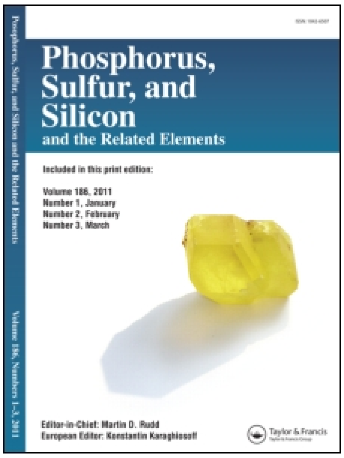

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The Synthesis and Characterization of a New Cobalt Dimethylphenylpiperazinium Cyclotetraphosphate Hexahydrate, $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$

Z. Aloui[a]; S. Abid[a]; M. Rzaigui[a]
[a] Faculté des Sciences de Bizerte, Laboratoire de Chimie des Matériaux, Zarzouna, Bizerte, Tunisie

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The Synthesis and Characterization of a New Cobalt Dimethylphenylpiperazinium Cyclotetraphosphate Hexahydrate, $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$

Z. Aloui
S. Abid
M. Rzaigui
Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte,
Zarzouna, Bizerte, Tunisie

Cobalt dimethylphenylpiperazinium cyclotetraphosphate hexahydrate, $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$, was synthesized by a reaction between cyclotetraphosphoric acid $H_4P_4O_{12}$, cobalt carbonate, and 1-(2,4-dimethylphenylpiperazine). It crystallizes in the triclinic system, space group $P\bar{1}$, with the following unit cell parameters: $a = 7.336(1)$, $b = 8.413(1)$, $c = 14.926(2)$ Å, $\alpha = 87.46(1)$, $\beta = 83.13(1)$, $\gamma = 82.98(1)^\circ$, $V = 907.3(2)$ Å^3, and $Z = 1$. The atomic arrangement can be described as layers containing P_4O_{12} rings a and $Co(H_2O)_6$ octahedra spreading in the (001) planes between which are located the dimethylphenylpiperazinium groups via H-bonds. The synthesis and characterization by X-ray diffraction, IR absorption, and thermal analysis are described.

Keywords Cyclotetraphosphate; hydrogen bonds; IR spectroscopy; layered compounds; X-ray diffraction

INTRODUCTION

The interest in metal-phosphate materials has been continuously growing because of their potential applications in catalysis, adsorption, ionic conduction, ion exchange, and electronic and opto-electronic.[1] Nevertheless, a bibliographical study on the metal organic condensed phosphate, and especially on the metal cyclotetraphosphate associated with an organic cation, reveals that this field remains practically unexplored. As a contribution to the elaboration of this compound family, we report in the present work the synthesis and the characterization of the first metal cyclotetraphosphate with aromatic cations $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$. This organic–inorganic

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Address correspondence to S. Abid, Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, Zarzouna, Bizerte, 7021 Tunisie. E-mail: sonia.abid@fsb.rnu.tn

hybrid compound results from an interaction between cyclotetraphosphoric acid, cobalt carbonate, and the dimethylphenylpiperazine molecule. The selected organic molecule is a biogenic diamine, which plays an important role as a deprotonated cation in biological systems.[2,3]

RESULTS AND DISCUSSION

Crystal Structure

Final atomic coordinate and anisotropic displacement thermal parameters (B_{eq}) of all nonhydrogen atoms are given in Table I. An ORTEP drawing of a molecular structure contains 37 nonhydrogen atoms,

TABLE I Final Atomic Coordinates and B_{eq} (Å^2) for Nonhydrogen Atoms in $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$. Estimated Standard Deviations are Given in Parentheses

Atoms	x (σ)	y (σ)	z (σ)	B_{eq} (Å^2)
Co	0.0000	0.0000	0.0000	2.067(3)
P(1)	−0.52696(3)	−0.35291(3)	0.121552(15)	1.707(3)
P(2)	−0.39444(3)	−0.33220(2)	−0.073947(15)	1.613(3)
O(E11)	−0.71557(10)	−0.29958(9)	0.16358(5)	2.661(13)
O(E12)	−0.36311(10)	−0.30640(8)	0.15853(5)	2.550(12)
O(L12)	−0.52529(9)	−0.29726(9)	0.01769(5)	2.428(12)
O(L21)	−0.50442(9)	−0.45564(8)	−0.11806(5)	2.355(12)
O(E21)	−0.20972(8)	−0.41269(8)	−0.05562(5)	2.225(11)
O(E22)	−0.41057(10)	−0.18252(8)	−0.12934(5)	2.645(13)
OW1	0.13530(10)	−0.00217(9)	0.11456(6)	2.662(13)
OW2	−0.03892(10)	0.25108(8)	−0.00993(6)	2.783(13)
OW3	0.24787(10)	0.01756(10)	−0.08484(7)	3.385(15)
N(1)	0.83703(11)	0.31930(11)	0.37234(6)	2.460(14)
N(2)	0.93509(13)	0.48192(13)	0.20568(7)	3.411(18)
C(1)	0.76389(12)	0.25170(12)	0.45615(6)	2.321(16)
C(2)	0.69541(15)	0.34877(15)	0.52860(8)	2.979(19)
C(3)	0.63363(17)	0.27959(19)	0.61158(8)	3.74(2)
C(4)	0.63713(16)	0.11669(19)	0.62121(9)	3.92(2)
C(5)	0.70399(14)	0.01770(15)	0.54988(9)	3.40(2)
C(6)	0.77209(13)	0.08365(13)	0.46616(7)	2.668(17)
C(7)	0.71073(19)	−0.16147(18)	0.56394(13)	4.93(3)
C(8)	0.85715(17)	−0.02530(15)	0.39197(10)	3.50(2)
C(9)	0.73896(14)	0.30092(14)	0.29445(7)	2.692(18)
C(10)	0.86828(16)	0.32090(16)	0.20932(8)	3.32(2)
C(11)	0.88347(16)	0.48223(14)	0.37234(8)	2.988(19)
C(12)	1.01534(16)	0.51393(17)	0.28917(9)	3.62(2)

including 1 cobalt atom, 4 phosphorus atoms, 18 oxygen atoms, 12 carbon atoms, and 2 nitrogen atoms, as shown in Figure 1. The atomic arrangement of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$ can be described as a typical layers organization. The layers, built by P_4O_{12} rings and $Co(H_2O)_6$ polyhedron, are parallel to the (a, b) plane and are centred at $z = 0$. Organic cations are located in the space delimited by the successive inorganic layers (Figure 2).

The phosphoric ring anion is localized around the (1/2, 1/2, 0) inversion center. So this centrosymmetrical ring is built by only two independent PO_4 tetrahedra, $P(1)O_4$ and $P(2)O_4$. The two P-P-P angle values, (82.16(1)° and 97.84(1)°), show that this P_4O_{12} ring is strongly distorted. This distortion is comparable with that observed in $C_{10}H_{28}N_4P_4O_{12}.4H_2O$,[4] where the P-P-P angles, 80.24(5)° and 99.76(5)°, exhibit the greatest distortion measured up to now. It should

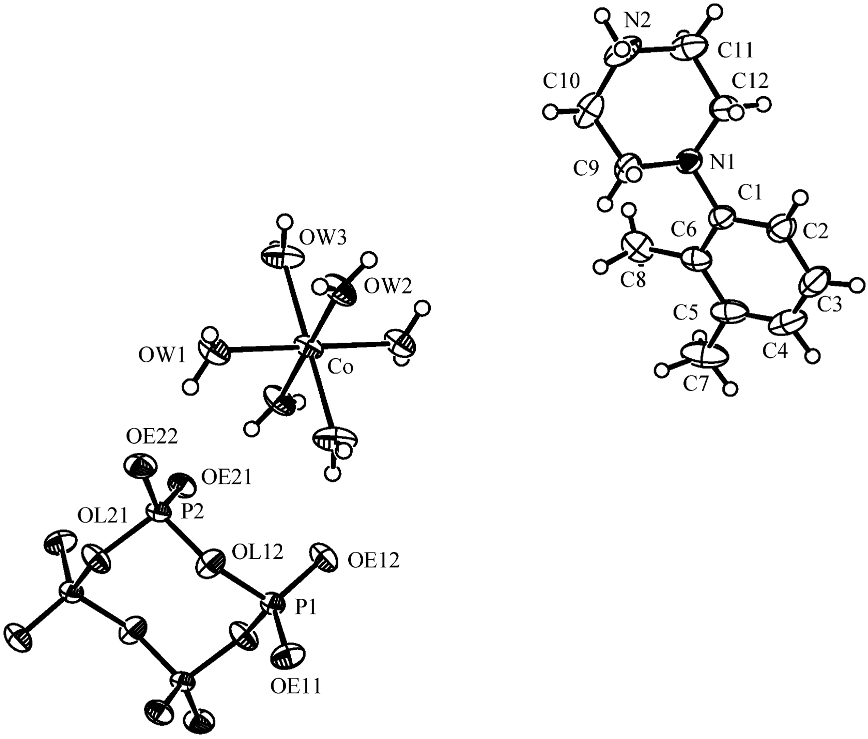

FIGURE 1 An ORTEP drawing of the molecular structure containing a $P_4O_{12}^{4-}$ ring, $Co(H_2O)_6$ octahedron, and dimethylphenylpiperazinium cation, with displacement ellipsoids drawn at the 50% probability level; H atoms shown small spheres of arbitrary radii.

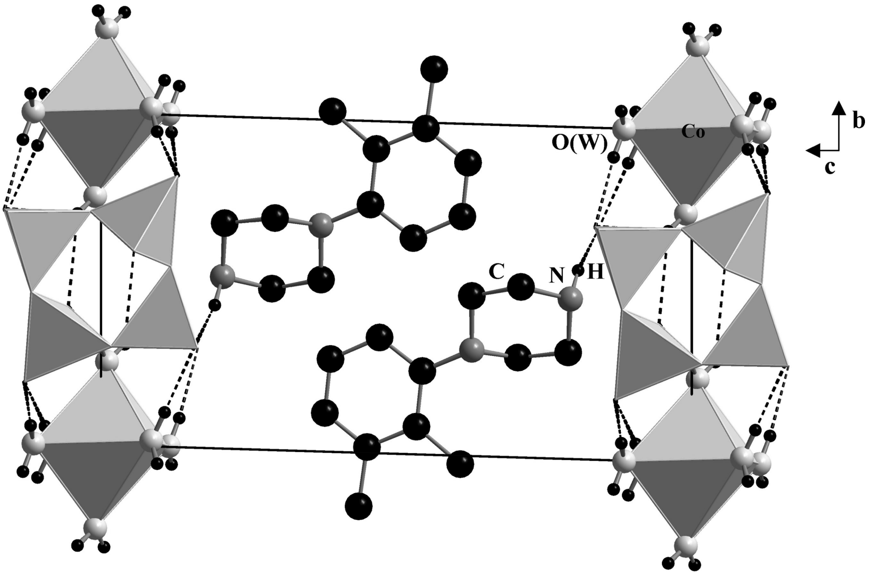

FIGURE 2 A projection along the a axis of the atomic arrangement of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$. Phosphoric anions and $Co(H_2O)_6$ octahedron are given in a polyhedral representation. Hydrogen bonds are denoted by dotted lines.

be noted that these large deviations from the ideal value 90° are commonly observed in the cyclotetraphosphates with low local symmetry Ci rings.[5,6] The P-O-P angle has an average of 134.15° with extrema of 131.3(7) and 137.0(7)°, while the average of the P-P distance is 2.941 (5)° with extrema of 2.914(5) and 2.968 (5) Å, which correspond also to values generally observed in such anions (Table II).[7]

Within a coordination sphere of 2.5 Å, the cobalt atom has a sixfold oxygen coordination formed by 6 water molecules, which form a centrosymmetrical slightly distorted octahedron.[8] The average Co-O distance is 2.085 Å in this octahedron. External and internal oxygen atoms of a phosphoric ring anion do not participate in the neighbors of the cobalt atom. $Co(H_2O)_6$, octahedra are connected to the external oxygen atoms of P_4O_{12} cycles through hydrogen bonds type $O(W)—H\cdots O_E$ to form inorganic layers, as shown in Figure 3. Inside each layer, the topology of the H-bonds network is different to the one observed in $[1,4\text{-}HOC_6H_4NH_3]_4P_4O_{12}.6H_2O$,[9] which has the same degree of hydration. This can be explained by the number of donors and acceptors center present in each structure.

TABLE II Main Interatomic Distances (Å) and Bond Angles (°) in the Inorganic Entities of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$. Estimated Standard Deviations are Given in Parentheses

			$P(1)O_4$ Tetrahedron		
	P(1)	OE11	OE12	OL12	OL21
	OE11	1.474(1)	2.569(2)	2.445(1)	2.520(1)
	OE12	120.74(7)	1.481(1)	2.532(1)	2.457(1)
	OL12	105.32(6)	110.46(6)	1.600(1)	2.452(2)
	OL21	109.97(6)	105.69(6)	103.40(6)	1.601(1)
			$P(2)O_4$ Tetrahedron		
	P(2)	OE21	OE22	OL21	OL12
	OE21	1.490(1)	2.575(1)	2.525(1)	2.538(1)
	OE22	120.58(6)	1.475(1)	2.470(1)	2.452(1)
	OL21	109.66(6)	106.97(6)	1.598(1)	2.512(1)
	OL12	110.92(6)	106.22(7)	100.59(6)	1.590(1)
P(2)-P(1)	2.968(5)	P(1)-P(2)-P(1)	97.84(1)	P(1)-OL12-P(2)	137.0(7)
P(1)-P(2)	2.914(5)	P(2)-P(1)-P(2)	82.16(1)	P(1)-OL21-P(2)	131.3(7)
			$Co(H_2O)_6$ Octahedron		
	Co-OW1	2.076(1)	OW1-Co-OW2	93.07(4)	
	Co-OW2	2.08(1)	OW1-Co-OW3	91.46(5)	
	Co-OW3	2.10(1)	OW3-Co-OW2	94.36(4)	
	OW1-H1W1	0.78(2)	OW1-H2W1	0.88(2)	
	OW2-H1W2	0.85(2)	OW2-H2W2	0.85(2)	
	OW3-H1W3	0.81(2)	OW3-H2W3	0.81(2)	
		H1W1-OW1-H2W1	102.8(2)		
		H1W2-OW2-H2W2	110.5(2)		
		H1W3-OW3-H2W3	110.5(2)		

The dimethylphenylpiperazinium cations are located between the anionic layers, compensating their negative charge. The piperazinium ring adopts a chair conformation (Figure 4) characterized by the torsion angles [N(1)-C(11)-C12-N2 = 56.0(1), C11-C12-N2-C10 = −51.1(1), N2-C10-C9-N1 = −58.9(1), C10-C9-N1-C11 = 65.1(1), and C9-N1-C11-C12 = −63.5(1)°]. The phenyl ring of the organic cation is planar with a mean deviation of 0.0077 Å and is oriented at an angle of 41.75° with respect to the piperazinium ring. Interatomic N—C, C—C bond lengths and N—C—C, C—C—C angles in these groups spread within these respective ranges: 1.375(4)–1.513(3) Å and 108.9(1)–120.8(1)°. These values do not differ significantly from what is usually reported for this kind of group in the literature.[10,11]

$(C_{12}H_{19}N_2)^+$ cations are anchored into inorganic layers via H-bonds type $N{-}H\cdots O_E$. Two types of hydrogen bonds (Table III) occur in this atomic arrangement: (i) $O(W){-}H\cdots O_E$, including 6 contacts with $H\cdots O$ distances ranging from 1.85 (2) to 2.37(2) Å, ensures the intralayer

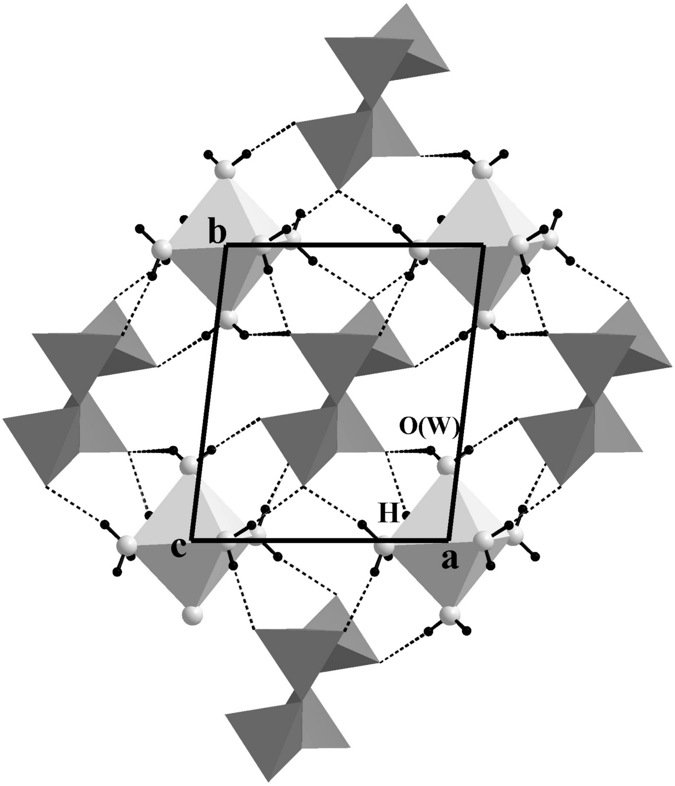

FIGURE 3 A projection along the c axis of the inorganic layer of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$.

cohesion between the cyclotetraphosphoric anion and the $Co(H_2O)_6$ octahedra in the layer,

(i) N—H· · ·O_E, involving 2 contacts with H· · ·O distances, in the range of 1.79(2)–2.38(2) Å, which connects the organic groups to the inorganic layers. The whole of hydrogen bonds (N—H· · ·O_E, O(W)—H· · ·O_E), Van Der Waals, and electrostatic interactions between organic cations and cyclotetraphosphate anions give rise to a stable three-dimensional network.

IR Spectroscopy

The IR spectrum of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$ is illustrated in Figure 5. Theoretically, the ideal symmetry of the $(P_4O_{12})^{4-}$ anions is D_{4h}. As previously mentioned, the symmetry of the studied ring is C_i,

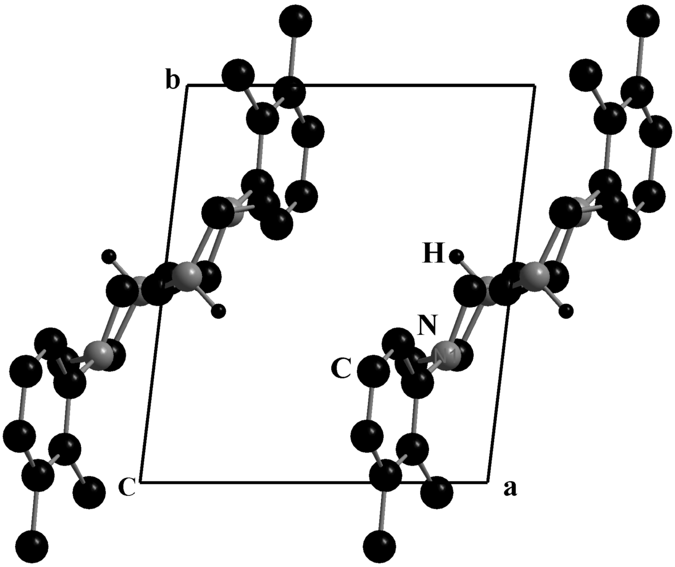

FIGURE 4 A projection along the c axis of the atomic arrangement of the organic groups.

according to the theoretical group analysis, and the number of normal modes is 42, given by the reduced representation $\Gamma_{\text{int}} = 21A_u + 21A_g$. A_u modes are active in the IR spectroscopy, whereas the A_g modes are active in Raman. The 21 IR-active modes could be divided into 8 stretching modes and 13 deformation modes. The 8 A_u modes are distributed as a

TABLE III Hydrogen–Bond Scheme in $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$. Estimated Standard Deviations are Given in Parentheses

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
OW1-H1W1···OE11	0.78(2)	1.94(2)	2.711(1)	173(2)
OW1-H2W1···OE22	0.88(2)	1.85(2)	2.728(1)	175(2)
OW2-H1W2···OE21	0.85(2)	1.86(2)	2.699(1)	171(2)
OW2-H2W2···OE11	0.85(2)	2.37(2)	3.06(1)	144(2)
OW3-H1W3···OE22	0.81(2)	2.03(2)	2.867(1)	170(2)
OW3-H2W3···OE12	0.81(2)	2.00(2)	2.806(1)	170(2)
N2-H1···OE12	1.01(2)	1.79(2)	2.785(1)	169(2)
N2-H2···E21	0.98(2)	2.38(2)	3.065(1)	143(2)
	H1W1-OW1-H2W1	102.8(2)		
	H1W2-OW2-H2W2	110.5(2)		
	H1W3-OW3-H2W3	110.5(2)		
	H1-N2-H2	111.8(2)		

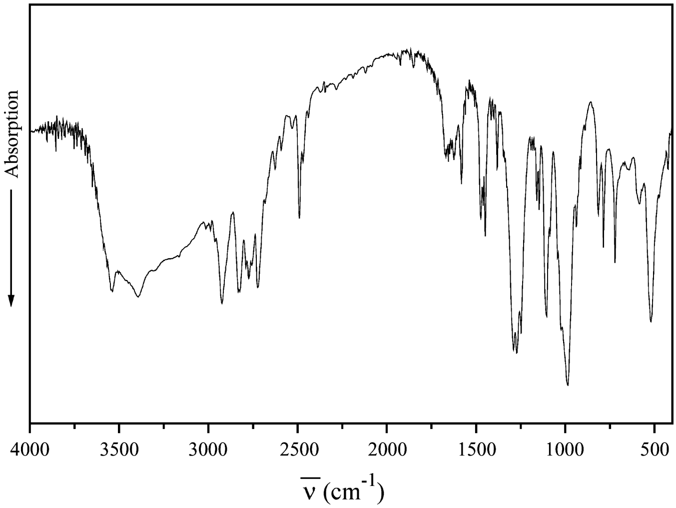

FIGURE 5 IR spectra of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$.

doublet in each region of the following four stretching domains: 1350–1180 cm^{-1} for $\nu_{as}(OPO)^-$, 1180–1060 cm^{-1} for ν_s (OPO), 1060–960 cm^{-1} for ν_{as}(POP), and 850–660 cm^{-1} for ν_s (POP).[12]

The IR spectrum of the organic cyclotetraphosphate is divided into three regions. Frequencies in the range of 4000–1350 cm^{-1} are attributed to O(N,C)—H stretching, bending vibrations, and (C=C) stretching modes. Those ranging from 1350–660 cm^{-1} are attributed to asymmetric and symmetric stretching OPO^- and POP atomic groups in the P_4O_{12}, and those below 660 cm^{-1} are attributed to bending, translation, and rotation of the P_4O_{12} ring anion.

We can note that it is difficult to attribute $\nu_{as}(OPO)^-$, ν_{as}(POP), and ν_s(POP) vibrations bands because of their possible overlapping with the $\nu(C—N)_{arom}$, $\nu(C—N)_{aliph}$ vibrations and δ(C—H) deformation vibration bands, respectively.[13]

Thermal Analysis

Figure 6 shows the simultaneously recorded differential thermal analysis and thermogravimetric analysis curves of the $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$. The DTA curve shows an important endothermic peak at 420 K followed by an exothermic peak at 541 k and other peaks between 663 and 711 K. The first one corresponds to the departure of six water molecules, well confirmed by the weight loss observed on the TGA curve (% water:experimental 12.17, calculated

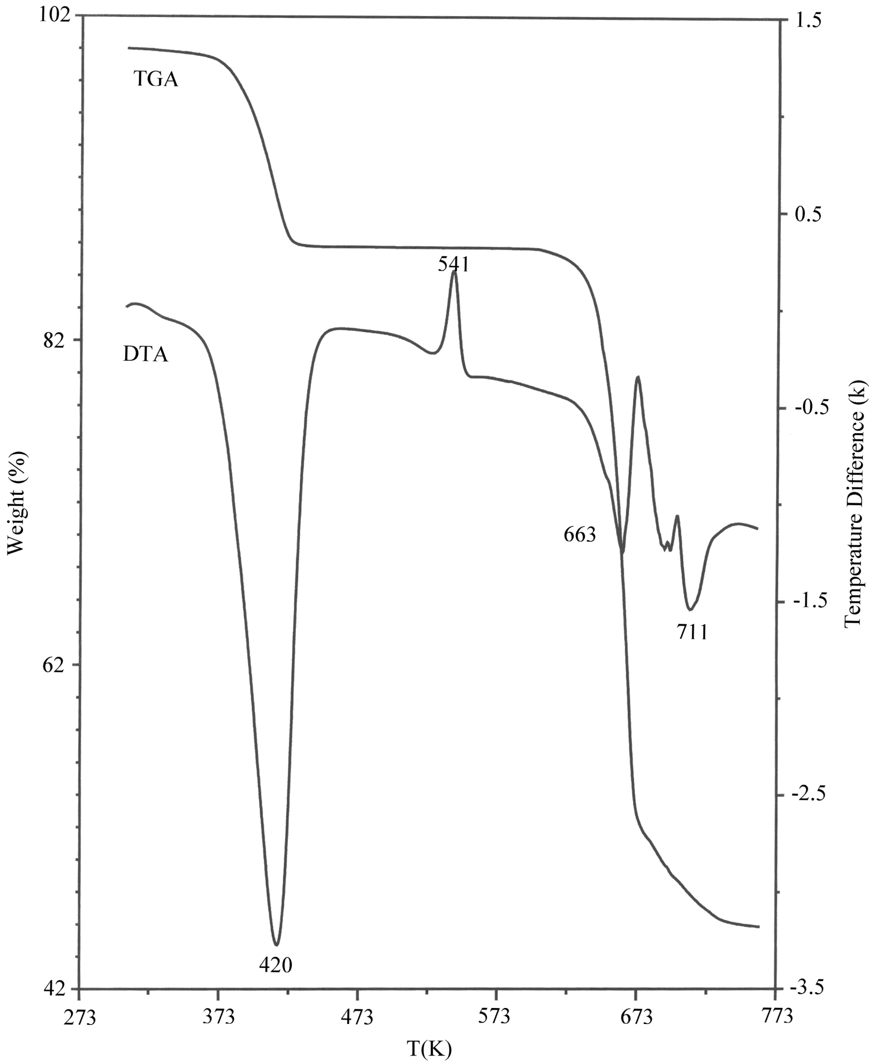

FIGURE 6 DTA and TGA curves of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$ at a rising temperature.

12.47). The exothermic peak at 541 K, without weight loss on the TGA curve, can be assigned to the crystallization of the anhydrous phase. The preparation of this anhydrous phase and the determination of its structure would be interesting for a comparative study with the initial hydrated phase. The last peaks between 623 and 750 K could be assigned to a degradation of the crystallized phase, since this phenomenon is accompanied by a significant weight loss (TGA curve) and gives a residue of black carbon and a consistent matter of polyphosphoric acid.

EXPERIMENTAL

The Synthesis of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$

The title compound is obtained by adding the cyclotetraphosphoric acid to an aqueous solution of dimethylphenylpiperazine and cobalt carbonate. The mixture is kept at a low temperature ($T < 278$ K). The chemical reaction is

$$H_4P_4O_{12} + CoCO_3 + 2(C_{12}H_{18}N_2) + 5H_2O$$
$$\longrightarrow Co[C_{12}H_{19}N_2]_2P_4O_{12} \cdot 6H_2O + CO_2$$

After some days of slow evaporation at r.t. of the obtained solution, prismatic-shaped crystals appear with suitable dimensions. These crystals are stable in air for many months under normal conditions of temperature and hygrometry.

Investigation Techniques

X- Ray Diffraction

A suitable single crystal of the title compound was selected with a polarizing microscope and measured by a Mach3 Enraf–Nonius diffractometer operating with silver radiation ($AgK\bar{\alpha} = 0.5608'$) for a structural determination. Unit cell dimensions have been measured and refined using a set of 25 angle reflections. The structure was solved using the direct method procedure of SIR92[14] and was refined by a full-matrix least-squares technique.[15] Six thousand six hundred eightysix reflections were collected and an omission of intensity with $I > 2\sigma$ (I_{obs}) gave 5053 observed reflections employed for analysis. The nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were localized through difference–Fourier maps and were refined isotropically. The final cycle of least-squares refinement included 332 parameters, which led to the reliability factors $R = 0.029$ and $wR = 0.036$, while the GOF was 1.22. Parameters used for X-ray data collection, structure determination conditions, and final results are reported in Table IV.

Crystallographic data (CIF) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data center as supplementary publication No. 278388. Copies of the data can be obtained, free of charge, on application to the CCDC, 12

TABLE IV Crystal Data, Intensity Measurements, and Structure Determination of $Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$

Empirical formula	$Co[C_{12}H_{19}N_2]_2P_4O_{12}.6H_2O$
Formula weight	865.50
Crystal system	Triclinic
Space group	$P\bar{1}$
a	7.336(1) (Å)
b	8.413(1) (Å)
c	14.926(2) (Å)
α	87.46(1)°
β	83.13(1)°
γ	82.98(1)°
Z	1
V	907.3(2) $Å^3$
ρcal.	1.580 (g. cm^{-3})
F(000)	453
$\mu(AgK\bar{\alpha})$	3.84 (cm^{-1})
Crystal size [mm]	0.60 × 0.50 × 0.20
Index ranges: ± h, ± k, l	$h_{max} = 11$, $k_{max} = 12$, $l_{max} = 22$
Reflexions collected	6686
Independent reflexions	6474
R_{int}	0.014
Refined parameters	332
R [$I > 2\sigma(I)$]	0.029
R(w)	0.036
Goodness-of-fit	1.22

Union Road, Cambridge CB12EZ, U (Fax: +44(1223)336-033 ; E-mail: deposit@ccdc.cam.ac.uk).

Physical Measurements

The IR spectrum was recorded in the range of 4000–400 cm^{-1} with a Perkin-Elmer Spectrum 1000 spectrophotometer using samples dispersed in a spectroscopically pure KBr pellet.

Thermal analysis was performed using the Thermal Analysis Instruments SDT2960 operating from r.t. up to 773 K in following argon at an average heating rate of 5 $K.min^{-1}$.

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