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Synthesis and X-Ray Structural Investigation of N,N'-1,6-diaminohexane *bis*-Salicylaldehyde

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A symmetrical potentially tetradentate N_2O_2 Schiff base N,N'-1,6-diaminohexane *bis*-salicylaldehyde (H^2L), (2-OH) C_6H_4-CH = N$(CH_2)_6$ N = CH-C_6H_4 (2-OH) was synthesized and characterized by spectroscopic methods (FT-IR, ^{1}H NMR, ^{13}C NMR) and C, H, N analysis. The tetradentate Schiff base was derived from the condensation reaction between 0.001 mol of 1,6-diaminohexane with 0.002 mol salicylaldehyde in ethanol as a solution. In the other part of this work the geometry of (H^2L) Schiff base compound was fully optimized in the gas phase by AM1 semi-empirical method. Mulliken population study shows two nitrogen atoms and two oxygen atoms are the coordination sites for binding to the metal ions.

Key Words: Schiff base, X-ray study, 1,6-Diaminohexane, AM1, Semi-empirical.

INTRODUCTION

In last 25 years, extensive chemistry has surrounded the use of Schiff bases in inorganic chemistry. Azomethine compounds or Schiff bases are typically formed by the condensation of a primary amine and an aldehyde or ketones. The resulting functional group, R^1-HC=N-R^2, is called an imine[1] and particularly for binding metal ions *via* the N atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands or macrocycles. (Ketones, of course, will also form imines of the type R^1R^2 C = NR^3, but the reactions tend to occur less readily than with aldehydes). During the past decades, there has been a great deal of interest in the synthesis and characterization of transition metal Schiff base compounds. They show biological activities including antibacterial[2-5], antifungal[6], anticancer[7] and herbicidal activities[8]. Furthermore, Schiff bases are utilized as starting material in the synthesis of industrial[9] and biological compounds such β-lactams[10]. Schiff-bases are becoming increasing important in the medicinal, pharmaceutical, dye and plastic industries as well as for liquid-crystal technology and mechanistic investigation of drugs used in pharmacology, biochemistry and physiology[11]. We have

recently reported the use of some Schiff-base compounds in construction of poly vinyl chloride powder (PVC)- based membrane selective sensors[12-15] for Co^{2+}, Ag^{+} , Fe^{3+} and Hg^{2+}. Also in some of recently works have been studied as NLO materials[16-19].

In present work we synthesize a tetradentate Schiff base (H^2L). The biological and analytical uses of this compound are under study. The structure of N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L) is given in the Fig. 1.

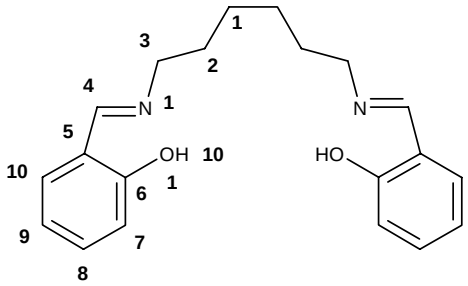

Fig. 1. Structure of N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L)

The structure was elucidated by direct methods, the atomic positions were calculated geometrically; the final R = 0.0531. The atomic coordinates and the isotropic thermal parameters are given in Table-1. Selected interatomic distances and bond angles for N,N´-*bis*-(salicyliden)-1,6-hexadiamine Schiff base compound are found in Table-2. All calculations were performed with SHELX-97 software[20]. The crystallographic data for N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L) is presented in Table-3.

TABLE-1
ATOMIC COORDINATED ($\times 10^4$) AND EQUIVALENT THERMAL PARAMETERS ($Å^2 \times 10^3$) FOR (H^2L) COMPOUND U (eq) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED UIG TENSOR

	X	Y	Z	U(eq)
N(1)	4086(1)	1605(2)	5785(1)	33(1)
O(1)	5880(1)	4944(2)	5862(1)	41(1)
C(1)	316(2)	1125(3)	4850(1)	42(1)
C(2)	1553(2)	2017(3)	5401(1)	39(1)
C(3)	2863(2)	482(3)	5379(1)	37(1)
C(4)	4783(1)	5557(3)	6364(1)	29(1)
C(5)	6048(1)	1609(3)	6754(1)	27(1)
C(6)	6560(2)	3760(3)	6474(1)	30(1)
C(7)	7799(2)	4693(3)	6836(1)	34(1)
C(8)	8511(2)	3532(3)	7472(1)	35(1)
C(9)	8006(2)	1434(3)	7761(1)	36(1)
C(10)	6789(2)	480(3)	7398(1)	32(1)

TABLE-2
SELECTED BOND ANGLES (Å) AND BOND LENGTHS FORM X-RAY DIFFRACTION DATA FOR N,N´-1,6-DIAMINOHEXANE *BIS*-SALICYLALDEHYDE (H^2L)

Selected bonds or bond angles	Bond length (Å) or and bond lengths (°)
N(1)-C(4)	1.2769(18)
N(1)-C(3)	1.4590(18)
O(1)-C(6)	1.3464(17)
O(1)-H(10)	0.9849
C(1)-C(1) # 1	1.514(3)
C(1)-C(2)	1.533(2)
C(1)-H(1B)	0.9700
C(1)-H(1C)	0.9700
C(2)-C(3)	1.516(2)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-(H3A)	0.9700
Selected angles	
C(4)-N(1)-C(3)	119.87(14)
C(6)-O(1)-H(10)	107.8
C(1) #1-C(1)-C(2)	113.74(17)
C(1) #1-C(1)-H(1B)	108.8
C(2)-C(1)-H(1B)	108.8
Selected torsion angles	
C(1) #1-C(1)-C(2)-C(3)	66.7(2)
C(4)-N(1)-C(3)-C(2)	126.97(15)
C(1)-C(2)-C(3)-N(1)	169.59(13)
C(3)-N(1)-C(4)-C(5)	177.36(12)

TABLE-3
CRYSTALLOGRAPHIC DATA FOR THE INVESTIGATED OF N,N´-1,6-DIAMINOHEXANE *BIS*-SALICYLALDEHYDE (H^2L)

Empirical formula	$C_{20}H_{24}N_2O_2$
Formula weight	324.41 g mol^{-1}
Temperature (k)	120 ± 2
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2 (1) /c
Unit cell dimensions	a=9.365(12) Å $\alpha = 90°$
	b=5.791(7) Å $\beta = 91.140(3)°$
	c=16.042(2) Å $\gamma = 90°$
Volume & Z	869.95(19)°A^3 & 2
Density (calculated)	1.238 mg m^3
Absorption coefficient	0.080 mm^{-1}
F(000)	348

Crystal size θ range for data collection	0.25 × 0.40 × 0.55 mm & 2.18 to 28.00º
Index ranges	$-8 \le h \le 12$, $-7 \le k \le 7$, $-20 \le 1 \le 21$
Reflections collected	5880
Independent reflections	2063 [R (int.) = 0.0559]
Completeness to θ = 28.00	98.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2063/0/109
Goodness – of fit on F^2	1.014
Final R indices for 1552 refl. with I 〉 2 sigma (I)	R1 = 0.0531, wR2 = 0.1008
R indices (all data)	R1 = 0.0736, wR2 = 0.1096
Largest diff. peak and hole (e. $Å^{-3}$)	0.265 and –0.229

EXPERIMENTAL

Salicylaldehyde and 1,6-diaminohexane (reagent grade, Merck). All solvents were dried before use by standard methods.

Preparation and characterization of Schiff base (H^2L): A mixture of 0.002 mol of salicylaldehyde in 10 mL methanol and 0.001 mol of 1,6-diaminohexane in 10 mL methanol was refluxed for 1.5 h. The reaction mixture changed to yellow colour. The precipitate was collected and washed with a little cold methanol. This product was recrystallized with a solution of 50 : 50 ethyl acetate and chloroform. Yellow crystalline N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L) was obtained: Yield 72%; m.p. 78ºC. Anal. (%) calcd. for $C_{20}H_{24}N_2O_2$: C, 74.07; H, 7.40; N, 8.64. Found: C, 74.02; H, 7.11; N, 8.34. The structure of Schiff-base was confirmed by using ^{1}H NMR, ^{13}C NMR and UV-Vis and FT-IR spectrometry. FT-IR spectra of salicylaldehyde and Schiff-base reveals that the absorption band of CO group 1669 cm^{-1} was disappeared and a new absorption band at 1624 cm^{-1} due to (C=N) group appeared upon the condensation. ^{1}H NMR (Bruker AM 400, $CDCl_3$ with TMS as internal standard), δ: 13.62 (2H, s, OH), 8.314 (2H, s, CH=N), 1.416-1.417 (12H, d. CH_2 groups) and 6.837-7.301 (8H, d, phenyl). ^{13}C NMR (Bruker AM 400, $CDCl_3$ with TMS as internal standard), δ: 26.838, 30.700, 59.346, 117.012, 118.405, 118.814, 131.111, 132.051, 161.359 and 164.600 the structure. UV-Vis spectral data (DMF as solvent): λ_{max} = 365 nm.

The structure of the N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L) compound with an atomic numbering scheme is shown in Fig.2. Two hydrogen bonds between H (10), N (1) and H (10´) N (1´) lying in this structure (Fig.2).

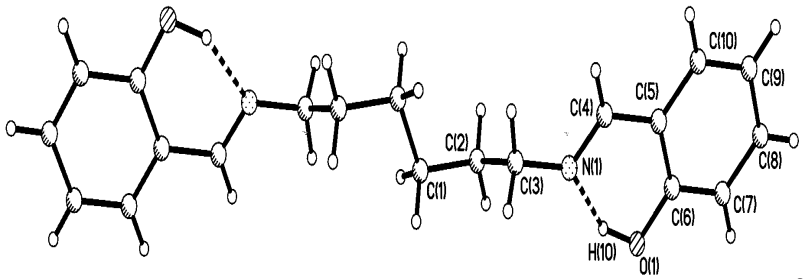

Fig. 2. Molecular structure of N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L)

The crystal-packing of N,N´-1,6-diaminohexane *bis*-salicylaldehyde compound is shown in Fig. 3.

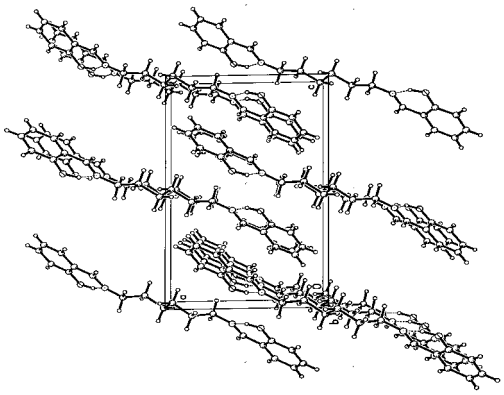

Fig. 3. Crystal packing diagram for N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L)

Theoretical calculations

The molecular geometry for Schiff base compound was fully optimized by using AM1 semi-empirical method. The Austin Model 1 (AM1) was the semi-empirical theory produced by Dewar,s group[21] an designed to eliminate the problems with MNDO[22] semi-empirical method, that were considered to arise from a tendency to overestimate repulsion between atoms separated by distances approximately equal to the sum of their Vander Waals radii. Geometry optimization calculations were performed on the Schiff base structure, using atoms with Hyperchem 5.0[23] atomic partial charges, and the results are presented in Fig. 4.

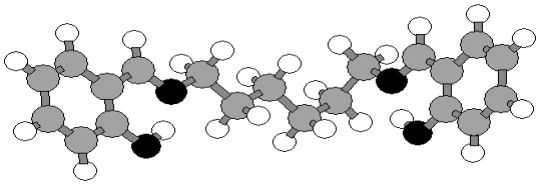

Fig. 4. Optimized geometry for N,N´-1,6-diaminohexane *bis*-salicylaldehyde (H^2L) by AM1 semi-empirical method

Mulliken population study shows O (10), O (10´), N (1) and N (1´) are the coordination sites for this Schiff base compound (H^2L). The charge density on O (10), O (10´´), N (1) and N (1´) are -0.259, -0.260, -0.233 and -0.235.

Conclusions

A tetradentate Schiff base compound is synthesized, this ligand is soluble in $CHCl_3$. Crystal data collection and refinements for the compound are listed in this work. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication No. CCDC 288853[24].

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REFERENCES

1. H. Schiff, *Ann. Chem. Suppl.*, **3**, 343 (1864).
2. M.A. Baseer, V.D. Jadhav, M.R. Phule, Y.V. Archana and Y.B. Vibhute, *Orient. J. Chem.*, **16**, 553 (2000).
3. P.G. More, R.B. Bhalvankar and S.C. Pattar, *J. Indian Chem. Soc.*, **78**, 474 (2001).
4. F.D. Karia and P.H. Parsania, *Asian J. Chem.*, **11**, 991 (1999).
5. A.H. El-Masry, H.H. Fahmy and A.S.H. Abdelwahed, *Molecules*, **5**, 1429 (2000).
6. W.M. Singh and B.C. Dash, *Pesticides*, **22**, 33 (1988).
7. S.B. Desai, P.B. Desai and K.R. Desai, *Hetrocycl. Commun.*, **7**, 83 (2001).
8. S. Samadhiya and A. Halve, *Orient. J. Chem.*, **17**, 119 (2001).
9. F. Aydogan, N. Ocal, Z. Turgut and C. Yolacan, *Bull. Korean Chem. Soc.*, **22**, 476 (2001).
10. A.E. Taggi, A.M. Hafez, H. Wack, B. Young, D. Ferraris and T. Lectka, *J. Am. Chem. Soc.*, **124**, 6626 (2002).
11. J. Casaszar, J. Morvay and O. Herczeg, *Acta. Phys. Chem.*, **31**, 717 (1985).
12 M.H. Mashhadizadeh and I. Sheikhshoaie, *Anal. Bioanal. Chem.*, **375**, 708 (2003).
13. T. Shamspur, M.H. Mashhadizadeh and I. Sheikhshoaie, *J. Anal. At. Spectrom.*, **18**, 1407 (2003).
14. M.H. Mashhadizadeh, I. Sheikhshoaie and N. Monadi, *Talanta*, **64**, 1048 (2004).
15. M.H. Mashhadizadeh and I. Sheikhshoaie, *Talanta*, **60**, 73 (2003).
16. M. Jalali-Heravi, A.A. Khandar and I. Sheikhshoaie, *Spectrochim. Acta*, **56A**, 1575 (2000).
17. I. Sheikhshoie and M.H. Mashhadizadeh, *Russ. J. Coord. Chem.*, **10**, 710 (2003).
18. I. Sheikhshoaie, M.H. Mashhadizadeh and S.S.-Nia, *J. Coord. Chem.*, **5**, 417 (2004).
19. I. Sheikhshoaie, M.H. Mashhadizadeh and N. Monadi, *Asian J. Chem.*, **18**, 25 (2006).
20. G.M. Sheldrick, SHELXTL, Version 5.10, Structure Determination Software Suite, Bruker AXS, Madison, WI (1998).
21. M.J.S. Dewar, E.G. Zeobisch, E.F. Healy and J.J.P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
22. M.J.S. Dewar and W. Theil, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
23. J.J.P. Stewart, MOPAC, A Semi-Empirical Molecular Orbital Program QCPE 455 1983, Version 6.00 (1990).
24. Further information may be obtained from: Cambridge CB21EZ, UK, by quoting the depository number CCDC 239985, e-mail: deposit@CCDC.com.au.uk.

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