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NEW METHOD FOR THE SYNTHESIS OF AMMONIUM SALTS OF O,O'-ALKYLENEDITHIOPHOSPHORIC ACID AND OCTATHIOTETRAPHOSPHETANE. CRYSTAL STRUCTURE FEATURES'S OF DIETHYLAMMONIUM SALT OF O,O'-PROPYLENEDITHIOPHOSPHORIC ACID

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Abstract

A new reaction of elemental phosphorus (P₄) with elemental sulfur and 1,3-propylene glycol in the presence of different amines has been investigated. Ammonium salts of O,O'-alkylenedithiophosphoric acids have been observed as main products of the reaction. Octathiotetraphosphetane ammonium salts were formed as minor products. The reaction is characterized by a complete conversion of white phosphorus and is not accompanied by the release of hydrogen sulfide. The crystal structure features's of diethylammonium salt of O,O'-propylenedithiophosphoric acid were determined using single crystal X-ray diffraction. Piperidinium salt of octathiotetraphosphetane in DMSO and DMF solutions possess significant antifungal activity against *Candida albicans*.

Keywords

Elemental phosphorus; ammonium salts of O,O'-alkylenedithiophosphoric acids and octathiotetraphosphetane; X-ray diffraction

INTRODUCTION

Syntheses, based on the cleavage of the phosphorus--phosphorus bond in the molecule of elemental phosphorus, open the easiest and environment-friendly opportunities to prepare many useful organophosphorus compounds. We have demonstrated that the reactions of

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elemental (white) phosphorus (P_4) and sulfur (S_8) in the presence proton donors (alcohols, phenols) and various amines proceed easily and yield ammonium salts of O,O'-diesters of dithiophosphoric acid.^{1–3} More recently we have shown⁴ that the use of aliphatic thiols as proton donors in the reaction of elemental (white) phosphorus with sulfur and amines led to the synthesis of two phosphorus-containing products. Ammonium salts of S,S'-dialkyltetraphosphoric acid were the main products while the four-membered cyclic phosphorus derivatives - ammonium salts of octathiotetraphosphetane were the minor products (yield 18–20%) in this reaction.

RESULTS AND DISCUSSION

In continuation of our studies of reactions of white phosphorus (P_4) with proton-donating reagents, we investigated an interaction of white phosphorus with different glycols in the presence of elemental sulfur and amines. We showed that the synthesis led to two phosphorus-containing products: ammonium salts of cyclic ether of dithiophosphoric acid **1a-c** and octathiotetraphosphetane **2a-c**.

P_4 - S_8 - 1,3-propylene glycol - amine system interaction was carried out in acetonitrile at 65°–80° C for 8–10 hours. The reaction is characterized by the full conversion of white phosphorus and is not accompanied by the release of hydrogen sulfide. Upon completion of the reaction, two signals of phosphorus in the ^{31}P NMR spectra of the reaction mixture were recorded at 121–122 ppm and 111–112 ppm; these were assigned to the ammonium salts of octathiotetraphosphetane **2a-c** and O,O'-propylenedithiophosphoric acid **1a-c**, respectively.

The structure of the ammonium salts of O,O'-propylenedithiophosphoric acid **1a-c** was determined by analytical and spectroscopic methods. The structure of diethylammonium salt **1b** was confirmed by X-ray diffraction. Single crystal X-ray diffraction analysis of salt **1b** showed that it crystallizes in the monoclinic system with 6 independent cation-anion pairs in the asymmetric part of the unit cell (Figure 1). Attempts to solve and to refine this structure in a more symmetric space group with a simultaneous decrease in the number of independent molecules were unsuccessful. However, the statistical analysis of the experimental reflections array evidenced the presence of noncentrosymmetric space group, leading to a doubling of the number of independent molecules. Thus, to obtain satisfactory statistics, the structure was solved and refined in the Sohncke space group $P2_1$ with 6 symmetry-independent anion-cation pairs in the unit cell.

It is clear that the presence of such a large number of independent molecules cannot be explained just by the differences in geometry and in conformation of cations and anions. This is especially true since they are not significantly different from each other (see Table 1). The explanation of this effect could be altogether different: the system of intermolecular contacts as realized in the crystal. In fact, analysis of the intermolecular interactions in the crystal of **1b** indicates a presence of several types of interactions, including classical hydrogen bonds $NH \dots O$, $NH \dots S$ types, as well as the weaker $C-H \dots O$ hydrogen bonds. The parameters of all interactions are shown in Table 2.

Arrangement of these NH...O and NH...S hydrogen bonds results in the formation of alternating cation-anion H-chains in the crystal (Figure 2,a), with one of the hydrogen atoms of the amino group participating in a bifurcate hydrogen bond. It is interesting to note that the formation of such H-chains is subject to the same rule: each of the six pairs of independent cation - anion forms its own H-chain, but the direction of all of chains is the same and along the crystallographic axis $0c$ (Figure 2,b).

Such an arrangement of supramolecular structures could, in principle, result in their complete cross-binding, but this does not occur. Only four of the six independent H-chains are interlinked by the C-H...O bonds, while the remaining two chains fail to participate in such interactions due to their unfavorable position (Figure 3,a). As such, the two chains are not involved in any additional hydrogen bonding within the crystal - at least as defined by the formal criteria of hydrogen bond formation of the PLATON and Mercury software.

Interestingly, while the cations and anions in all other H-chains are arranged in a uniform (nearly layered) manner, the arrangement of the independent anion-cation pairs in those two unconnected H-chains is staggered (as shown in the other crystal packing projection Figure 3,b). The crystal regions in which the anion-cation pairs are located are spatially relatively localized regions of the crystal (Figure 4). Apparently, it is their presence that leads to a decrease in the density of the molecule parking in the crystal; the calculated coefficient of crystal packing is equal to 64.9%, near the smallest values characteristic of crystals of organic compounds (0.65 -- 0.75). Nonetheless, this does not lead to an appearance of voids in the crystal at least not accessible to solvent molecules.

Previously the ammonium salts of octathiotetraphosphetane **2a-c** were synthesized in the reactions of white phosphorus with aliphatic thiols, sulfur and amines.⁵ The physico-chemical and the spectral parameters of the octathiotetraphosphetane ammonium salts **2a-c** coincide with the same characteristics given in our previous publications.⁵ Structures of salts **2a-c** were confirmed by the XRD analysis as well.^{8, 9} It is relevant to note that these salts, as well as other cyclic thiophosphates, can also be obtained in reactions of white phosphorus with polysulfide polysulfides, hydrogen sulfide and amines.^{6, 7}

The ratio between two of the products **1a-c** and **2a-c** depends on which amine is being used. In the reaction of white phosphorus with piperidine, sulfur and 1,3-propylene glycol, the piperidinium salt of octathiotetraphosphetane was obtained with the highest yield (45%). When using triethyl- and diethylamine the corresponding salts yield was lower, and we observed a preferable formation of ammonium salts of O,O'-propylenedithiophosphoric acid. Octathiotetraphosphetanes as ammonium salts bearing the various functional groups in the molecule (amine groups, thio groups, thiophosphoryl groups) have recently been the subject of our studies as ligands in complexation with transition d-metals.¹⁰ In addition, ammonium salts of octathiotetraphosphetane were tested for their biological activity. It was found that DMSO and DMF solutions of piperidinium salt of octathiotetraphosphetane possess significant anti-fungal activity against *Candida albicans* (Table 3). The 12 hour MIC for this compound in DMSO solution is 12uM and slightly lower in DMF solution (6uM). Anti-fungal activity decreases 4 fold for both solutions within the first 24 hours but thereafter

stabilizes for at least a month at room temperature, confirming extended stability of the biologically active component in solution.

Finally, it should be noted that the use of 1,3-propylene glycol provides relative environmental safety of the proposed synthetic method for biologically active salts of octathiotetraphosphetane, that it eliminates toxic thiols from the process, and that it furthermore increases the yield of the target compounds to 45% (best result).

EXPERIMENTAL

IR spectra were recorded with the Bruker Tensor-27 Fourier spectrometer (KBr, 4000-400 cm^{-1}). ^1H NMR spectra were recorded with the Bruker MSL-400 (162.0 MHz) spectrometer with internal TMS reference. ^{31}P NMR spectra were recorded with the Bruker CPX (36.48 MHz) spectrometer with 85% phosphoric acid reference. C, H, N, and S content were determined using the CHN-3 analyzer. Content of phosphorus was evaluated by means of the standard pyrolysis procedure.

Solvent and reagents were purified by standard methods. All preparations were carried out in argon atmosphere.

The X-ray diffraction data for the crystal of **1b** were collected at 296 K on a Bruker AXS Smart Apex II CCD diffractometer in the ω and ϕ -scan modes using graphite monochromated $\text{MoK}\alpha$ (λ 0.71073 Å) radiation: $-8^\circ \leq \theta \leq 9^\circ$, $-47^\circ \leq \phi \leq 46^\circ$, $-19^\circ \leq \chi \leq 19^\circ$, $2.17^\circ \leq \theta \leq 27.96^\circ$.

Crystallographic data for **1b** $\text{C}_3\text{H}_6\text{O}_2\text{PS}_2 \cdot \text{C}_4\text{H}_{12}\text{N}^+$, colourless prism crystal $0.27 \times 0.20 \times 0.10$ mm, formula weight 243.31, monoclinic, $P2_1$, $a = 6.956(1)$ Å, $b = 36.007(6)$ Å, $c = 15.236(3)$ Å, $\beta = 100.047(2)^\circ$, $V = 3757.5(11)$ Å³, $Z = 12$, $Z' = 6$, $\rho_{\text{calc}} = 1.290$ g·cm⁻³, $\mu(\lambda\text{MoK}\alpha) = 5.27$ cm⁻¹. $R(000) = 1560$, reflections collected = 29053, unique = 15602, $R(\text{int}) = 0.0665$. Full-matrix least-squares on F^2 with 709 parameters and 35 restraints. Final R values are $R_1 = 0.0718$, $wR_2 = 0.1650$ for 7078 reflections with $I > 2\sigma(I)$ and $R_1 = 0.1714$, $wR_2 = 0.2133$ for all data, goodness-of-fit on $F^2 = 0.942$, largest difference in peak and hole (1.111 and -0.348 eÅ⁻³).

Data were corrected for the absorption effect using SADABS program.¹¹ The structure was solved by direct method and refined by the full matrix least-squares using SHELXTL¹² and WinGX¹³ programs. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at calculated positions and refined as riding atoms except the hydrogen atoms on N atoms which were located from difference maps and refined using a riding model. Data collections: images were indexed, integrated, and scaled using the APEX2¹⁴ data reduction package. Analysis of the intermolecular interactions was performed using the program PLATON.¹⁵ Mercury program package¹⁶ was used for figures preparation. Selected geometric parameters of the molecules are presented in the Table 1.

Crystallographic data (excluding structure factors) for the structure of **1b** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1026188. Copies of the data can be obtained, free

of charge, by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: + 44-(0)1223-336033 or deposit@ccdc.cam.ac.uk).

CAUTION: White phosphorus is a very toxic and flammable compound.

Reaction of P₄ with Sulfur, 1,3-propylene glycol and trimethylamine

Triethylamine 3.9 g (39 mmol) was added dropwise at room temperature to stirred mixture of 1 g (32 mmol) of white phosphorus, 2.08 g (65 mmol) of sulfur, and 2.4 g (32 mmol) of 1,3-propanediol in CH₃CN (8 mL). The mixture was stirred during at 65--70°C 8 h (complete conversion of P₄). The resulting yellow solution was cooled to give white solid. The so formed crystals were filtered off, washed with mixture of CH₃CN : Et₂O 1:1 (2×5 ml) and dried under vacuum. Yield of triethylammonium salt of O,O'-propylenedithiophosphoric acid **1a** 4.5g (51%). ¹H NMR (CD₃CN, δ): 0.96 (t, 9H, CH₃), 1.67 (m, 2H, OCH₂CH₂), 2.74 (m, 6H, CH₂CH₃), 3.53 (m, 4H, CH₂O); ³¹P NMR (CD₃CN, δ): 111. IR spectrum (KBr), ν, cm⁻¹: 2678, 2469 (HN⁺), 1035 P-O-C, 674 (P = S). Anal. Calcd for C₉H₂₂NO₂PS₂ (271): C 39.85; H 8.12; N 5.16; P 11.44; S 23.61. Found: C 39.43; H 7.72; N 5.03; P 11.76; S 24.05.

The solution after filtration of salt **1a** was evaporated under reduced pressure to give yellow oil. Upon further refrigeration, 0.3 g of 1,2,3,4-tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(triethylammonium) salt **2a** crystallized from the mother liquor in three days. Physical, analytical, and spectral data for **2a** was given in previous publications.⁸

Reaction of P₄ with Sulfur, 1,3-propylene glycol and diethylamine

Diethylamine 2.4 g (32.7 mmol) was added dropwise at room temperature to stirred mixture of 1 g (32 mmol) of white phosphorus, 2.1 g (64.6 mmol) of sulfur, and 2.5 g (33 mmol) of 1,3-propanediol in CH₃CN (10 mL). The mixture was stirred during at 65--80°C 10 h (complete conversion of P₄). The resulting yellow solution was evaporated under vacuum to half of the volume and cooled to give white solid. The crystals were filtered off, washed with Et₂O (2×5 ml) and dried under vacuum. Yield of diethylammonium salt of O,O'-propylenedithiophosphoric acid **1b** 3.6 g (46%), mp 136-138 °C. ¹H NMR (CD₃CN, δ): 1.00 (t, 6H, CH₃), 1.68 (m, 2H, OCH₂CH₂), 2.4 (m, 4H, CH₃CH₂), 3.54 (m, 4H, CH₂O); ³¹P NMR (CD₃CN, δ): 112. IR spectrum (KBr), ν, cm⁻¹: 2668, 2483 (HN⁺), 666 (P = S). Anal. Calcd for C₇H₁₈NO₂PS₂ (243): C 34.56; H 7.41; N 5.76; P 12.75; S 26.33. Found: C 34.39; H 7.09; N 5.46; P 12.25; S 25.87.

The solution after filtration of salt **1b** was then evaporated under reduced pressure to give yellow oil. Upon further refrigeration 0.7 g of 1,2,3,4-tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(diethylammonium) salt **2a** crystallized from the mother liquor within a week. Physical, analytical, and spectral data for **2a** was given in previous publications⁸.

Reaction of P₄ with Sulfur, 1,3-propylene glycol and piperidine

Piperidine 3.3 g (39 mmol) was added dropwise at room temperature to stirred mixture of 1 g (32 mmol) of white phosphorus, 2.1 g (64.6 mmol) of sulfur, and 2.5 g (33 mmol) of 1,3-

propanediol in CH₃CN (8 mL). The mixture was stirred during at 75--80°C 10 h (complete conversion of P₄). Evaporation the resulting dark yellow solution and addition of Et₂O to the solution gave beige solid. The crystals were filtered off, washed with cooling CH₃CN (2 ml), Et₂O (3×5 ml) and dried under vacuum. Yield of 1,2,3,4-tetrathio-1,2,3,4-tetrathioxotetraphosphetane tetrakis(piperidinium) salt **2c** 2.6 g (45%), pale yellow solid. Physical, analytical, and spectral data for **2c** was given in previous publications.⁹ The solution after filtration of salt **2c** was then evaporated under reduced pressure to give red oil. Salt **1c** was purified by column chromatography on silica gel. Yield of salt of O,O'-propylenedithiophosphoric acid with piperidine **1c** 0.4 g, pale yellow oil. ¹H NMR (CD₃OD, δ): 1.35 (m, 2H, OCH₂CH₂), 1.87 (m, 6H, NCH₂(CH₂)₃), 3.2 (m, 4H, CH₂NCH₂), 4.0 (m, 4H, CH₂O); ³¹P NMR (CD₃CN, δ): 112. IR spectrum (KBr), ν, cm⁻¹: 2700, 2469 (HN⁺), 1060 P-O-C, 655 (P = S). Anal. Calcd for C₈H₂₂NO₂PS₂ (255): C 37.65; H 8.63; N 5.49; P 12.16; S 25.09. Found: C 37.25; H 8.28; N 5.61; P 12.45; S 25.55.

Testing of DMSO and DMF solutions of compound **2c** against *Candida albicans*

Inoculated Yeast Mold (YM) media with *Candida albicans* (ATCC 26555) and incubated for cells to grow for 18 hours at 37°C. Cells were thereafter diluted 1:20ml with YM media. Three rows of cells were placed in a 48 well plate for treatment with each drug. Solutions of **2c** in DMSO and **2c** in DMF had starting concentration at 100uM. Final solvent concentration did not exceed 5%. Each row of target cells was prepared for a two-fold serial dilution by placing 1ml of diluted cells in the first column and 0.5ml for the remaining dilution-series wells. Drug is added in each of the 1ml wells in the first column and mixed thoroughly by pipetting. Then 0.5ml is withdrawn from the 1ml drug-treated well and added to the next 0.5 ml well to generate a drugdilution series while keeping the cell concentration the same in each well. Controls for this experiment included: a positive growth control (no drug added; ensures unobstructed growth of *Candida* and provides an untreated baseline); a negative growth control (cells treated with Amphotericin B 10ug/ml to ensure full killing and provide a no-growth/viability baseline); and DMSO and DMF solvent control (to observe/document any toxicity of the solvents against *Candida*). Colorimetric MTT assay¹⁷ was used to evaluate cell viability.

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Figure 1.

The geometry of cations and anions in the **1b** crystals and the partial numbering scheme. Non-hydrogen atoms are represented by probability ellipsoids of thermal vibrations ($p = 30\%$). Hydrogen atoms are not shown for clarity.

Figure 2. Two projections of the system of classic NH...O, NH...S hydrogen bonds (shown in thin dotted lines) between anions and cations in the crystal **1b**. (a) View along Oc axis, showing one H-chain; (b) View along Oa axis, showing H-chains of all six independent anions-cations pairs.

Figure 3. System of NH...O, NH...S and C-H...O hydrogen bonds (thin dotted lines) in crystal **1b**. Two independent anion-cation pairs are shown in the ball-stick model and the rest in the stick model. (a) View along *Oa* axis; (b) View along *Oc* axis.

Figure 4.

Fragment of the anions and the cations crystal packing in **1b** (Van der Waals representation). The view is along the axis Oa . The two selected H chains, mentioned in the discussion, are presented by green and purple colors.

Table 1

Some geometric parameters of the molecules in the **1b** crystals: bond lengths (d, Å), bond angles (ω , °) and torsion angles (τ , °)

Bond	d (Å)	Bond angle	ω (°)
C1-O1	1.47(1)	O1-C1-C2	112.1(8)
C3-O2	1.36(1)	O2-C3-C2	115.4(9)
C4-C5	1.46(1)	C20-C19-N1	109.5(1)
C4-O3	1.50(1)	C22-C21-N1	120.0(1)
C6-O4	1.39(1)	O1-P1-O2	101.9(4)
C7-O5	1.47(1)	O1-P1-S2	111.3(3)
C9-O6	1.513(16)	O2-P1-S2	108.9(3)
C19-N1	1.484(11)	O1-P1-S1	108.8(3)
C23-N2	1.493(11)	O2-P1-S1	105.5(3)
C27-N3	1.493(14)	S2-P1-S1	118.9(2)
C31-N4	1.475(16)	O3-P2-O4	101.0(4)
C35-N5	1.504(11)	O3-P2-S4	112.0(3)
C39-N6	1.450(12)	O4-P2-S4	109.0(3)
C41-N6	1.543(12)	O3-P2-S3	108.8(3)
O1-P1	1.530(7)	O4-P2-S3	105.7(3)
O2-P1	1.643(7)	S4-P2-S3	118.8(2)
O3-P2	1.542(8)	O6-P3-O5	100.7(4)
O4-P2	1.619(7)	O6-P3-S5	107.4(3)
O5-P3	1.617(6)	O5-P3-S5	107.4(3)
O6-P3	1.589(7)	O6-P3-S6	111.0(3)
O7-P4	1.585(7)	O5-P3-S6	110.0(3)
O8-P4	1.666(7)	S5-P3-S6	118.8(2)
O9-P5	1.579(7)	O7-P4-O8	100.4(4)
O10-P5	1.659(7)	O7-P4-S8	107.0(3)
O11-P6	1.597(6)	O8-P4-S8	107.1(3)
O12-P6	1.628(6)	O7-P4-S7	112.6(3)
P1-S2	1.959(4)	O8-P4-S7	109.4(3)
P1-S1	1.989(4)	S8-P4-S7	118.6(2)
P2-S4	1.964(4)	O9-P5-O10	101.4(4)
P2-S3	1.980(4)	O9-P5-S10	107.2(3)
P3-S5	1.946(3)	O10-P5-S10	105.8(3)
P3-S6	1.955(4)	O9-P5-S9	112.6(3)
P4-S8	1.915(4)	O10-P5-S9	109.5(3)
P4-S7	1.970(4)	S10-P5-S9	118.7(2)
P5-S10	1.924(4)	O11-P6-O12	101.5(4)
P5-S9	1.961(4)	O11-P6-S11	110.2(3)

Bond	d (Å)	Bond angle	ω (°)
P6-S11	1.945(4)	O11-P6-S12	107.7(3)
P6-S12	1.956(3)	S11-P6-S12	119.4(2)
Torsion angle	τ (°)	Torsion angle	τ (°)
O1-C1-C2-C3	-52.7(12)	C17-C16-O11-P6	64.3(12)
C1-C2-C3-O2	58.5(12)	C1-O1-P1-S2	66.8(7)
C4-C5-C6-O4	60.0(11)	C1-O1-P1-S1	-160.3(6)
O5-C7-C8-C9	-53.4(16)	C4-O3-P2-O4	-50.6(8)
C7-C8-C9-O6	52.5(17)	C4-O3-P2-S4	65.3(8)
C22-C21-N1-C19	179.7(14)	C4-O3-P2-S3	-161.5(7)
C26-C25-N2-C23	-173.5(13)	C7-O5-P3-O6	-51.7(7)
C38-C37-N5-C35	170.1(11)	C7-O5-P3-S5	-163.9(6)
C2-C1-O1-P1	56.1(11)	C7-O5-P3-S6	65.5(7)
C2-C3-O2-P1	-60.0(10)	C12-O8-P4-O7	56.3(8)
C5-C4-O3-P2	59.7(11)	C12-O8-P4-S8	167.9(7)
C8-C7-O5-P3	55.6(12)	C12-O8-P4-S7	-62.3(8)
C11-C10-O7-P4	57.0(10)	C13-O9-P5-O10	-56.2(7)
C14-C13-O9-P5	58.2(9)	C13-O9-P5-S9	60.6(7)
C16-O11-P6-S12	-167.3(8)	C15-O10-P5-S10	167.4(6)

Table 2Parameters of the intermolecular H-bonds for **1b** crystals

D--H A	H A, Å	D A, Å	∠ DHA, °	Symmetry operation
N1--H1 ..S4	2.52	3.399(8)	167	[1+x,y,z]
N3--H3 ..S9	2.44	3.335(9)	171	[1+x,y,z]
N4--H4 ..S7	2.46	3.35(1)	170	[1+x,y,z]
N2--H2 ..S2	2.49	3.368(8)	165	[1+x,y,-1+z]
N5--H5 ..S5	2.61	3.354(8)	141	[-x,-1/2+y,1-z]
N5--H5 ..O5	2.36	3.158(10)	148	[-x,-1/2+y,1-z]
N6--H6 ..S12	2.59	3.331(9)	140	[-1+x,y,z]
N6--H6 ..O12	2.36	3.165(10)	149	[-1+x,y,z]
N1--H10 ..S3	2.58	3.359(8)	145	-
N1--H10 ..O4	2.56	3.355(10)	147	-
N2--H20 ..S1	2.61	3.356(8)	141	[x,y,-1+z]
N2--H20 ..O2	2.5	3.339(10)	147	[x,y,-1+z]
N3--H30 ..S10	2.57	3.363(9)	147	-
N3--H30 ..O9	2.49	3.256(11)	144	-
N4--H40 ..S8	2.59	3.389(11)	148	-
N4--H40 ..O7	2.50	3.274(12)	144	-
N5--H50 ..S6	2.48	3.374(8)	170	[1-x,-1/2+y,1-z]
N6--H60 ..S11	2.52	3.402(8)	168	

Table 3

The activity of DMSO and DMF solutions of piperidinium salt of octathiotetraphosphetane against *Candida albicans*.

MIC	0	18hours	7days	14days	21days
DMSO	12uM	50uM	50uM	50uM	50uM
DMF	6uM	25uM	25uM	25uM	25uM