

Synthesis and structural characterization of 1,3-bis(4-formylphenoxyethyl)-2,4,5,6-tetrachlorobenzene and 1,3-bis(4-(2-hydroxyphenyliminomethyl)phenoxyethyl)-2,4,5,6-tetrachlorobenzene

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Abstract – Two new macromolecular ligands, 1,3-bis(4-formylphenoxyethyl)-2,4,5,6-tetrachlorobenzene and 1,3-bis(4-(2-hydroxyphenyliminomethyl)phenoxyethyl)-2,4,5,6-tetrachlorobenzene were made from simple available starting materials and reported in this article. Their structures were also determined via FT-IR and NMR analysis of the pure compounds.

Index Terms - Dialdehyde, Diamine, Di-imine, Diols, FT-IR, Macromolecules, NMR, Spectroscopy.

1. INTRODUCTION

Macromolecular compounds particularly Schiff bases, received greater consideration in the recent medical and scientific advancements due to their relationship to catalytic, and biomimetic systems. They are applied as chelating agents to biology and medicine as well as in chemical techniques like magnetic resonance imaging (MRI), imaging with radioisotopes and radiotherapy due to their high kinetic and thermodynamic stability toward release of metal ions [1].

Designation and modification of macromolecular compounds into special ligands in order to mimic the functions of some important natural carrier molecules and enzymes has been employed in recognizing and transporting specific metal cations, anions or neutral molecules, as well as in understanding and reproducing the catalytic activity of metallo-enzymes and proteins [2], [3], [4], [5], [6], [7], [8].

Such macromolecules have been synthesized to specifically identify the role

played by the different donor atoms relative to their position, number and size of the chelating rings formed, flexibility and the shape of the coordinating moiety on the selective binding of charged or neutral species and on the properties arising from these aggregations [9], [10].

Emphasis has also been given to the coordination of various macromolecules and cyclophane systems with certain metal ions in both the lanthanide and the transition series to produce complex compounds of desired medical and pharmaceutical importance [11], [12], [13], [14], [15], [16].

Hetero macromolecular compounds incorporated in a macrocyclic ring provide rigidity and are able to participate in complexation through their soft donor atoms; for example macrocyclic ethers with pyridine and other nitrogen containing heterocyclic subunits were reported to form strong and selective interactions with various charged and neutral guest molecules [17], [18], [19], [20], [21].

Such macromolecular ligands complexes otherwise called organometallics had achieved positive application in medical diagnosis and treatments. For example, Gadolinium complexes of certain macromolecular ligands were used in hospitals to improve the contrast of magnetic resonance images (MRI) [22]. Manganese macromolecular complexes have achieved significant progress owing to the increase recognition of Mn (II) functions in biological system [23], [24]. Two new ligands of such kind are synthesized and structurally characterized in this article.

2. EXPERIMENTAL

2.1 Chemistry

All reagents and solvents are of standard grade and were used as without purification. Electro-thermal 9100 melting point apparatus was used in determining the Melting points of the new ligands. FT-IR spectra were recorded on the Bruker Alpha-P in the range of 4000-400 cm^{-1} . Routine ^1H (400 MHz) and ^{13}C (100 MHz) spectra were recorded in DMSO- d_6 or CDCl_3 at ambient temperature on a Bruker Ultrashield Plus 400MHz instrument. Chemical shifts (δ) are expressed in units of parts per million relative to TMS.

2.2 Synthesis

2.2.1 1,3-bis(4-formylphenoxy)methyl)-2,4,5,6-tetrachlorobenzene (L_1). To a solution of KOH (600mg, 10.70mmol) in Ethanol (20mL) was added *Para*-hydroxybenzaldehyde (1.30g, 10.60mmol) and stirred at 60°C for 45 minutes in an external oil bath. 2, 4, 5, 6-tetrachloro-1,3-bis(chloromethyl)benzene (1.0 g, 3.20 mmol) was then added slowly in 30 minute interval and the mixture was stirred overnight at the same temperature. The resulting product was stirred in cold distilled water, in order to remove unreacted starting materials. The purification was repeated two more times

and a white solid was obtained. $\text{C}_{22}\text{H}_{14}\text{Cl}_4\text{O}_4$: 1.41 g, yield 88%, MP: 148-150°C. FT-IR (solid cm^{-1}): 3074 $\nu(\text{C}=\text{H})$, 2806 and 2742 $\nu(\text{CHO})$, 1685 $\nu(\text{C}=\text{O})$, 1599 $\nu(\text{C}=\text{C})$, 1243 $\nu(\text{C}-\text{O})$, 788 $\delta(\text{C}=\text{C}-\text{H})$. ^1H NMR (CDCl_3), δ_{H} ppm: 5.45 (s, 4H, CH_2), 7.21 (d, $J = 8.28$ Hz, 4H), 7.89 (d, $J = 8.28$ Hz, 4H), 9.93 (s, 2H, CHO). ^{13}C NMR (CDCl_3), δ_{C} ppm: 66.51 (CH_2), 115.01, 130.60, 132.08, 132.29, 132.54, 137.02, 137.54, 163.38, 190.74 (CHO).

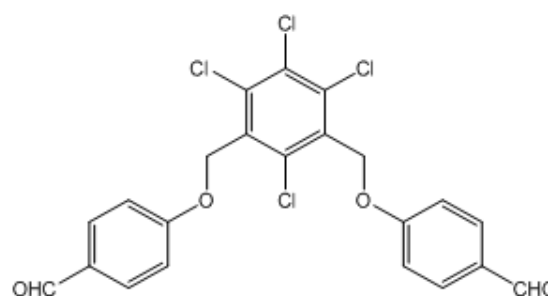


Figure 1: 1,3-bis(4-formylphenoxy)methyl)-2,4,5,6-tetrachlorobenzene (L_1).

2.2.2 1,3-bis(4-(2-hydroxyphenyliminomethyl)phenoxy)methyl)-2,4,5,6-tetra-chlorobenzene (L_2). To a stirred solution of *ortho*-aminophenol (150 mg, 1.37 mmol) in methanol (7 mL) was added dialdehyde (L_1) (300 mg, 0.62 mmol). The reaction mixture was stirred for 3 hours at 70°C. The resulting product was cooled, filtered and cleaned two times with methanol (5 mL). A pure pale yellow solid di-imines (L_2) was obtained. $\text{C}_{34}\text{H}_{24}\text{Cl}_4\text{N}_2\text{O}_4$: 374mg, yield 83%. Mp:182-184°C, FT-IR: (solid, cm^{-1}) 3375 $\nu(\text{OH})$, 3035 $\nu(\text{C}=\text{H})$, 1623 $\nu(\text{C}=\text{N})$ 1597 $\nu(\text{C}=\text{C})$, 1243 $\nu(\text{C}-\text{O})$, 745 $\delta(\text{C}=\text{C}-\text{H})$. ^1H NMR (DMSO), δ_{H} ppm: 5.45 (s, 4H, CH_2), 6.84 (t, $J = 7.53$ Hz, 2H), 6.90 (d, $J = 7.28$ Hz, 2H), 7.07 (m, 4H), 7.22 (m, 4H), 8.04 (d, $J = 8.53$ Hz, 4H), 8.67 (s, 2H, CHN), 8.94 (s, 2H, OH). ^{13}C NMR (DMSO), δ_{C} ppm: 66.55 (CH_2), 114.71, 115.83, 118.72, 119.41, 127.05, 130.09,

130.73, 131.09, 132.96, 136.24, 136.70,
137.83, 151.24, 158.15, 160.65

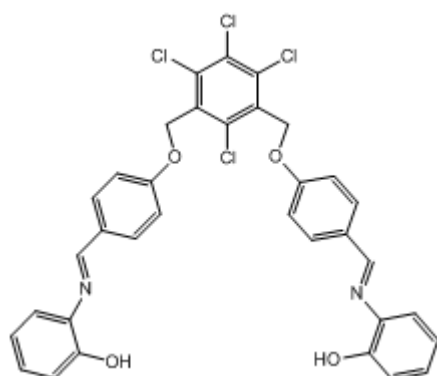


Figure 2: 1,3-bis(4-(2-hydroxyphenyliminomethyl)phenoxy)methyl)-2,4,5,6-tetra-chlorobenzene (L_2).

3. RESULT AND DISCUSSION

3.1 FT-IR analysis

The vibrational Spectra of L_1 and L_2 were studied in comparison in order to point out clearly the synthesis of L_2 from L_1 by reacting L_1 with ortho-aminophenol there by indicating the success of the reaction pathways. The comparative FT-IR Spectra show the following success:

Vibrational spectroscopy of (L_1) is studied in terms of the following important peaks: 2750-2850 cm^{-1} weak for aldehydic $\nu(\text{C-H})$ which are always two peaks. 1685-1700 cm^{-1} strong for Carbonyl $\nu(\text{C=O})$. 1580-1600 cm^{-1} strong for aromatic $\nu(\text{C}=\text{C})$, 1200-1250 cm^{-1} for $\nu(\text{C-O})$ and finally strong peak around 700 cm^{-1} for $\delta(\text{C}=\text{C}-\text{H})$. Disappearance of strong $\nu(\text{O-H})$ vibrations of phenyl (OH) groups of hydroxybenzaldehyde within the region of 3160-3250 cm^{-1} also confirm the formation of the dialdehyde ligand L_1 . The $\nu(\text{C=O})$ of the hydroxybenzaldehyde which was at around 1673 cm^{-1} slightly shift to 1685 cm^{-1} in the dialdehyde. See figures 3.

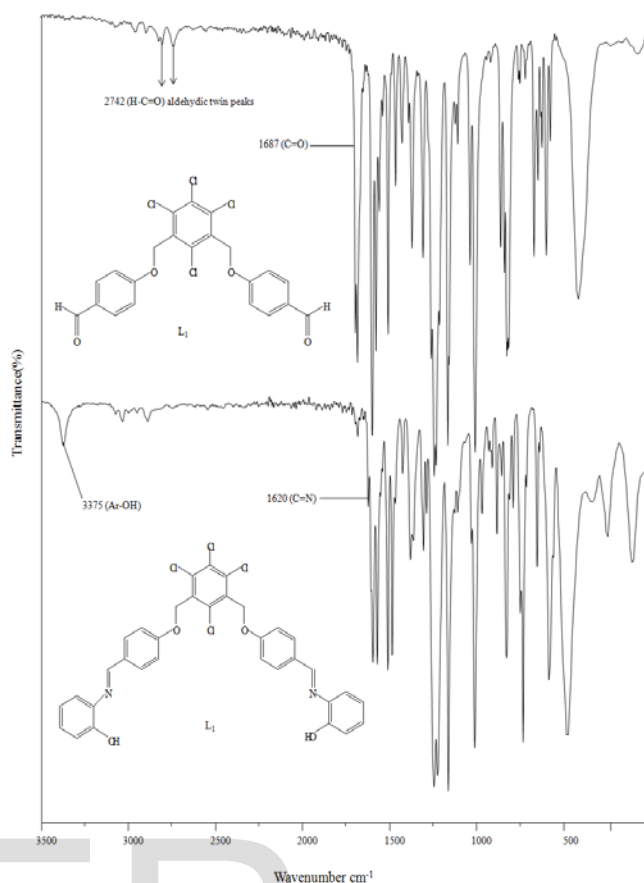


Fig 3: Comparative FT-IR spectra of L_1 and L_2

3.2 NMR analysis

^1H NMR of dialdehydes (L_1) shows a singlet for ethylene (CH_2) protons at around 5 - 5.20 ppm, and (CHO) protons at around 10 - 10.50 ppm. The integration for aromatic protons is significantly consistent with the structure of the dialdehyde (L_1). ^{13}C NMR of L_1 shows 10 different carbons atoms as expected in the chemical structure. See figure 4.

^1H NMR of di-imines (L_2) shows singlet for ethylene (CH_2) protons, around 5.2 - 5.50 ppm, and a new peak for ($\text{HC}=\text{N}$) protons at ~ 8.70 ppm while the (OH) protons were observed within the region of 9.00 - 9.20 ppm. ^{13}C NMR of di-imine (L_2) shows 15 expected number of carbon atoms as in the chemical structure. See figure 5.

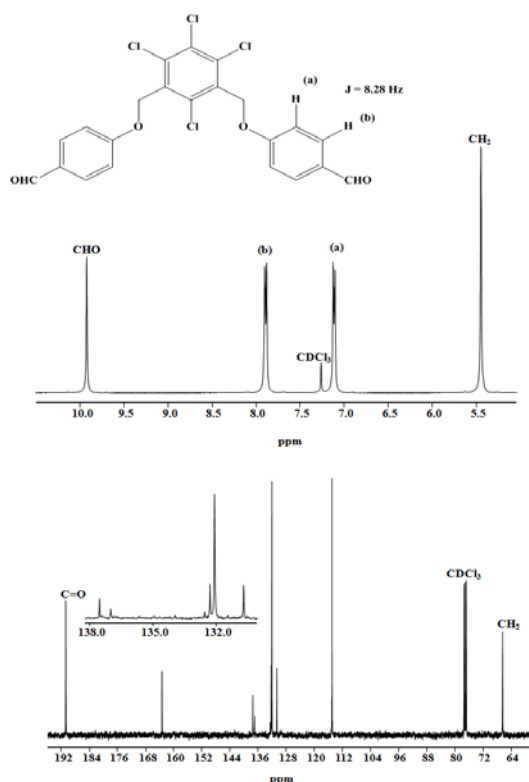


Figure 4: ^1H NMR and ^{13}C NMR spectra of dialdehyde (L_1) in CDCl_3 .

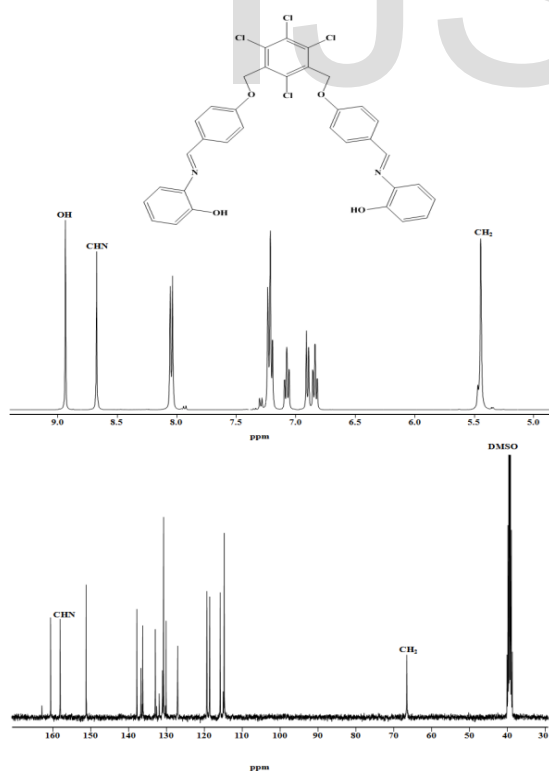


Figure 5: ^1H NMR and ^{13}C NMR spectra of di-imine (L_2) in DMSO.

4. CONCLUSION

Synthesis and structural characterization of the compounds via FT-IR and NMR have been accounted for. The synthetic steps have been carefully monitored and observed. The FT-IR and the NMR of L_1 and L_2 have been compared in order to assure the success of the synthesis of one ligand from the other. Test on microbial and other biological activities of either the ligands alone or in metal complexes would be investigated.

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REFERENCES

- [1] Lakshmi, B., Prabhavathi, A., Devi, M., Nagarajan, S. *J. Chem. Soc. Perkin Trans.* Pp. 1495, 1997. and Refs. cited therein.
- [2] (a) Curtis, N.F. *Coord. Chem. Rev.* Vol. 3, pp. 3, 1968 ; (b) Busch, D.H. *Science direct* Vol. 171, pp 241, 1971; (c) Nelson, S.M. *Pure Appl. Chem.* Vol. 52, pp. 2461, 1980.
- [3] Alexander, V. *Chem. Rev.* Vol. 95, pp. 273, 1995.
- [4] (a) Okawa, H., Furutachi, H., Fenton, D.E. *Coord. Chem. Rev.* Vol. 174, pp. 51, 1998; (b) Fenton, D.E., Okawa, H. *Chem. Ber.* Vol. 130, pp. 433, 1997; (c) Collinson, S.R., Fenton, D.E. *Coord. Chem. Rev.* Vol. 148, pp. 19, 1996; (d) Fenton, D.E. *Pure Appl. Chem.* Vol. 58, pp. 1986, 1437.
- [5] (a) Lindoy, L.F. *The Chemistry of Macrocyclic Ligand Complexes, Cambridge University, Cambridge, UK, 1989*; (b) Lindoy, L.F. *Pure Appl. Chem.* Vol. 61, pp. 1575, 1989.
- [6] Guerriero, P., Tamburini, S., Vigato, P.A. *Coord. Chem. Rev.* Vol. 139, pp.

- 17, 1995.
- [7] Kahn, O. in: Sikes A.G. (Ed.), *Advances in Inorganic Chemistry*, Academic Press, S. Diego, USA, pp. 179, 1995.
- [8] Murray, K.S. in: Sikes A.G. (Ed.), *Advanced in Inorganic Chemistry*, vol. 43, Academic Press, S. Diego, USA, pp. 261, 1995.
- [9] Coper S.R. (Ed.), *Crown Compounds: Toward Future Applications*, VCH Publisher Inc., New York, 1992.
- [10] Penitka, A. J., Kong, D. *Coord. Chem. Rev.* Vol. 216, pp. 55, 2001.
- [11] McKee, V. in: Sikes A.G. (Ed.), *Advanced in Inorganic Chemistry*, Vol. 49, 2000.
- [12] Bandi'n, R., Bastida, R., de Blas, A., Castro, P., Fenton, D.E. Maci'as, A. Rodri'guez, A., Rodri'guez-Blas, T. *J. Chem. Soc., Dalton Trans.* Pp. 1185, 1994.
- [13] R. Bastida, A. de Blas, P. Castro, D.E. Fenton, A. Maci'as, R. Rial, A. Rodri'guez, T. Rodri'guez-Blas, *J. Chem. Soc., Dalton Trans.* Pp. 1493, 1996.
- [14] Adams, H., Bastida, R., de Blas, A., Carnota, M., Fenton, D.E., Maci'as, A., Rodri'guez, A., Rodri'guez-Blas, T. *Polyhedron* 16, pp. 567, 1997.
- [15] Lodeiro C., Bastida, R., de Blas, A., Fenton, D.E., Maci'as, A., Rodri'guez, A., Rodri'guez-Blas, T. *Inorg. Chim. Acta* Vol. 267, pp. 55, 1998.
- [16] Be'rtolo, E., Bastida, R., de Blas, A., Fenton, D.E., Maci'as, A., Rodri'guez, A., Rodri'guez-Blas, T., Villar, Naturforsch., A. Z. *Teil B* Vol. 53, pp. 1445, 1998.
- [17] (a) Izatt, R. M., Bordunov, A. V., Zhu, C. Y., Hathaway, J. K. In *Comprehensive Supramolecular Chemistry*, (b) Gokel, G. W. Ed.; Pergamon: New York, Vol. 1, pp. 3595, 1996.
- [18] Izatt, R. M., Pawlak, K., Bradshaw, J. S., Bruening, R. L. *Chem Rev.* Vol. 91, pp. 1721, 1991.
- [19] (a) Gokel, G. W. *Crown Ethers and Cryptands (Monographs in Supramolecular Chemistry); The Royal Society of Chemistry: Cambridge*, Vol. 3, 1991; (b) Cram, D. J. *Container Molecules and their Guests (Monographs in Supramolecular Chemistry); The Royal Society of Chemistry: Cambridge*, Vol. 4, 1994; (c) Bell, T. W., Salmi, S. K. In *Inclusion Compounds*; J. L. Atwood, J. E. Davies, D. D. Macnicol, Eds.; *Oxford University Press: Oxford*, Vol. 4, pp. 325, 1991.
- [20] Kohler, E. W., Reuter, H. J. *J. Org. Chem.* Vol. 56, 1236, 1991.
- [21] Kohler, E. W., Prakt, H. J. *J. Org. Chem.* Vol. 56, pp. 12, 1991.
- [22] Chin, K.O., Morrow, A. J.R., Lake, C.H., Churchill, M.R. *Inorg. Chem.* Vol. 33, pp. 656, 1994.
- [23] Adams, H., Bastida, R., de Blas, A., Carnota, M., Fenton, D.E., Macias, A. *Inorg chem.* Pp. 337 – 451, 1995.
- [24] Sanyog S. et al *From Tetrahedron Letters*, Vol. 54 (19), pp. 2423- 2427, 2013.

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