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Hydrothermal Synthesis and Characterization of Chabazite-Type Cobaltoaluminophosphate with an Encapsulated Cobalt Complex: $Co_3Al_3(PO_4)_6Co(DETA)_2 \cdot (H_2O)_3$

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A chabazite-type cobaltoaminophosphate containing mixed-valence Co atoms with the encapsulated cobalt complex $Co_3Al_3(PO_4)_6Co(DETA)_2 \cdot 3(H_2O)$ (DETA, diethyltriamine) has been hydrothermally synthesized and structurally determined. The compound with a chabazite structure crystallizes in the rhombohedral space group $R\bar{3}$ with $a = 13.792(2)$ Å, $c = 14.997(4)$ Å, $V = 2470.6(9)$ Å^3, and $Z = 2$. The negative open framework contains $Co^{II}O_4$ units and is disordered with AlO_4 units in the same position. The charge-balancing cations, $[Co(DETA)_2]^{3+}$, are located in the big cages. The compound was characterized by infrared spectroscopy, diffuse reflectance spectrocopy, X-ray photoelectron spectroscoy, and differential thermal analyses thermogravimetry. The results show that the compound can exist up to 300°C in N_2. © 1999 Academic Press

Key Words: **chabazite-type; cobaltoaluminophosphate; encapsulation; zeolite.**

INTRODUCTION

Zeolites are materials with uniform pores which are applied in many fields such as separation and purification of gases, ion exchange, and catalysis. A recently increasing trend in the fields of catalysis, semiconductors, and related processes (1, 2) is the preparation of host–guest compounds with zeolites as the matrix. These compounds were prepared by ship-in-bottle, dispersion, or synthesis *in situ* processes, for example, MOR and AFI zeolites with BiI_3 (3), zeolite Y with enclosed $[Cu(His)_2]^+$ ions (4), and other zeolites with guest species (5–7). Very recently, some zeolites with an encapsulated cobalt complex were also investigated such as clathrasils with $[Co^{III}(\eta^5\text{-}C_5H_5)_2]^+$ and aluminum phosphates with $[Co(en)_3]^{3+}$, $[Co(tn)_3]^{3+}$, and $[Co(DETA)_2]^{3+}$ (DETA, diethyltriamine) (8–12). Although the most synthesized compounds containing these cobalt complex ions are almost layered phosphates with similar structures (10–12), the successful synthesis of v-$Co(en)_3[H_3Ga_{2-x}Al_xP_4O_{16}]$, which has a chiral three-dimensional (3D) structure (13), gives enlightenment on how to prepare chiral structure.

The framework of chabazite, a natural silicoaluminate having ion-exchanged properties (14), consists of double six-rings building units and ellipsoidal cages which share eight-rings to generate a three-dimensional channel system. Aluminophosphate or silicoaluminophosphate with the chabazite-type framework has also been synthesized using cyclohexylamine, tetraethylammonium, or 1,4-methylbutylammonium as a structure-directing agent (15–17). So far, there is no reported example of phosphates containing a cobalt complex with an open framework. Although the ellipsoidal cages of chabazite-type zeolites are not the biggest ones among zeolites, we have successfully synthesized cobaltoaluminophosphate with a chabazite-type structure containing $[Co^{III}(DETA)_2]^{3+}$ ions in the ellipsoidal cages.

EXPERIMENTAL

Synthesis and Methods

All starting materials purchased were reagent grade. The compound $Co_3Al_3(PO_4)_6Co(DETA)_2 \cdot (H_2O)_3$ was synthesized by a hydrothermal reaction. A mixture of $Al(OH)_3$, $CoCl_2 \cdot 6H_2O$, 85% phosphoric acid, diethyltriamine (DETA), NaOH, and water with an initial composition in the molar ratio Al_2O_3:(1–4)Co_2O_3:(3–5)P_2O_5: (3–10)DETA: (1–5)Na_2O:(100–200)H_2O was sealed in a Teflon-lined autoclave and heated at 140°C for 3 days under autogenous pressure. The crystal product was filtered, washed with distilled water, and dried at ambient temperature.

The elemental analysis was performed on a PE 240C elemental analyzer. The infrared spectrum (IR) was recorded on a Nicolet FT-170 SX Fourier spectrophotometer with pressed KBr Pellets. The Al, Co, and P components of the product were determined with inductively coupled plasma (ICP) on a Perkin–Elmer 40 plasma emission

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spectrometer. Simultaneous differential thermal analysis and thermogravimetric analysis (DTA–TG) were performed on a SDT 2960 simultaneous DTA–TG thermal analysis instrument with a heating rate of 10°C/min in flowing N_2. UV–vis diffuse reflectance spectra (DRS) were recorded and UV-240 UV–visible recording spectrophotometer with MgO as the background. X-ray photoelectron spectroscopy (XPS) was carried out on ESCALab MK2 with Al*K*α radiation, and the binding energy (BE) was corrected with CIS (BE = 285 eV).

Crystallography

A black crystal with the size $0.4 \times 0.3 \times 0.3$ mm was selected from the product for indexing and intensity data collection at 293(2) K on a Siemens P4 four-circle diffractometer with monochromatic Mo*K*α ($\lambda = 0.71073$ Å) radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the data of 33 reflections in the range $5^\circ \leq \theta \leq 9^\circ$, preferring a rhombohedral cell. Intensity data were collected using the θ–2θ scan mode with a variable scan speed of 5–55°/min in ω. The data were corrected for Lorentz polarization effects during data reduction using XSCANS (18). An empirical absorption correction based on Ψ-scan measurements was applied.

The structure was solved by the direct method and refined on F^2 by full-matrix least-squares using SHELXTL (19). Al and Co1, which were disordered in the same position, were dealt with by refining with a free variable, in which FVAR = 0.47417 was obtained, and then fixing the same thermal parameters and site occupation factors (i.e., 0.5) and combining the results of elemental analysis. The C1 and C2 atoms of diethylenetriamine, which were disordered, were assigned equal occupancies of the possible positions, and the remaining occupancy of the space was assigned to water. All the nonhydrogen atoms were refined anisotropically. The hydrogen atoms of DETA were placed in calculated positions (C–H = 0.96 Å; N–H = 0.90 Å), and the disordering hydrogen atoms of N were dealt with by fixing their site occupation factors to certain positions. The hydrogen atoms of water were found in the Fourier-difference map. All the hydrogen atoms were assigned fixed isotropic thermal parameters 1.2 times those of the atoms to which they are attached. The contributions of these hydrogen atoms were included in the structure-factor calculations. In the final Fourier-difference map the deepest hole was -0.740 e Å^{-3} and the highest peak 0.701 e Å^{-3}.

All computations were carried out on a PC-586 computer using the SHELXTL package. Analytical expressions for neutral-atom scattering factors and anomalous dispersion corrections were incorporated (20). Details of the data collection and structure refinement can be found in Table 1. Atom positions are listed in Table 2, and some selected distances and angles are given in Table 3. Anisotropic temperature factors of the atoms are listed in Tables 4 and 5.

TABLE 1
Crystal Data and Structure Refinement for 1

Identification code	*xyh*2
Empirical formula	$C_8H_{32}Al_3Co_4N_6O_{27}P_6$
Formula weight	1146.88
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	$R\bar{3}$
Unit cell dimensions	$a = 13.792(2)$ Å, $\alpha = 90^\circ$
	$b = 13.792(2)$ Å, $\beta = 90^\circ$
	$c = 14.997(4)$ Å, $\gamma = 120^\circ$
Volume, Z	2470.6(9) Å^3, 3
Density (calculated)	2.313 Mg/m^3
Absorption coefficient	2.464 mm^{-1}
$F(000)$	1725
Crystal size	$0.40 \times 0.30 \times 0.30$ mm
θ Range for data collection	2.18 to 27.47°
Limiting indices	$-1 \leq h \leq 16$, $-17 \leq k \leq 1$, $-1 \leq l \leq 19$
Reflections collected	1638
Independent reflections	1247 ($R_{int} = 0.0700$)
Absorption correction	Semiempirical from psi scans
Max. and min. transmission	0.5788 and 0.4338
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1244/0/95
Goodness-of-fit on F^2	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0580$, w$R_2 = 0.1532$
R indices (all data)	$R_1 = 0.0803$, w$R_2 = 0.1740$
Largest diff. peak and hole	0.701 and -0.740 eÅ^{-3}

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$

w$R_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]]^{1/2}$

RESULTS AND DISCUSSION

Formation and Composition

In hydrothermal synthesis, the product was sensitively influenced by the pH value of the system. In the system $0.5Al_2O_3$:CoO:$2P_2O_5$:2DETA:$100H_2O$, NaOH solution was used to adjust the pH value. When the pH was 5, the product was an amorphous phase. When the pH was 6, the product was a mixture of an amorphous phase, black crystals (title compound), and yellow plate crystals, which were the same layered compound as that reported in the literature (10). When the pH was 7, the product was a mixture of black crystals and yellow plate crystals. When the pH was 8, the product was a mixture of a few yellow plate crystals and more yellow balls. Under different conditions, the appearance of the title compound was different and usually irregular. By carefully controlling the pH at 6–7, the title compound could be obtained with regular appearance. In this synthesis process, Co^{II} was oxidized and formed the $[Co(DETA)_2]^{3+}$ ion, which may be caused by O_2 existing in the system.

TABLE 2
Atomic Coordinates [$\times 10^4$] and Equivalent Isotropic Displacement Parameters [Å$^2 \times 10^3$] for 1

	x	*y*	*z*	*U*(eq)
Co(2)	3333	− 3333	− 3333	34(1)
P	1091(1)	− 3218(1)	544(1)	29(1)
Al(1)	3437(1)	− 1002(1)	676(1)	34(1)
Co(1)	3437(1)	− 1002(1)	676(1)	34(1)
O(1)	160(3)	− 3337(3)	− 55(3)	71(1)
O(2)	758(3)	− 3216(3)	1502(2)	59(1)
O(3)	1319(3)	− 4161(3)	365(3)	66(1)
O(4)	2106(4)	− 2131(3)	303(3)	78(2)
N(1)	2051(4)	− 3700(4)	− 2539(3)	65(1)
C(1)	1997(10)	− 4547(9)	− 1832(8)	98(4)
C(2)	2346(9)	− 2645(9)	− 1997(8)	106(4)
O(2W)	1796(12)	− 5591(12)	− 1620(10)	96(5)
O(1W)	3333	− 3333	1667	213(11)

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

The elemental analysis revealed that the C, H, and N contents were 8.35, 3.51, and 7.25; ICP analysis results showed that the Co, Al, and P components were 20.3, 6.13, and 13.3, so that the formula $Co_3Al_3(PO_4)_6Co(DETA)_2 \cdot 3H_2O$, which has C 8.38, N 7.33, H 2.81, Al 7.06, Co 20.55, and P 16.20, is prefered. That the (Al + Co)/P ratio is greater than 1:1 is attributed to the cobalt-containing complexes in the cages.

The infrared spectrum of the compound also shows the characteristics of a phosphate-containing amine.

DRS and XPS

The UV–vis diffuse reflectance spectrum (DRS) of the product (Fig. 1) shows four absorption peaks lying at 400–500, 480–550, 550–600, and 600–680 nm, respectively. The latter three absorption peaks, which are ascribed to *d–d* absorption bands of four-coordinated Co^{II}, are similar to that of Co-NJU-1 which contains tetrahedral $Co^{II}O_4$. This is in agreement with the results shown in the literature (21), indicating that the title compound contains a tetrahedral $Co^{II}O_4$ unit in the framework. The peak between 400 and 500 nm, which is referred to *d–d* electron transference in six-coordinated Co^{III}, is similar to that of $Co(en)_3Cl_3 \cdot xH_2O$. This indicates that the title compound contains six-coordinated Co^{III} species.

Although the starting reaction material is Co^{II} species, the reaction vessel contains oxygen, and when the complexes are formed by the reaction of Co^{II} ions with DETA, the Co^{II} species is oxidized into Co^{III} species.

The XPS spectrum of the compound shows that there are two kinds of Co atom with BE = 781.5 and 782.75 eV, which are attributed to $2P_{3/2}$ of Co^{II} and Co^{III}, respectively. This is in agreement with the DRS result.

Crystal Structure

The results of single-crystal X-ray diffraction analysis show that the compound crystallizes in the rhombohedral space group $R\overline{3}$ with $a = 13.792(2)$ Å, $c = 14.997(4)$ Å, $V = 2470.6(9)$ Å^3, and $Z = 3$. The crystal cell is shown in Fig. 2. It is clear that its opening framework in three dimensions is analogous to that of chabazite (CHA).

TABLE 3
Bond Lengths (Å) and Angles (°) for 1

Co(2)–N(1)	1.976(4)	Co(2)–N(1)#1	1.976(4)
Co(2)–N(1)#2	1.976(4)	Co(2)–N(1)#3	1.976(4)
Co(2)–N(1)#4	1.976(4)	Co(2)–N(1)#5	1.976(4)
P–O(4)	1.497(3)	P–O(1)	1.507(4)
P–O(3)	1.508(4)	P–O(2)	1.508(3)
Al(1)–O(2)#6	1.800(3)	Al(1)–O(4)	1.803(4)
Al(1)–O(3)#1	1.814(4)	Al(1)–O(1)#7	1.820(4)
Co(1)–O(2)#6	1.800(3)	Co(1)–O(4)	1.803(4)
Co(1)–O(3)#1	1.814(4)	Co(1)–O(1)#7	1.820(4)
O(1)–Co(1)#8	1.820(4)	O(1)–Al(1)#8	1.820(4)
O(2)–Co(1)#9	1.800(3)	O(2)–Al(1)#9	1.800(3)
O(3)–Co(1)#5	1.814(4)	O(3)–Al(1)#5	1.814(4)
N(1)–C(2)	1.534(11)	N(1)–C(1)	1.552(13)
C(1)–C(2)#5	1.36(2)	C(2)–C(1)#1	1.36(2)
N(1)–Co(2)–N(1)#1	87.5(2)	N(1)–Co(2)–N(1)#2	92.5(2)
N(1)#1–Co(2)–N(1)#2	92.5(2)	N(1)–Co(2)–N(1)#3	92.5(2)
N(1)#1–Co(2)–N(1)#3	180.0	N(1)#2–Co(2)–N(1)#3	87.5(2)
N(1)–Co(2)–N(1)#4	180.0	N(1)#1–Co(2)–N(1)#4	92.5(2)
N(1)#2–Co(2)–N(1)#4	87.5(2)	N(1)#3–Co(2)–N(1)#4	87.5(2)
N(1)–Co(2)–N(1)#5	87.5(2)	N(1)#1–Co(2)–N(1)#5	87.5(2)
N(1)#2–Co(2)–N(1)#5	180.0	N(1)#3–Co(2)–N(1)#5	92.6(2)
N(1)#4–Co(2)–N(1)#5	92.6(2)	O(4)–P–O(1)	106.5(2)
O(4)–P–O(3)	109.1(3)	O(1)–P–O(3)	109.5(2)
O(4)–P–O(2)	111.2(2)	O(1)–P–O(2)	109.0(2)
O(3)–P–O(2)	111.5(2)	O(2)#6–Al(1)–O(4)	113.7(2)
O(2)#6–Al(1)–O(3)#1	114.8(2)	O(4)–Al(1)–O(3)#1	108.5(2)
O(2)#6–Al(1)–O(1)#7	105.1(2)	O(4)–Al(1)–O(1)#7	100.3(2)
O(3)#1–Al(1)–O(1)#7	113.6(2)	O(2)#6–Co(1)–O(4)	113.7(2)
O(2)#6–Co(1)–O(3)#1	114.8(2)	O(4)–Co(1)–O(3)#1	108.5(2)
O(2)#6–Co(1)–O(1)#7	105.1(2)	O(4)–Co(1)–O(1)#7	100.3(2)
O(3)#1–Co(1)–O(1)#7	113.6(2)	P–O(1)–Co(1)#8	138.0(3)
P–O(1)–Al(1)#8	138.0(3)	P–O(2)–Co(1)#9	146.5(3)
P–O(2)–Al(1)#9	146.5(3)	P–O(3)–Co(1)#5	145.9(3)
P–O(3)–Al(1)#5	145.9(3)	P–O(4)–Co(1)	145.9(3)
P–O(4)–Al(1)	145.9(3)	C(2)–N(1)–C(1)	104.0(7)
C(2)–N(1)–Co(2)	107.4(5)	C(1)–N(1)–Co(2)	107.8(5)
C(2)#5–C(1)–N(1)	115.7(8)	C(1)#1–C(2)–N(1)	113.5(9)

Note. Symmetry transformations used to generate equivalent atoms: #1, $-x+y+1, -x, z$; #2, $y+\frac{2}{3}, -x+y+\frac{1}{3}, -z-\frac{2}{3}$; #3, $x-y-\frac{1}{3}, x-\frac{2}{3}, -z-\frac{2}{3}$; #4, $-x+\frac{2}{3}, -y-\frac{2}{3}, -z-\frac{2}{3}$; #5, $-y, x-y-1, z$; #6, $y+\frac{2}{3}, -x+y+\frac{1}{3}, -z+\frac{1}{3}$; #7, $x-y, x, -z$; #8, $y, -x+y, -z$; #9, $x-y-\frac{1}{3}, x-\frac{2}{3}, -z+\frac{1}{3}$.

TABLE 4
Anisotropic Displacement Parameters [Å^2× 10^3] for 1

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co(2)	41(1)	41(1)	18(1)	0	0	21(1)
P	31(1)	30(1)	20(1)	0(1)	− 4(1)	10(1)
Al(1)	32(1)	39(1)	22(1)	4(1)	0(1)	10(1)
Co(1)	32(1)	39(1)	22(1)	4(1)	0(1)	10(1)
O(1)	70(2)	87(2)	58(2)	2(2)	− 29(2)	41(2)
O(2)	75(2)	77(2)	27(1)	− 1(1)	7(2)	40(2)
O(3)	83(2)	57(2)	69(2)	− 5(2)	3(2)	44(2)
O(4)	72(3)	53(2)	55(2)	19(2)	− 2(2)	− 8(2)
N(1)	54(2)	104(3)	41(2)	3(2)	11(2)	44(2)
C(1)	102(7)	75(6)	86(6)	34(5)	54(6)	22(5)
C(2)	97(6)	118(7)	93(7)	− 52(6)	25(6)	47(6)
O(2W)	82(9)	74(9)	87(9)	26(7)	− 11(8)	7(7)

Note. The anisotropic displacement factor exponent takes the form $-2\pi^2[(ha^*)^2U_{11} + \cdots + 2hka^*b^*U_{12}]$.

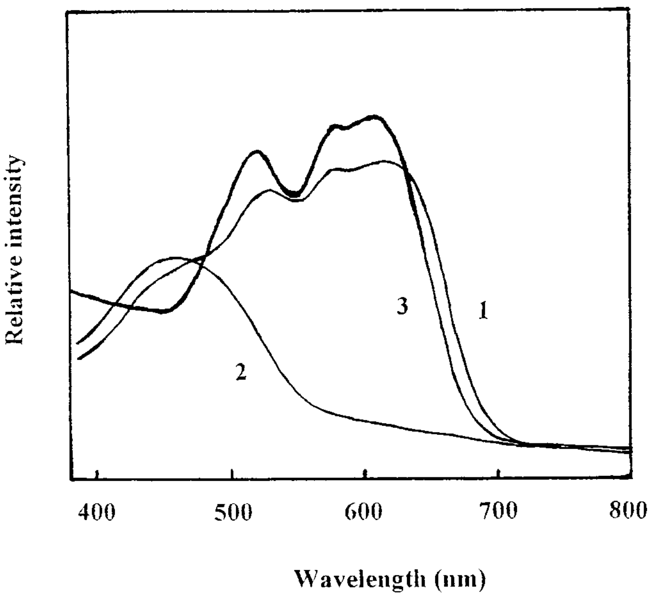

FIG. 1. The DRS of the compound (1) $Co_3Al_3(PO_4)_6Co(DETA)_2 \cdot 3H_2O$, (2) $Co(en)_3Cl_3 \cdot xH_2O$, and (3) Co-NJU-1.

The CHA framework is composed of double six-membered rings stacked in the sequence AABBCC. There are two kinds of cages: the smaller cages are formed by double six-membered rings and the bigger ones, which are bounded by eight-membered rings and four-membered rings, are formed by the smaller stacking. In this compound, Al and Co^{II} are disordered in the same position in the framework with Al/Co = 1. The ratio *T*(Al + Co):P is 1:1, so the framework is negative. One molecule of water is located in the double six-membered ring cage, and in the bigger cage two molecules of water and one $[Co(DETA)_2]^{3+}$ ion are located, which is in charge balance with the negative framework. There are only one kind of N atom and two kinds of C atoms in crystallography (Table 2), so DETA is disordered in the cage. Four C atoms of DETA occupy four of six possible positions in the cage at random, and the remaining space is occupied by water. The terminal N atoms of DETA are hydrogen-bonding with water with a O···H–N distance of 2.802 Å. If the water is nearby, they are also hydrogen bonding together with a O···H–O distance of 2.954 Å. So the cobalt complexes and water are linked together by a hydrogen bond in the channels of the compound.

There are two kinds of Co atoms in the compound: Co^{II} is in the negative framework and Co^{III} coordinated with DETA is in the bigger cage. So the compound contains mixed-valence Co atoms.

TABLE 5
Hydrogen Coordinates (×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1

	x	*y*	*z*	*U* (eq)
H (1E)	2204(4)	− 3068(4)	− 2250(3)	78
H(1D)	1989(4)	− 4231(4)	− 2157(3)	78
H(1C)	1385(4)	− 3957(4)	− 2810(3)	78
H(1A)	2215(10)	− 4169(9)	− 1260(8)	117
H(1B)	1226(10)	− 5145(9)	− 1780(8)	117
H(2A)	2090(9)	− 2205(9)	− 2319(8)	127
H(2B)	1947(9)	− 2866(9)	− 1434(8)	127
H(2WB)	1179(12)	− 6158(12)	− 1772(10)	115
H(2WA)	1680(12)	− 5044(12)	− 1561(10)	115
H(1WA)	2863	− 3107	1681	255

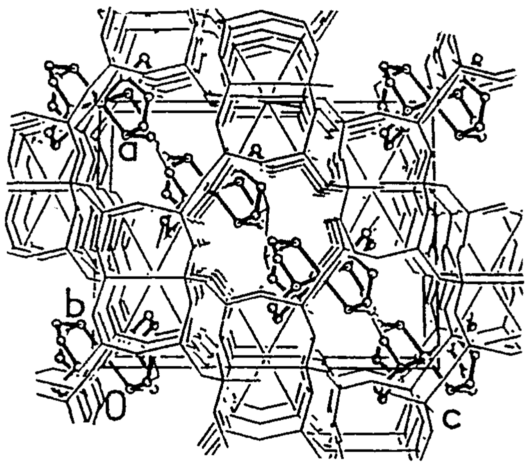

FIG. 2. The crystal cell of the title compound (water and DETA, which has four carbon atoms in six positions, are disordered).

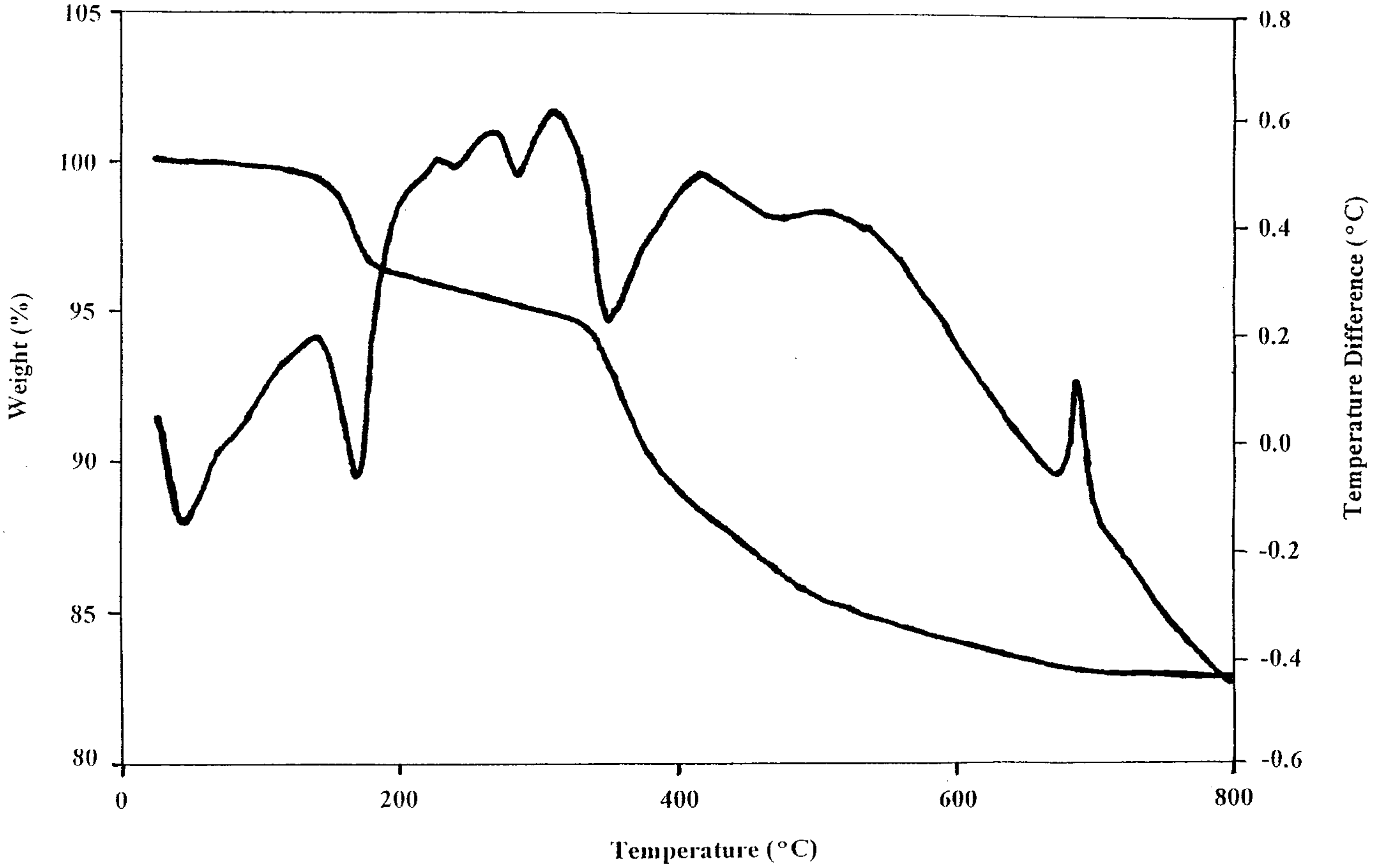

FIG. 3. The DTA–TG curves of the title compound (in N_2 flow).

Thermal Properties

DTA and TG curves (Fig. 3) show that there are five endothermic peaks and one exothermal peak with two-stage weight losses. The first-stage weight loss of about 4.8 wt% between 100 and 300°C with three endothermic peaks at 170, 241, and 287°C is attributed to the absorption of water. The second-stage weight loss of 11.8 wt% with two endothermic peaks at 353 and 472°C is attributed to the decomposition of the cobalt complexes and partial loss of the amine. The exothermic peak at 687°C with no weight change is ascribed to the phase transition of the compound. The amine decomposed at high temperature and the carbon formed in this process was partly left in the solid, so the weight loss value is lower than that of the theoretical calculation. The calculated weight losses are 4.7 and 17.9 wt%, respectively. The reactions of the compound below 550°C may be as follows:

(1) $Co_3Al_3(PO_4)_6Co(DETA)_2 \cdot 3H_2O \rightarrow Co_3Al_3(PO_4)_6Co(DETA)_2 + 3H_2O$ 170°C

(2) $Co_3Al_3(PO_4)_6Co(DETA)_2 \rightarrow Co_4Al_3(PO_4)_6 + 2DETA$ 353°C.

CONCLUSION

The microporous cobalt aluminum phosphate with mixed-valence cobalt, $Co_3Al_3(PO_4)_6Co(DETA)_2 \cdot 3H_2O$, consisting of an open chabazite-type framework, has been hydrothermally synthesized. The product is sensitively influenced by the pH value of the system. The cobalt complex ions with Co^{III} lie in the ellipsoidal cages and DETA is disordered by water. The compound can exist stably at high temperatures up to 300°C.

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