2778(7)	1424(8)	5002(7)	19(2)
N(1)	2950(13)	5409(12)	6853(11)	48(4)
C(2)	2233(18)	4231(19)	7949(15)	66(7)
N(2)	2670(9)	3359(10)	7484(9)	27(3)
C(3)	5378(15)	4736(18)	5240(18)	61(6)
C(1)	2476(14)	5197(16)	7863(14)	31(13)
C(1A)	2127(13)	5204(13)	7396(11)	49(7)
N(3)	4951(15)	4777(15)	6223(13)	23(4)
N(3A)	4425(10)	4980(14)	6233(14)	36(12)

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

Table 4
Selected bond distances in $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$, **I**.

Moiety	Distance (Å)	Moiety	Distance (Å)
Ge(1)–O(2)	1.718(9)	Ge(4)–O(5)^a	1.870(9)
Ge(1)–O(1)	1.735(9)	Ge(4)–O(10)	1.944(8)
Ge(1)–O(3)	1.769(9)	Ge(5)–O(6)	1.873(8)
Ge(1)–O(4)	1.771(8)	Ge(5)–O(6)^b	1.873(8)
Ge(2)–O(5)	1.745(9)	Ge(5)–O(1)^b	1.893(9)
Ge(2)–O(6)	1.750(9)	Ge(5)–O(1)	1.893(9)
Ge(2)–O(7)	1.760(9)	Ge(5)–O(10)^b	1.901(8)
Ge(2)–O(3)	1.775(9)	Ge(5)–O(10)	1.901(8)
Ge(3)–O(7)	1.769(9)	Co(1)–N(3A)	1.77(5)
Ge(3)–O(8)	1.771(9)	Co(1)–O(4)	2.099(9)
Ge(3)–O(9)	1.776(9)	Co(1)–N(2)	2.100(13)
Ge(3)–O(2)^c	1.845(9)	Co(1)–N(3)	2.13(2)
Ge(3)–O(10)	2.039(9)	Co(1)–N(1)	2.23(2)
Ge(4)–O(11)	1.758(10)	Co(1)–O(8)^d	2.282(9)
Ge(4)–O(9)	1.806(9)	Co(1)–O(5)^a	2.318(9)
Ge(4)–O(4)	1.817(9)		
Organic moiety			
N(1)–C(1A)	1.43(3)	C(2)–C(1A)	1.51(4)
N(1)–C(1)	1.65(6)	C(3)–C(3)^e	1.45(4)
C(2)–C(1)	1.31(6)	C(3)–N(3)	1.57(3)
C(2)–N(2)	1.46(3)		

Symmetry transformations used to generate equivalent atoms:
^{a} $x - 1/2, -y + 1/2, -z + 1$.
^{b} $-x + 1, -y, -z + 1$.
^{c} $x, -y + 1/2, z - 1/2$.
^{d} $x, -y + 1/2, z + 1/2$.
^{e} $-x + 1, -y + 1, -z + 1$.

Table 5
Selected bond angles in $Co_2(NH_2(CH_2)_2NH_2)_3[Ge_9O_{18}(OH)_4]$

Moiety	Angle (deg)	Moiety	Angle (deg)
O(2)–Ge(1)–O(1)	106.6(4)	O(5)^a–Ge(4)–O(10)	170.5(4)
O(2)–Ge(1)–O(3)	109.4(4)	O(6)–Ge(5)–O(6)^b	180
O(1)–Ge(1)–O(3)	109.9(4)	O(6)–Ge(5)–O(1)^b	89.4(4)
O(2)–Ge(1)–O(4)	108.8(4)	O(6)^b–Ge(5)–O(1)^b	90.6(4)
O(1)–Ge(1)–O(4)	113.2(4)	O(6)–Ge(5)–O(1)	90.6(4)
O(3)–Ge(1)–O(4)	108.9(4)	O(6)^b–Ge(5)–O(1)	89.4(4)
O(5)–Ge(2)–O(6)	105.7(4)	O(1)^b–Ge(5)–O(1)	179.999(1)
O(5)–Ge(2)–O(7)	104.9(4)	O(6)–Ge(5)–O(10)^b	90.9(4)
O(6)–Ge(2)–O(7)	111.5(4)	O(6)^b–Ge(5)–O(10)^b	89.1(4)
O(5)–Ge(2)–O(3)	113.8(4)	O(1)^b–Ge(5)–O(10)^b	88.5(4)
O(6)–Ge(2)–O(3)	108.1(4)	O(1)–Ge(5)–O(10)^b	91.5(4)
O(7)–Ge(2)–O(3)	112.7(5)	O(6)–Ge(5)–O(10)	89.1(4)
O(7)–Ge(3)–O(8)	119.4(5)	O(6)^b–Ge(5)–O(10)	90.9(4)
O(7)–Ge(3)–O(9)	122.2(5)	O(1)^b–Ge(5)–O(10)	91.5(4)
O(8)–Ge(3)–O(9)	117.3(5)	O(1)–Ge(5)–O(10)	88.5(4)
O(7)–Ge(3)–O(2)^c	90.2(4)	O(10)^b–Ge(5)–O(10)	180
O(8)–Ge(3)–O(2)^c	96.0(4)	O(4)–Co(1)–N(2)	101.8(5)
O(9)–Ge(3)–O(2)^c	94.5(4)	O(4)–Co(1)–N(3)	90.9(6)
O(7)–Ge(3)–O(10)	89.1(4)	N(2)–Co(1)–N(3)	155.0(6)
O(8)–Ge(3)–O(10)	91.3(4)	O(4)–Co(1)–N(1)	168.6(5)
O(9)–Ge(3)–O(10)	79.2(4)	N(2)–Co(1)–N(1)	82.3(6)
O(2)^c–Ge(3)–O(10)	172.1(4)	N(3)–Co(1)–N(1)	89.4(7)
O(11)–Ge(4)–O(9)	123.3(5)	O(4)–Co(1)–O(8)^d	88.4(3)
O(11)–Ge(4)–O(4)	116.7(4)	N(2)–Co(1)–O(8)^d	85.6(4)
O(9)–Ge(4)–O(4)	120.0(5)	N(3)–Co(1)–O(8)^d	73.2(6)
O(11)–Ge(4)–O(5)^a	93.7(4)	N(1)–Co(1)–O(8)^d	102.6(5)
O(9)–Ge(4)–O(5)^a	91.5(4)	O(4)–Co(1)–O(5)^d	70.2(3)
O(4)–Ge(4)–O(5)^a	87.4(4)	N(2)–Co(1)–O(5)^d	95.0(4)
O(11)–Ge(4)–O(10)	95.5(4)	N(3)–Co(1)–O(5)^d	109.7(6)
O(9)–Ge(4)–O(10)	81.2(4)	N(1)–Co(1)–O(5)^a	99.0(5)
O(4)–Ge(4)–O(10)	90.9(4)	O(8)^d–Co(1)–O(5)^a	158.3(4)

Symmetry transformations used to generate equivalent atoms:
^{a} $x - 1/2, -y + 1/2, -z + 1$.
^{b} $-x + 1, -y, -z + 1$.
^{c} $x, -y + 1/2, z - 1/2$.
^{d} $x, -y + 1/2, z + 1/2$.

disordered atoms) and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out using the SHELXTL-PLUS [19] suit of programs. Details of the final refinements are given in Table 2. The final atomic coordinates, selected bond distances and bond angles are given for **I** in Tables 3–5.

3. Results and discussion

The structure of $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$, **I**, is constructed from hour-glass-like Ge_9 clusters. The clusters are connected in such a way as to form intersecting three-dimensional channels. The Co–en complex is grafted inside the channel and balances the charge, besides stabilizing the channel. The structure is analogous to $[Zn_2Ge_9O_{18}(OH)_4] \cdot 3(NH_2(CH_2)_2NH_2)$ [12] but with certain differences discussed later.
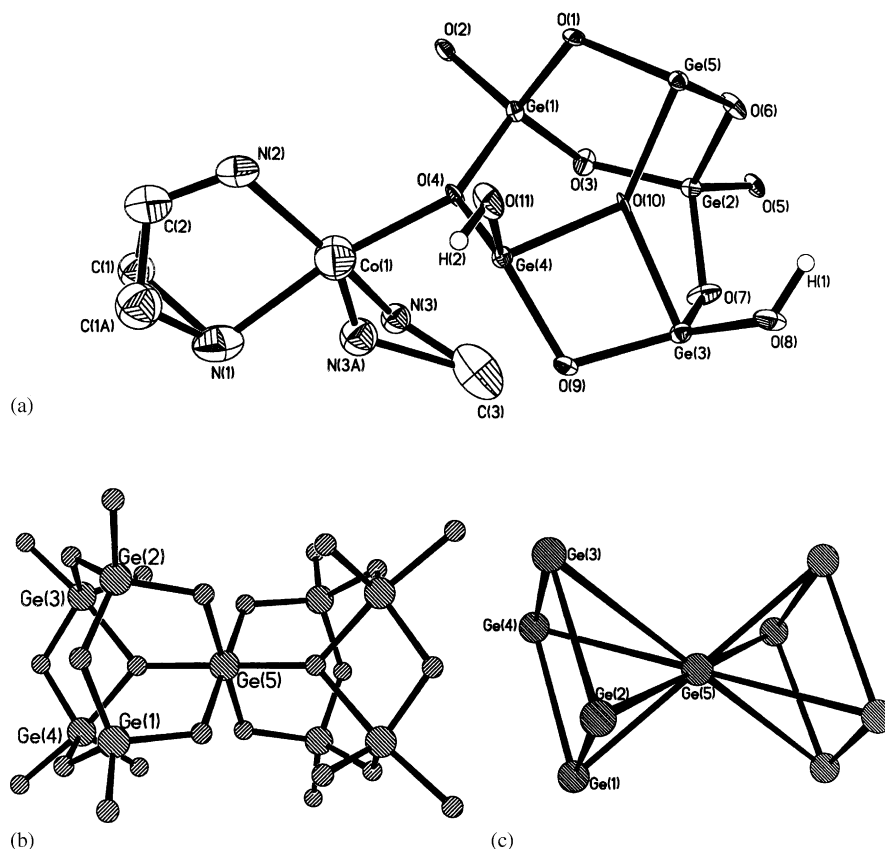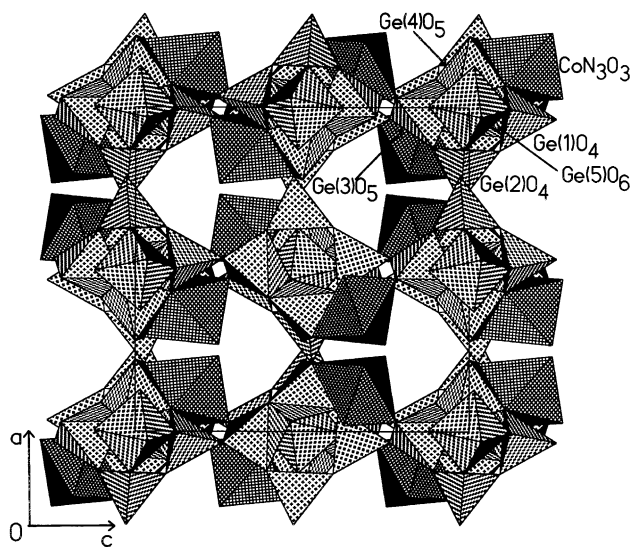
Fig. 1. ORTEP plot of **I**. The asymmetric unit is labeled and thermal ellipsoids given at 50% probability: (a) ball and stick representation of the hour-glass-like Ge_9O_{18} cluster and (b) the T atom (Ge sites) connectivity of the Ge_9 hour-glass-like cluster.
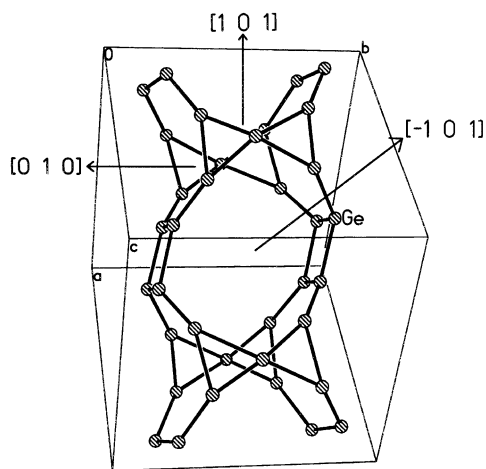
The asymmetric unit of **I** contains 23 non-hydrogen atoms, out of which 17 atoms (5 Ge, 1 Co, 11 O) belong to the inorganic framework and six belongs to the organic ligand (3 C and 3 N), which constitutes a full fragment of bis-chelated en and half of end-to-end connected en (Fig. 1(a)). There is disorder in one of the C (C1) and N (N3) sites in the chelated and end-to-end en, respectively. There are five crystallographically distinct Ge atoms and one Co atom. Ge(1) and Ge(2) have nearly regular tetrahedral coordination, while Ge(3) and Ge(4) have slightly distorted trigonal bipyramidal coordination of oxygen neighbors, one of them being a terminal –OH group (O11). Ge(5), on the other hand, is located at the inversion center and adopts an octahedral coordination. The Ge–O distances in the tetrahedral Ge sites are in the range 1.718(9)–1.775(9) Å [$(Ge(1)–O)_{av}$ = 1.748 and $(Ge(2)–O)_{av}$ = 1.757 Å], for the trigonal bipyramidal Ge sites the range is 1.758(10)–2.039(9) Å [Ge(3/4)–O = 1.84 Å], and for the octahedral site the range is 1.873(3)–1.9011(8) Å [avg = 1.889 Å]. So the Ge–O distances vary in the order $(Ge–O)_{Td}$ < $(Ge–O)_{tbp}$ < $(Ge–O)_{Oh}$, which is in general agreement with those observed in similar compounds [6,20]. The Co site on the other hand adopts a very distorted octahedral coordination with three framework oxygen atoms and three nitrogen atoms from two types of en

molecules. Out of the three Co–O distances, two are rather long [Co(1)–O(8) = 2.282(9), Co(1)–O(5) = 2.318(9)]. One of these (O8) belong to the bridging hydroxide group. Co–N distances on the other hand are regular, though one of the nitrogens bonded to Co is disordered. Bond valence calculations [21] indicate that all the Ge atoms are in the +4 state while Co is in the +2 state, giving rise to the formula $[Co_2(NH_2(CH_2)_2NH_2)_3][Ge_9O_{18}(OH)_4]$.

The tetrahedral Ge sites [Ge(1) and Ge(2)] and the trigonalbipyramidal (tbp) Ge sites [Ge(3) and Ge(4)] are linked to each other to form a four-membered Ge_4 unit. In the four-membered ring, only the tbp $GeO_4(OH)$ units are edge-shared between themselves, while rest of the connectivities are corner-shared. Two such Ge_4 units are linked by the $Ge(5)O_6$ octahedra and related by an inversion center, resulting in the hour-glass-like Ge_9 cluster building unit as shown in Figs. 1(b) and (c). In the cluster, the Ge_4 units are connected to the center through the utilization of both bi- and tri-connected oxygens, thereby creating six three-membered rings. Three-membered rings are characteristic of open-framework germanates [3,13]. In each Ge_9 cluster, excepting the terminal –OH (O11–H) and the bridging –OH (O8–H) groups, the remaining oxygen atoms at the corners links to eight neighboring Ge_9 cluster, thus
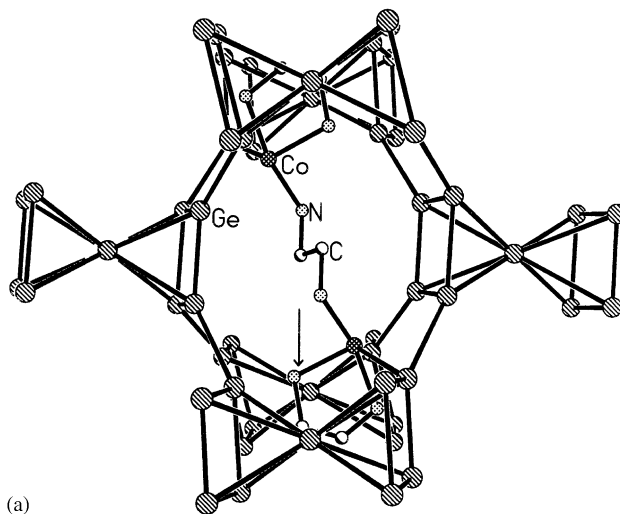
(a)

be seen from Fig. 3(a). Apart from this, the Co atom is connected to the framework through O(4), O(5) and O(8)(–H) oxygens, out of which O(4) and O(5) are involved in inter- and intra-cluster binding. O(8)H is only used to solely connect the Co-site. The distorted Co octahedron partially blocks the channel along the *b*-axis as can be seen form Fig. 2(a), while there is reasonable free space along the [101] and [−101] directions (Fig. 3(b)). Only Co–O(4) connectivity is strong, while Co–O(5) and Co–O(8)H connectivities are weak. These connections are different from those in the Zn-analog [12]. In the Zn-analog, the O(8)H hydroxyl group remains terminal to the Ge-site and does not form a bond with Zn (Zn–OH = 2.7 Å). The presence of the Co-complex grafted on to the channels of the frame-

(b)

Fig. 2. (a) Polyhedral arrangement of the structure of **I** along the *b*-axis, showing the eight-membered channel. Partial blocking of the eight-membered channel by Co-octahedra is also shown. Amine molecules are omitted for clarity and (b) T atom (Ge sites) connectivity showing the openings of the eight- and ten-membered intersecting channels from different directions.

forming an open-framework structure with intersecting three-dimensional channels. The long axis of the Ge_9 cluster is aligned with the *b*-axis and create an eight-membered ring channel as shown in Fig. 2(a), while it creates a ten-membered channel along [101] and [−101] directions [Fig. 2(b)].

The Co atom does not participate in the construction of the framework, but the amine plays a dual role. Between the two types of en molecules, which bind to the Co site, one acts as a bis-bidentate chelating agent and protrudes into the eight-membered channel and the other connects the two Co sites (one symmetrically generated) in a end-to-end fashion (Co–N–C–C–N–Co), acting as a pillar inside the ten-membered channel as can

(a)

(b)

Fig. 3. (a) The pillaring role of the end-to-end connected en molecule in the ten-membered tunnel has been shown. Arrow indicates the complex in the eight-membered channel and (b) T atom (Ge sites) connectivity in the structure of **I** along the [101] direction showing the ten-membered channel. The Co-amine complex has been removed for clarity.
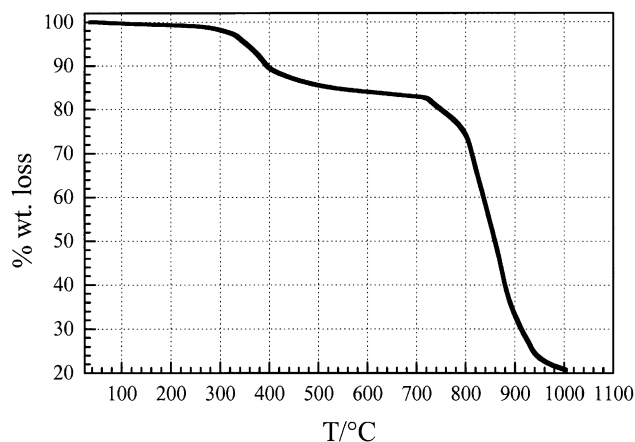
Fig. 4. TGA curve of **I**.

work in **I** can be taken as an example of a metal coordintaion complex-grafted microporous material.

There are other interesting features in **I**. The hourglass-like cluster unit is versatile and has been observed previously in $[Ge_{18}O_{38}(OH)_4][(C_2N_2H_{10})_4] \cdot 2H_2O$ (2), and $[Ge_9O_{18}(OH)_4] \cdot [(C_4N_2H_{12})_2] \cdot 0.5H_2O$ (ASU-14) (6). In $Ge_{18}O_{38}(OH)_4^{-8}$, the two terminal –OH groups condense to form a bridging oxide that links two Ge_4 units in the same Ge_9 cluster. In ASU-14, the inter-cluster connectivities are similar to **I**, except that there are four terminal –OH groups in the Ge_9 unit. A significant finding is the isolation of individual Ge_9 cluster in the supramolecular assembly of $[C_4N_4H_{12}][Ge_9O_{14}(OH)_{12}] \cdot 14H_2O$ by Tripathi et al. [20] where all the terminal oxygens are dangling –OH groups. This provides definitive evidence for the existence of such isolated clusters in the solution phase and the likely build-up of the framework structure by the polycondensation of such clusters according to the concept of scale chemistry of Ferey [22].

TGA carried out in flowing nitrogen (commercial grade) at a heating rate of $10°C\,min^{-1}$ from 25–1000°C indicates two major mass loses in the regions 300–400°C and 720–950°C (Fig. 4). The first step corresponds to the loss of three en molecules and two water molecules (calc. = 16.5%, obs. = 16.6%), leading to the collapse of the framework. The second huge mass loss (62%) can be assigned to the removal of the volatile germanium oxide phases. Pxrd of the remaining annealed sample at 1000°C revealed Ge metal (JCPDS file, card no.: 04–0545) and CoO (JCPDS file, card no.: 42–1300). EDAX analysis also showed the presence of Ge and Co in the annealed product.

4. Conclusions

The synthesis of an organically templated open-framework cobalt germanate has been accomplished by the solvo/hydrothermal method. The germanate formed by Ge_9O_{18} clusters has eight- and ten-membered channels with the cobalt amine complex protruding in the eight-membered channels. This germanate may be considered to be an example of a metal complex-grafted microporous solid.

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