International Journal of Advance Research in Science and Engineering
Volume No 06, Special Issue No. 03, September 2017, AFM-2017
www.ijarse.com
IJARSE
ISSN: 2319-8354

COMPUTATIONAL STUDIES AND SPECTRAL CHARACTERISATIONS OF A N, S DONOR ^{4}N - THIOSEMICARBAZONE

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Abstract

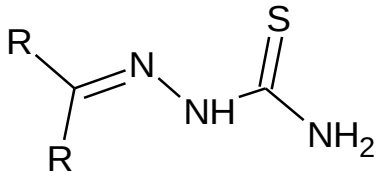
Thiosemicarbazones are well-known class of Sulphur/Nitrogen donor ligands. They have wide range of applications. Thiosemicarbazones are obtained by the condensation of thiosemicarbazides with suitable aldehydes or ketones. A salicylaldehyde derivative was selected for the synthesis of the present thiosemicarbazone. After synthesis of the thiosemicarbazone, a single crystal of the same was grown by slow evaporation method and it was subjected to Single Crystal X-Ray Diffraction Study (SXRD). The compound was analyzed using various spectral methods like FT-IR, NMR, and electronic spectroscopy. NLO activity measurement was also has been done. The DFT studies of the same compound were also done.

Keywords: Thiosemicarbazone, SXRD, DFT, NLO

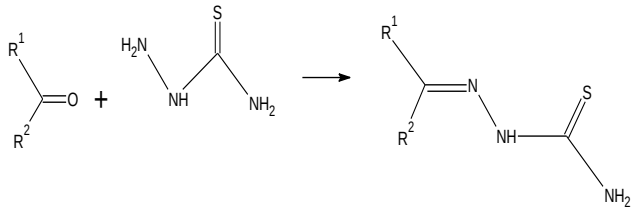
I. INTRODUCTION

Thiosemicarbazones are compounds having the formula R2C=N–NH–(CS)–NH2 (Scheme: 1). Thiosemicarbazones are obtained by the condensation of thiosemicarbazides with suitable aldehydes and ketones (Scheme: 2). they exist in two tautomeric forms, thione and thiol. Due to the wide-range of biological properties such as antitumor [1, 5], fungicidal [2], bactericidal [3], and antiviral [7] thiosemicarbazones and their metal complexes are now established as an important class of Sulphur/Nitrogen donor ligands. Being chelating ligands they are able to form an extensive variety of coordination compounds with both transition and main group metal ions [4]. Due to their broad biological activities and complexing ability, thiosemicarbazones are well-known ligands particularly for transition metal ions [6].

Scheme: 1



Scheme: 2



II. EXPERIMENTAL

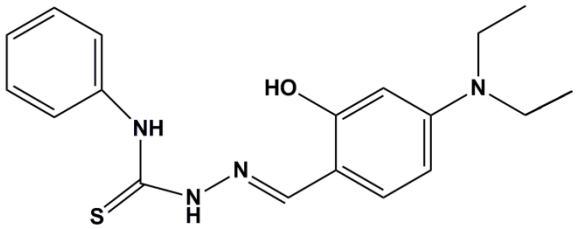
2.1 Materials and methods

4-[N, N-Diethyl amino] Salicylaldehyde (Sigma Aldrich) and N4-phenylthiosemicarbazide (Sigma Aldrich) used were of AR grade. AR ethanol (Merck) used without purification for synthesis.

2.2 Synthesis of 4 - (N, N Diethyl amino) salicylaldehyde thiosemicarbazone [NPSL]

The present compound, 4-[N,N-Diethyl amino] Salicylaldehyde thiosemicarbazone, was prepared by refluxing a mixture of N-phenyl thiosemicarbazide (0.167g;1mmol) in 20ml ethanol and 4-(N,N-Diethyl amino)salicylaldehyde (0.193g;1mmol) in 20ml ethanol for 2-3 hours (Scheme:3).The resultant solution was concentrated and cooled to room temperature. Dark green coloured crystalline precipitate was formed. It was then filtered, washed with ethanol and water. The resultant ligand was re-crystallized from ethanol by slow evaporation method [11].

Scheme: 3



III. RESULTS AND DISCUSSIONS

3.1 NLO ACTIVITY STUDY

NPSL has NLO value 25. It shows 41.67% NLO activity of NPSL with respect to the reference KDP which has an NLO value 60.

3.2 SINGLE CRYSTAL X-RAY DIFFRACTION STUDY

From single crystal X-ray diffraction studies the compound was found to be recrystallized in the monoclinic system.

CCDC Deposition

CCDC NO of the compound is 1511773. This data can be obtained from Cambridge crystallographic data centre or http:// www.ccdc.cam.ac.uk/concs/

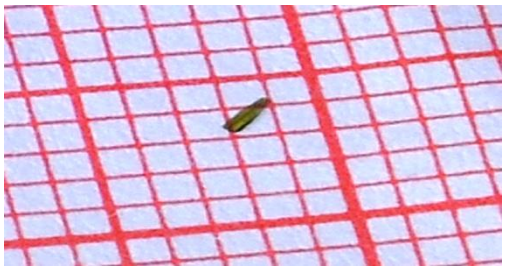


Fig.1

Photograph of the crystal

International Journal of Advance Research in Science and Engineering
Volume No 06, Special Issue No. 03, September 2017, AFM-2017
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ISSN: 2319-8354

Table 1 Crystal data and experimental parameters

Empirical formula	$C_{18}H_{22}N_4OS$
Formula weight	342.45
Temperature	173(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
a	8.7644(2) Å
b	18.0690(5) Å
c	11.4200(3) Å
α	90°
β	95.344(2°)
γ	90°
Volume	1800.66(8) $Å^3$
Z	4
Calculated density	1.263 g/cm^3
Absorption coefficient	0.192 mm^{-1}
F(000)	728
Crystal size/	0.47 × 0.14 × 0.1 mm^3
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.492 to 65.534
Index ranges	$-7 \le h \le 13$, $-25 \le k \le 26$, $-16 \le l \le 17$
Reflections collected	13441
Independent reflections	5998 [R_{int} = 0.0272, R_{sigma} = 0.0379]
Data/restraints/parameters	5998/0/220
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0449, wR_2 = 0.1080
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1190

Table 2 Bond Lengths of NPSL

Atom	Atom	Length/Å	Atom	Atom	Len
S1	C1	1.6826(12)	C4	C5	1.38
O1	C4	1.3530(15)	C5	C6	1.40
N1	C1	1.3542(15)	C6	C7	1.41
N1	C9	1.4147(15)	C7	C8	1.37
N2	C1	1.3440(16)	C9	C14	1.38
N3	C2	1.2931(15)	C10	C11	1.38
N4	C6	1.3723(15)	C11	C12	1.38
N4	C15	1.4605(19)	C12	C13	1.38
N4	C17	1.4592(18)	C13	C14	1.38
C2	C3	1.4379(15)	C15	C16	1.51
C3	C4	1.4160(16)	C17	C18	1.51
C3	C8	1.4010(16)			

Table 3 Bond Angles of NPSL

Atom	Angle/°	Atom	Angle/°
C1-N1-C9	129.14	C4-C5-C6	121.03
C1-N2-N3	119.96	N4-C6-C5	121.06
C2-N3-N2	116.68	N4-C6-C7	121.27
C6-N4-C15	121.4	C5-C6-C7	117.67
C6-N4-C17	121.49	C8-C7-C6	120.63
C17-N4-C15	116.62	C7-C8-C3	122.24
N1-C1-S1	125.48	C10-C9-N1	122.39
N2-C1-S1	120.02	C14-C9-N1	117.65
N2-C1-N1	114.46	C14-C9-C10	119.7
N3-C2-C3	121.41	C11-C10-C9	119.25
C4-C3-C2	122.7	C12-C11-C10	121.18
C8-C3-C2	120.36	C13-C12-C11	119.31
C8-C3-C4	116.83	C12-C13-C14	120.26
O1-C4-C3	121.34	C9-C14-C13	120.29
O1-C4-C5	117.12	N4-C15-C16	112.81
C5-C4-C3	121.52	N4-C17-C18	113.27

Table 4 Hydrogen bonding interactions

D-H···A	d(D-H)	d(H-A)	d(D-A)	D-H-A
O(1)-H(1)···N(3)	0.84	1.89	2.6319(13)	146.4
N(2)-H(2)···S(1)	0.88	2.58	3.3491(11)	146

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ISSN: 2319-8354

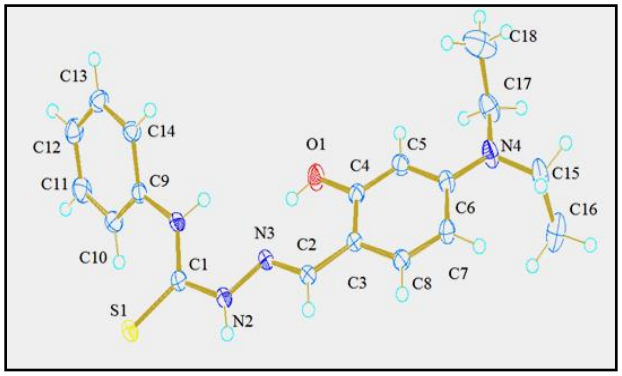

Fig.2 The molecular structure of NPSL

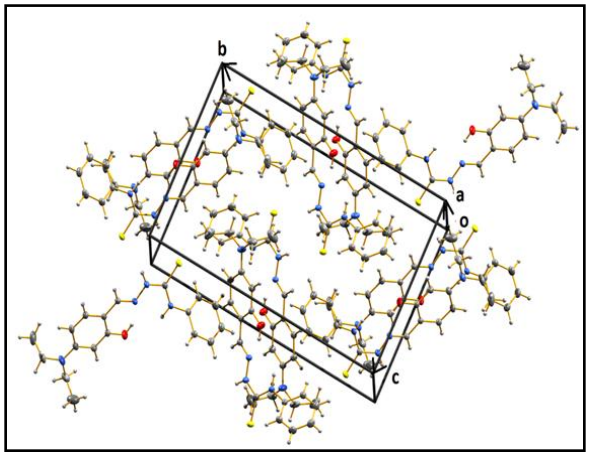

Fig.5 Packing Diagram along a-axis

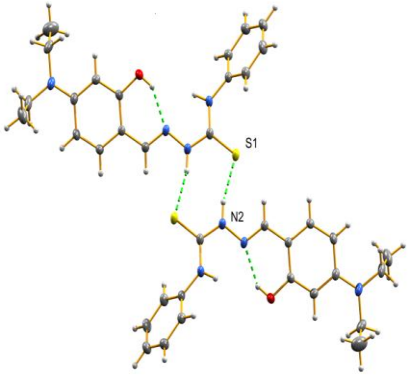

Fig.3Asymmetric Unit

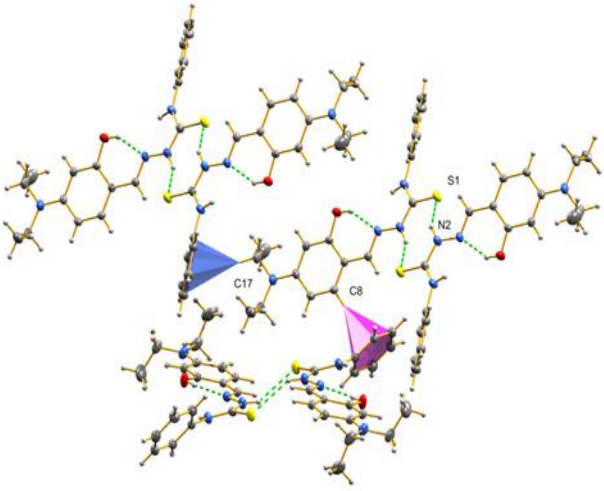

Fig.4 3D supramolecular network.

This molecule adopts an E conformation about the C2=N3 bond (Fig. 2) and an intramolecular O···H\\u008943N hydrogen bond increases the rigidity. They form a centrosymmetric dimers by means of N···H···S hydrogen bond interaction (Fig. 3) and the formed dimers are linked by two types of C-H···π interactions (Fig. 3) thereby generating a 3D-supramolecular architecture. There are no significant stacking intercalations. The packing diagram viewed on a - axis is shown in Fig. 5. The title compound, has two molecules in the asymmetric unit and both have trans configurations with respect to azomethine double bond and an intramolecular O···H\\u008943N hydrogen bond. The N---H...S hydrogen bond interaction forms centrosymmetric dimers and two kinds of C---H ...\p interactions present in the molecular crystal connect such dimers to generate a 3D-supramolecular architecture in the lattice. There are no significant stacking intercalations present in the crystal.

3.3 ELEMENTAL ANALYSIS

From elemental analysis it is clear that the experimental values are in good agreement with the theoretical values.

Table 5 CHNS values

NPSL	C%	N%	H%	S%
OBSERVED	64.63	17.14	6.78	11.7
CALCULATED	63	16.37	6.43	9.35

3.4 SPECTRAL STUDIES

a) FT-IR

The peak at 3363 cm–1 is assigned to OH stretching frequency. The 2NH stretching frequency is observed at 3137 cm–1. The =CH stretching frequency is observed at 2971 cm–1. The IR spectrum shows a band at 1422cm–1 which is due to υ (C=N) stretching mode vibration. The υ (N-N) band of the compound is at 1100cm-1. Band at 1220 cm–1 is assigned to C=S stretching vibrations. The band at 817 cm-1 is due to C=S bending mode. Since there is no band near 2600-2500 cm-1due to SH group the compound is in the neutral form.

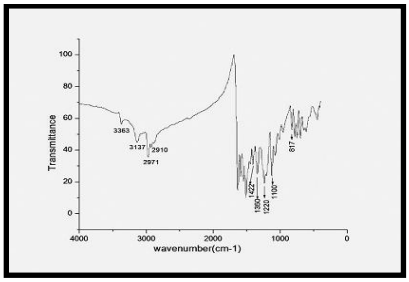

Fig.6 IR Spectrum of NPSL

b) NMR Spectra

^{1}H NMR

^{1}H NMR studies shows the proton atmosphere of the ligand. Triplets at 1.105 is due to CH3 protons in diethyl amino group. The quartets around 3.600ppm are due to CH2 protons in diethyl amino group. Multiplets between 6 & 7 ppm indicates phenyl ring protons. A singlet around 9.824 ppm indicates protons attached to N=C. A singlet around 11.444 ppm shows the presence of hydroxyl proton.

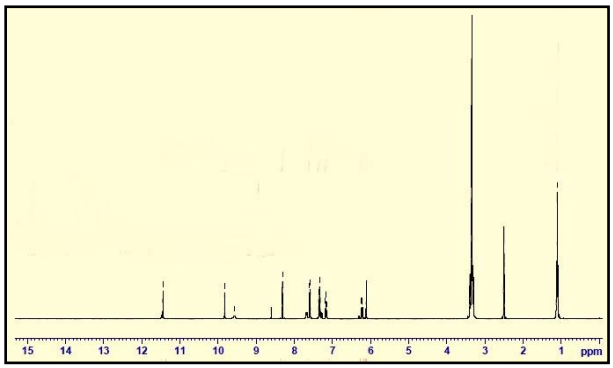

Fig.7

^{1}H NMR of NPSL

^{13}C NMR

^{13}C spectrum can be used to find out the types of carbon present in the compound. A peak at 174.456ppm shows the presence of C=S carbon. The peak at 158.306 is due to the presence of CH=N carbon. The singlet at 150.295 is due to NH-C from the phenyl part. The carbon atom attached to azomethine carbon (C-CH=N) show signal at a low field, 97.281 ppm. The singlet at 104.008 is due to the carbon atom in the phenyl ring which is substituted with OH group. The singlet at 107.384 is due to the presence of carbon which is attached to the diethyl amino group. The remaining aryl carbons (C 4, C 7 and C 8) gives signals at 128.9, 140.5 and149. The signals at 43.824ppm and at 12.531ppm are due to the methylene and methyl groups in the diethyl amino group. The signals at 139.315, 129.20, 127.952, 125.074 and 124.750 are due to the other carbon atoms in the two phenyl rings.

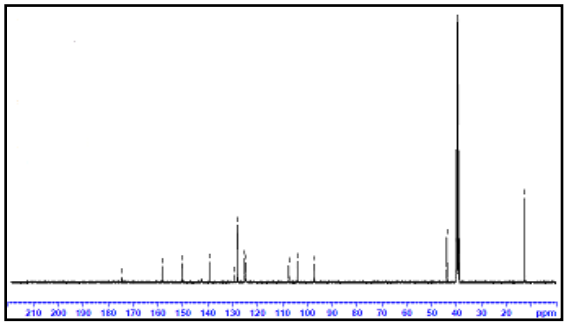

Fig.8

^{13}C NMR of NPSL

c) UV-VIS Spectrum

The UV-VIS spectrum of NPSL shows two absorption maxima. .The absorption peak at 313 nm corresponds to π–π* transition and the peak at 410nm is due to n–π* transition.

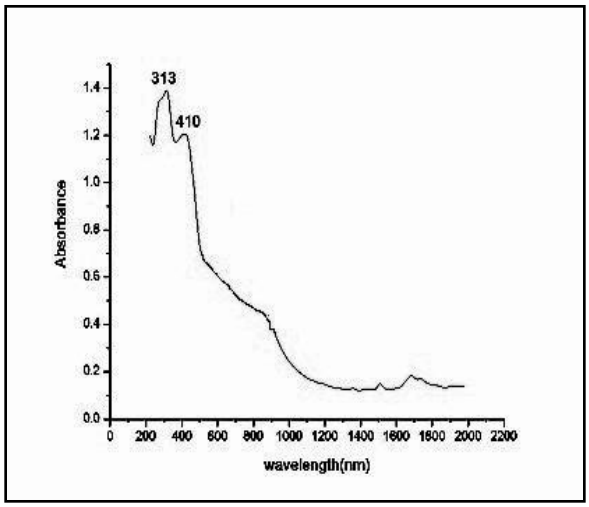

Fig.9 UV-VIS Spectrum of NPSL

3.5 COMPUTATIONAL STUDIES

a) Geometry Optimization

The optimized structure parameters of NPSL are calculated by B3LYP basis set and are listed in the below Tables (6 to 10). The optimized geometry of the compound calculated by the B3LYP method of DFT agrees well with the experimental results. The gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [9]. The calculated vibrational frequencies have also been scaled by a factor of 0.9673. By combining the results of the GAUSSVIEW'S program [10] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. This approach was found to be very straight forward for the prediction of IR frequencies of the ligand. DFT calculations provide excellent vibrational frequencies of organic compound if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies.

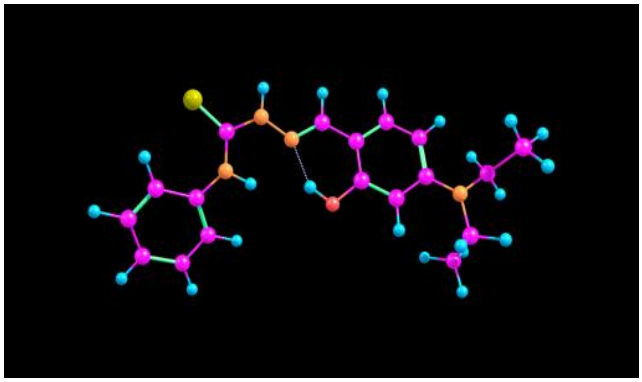

Fig.10

Optimized geometry of NPSL

b) Optimized geometrical parameters of NPSL

Table 6 Comparison Of Bond Length

Bond Length	Calculated	Experimental
R(1,2)	1.3812	1.3843
R(1,6)	1.401	1.4
R(2,3)	1.403	1.416
R(2,8)	1.3341	1.353

R(3,4)	1.3966	1.416
R(5,6)	1.4152	1.4196
R(3,10)	1.454	1.4379
R(6,14)	1.3666	1.3723
R(14,22)	1.4554	1.4605
R(8,9)	0.946	0.84
R(10,11)	1.0851	0.95
R(10,29)	1.2634	1.2931
R(14,15)	1.4551	1.4592
R(29,30)	1.3656	1.387
R(30,31)	0.9961	0.88
R(30,32)	1.3457	1.344
R(32,33)	1.6815	1.6826
R(32,34)	1.3366	1.3542
R(34,36)	1.4265	1.4147
R(30,31)	0.9961	0.88
R(34,35)	0.9941	0.88
R(36,37)	1.3833	1.3877
R(36,41)	1.3846	1.3931

Table 7 Comparison Of Bond Angle

Bond Angle	Calculated	Experimental
A(2,1,6)	121.6576	121.03
A(1,2,3)	121.1799	121.52
A(1,2,8)	116.6679	117.12
A(3,2,8)	122.1521	121.34
A(2,3,4)	116.618	116.83
A(2,3,10)	124.2514	122.7
A(4,3,10)	119.1278	120.36
A(3,4,5)	123.1486	122.24
A(4,5,6)	120.1061	120.63
A(1,6,14)	121.3657	121.06
A(2,8,9)	110.1902	109.5
A(3,10,11)	115.4658	119.3
A(3,10,29)	124.6408	121.41
A(11,10,29)	119.8932	119.3
A(30,32,33)	118.7842	120.02
A(30,32,34)	115.5578	114.46
A(33,32,34)	125.6556	125.48
A(32,34,36)	126.3923	129.14
A(35,34,36)	116.715	115.4
A(29,30,31)	120.405	120

Table 8 Comparison of IR Values

IR Intensity	Wave Number (Experimental)	Wave Number (Theoretical)	Assignments
0.7619	1013	1017.008	C-C Stretch
8.345	1350	1359.9587	C-C Stretch
8.5827	1100	1112.1282	N-N Stretch
8.9923	817	811	C-S Bend
13.0676	954	944	C-H Bend
21.0609	3137	3191.6573	N-H Stretch
25.6251	1220	1217.3332	C-S Stretch
29.2657	2971	2972	C-H Stretch
33.4495	3363	3535.4668	O-H Stretch
188.5771	1422	1426.7628	C-N Stretch
309.2376	1549	1533.7846	O-H Bend

Table 9 Comparison of ^{1}H NMR

Atoms	Experimental	Theoretical
H7	9.84	25.62
H9	11.83	8.824
H11	7.602	7.161
H12	6.24	6.563

H13	6.234	5.871
H16	3.096	3.5
H17	2.85	3.6
H19	0.656	1.105
H20	0.874	1
H21	0.099	0.89
H23	3.08	3.5
H24	2.86	3.61
H26	0.87	0.65
H27	0.66	1.1
H28	1.06	1.16
H31	7.13	9.56
H35	7.61	8.31
H42	6.54	7.321
H43	7.03	7.36
H44	6.88	7.341
H45	7.14	7.583
H46	8.9	7.602

Table 10

Comparison of ^{13}CNMR

Atoms	Experimental	Theoretical
C1	95.1515	129.12
C2	160.182	107.384
C3	107.3198	97.28
C4	132.6066	127.952
C5	102.2402	104.1
C6	150.4502	104.008
C10	144.5281	158.306
C18	8.7077	12.4
C22	42.868	43.824
C25	8.607	12.531
C32	169.5561	174.456
C36	139.5344	150.295
C37	118.5039	119.5
C38	128.2	139.315
C39	123.1	120.75
C40	127.26	123.6
C41	116.23	124.75

IV. CONCLUSION

We have synthesised 4-(N, N-diethyl amino) salicylaldehyde and the single crystal was grown using ethanol as solvent by slow evaporation method. The compound crystallizes in the monoclinic crystal system, space group $P2_1/c$, Z=4, V= 1800.66(8) $Å^3$, with unit cell parameters α= 90°, β= 95.344(2°), γ=90°. The compound was analyzed by FT-IR, NMR, UV-VIS spectral methods. From spectral analysis it is clear that the compound is present in the neutral form. The DFT study of the compound was also done. Comparison of theoretical and experimental values shows good agreement with each other except for a few values. The difference may be due to the difference in physical states during theoretical and experimental studies.

V. ACKNOWLEDGEMENTS

The authors are thankful to Jerry P. Jasinskic and Victoria A Smolenskic (Department of Chemistry, Keene State College 229 Main Street, Keene, NH 03435-2001 (603) 358-2563) for providing instrumental facilities and refining the data. We are also thankful to Dr. M Sithambaresan, Dept. Of chemistry, Eastern University, Sree Lanka and Dr.Prathapachandra Kurup for their valuable

suggestions in XRD studies. We are also thankful to SAIF, STIC, KOCHIN for the spectral studies done.

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