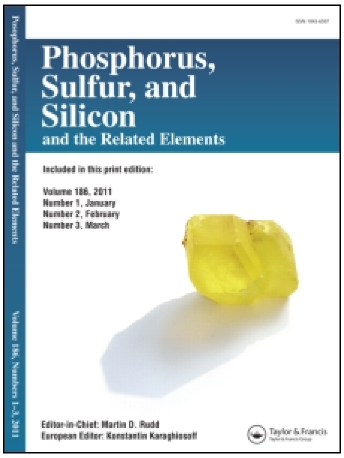

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Venkatachalam, V. , Thirumaran, S. , Ramalingam, K. , Mak, T. C. W. and Sheng, L. B.(1998) 'INFRARED SPECTRAL, VALENCE BOND SUM ANALYSIS AND SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION OF 2,2'-BIS (PHTHALIMIDOETHYL) AMMONIUM 2,2'-BIS (PHTHALIMIDO-ETHYL)DITHIOCARBAMATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 142: 1, 239 — 248

To link to this Article: DOI: 10.1080/10426509808029678

URL: http://dx.doi.org/10.1080/10426509808029678

Phosphorus, Sulfur and Silicon, 1998, Vol. 142, pp. 239-248
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INFRARED SPECTRAL, VALENCE BOND SUM ANALYSIS AND SINGLE CRYSTAL X-RAY STRUCTURE DETERMINATION OF 2,2'-BIS (PHTHALIMIDOETHYL) AMMONIUM 2,2'-BIS (PHTHALIMIDO-ETHYL)DITHIOCARBAMATE

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(Received 28 May, 1998; In final form 18 August, 1998)

Synthesis and X-ray crystal structure of 2,2'-bis(phthalimidoethyl) ammonium 2,2'-bis(phthalimido ethyl)dithiocarbamate ((padtc)$^-$(paH)$^+$) is reported. Crystal parameters are : space group : Pl, a = 10.252(2), b = 13.692(3), C = 15.072(4)Å, α = 103. 680 (1)°; β = 99.710(1)°; v = 107.300(1)°, Z = 2, R = 0.048 for 6288 reflections. The two, C-S distances significantly differ from each other and are in between the single and double bond distances [C(41)-S(1) = 1.701(3)Å and C(41)-S(2) = 1.682(4)Å]. Asymmetry in the C-S distances shows localization of high electron density between the C and S bonds. Contribution of thioureide form to the dithiocarbamate is explicitly supported by the thioureide distance observed. The valence bond sum (VBS) was found to be 1.4 for the thioureide C-N bond indicating a partial double bonded nature.

Keywords: Synthesis; IR; VBS; Crystal Structure; (padtc)$^-$(paH)$^+$

INTRODUCTION

Many of the dithiocarbamate ligands find use as analytical reagents and the sodium salt of diethyldithiocarbamate will precipitate more than 25 different metal ions.[1] Interest on these complexes is due to their chemis-

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try and their applications as analtycal reagents.[2,3] In continuation of our interest in these type of ligands and their complexes,[4–6] the synthesis, IR spectral, and X-ray structure determination of a new dithiocarbamate ligand, $(padtc)^-$ $(paH)^+$ is presented in this paper. The crystal structure provides unambiguous evidence for the contribution of the thioureide form to the dithiocarbamate.

RESULTS AND DISCUSSION

Infrared Spectral Studies

A set of three bands at 1463, 1434, and 1394 cm^{-1} in the IR-spectrum is observed in the amine (pa), which appears unaffected in the corresponding dithiocarbamate salt $(padtc)^-$ $(paH)^+$. Clearly, the band at 1394 cm^{-1} is due to the tertiary νC-N stretch in the compound and the other two bands are due to the νC-H bending vibrations of the $-CH_2-$ groups.[7] However, formation of a dithiocarbamate from the amine introduces another νC-N vibration indicating a partial double bond character which might also appear in the 1380–1450cm^{-1} region and hence could not be differentiated from a band due to a typical C-N single bond. A strong band at 719 cm^{-1} is attributed to the disubstituted aromatic system with four adjacent hydrogen atoms.[8] Characteristic νC=O frequencies are the least affected on condensation of phthalic anhydride with diethylene triamine to form the amine, (pa) and then the corresponding dithiocarbamate salt $(padtc)^-$ $(paH)^+$.

Structure Analysis

The structure of $(padtc)^-$ $(paH)^+$ is shown in Fig.1. The molecule is monomeric with two molecuels present in the unit cell. In $(padtc)^-$, the two C-S distances are C(41)-S(1) = 1.701(3)Å and C(41)-S(2) = 1.682(4)Å, which significantly differ from each other (and are in between the single and double bond distances). Asymmetry in the C-S distances indicates localization of high electron density between one of the C and S atoms. The angles around C(41) average to 119.8°(S(1) -C(41) -S(2), S(1)-C(41)-N(6), S(2)-C(41)-N(6)), which indicates a planar arrangement as expected of the

sp^2 hybridized carbon. This observation supports the statement that one of the C-S bonds is a double bond.

TABLE I Crystal data, solution and refinement parameters for $(padtc)^-$ $(paH)^+$

Empirical formula	$C_{41}H_{34}N_6O_8S_2 \cdot 1/2\ (H_2O)$
Color and shape	Yellow, prism
Formula weight	811.87
Crystal dimensions,mm	0.20 × 0.40 × 0.45
Crystal system	Triclinic
Space group	$P\bar{1}$
Temp., °K	293
Cell Constants	
a, Å	10.252(2)
b, Å	13.692(3)
c, Å	15.072(4)
α. deg	103.680(1)
β. deg	99.710(1)
v, deg	107.300(1)
Cell volume, Å^3	1896.3(8)
Formula units/unit cell	2
D_{calc}, gcm^{-3}	1.422
μ_{calc}, mm^{-1}	0.208
F(000)	846
Diffractometer/scan	Siemens R3m/V/ /2θ
Radiation, graphite monochromator	MoKα (λ= 0.71073Å)
2θ range, deg	3.0 to 48.0
Standard reflections	2 measured for every 123 reflections
Index ranges	$0\le h\le 11$, $-15\le k\le 14$ $-17\le l\le 17$
Reflections collected	6288
Observed reflections (F > 4.0 σ (F))	4139
System used	Siemens SHELXTL PLUS (PC Version)[10]
Structure solution	Direct methods
Refinement method	Full-matrix least-squares
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0012F^2$
No. of parameters refined	532
R	0.048
Rw	0.065
GOF	1.37
Largest feature final diff. map, e^- Å^{-3}	0.38

TABLE II Bond lengths (Å) and bond angles (°) for $(padtc)^-$ $(paH)^+$

C(1)-C(2)	1.373 (4)	C(1)-C(6)	1.388 (5)
C(2)-C(3)	1.386 (5)	C(3)-C(4)	1.373 (5)
C(4)-C(5)	1.382 (4)	C(5)-C(6)	1.386 (4)
C(5)-C(8)	1.476 (4)	C(6)-C(7)	1.475 (4)
C(7)-O(1)	1.205 (3)	C(7)-N(1)	1.407 (4)
N(1)-C(8)	1.394 (3)	N(1)-C(9)	1.448 (3)
C(8)-O(2)	1.211 (4)	C(9)-C(10)	1.511 (3)
C(10)-N(3)	1.475 (4)	N(3)-C(20)	1.506 (4)
C(11)-C(12)	1.376 (4)	C(11)-C(16)	1.375 (4)
C(12)-C(13)	1.383 (5)	C(13)-C(14)	1.380 (4)
C(14)-C(15)	1.377 (4)	C(15)-C(16)	1.381 (4)
C(15)-C(18)	1.467 (3)	C(16)-C(17)	1.483 (4)
C(17)-O(3)	1.205 (4)	C(17)-N(2)	1.414 (3)
N(2)-C(18)	1.394 (4)	N(2)-C(19)	1.457 (3)
C(18)-O(4)	1.221 (3)	C(19)-C(20)	1.506 (4)
C(21)-C(22)	1.380 (5)	C(21)-C(26)	1.371 (4)
C(22)-C(23)	1.374 (5)	C(23)-C(24)	1.390 (4)
C(24)-C(25)	1.384 (4)	C(25)-C(26)	1.386 (4)
C(25)-C(28)	1.477 (3)	C(26)-C(27)	1.474 (4)
C(27)-O(5)	1.206 (4)	C(27)-N(4)	1.399 (3)
N(4)-C(28)	1.385 (4)	N(4)-C(29)	1.454 (3)
C(28)-O(6)	1.212 (4)	C(29)-C(30)	1.523 (4)
C(30)-N(6)	1.460 (3)	N(6)-C(40)	1.467 (4)
N(6)-C(41)	1.359 (3)	C(31)-C(32)	1.393 (4)
C(31)-C(36)	1.369 (4)	C(32)-C(33)	1.374 (6)
C(33)-C(34)	1.375 (4)	C(34)-C(35)	1.381 (4)
C(35)-C(36)	1.381 (4)	C(35)-C(38)	1.475 (3)
C(36)-C(37)	1.491 (3)	C(37)-O(7)	1.212 (4)
C(37)-N(5)	1.384 (4)	N(5)-C(38)	1.401 (4)
N(5)-C(39)	1.451 (3)	C(38)-O(8)	1 .200 (4)
C(39)-C(40)	1.520 (4)		
C(41)-S(1)	1.701 (3)	C(41)-S(2)	1.682 (4)
C(41)-S(2′)	1.736 (4)	N(3)...S(1)	3.195 (5)
O(1W)...S(2)	3.207 (5)		
C(2)-C(1)-C(6)	117.4(3)	C(1)-C(2)-C(3)	121.7(3)
C(2)-C(3)-C(4)	121.3(3)	C(3)-C(4)-C(5)	117.2(3)
C(4)-C(5)-C(6)	121.8(3)	C(4)-C(5)-C(8)	130.4(3)
C(6)-C(5)-C(8)	107.9(2)	C(1)-C(6)-C(5)	120.6(2)
C(1)-C(6)-C(7)	130.7(3)	C(5)-C(6)-C(7)	108.6(3)
C(6)-C(7)-O(1)	130.2(3)	C(6)-C(7)-N(1)	105.8(2)
O(1)-C(7)-N(1)	124.0(3)	C(7)-N(1)-C(8)	111.1(2)
C(7)-N(1)-C(9)	124.8(2)	C(8)-N(1)-C(9)	123.6(2)
C(5)-C(8)-N(1)	106.6(2)	C(5)-C(8)-O(2)	129.2(2)

N(1)-C(8)-O(2)	124.2(3)	N(1)-C(9)-C(10)	114.8(2)
C(9)-C(10)-N(3)	114.6(2)	C(10)-N(3)-C(20)	117.9(2)
C(12)-C(11)-C(16)	117.5(3)	C(11)-C(12)-C(13)	121.7(2)
C(12)-C(13)-C(14)	120.6(3)	C(13)-C(14)-C(15)	117.7(3)
C(14)-C(15)-C(16)	121.3(2)	C(14)-C(15)-C(18)	130.3(3)
C(16)-C(15)-C(18)	108.5(2)	C(11)-C(16)-C(15)	121.2(3)
C(11)-C(16)-C(17)	130.8(3)	C(15)-C(16)-C(17)	108.0(2)
C(16)-C(17)-O(3)	130.0(2)	C(16)-C(17)-N(2)	106.2(2)
O(3)-C(17)-N(2)	123.8(2)	C(17)-N(2)-C(18)	110.2(2)
C(17)-N(2)-C(19)	122.7(2)	C(18)-N(2)-C(19)	126.9(2)
C(15)-C(18)-N(2)	107.2(2)	C(15)-C(18)-O(4)	128.2(3)
N(2)-C(18)-O(4)	124.6(2)	N(2)-C(19)-C(20)	115.1(2)
N(3)-C(20)-C(19)	110.9(2)		
C(22)-C(21)-C(26)	118.0(3)	C(21)-C(22)-C(23)	120.2(3)
C(22)-C(23)-C(24)	122.6(3)	C(23)-C(24)-C(25)	116.5(3)
C(24)-C(25)-C(26)	120.8(2)	C(24)-C(25)-C(28)	131.0(3)
C(26)-C(25)-C(28)	108.1(2)	C(21)-C(26)-C(25)	121.8(3)
C(21)-C(26)-C(27)	130.1(3)	C(25)-C(26)-C(27)	108.1(2)
C(26)-C(27)-O(5)	130.0(2)	C(26)-C(27)-N(4)	105.9(2)
O(5)-C(27)-N(4)	124.0(2)	C(27)-N(4)-C(28)	111.6(2)
C(27)-N(4)-C(29)	122.8(3)	C(28)-N(4)-C(29)	125.5(2)
C(25)-C(28)-N(4)	106.2(2)	C(25)-C(28)-O(6)	129.2(3)
N(4)-C(28)-O(6)	124.7(2)	N(4)-C(29)-C(30)	109.5(2)
C(29)-C(30)-N(6)	112.4(2)	C(30)-N(6)-C(40)	113.8(2)
C(30)-N(6)-C(41)	123.4(2)	C(40)-N(6)-C(41)	122.7(2)
C(32)-C(31)-C(36)	117.2(3)	C(31)-C(32)-C(33)	120.5(3)
C(32)-C(33)-C(34)	122.3(3)	C(33)-C(34)-C(35)	117.1(3)
C(34)-C(35)-C(36)	120.9(2)	C(34)-C(35)-C(38)	129.9(3)
C(36)-C(35)-C(38)	109.2(2)	C(31)-C(36)-C(35)	122.0(3)
C(31)-C(36)-C(37)	130.6(3)	C(35)-C(36)-C(37)	107.4(2)
C(36)-C(37)-O(7)	128.1(3)	C(36)-C(37)-N(5)	106.0(2)
O(7)-C(37)-N(5)	125.9(2)	C(37)-N(5)-C(38)	112.2(2)
C(37)-N(5)-C(39)	124.1(2)	C(38)-N(5)-C(39)	123.7(2)
C(35)-C(38)-N(5)	105.2(2)	C(35)-C(38)-O(8)	130.2(3)
N(5)-C(38)-O(8)	124.6(2)	N(5)-C(39)-C(40)	112.9(2)
N(6)-C(40)-C(39)	113.0(2)		
N(6)-C(41)-S(1)	119.8(2)	N(6)-C(41)-S(2)	119.7(2)
S(1)-C(41)-S(2)	119.8(2)	N(6)-C(41)-S(2)'	118.8(2)
S(1)-C(41)-S(2)'	120.8(1)	N(3)-H(3B)...S(1)	160.4(3)

One of the S atoms in the CS_2 group exhibits two fold disorder and a molecule of water of crytallisation exists for two (padtc)(paH) units. Of the two sulfhur, atoms S(2) shows a very large disorder and it has a non-bonded interaction with a water molecule, S(2)....O(1W) (distance is 3.207(5)Å). The disorder associated with the S(2) atom results in another occupancy at S(2'). The longer C(41)-S(1) distance, 1.701(3)Å, is due to S(1)...N(3) non-bonded interaction with the $(paH)^+$ cation at a distance of 3.195(5)Å. Bond parameters of the alkyl chains attached to the N atom and the phenyl rings are normal except C(20)-N(3) for a relatively long distance of 1.506(4)Å, which is caused by packing requirements. The packing diagram is shown in Fig.2. It clearly shows the non-bonded interaction involving sulfur and the water molecule as well as the sulfur and the protonated amine (Table II).

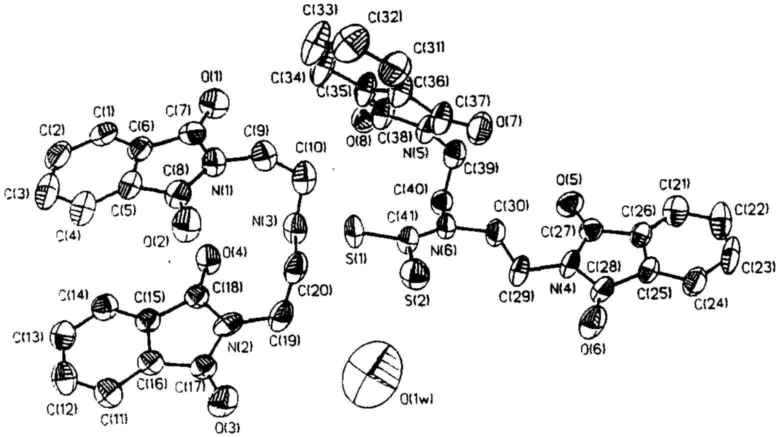


FIGURE 1 ORTEP Plot of $(padtc)^-$ $(paH)^+$

The thioureide, N(6)-C(41) bond distance is 1.359(3)Å, and possesses a partial double bond character. This is well recognised when compared with the N(6)-C(30) and N(6)-C(40) bond distances which are 1.460(3)Å and 1.467(4)Å, respectively. A clear N-C single bonded distance in the same compounds is 1.460(3)Å and the thioureide C-N distance was found to be 1.359(3)Å which unequivocally supports the contribution of the thioureide form to the structure. Valence bond sum (VBS) analysis of a compound whose crystal structure is known gives information about the nature of the bonds invovled.[9,10] The valency Vi of an atom connected to j atoms is equivalent to the sum of the individual valence contributions of each bond:

$$\sum_j v_{ij} = V_i$$

$$\text{where } v_{ij} = \exp\left[(R_{ij} - d_{ij})/b\right]$$

$$\text{where } R_{ij} = r_i + r_j - \frac{r_i r_j (\sqrt{c_i} - \sqrt{c_j})^2}{c_i r_i + c_j r_j}$$

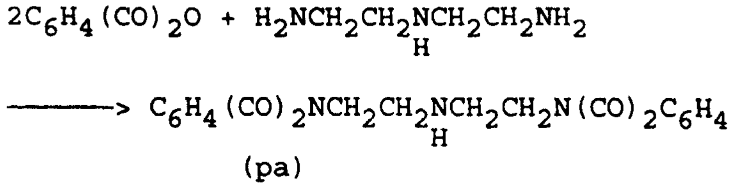
and b is a universal constant equal to 0.37. Valence bond sum calculations give a value of 1.4 for the thioureide bond (v_{ij}) whereas, a typical C-N single bond (C(40)N(6) or C(30)-N(6)) gives only 1.0 ± 0.2. This fact also supports the contribution of the thioureide bond to the dithiocarbamate described in this report.

EXPERIMENTAL

All reagents and solvents employed were commercially available. High grade purity materials (E-Merck) were used as supplied without further purification. Infrared spectra were recorded on a JASCO IR-700 spectrophotometer (range 4000–400 cm^{-1}) as KBr pellet.

(i) Preparation of 2,2'-Bis (phthalimidoethyl)amine (pa)

The parent amine, pa was synthesised from phthalic anhydride and Di(2-aminoethyl)amine (dien)[11]



$$2C_6H_4(CO)_2O + H_2NCH_2CH_2\underset{H}{N}CH_2CH_2NH_2$$

$$\longrightarrow C_6H_4(CO)_2NCH_2CH_2\underset{H}{N}CH_2CH_2N(CO)_2C_6H_4$$

(pa)

(ii) Preparation of 2,2'-bis(phthalimidoethyl)ammonium 2,2'-bis (phthalimidoethyl) dithiocarbamate ($(padtc)^{-}(paH)^{+}$).

Equimolar concentrations of the amine, pa and CS_2 were mixed together in acetonitrile to give a yellow solution of the dithiocarbamate. After an hour of mixing, yellow crystals of $(padtc)^{-}$ $(paH)^{+}$ separated from the solution. The analysis of crystals agreed with the proposed formula (C,H,N

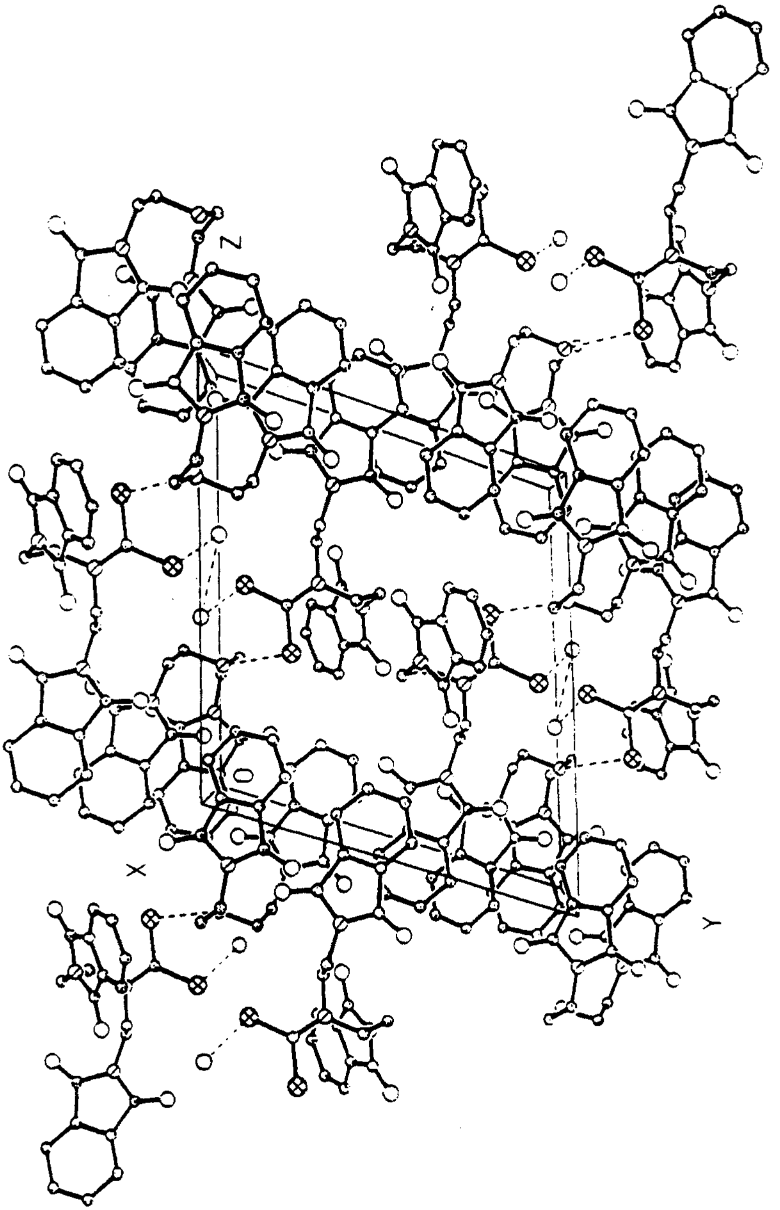
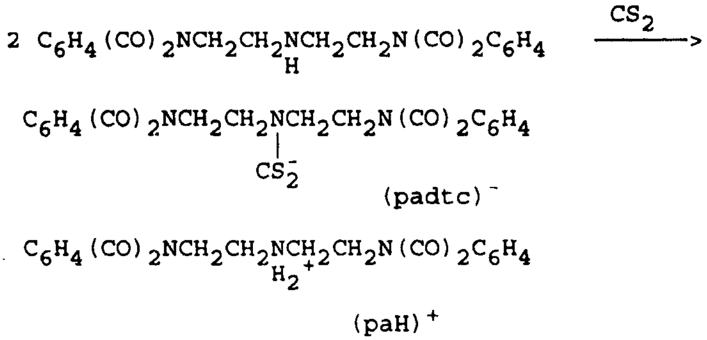


FIGURE 2 PACKING Diagram of (padtc)$^-$ (paH)$^+$

analysis. Found(Calcd) C: 60.4(60.6); H:4.3(4.4); N:10.2(10.3); S:7.7(7.9).



$$2\ C_6H_4(CO)_2NCH_2CH_2\underset{H}{N}CH_2CH_2N(CO)_2C_6H_4 \xrightarrow{CS_2}$$

$$C_6H_4(CO)_2NCH_2CH_2\underset{CS_2^-}{N}CH_2CH_2N(CO)_2C_6H_4$$

(padtc)$^-$

$$\cdot\ C_6H_4(CO)_2NCH_2CH_2\underset{H_2^+}{N}CH_2CH_2N(CO)_2C_6H_4$$

(paH)$^+$

X-ray Crystallography

Details of the crystal data, data collection and refinement parameters are summarized in Table I. Intensity data were collected on a Siemens R3m/v difractometer at room temperature using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$Å). The cell parameters were obtained from a least-squares refinement of 25 low angle reflections. Intensity of two standard reflections measured for every 123 reflections showed no significant change. Lorentz and polarization correctiones were made. Semi empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares technique. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed isotropically using a riding model. All the calculations were performed on SHELXTL plus PC version[12]. The measured bond distances and angles are presented in Table II.

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