



April 2008

Volume 3 Issue 2

Inorganic CHEMISTRY

Trade Science Inc.

An Indian Journal

Full Paper

ICAIJ, 3(2), 2008 [113-117]

Structure, thermal behavior, and IR investigations of $(C_4H_{12}N)_2H_2P_2O_7$

A.Gharbi, L.Guelmami, A.Jouini*

Laboratoire de Chimie du Solide, Departement de chimie, Faculte des Sciences de Monastir,

Universite de Monastir, 5019 Monastir, (TUNISIA)

Fax: 00216-73 500 278, Tel: 00216-73 500 280

E-mail: jouini_amor@yahoo.fr; amor.jouini@fsm.rnu.tn

Received: 19th November, 2007 ; Accepted: 24th November, 2007

ABSTRACT

Chemical preparation, X-ray single crystal, thermal behaviour, and IR spectroscopic studies on a new organic compound, the bis (tert-butylammonium) dihydrogendiphosphate denoted TBAP, are described. The TBAP crystallizes in the monoclinic system with C2/c space group. The unit cell dimensions are $a=19.840(7)\text{\AA}$, $b=8.932(4)\text{\AA}$, $c=12.518(5)\text{\AA}$, $\beta=136.81(2)\text{\AA}$, with $V=1518.3(11)\text{\AA}^3$ and $Z=4$. The structure has been solved by a direct method and refined to a reliability R factor of 0.0444 using 1649 independent reflections. The central oxygen atom of the $H_2P_2O_7$ group is located on a twofold axis providing a binary internal symmetry of the phosphoric entity. Two kinds of hydrogen bonds coexist in the structure. The mineral anions, linked by the first one O-H...O, built chains running parallel to the c axis. The organic cations, assemble these chains by the second one N-H...O to perform a three dimensional network.

© 2008 Trade Science Inc. - INDIA

KEYWORDS

Inorganic compounds;
Chemical synthesis;
X-ray diffraction;
Infrared spectroscopy;
Thermogravimetric analysis
(TG-DTA),
Crystal structure.

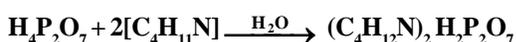
INTRODUCTION

A small number of anhydrous organic dihydrogen diphosphates has been reported. Only four compounds with a well known structural investigation can be cited: $(C_4H_{14}N_2)H_2P_2O_7$ ^[1], $(C_2H_8NO)_2H_2P_2O_7$ ^[2], $(C_2H_{10}N_2)H_2P_2O_7$ ^[3], $(C_4H_{12}NO)_2H_2P_2O_7$ ^[4]. This work deals with the structure of TBAP giving a new example of such compounds. As can be expected, acidic anions in all atomic arrangements of phosphates have a tendency to assemble via their hydrogen bonds to build infinite networks. In particular the acidic diphosphate anions of formula $HP_2O_7^{3-}$, $H_2P_2O_7^{2-}$ and $H_3P_2O_7^-$, adopt various geometrical configurations such as infinite chains, bidimensional layers or tridimensional networks^[5]. The aim of the present work is devoted to a detailed structural investigation of the TBAP. The thermal behavior and the results of spectroscopic study on this new compound

are discussed.

EXPERIMENTAL

The title compound is synthesised by action of diphosphoric acid and aqueous solution of 2-amino-2-methylpropane (fluka chemica, >97%). The diphosphoric acid $H_4P_2O_7$ is produced from a solution of $Na_4P_2O_7$ going through an ion exchange-resin (Amberlite IR120). The addition of the diphosphoric acid to the organic solution is stopped when the pH of the final solution reaches the value 5. Schematically the reaction is:



Thick, prismatic, colourless and transparent single crystals appear after some weeks of evaporation of the solution at room temperature. Crystals, with suitable

Full Paper

TABLE 1: Crystal structure data for $(C_4H_{12}N)_2H_2P_2O_7$

I. Crystal data	
Compound	CCDC653210
Formula/Formular weight	$(C_4H_{12}N)_2H_2P_2O_7$ / 324.25 gmol ⁻¹
Crystal system	Monoclinic
Space group/Z	C2/c/4
Lattice parameters	a= 19.840 (7)Å b= 8.932(4)Å; β=136.81(2)° c= 12.518 (5)Å
Volume	1518.3(11)Å ³
Density(calculated) (g/cm ³)	1.418
Absorption coefficient μ(mm ⁻¹)	0.315
F(000)	696
Size (mm ³)/color	0.29×0.25×0.20/ Colorless
II. Instrument measurement	
Diffractometer	Enraf-Nonius CAD4
Monochromator	Graphite
Wavelength, Mo K _α	λ=0.71073 Å
Temperature	293(2)
Theta range	3° / 27°
h, k, l range	-15/25, 0/11, -15/15
No. of measured reflections	1711
No. of independent reflections	1649
III: Structure determination	
Unic reflections included: (I>2σI)	1164
Programs used	SHELX-97 []
No. of refined parameters	140
Goodness-of-fit on F ²	1.010
R (anisotropic)	0.0444
Rw (anisotropic)	0.1146
Δρ _{min} /Δρ _{max} . (e/Å ³)	-0.612/ 0.549
Largest shift/error	0.000

TABLE 2: The final atomic coordinates and equivalent temperature factors for $(C_4H_{12}N)_2H_2P_2O_7$

Atomes	X	Y	Z	U _{eq}
P1	0.06532(4)	0.03942(6)	0.42049(6)	0.0205(2)
OE1	0.15164(11)	0.1164(2)	0.47137(19)	0.0313(4)
OE2	-0.00237(13)	0.15781(18)	0.3980(2)	0.0296(4)
OE3	0.08687(12)	-0.08759(19)	0.52000(19)	0.0268(4)
OL	0.0000	-0.0307(2)	0.2500	0.0245(5)
N	0.23722(15)	-0.1229(2)	0.8632(2)	0.0265(4)
C1	0.30216(17)	0.0154(3)	0.9359(3)	0.0285(5)
C2	0.2333(2)	0.1499(3)	0.8550(3)	0.0367(6)
C3	0.3649(2)	0.0125(4)	1.1088(3)	0.0446(7)
C4	0.3643(3)	0.0082(4)	0.9073(5)	0.0490(8)

dimensions for crystallographic study, are stable under normal conditions of temperature and humidity.

For the structure determination, the crystal was mounted on an Enraf-Nonius CAD4 diffractometer using monochromatic MoK_α radiation (λ=0.71073Å). The main crystal data, the parameters used for the intensity data collection and the final reliability factors

are summarized in TABLE 1. A total number of 1711 reflections have their intensities integrated and scaled; among them 1649 reflections are independent. X-ray diffraction study shows that the space group is the Centro symmetric C2/c. The crystal structure was solved by direct methods from the SHELXS-97 programs and refined on intensities by a full-matrix least-squares method using SHELXL-97^[6] programs. Heavy atom positions were deduced from the Fourier maps, whereas the hydrogen atoms were located by difference-Fourier syntheses during the refinement of the structure. The final cycle of the refinement, including 140 parameters, leads to the reliability factors R=4.44% and Rw=11.46%. The average density, D_m=1.30g/cm³, measured at room temperature using toluene as pycnometric liquid, is in agreement with the calculated D_x=1.418g/cm³.

Setaram thermoanalysers, TG-DTA92, and DSC92 were used to perform thermal treatment on samples of TBAP. TG-DTA thermograms were obtained with 20.47mg sample in an open platinum crucible. The differential scanning calorimetry (DSC) was carried out using a weighed 15mg sample sealed in an aluminum DSC crucible. In both techniques, the samples were heated in air with 3°C/min heating rate from room temperature to 300°C; an empty crucible is used as reference.

IR spectrum was recorded at room temperature with a Bioered FTS 6000 FTIR spectrometer over the wave numbers 4000-400cm⁻¹ with a resolution of about 4cm⁻¹. Thin and transparent pellet was made by compacting an intimate mixture obtained by shaking 2mg of the samples in 100mg of KBr.

RESULTS AND DISCUSSION

The final coordinates and U_{eq} are given in TABLE 2. Interatomic distances and angles are listed in TABLE 3. The projection of the anionic arrangement along the b direction is displayed in figure 1. It is shown that the connection between mineral groups is made by the first type of hydrogen bond, O-H...O, of the structure. This interaction has a strong character since the distance value H...O 1.73(3)Å is the shortest in the hydrogen network (TABLE 4). This connection leads to chains, of formula [H₂P₂O₇]²⁻, running along the c axis and located at x=0 and x=1/2. In addition, the acceptor-donor dis-

TABLE 3. Main interatomic distances (Å) and bond angles (°) for $(C_4H_{12}N)_2H_2P_2O_7$

PO ₄ tetrahedron				
P(1)	O(E1)	O(E2)	O(E3)	O(L)
O(E1)	1.490(2)	109.48(1)	116.84(1)	108.03(1)
O(E2)	2.495(2)	1.565(2)	110.38(1)	105.58(1)
O(E3)	2.546(2)	2.516(2)	1.498(2)	105.87(1)
O(L)	2.510(2)	2.529(2)	2.482(2)	1.611(1)

P(1)-O(L)-P(1)=134.22(1)°; P(1)-O(E2)-H=116(2); O(E2)-H=0.87(3)

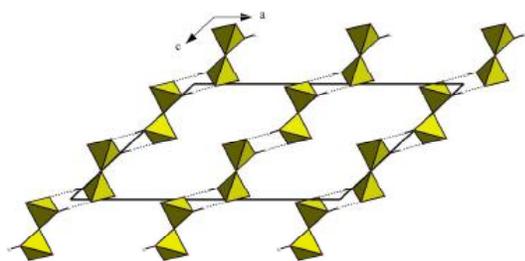
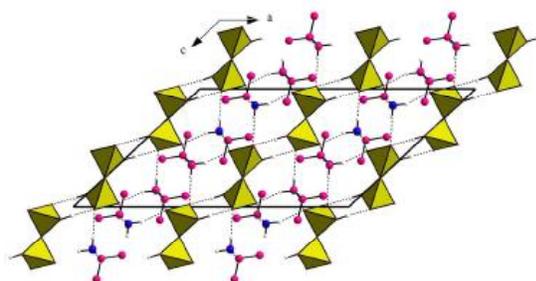
Organic group			
C(1)-N	1.518(3)	C(4)-C(1)-C(3)	111.9(3)
C(1)-C(2)	1.522(3)	N-C(1)-C(3)	107.2(2)
C(1)-C(3)	1.519(4)	C(4)-C(1)-C(2)	111.5(2)
C(1)-C(4)	1.515(4)	N-C(1)-C(2)	106.6(2)
C(4)-C(1)-N	107.8(2)	C(3)-C(1)-C(2)	111.5(2)

TABLE 4: Bond lengths (Å) and angles (°) in the Hydrogen-bonding scheme^a of $(C_4H_{12}N)_2H_2P_2O_7$

	D-H	H...A	D...A	D-H...A
N-H(1N)...O(E1 ⁱⁱ)	0.97(3)	1.91(4)	2.841(3)	159(3)
N-H(2N)...O(E3)	0.89(4)	2.07(4)	2.961(3)	177(3)
N-H(3N)...O(E1 ⁱⁱⁱ)	0.83(3)	2.02(3)	2.814(3)	162(3)
O(E2)-H(OE2)...O(E3 ^{iv})	0.87(3)	1.73(3)	2.601(2)	175(3)

^aSymmetry code: (i) : -X, Y, -Z+1/2; (ii) : X, -Y, Z+1/2; (iii) : -X+1/2, Y-1/2, -Z+3/2 (iv) : -X, -Y, -Z+1

tance 2.601(2)Å, involved in the chain, is of the same order of magnitude as the O...O distances inside the PO₄ tetrahedra; this contributes to consider the

**Figure 1 :** Projection of infinite chains of anions viewed down the crystallographic b axis**Figure 2 :** Projection along the b axis of the atomic arrangement in $(C_4H_{12}N)_2H_2P_2O_7$

$[H_2P_2O_7]_n^{2n-}$ as a linear polyanion. The location of the bridging oxygen atom on the twofold axis of the monoclinic unit cell induces a twofold internal symmetry of the anionic group which is being built by one independent HPO₄ tetrahedron. This type of internal binary symmetry is not very common in the diphosphate groups. Inside the HPO₄ tetrahedron, there are three types of P-O distances: A long one of 1.611(1)Å corresponds to the bridging oxygen atom P-O(L), an intermediate one of 1.565(2)Å for the P-OH bending and two short ones of 1.490(2), and 1.498(2)Å to the external oxygen atoms P-O(E). The calculated average values of the distortion indices^[7] for the different angles and distances in the PO₄ tetrahedron, DI(PO)=0.0304, DI(OPO)=0.0262, DI(OO)=0.0068, exhibit a pronounced distortion of the PO distances and OPO angles if compared to OO distances. The P-O-P bridging angle of 134.22(1)° is close to what is observed in P₂O₇ groups having the same local symmetry in similar reported compounds^[8-12].

The organic entities, located at $x=1/4$ and $x=3/4$ (Figure 2) are anchored between mineral linear polyanions and seem to be organized as chains parallel to the c direction. In fact, having no connection between them, each organic cation is linked to two successive mineral chains giving rise to a structural layer in the (a,c) plane. In deed the second kind of the hydrogen bonds, N-H...O, constitute the principal contacts between the mineral chains by linking three different anions, two in the same chain ($x=0$), the other belonging to the adjacent one ($x=1/2$). Nevertheless, this contact is weaker than the first one since the corresponding N...O distances, spreading in the range 2.841(3)-2.961(3)Å, are longer than the value of 2.601(2)Å relative to the O...O distance^[13,14]. The hydrogen bond characteristics, reported in TABLE 4, indicate that each of the two external oxygen atoms, O(E1) and O(E3) is twofold acceptor whereas the remaining O(E2) oxygen atom is donor. All distances and angles relating to the conformation of the tert-butylammonium group, (TABLE 3) spread within the respective ranges 1.515(4) to 1.522(3)Å and 106.6 to 111.9(3)Å. For instance, they are quite similar to those observed in the same organic cation involved in other phosphoric anions^[15,16].

Thermal behavior

Full Paper

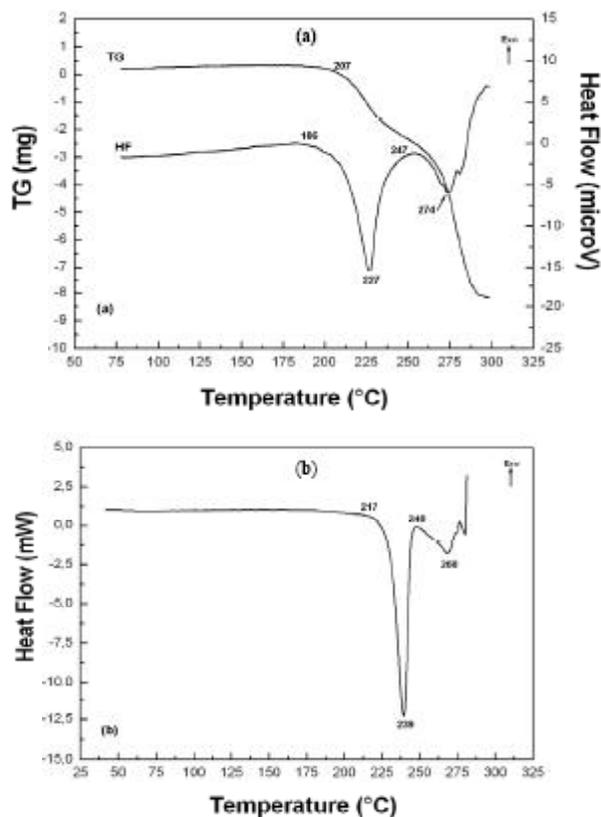


Figure 3 : Thermal analyses: (a) TG-DTA thermograms, (b) DSC thermogram

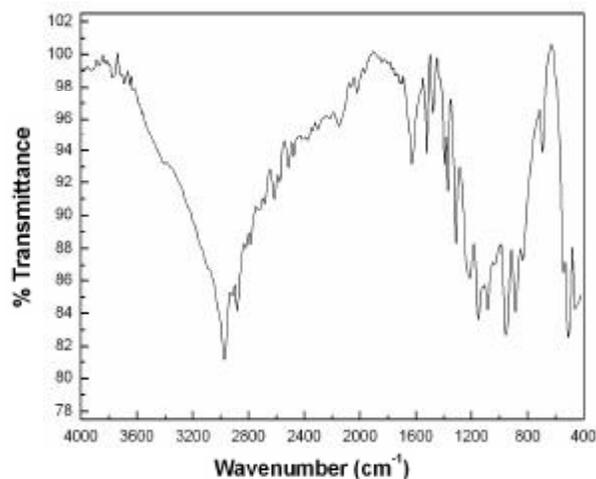
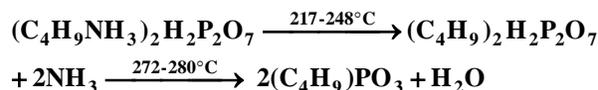


Figure 4 : IR spectrum of $(C_4H_{12}N)_2H_2P_2O_7$

The TG, DTA thermograms of the title compound, depicted in figure 3, are registered, from room temperature to 300°C. They show that the anhydrous compound conserves its stability until 186°C. The decomposition begins at 207°C with evolution of ammonia represented by the endothermic peak at

227°C^[17]. The weight loss deduced from the TG curve, 2.34mg, (Theo.: 2.14mg) corresponds to the elimination of two ammonia molecules. With further increase in temperature, the sample melts in a nearly one step with maximum temperature at 247°C. The DTA curve shows a small exothermic peak at 278°C which can, may be, attributed to the crystallization of a long chain polyphosphate. The fusion is confirmed by an additional thermal treatment in a separate carbolite furnace with run heating of 3°C/min from room temperature to 275°C. The DSC thermogram, registered from room temperature to 325°C, is given in figure 4. It exhibits the same thermal behavior observed in the TG-DTA analyses of the TBAP compound. Thus the first endothermic peak, occurring in the temperature range 217-248°C, is ascribed to the evolution of ammonia with ΔH of 54.8KJ.mol⁻¹, the second one is relative to the melting of the sample. The thermal behaviour of the title compound can be summarized by the following reaction:



The reaction process can be deduced from the hydrogen bonds described in the structure. Indeed, the breaking of the weak second type of hydrogen bond, N-H...O, followed by a displacement of the unbalanced electron pair on the -NH₃⁺ group, induces the evolution of ammonia in the temperature range 217-248°C. The second step of this reaction must be regarded as combined processes including (i) the melting of the obtained new compound, (ii) the breaking of the strong first type of hydrogen bond O-H...O followed by the crystallization of the polyphosphate with elimination of water, and (iii) the degradation begins at 280°C. It is to be noted that the temperature of ammonia elimination and of the degradation are somewhat shifted since the sensibilities of the two techniques are different. The TG-DTA analyser, used in this experience, is more reliable in high temperature domain and the sample is placed in an open crucible, whereas the temperature range of the DSC analyser does not exceed 600°C and the sample is used in a partly sealed crucible.

IR spectroscopic investigation

The group-theoretical analysis for the isolated P₂O₇ group in its ideal symmetry D_{3h}, leads to the

representation $\Gamma_{\text{int}} = 3A'_1 + 4E' + A''_1 + 3A''_2 + 3E''$. These normal modes are distributed in: (i) Six stretching bands in the range $975\text{--}1200\text{cm}^{-1}$ ^[18-19] and eleven bending vibrations in the interval $370\text{--}610\text{cm}^{-1}$ for the PO_3 terminal groups (ii) Two stretching and two bending modes, observed in the domain $740\text{--}950$ ^[20-21], for the P–O–P bridging group. The localization of two protons on the oxygen atoms reduces the ideal symmetry from D_{3h} to C_{2v} . The correlation of group to subgroup shows that the modes of $\text{H}_2\text{P}_2\text{O}_7$ have the representation: $\Gamma_{\text{int}} = 9A_1 + 5A_2 + 5B_1 + 8B_2$. The structural study shows that the local symmetry of the anionic group is C_2 . The interpretation of the IR spectrum, depicted in figure 4, is made in terms of internal modes of the two atomic groups, PO_3 and $\text{P}(\text{OH})_2$, included in the $[\text{H}_2\text{P}_2\text{O}_7]^{2-}$ anion. The two stretching vibrations, asymmetric and symmetric of PO_3 group, are observed in the range $1149\text{--}1080\text{cm}^{-1}$; while those related to $\text{P}(\text{OH})_2$ occur, as two strong bands in the domain $885\text{--}840\text{cm}^{-1}$. On the other hand, the bending modes are observed at lower frequencies. The strong and the very strong bands, respectively at 542 and 508cm^{-1} , correspond to the bending $\delta(\text{PO}_3)$ vibrations. The strong band at 955cm^{-1} is attributed to the asymmetric stretching vibration ν_{as} (POP) and the weak one, at 691cm^{-1} , corresponds to the symmetric motion ν_{s} (POP) present in the bridging group.

The two types of the hydrogen bonds are recognized, in the IR spectrum, as broad bands in the region $3710\text{--}1630\text{cm}^{-1}$ ^[22]. The high-frequency peak at 1211cm^{-1} and the weak one at 828cm^{-1} are assigned respectively to the out-of-plane bending $\tau(\text{POH})$ and to the in-plane bending (POH) vibrations^[23,24]. The stretching vibrations of the CH_3 groups can be observed in the region $3566\text{--}2613\text{cm}^{-1}$ where bands are almost overlapped by those of the stretching N-H and O-H vibrations. These tentative of attributions are based on the reported data corresponding to organic phosphates; they are of approximate character since the combinations, the harmonics^[25] and the coupling between the four formulas units in the cell may occur by increasing the number of bands in the spectrum.

REFERENCES

- [1] E.Bartoszak and M.Jaskolski; *Acta Cryst.*, **C46**, 2158 (1990).
- [2] M.T.Averbuch-pouchot and A.Durif; *Eur.J.Solid State Inorg.Chem.*, **29**, 411 (1992).
- [3] M.T.Averbuch-pouchot and A.Durif; *C.R.Acad. Sci.*, **316(2)**, 187 (1993).
- [4] A.Gharbi and A.Jouini; *J.Soc.Chim.Tunisie*, **3(11)**, 813 (1996).
- [5] M.T.Averbuch-pouchot, A.Durif; 'Topics In Phosphat Chemistry', World Scientific, (1996).
- [6] G.M.Sheldrick; SHELXS97 and SHELXL97. Program for Crystal Structure Solution and Refinement University of Gottingen, Germany, (1997).
- [7] W.H.Baur; *Acta Cryst.*, **B30**, 1195 (1974).
- [8] R.L.Collin and M.Willis; *Acta Cryst.Sect.*, **B27**, 291 (1971).
- [9] A.Larbort, A.Norbert, L.Cot; *C.R.Acad.Sci.Ser.*, **C289**, 185 (1979).
- [10] M.T.Averbuch-pouchot, A.Durif; *Eur.J.Solid State Inorg.Chem.*, **29**, 993 (1992).
- [11] E.Bartozak, M.Jaskolski; *Acta Cryst.*, **C46**, 2158 (1990).
- [12] S.Kamoun, A.Jouini, A.Daoud; *J.Solid State Chem.*, **99**, 18 (1992).
- [13] R.H.Blessing; *Acta Cryst.*, **B42**, 613 (1986).
- [14] D.Brown; *Acta Cryst.*, **A32**, 24 (1976).
- [15] M.Charfi, A.Jouini; *Acta Cryst.*, **C35**, 463 (1997).
- [16] V.A.Chavez, M.Tina, N.L.Hannooman; W.T.A. Harrison; *J.Solid State Chem.*, **147**, 584 (1999).
- [17] A.Chtioui and A.Jouini; *Journal of Crystallography*, **34**, (2004).
- [18] M.Gabelica-Robert, P.Tarte; *J.Mol.Struct*, **79**, 251 (1982).
- [19] R.w.Mooney, S.Z.Toma, J.Brunvoll; *Spectrochim. Acta*, **A23**, 1541 (1967).
- [20] R.w.Mooney, R.L.Goldsmith; *J.Inorg.Nucl.Chem.*, **4**, 933 (1969).
- [21] Z.Iqbal, H.Arend, P.Wachter; *J.Phys.C.Solid State Phys.*, **14**, 1497 (1981).
- [22] Nemeč, I.Cisarova, Z.Micka; *J.Solid State Chem.*, **140**, 71 (1998).
- [23] A.C.Chapman, L.E.Tirlwell; *Spectrochim.Acta*, **20**, 937 (1964).
- [24] L.Ben Hamada, A.Jouini; *Materials Research Bulletin*, **40**, 459 (2005).
- [25] K.Y.Leung, C.Calvo; *Can.J.Chem.*, **50**, 2519 (1972).