

Available online at www.sciencedirect.com



CHINESE CHEMICAL LETTERS

Chinese Chemical Letters 22 (2011) 439-442

www.elsevier.com/locate/cclet

Synthesis and characterization of new azo containing Schiff base macrocycle

Saeed Malek-Ahmadi, Amir Abdolmaleki*

Department of Chemistry, Isfahan University of Technology, Isfahan-84156/83111, Iran

Received 24 August 2010 Available online 15 January 2011

Abstract

Fully conjugated Schiff base macrocycle has been prepared through a simple and mild condition, a one-pot cyclization procedure of four-component without using a template. The condensation reaction of related bis (hydroxybenzaldehyde) with phenylenediamines to prepare a conjugated [2 + 2] Schiff base macrocycle has been investigated and fluorescent [2 + 2] Schiff base macrocycles with N₂O₂ binding pockets has been prepared and characterized by elemental analysis, ¹H NMR, IR, Fluorescent, UV–visible and MALDI mass spectroscopies.

© 2010 Amir Abdolmaleki. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Schiff base macrocycle; Non-template; Azo compounds

During the last two decades, considerable efforts have been made for developing metal-free methods for macrocyclic synthesis [1–9]. Condensation of diamines and dialdehydes to form Schiff base macrocycles has been used by many researchers to form both small and large macrocycles, usually templated with transition metals [10–15]. Indeed, this reaction is used to synthesize an important class of ligands known as salen (short for N,N'-bis (salicylidene)ethylenediamine) and salphen (N,N'-bis(salicylidene)phenylenediamine). When these ligands are bound to transition metals, they form coordination complexes that can be useful for catalysis and can have very interesting optical properties. Specifically, Jacobsen's catalyst is a potent asymmetric epoxidation catalyst [16]. Recently, MacLachlan group prepared the soluble rings in good yield through the thermodynamically favored cyclocondensation of the corresponding dialdehyde and diamine [16] with potential to be used as shape-persistent macrocycles with optical properties.

In this paper; in an effort to obtain fully conjugated shape-persistent macrocycles, we have prepared the new azo containing Schiff base macrocycles. The incorporation of metals into rigid, conjugated covalently bonded macrocycle may offer opportunities for developing supramolecular materials and sensors triggered by ligand coordination to the metal [17].

1. Experimental

All of the chemical reagents were of analytical grade and used without further purification. Benzene-1, 2-diamine was sublimated for further purification.

* Corresponding author.

E-mail address: abdolmaleki@cc.iut.ac.ir (A. Abdolmaleki).

^{1001-8417/\$ –} see front matter © 2010 Amir Abdolmaleki. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved. doi:10.1016/j.cclet.2010.10.040

Preparing N,*N'-bis-(2-hydroxybenzaldehyde-5-yl)-benzene-1,3-diazene:* The benzene-1, 3-diamine (2.7 g, 25 mmol) is dissolved in (35 mL) of water and then hydrochloric acid (36%) (13 mL, 140mmol) is added and the temperature was adjusted to 0–5 °C by using ice bath and adding 25 g of ice in mixture of reaction, then a solution of sodium nitrite (3.6 g, 52 mmol) in (35 mL) of water were added by drop funnel in 30 min and then for 1 h the above solution was stirred. To prepare the second solution, sodium hydroxide (1.04 g) was dissolved in (13 mL) of water (2 mol/L), and then 2-hydroxybenzaldehyde (7.5 g, 54 mmol) was added. To form azo coupled compound the second solution was added to the first solution during 30 min by drop funnel and reaction was stirred for 3 h. A yellow solid precipitated when pH was adjusted to 7 and filtered and washed with ethanol to remove unreacted materials (yield was 40%). *R*_f 0.642(40/60) ethyl acetate/cyclohexane; ¹H NMR (400 MHz, CDCl₃): δ 13.10 (s, 2H, OH), 8.62 (s, 2H, CHO), 7.14 (m, 10H, Ar); ¹³C NMR (400 MHz, CDCl₃): δ 190.3, 160.4, 134.3, 132.3, 129.5, 129.0, 122.5, 122.3, 119.6. Anal. Calcd. for C₂₀H₁₄N₄O₄: C, 64.17; H, 3.77; N, 14.97. Found: C, 64.09; H, 3.80; N, 14.88. UV-vis (DMSO-*d*₆) λ_{max} = 259 nm. IR (KBr): ν = 3447, 1619, 1590, 1566, 1262 cm⁻¹.

Macrocycle 1: Benzene-1,2-diamine (0.220 g, 1.5 mmol) was dissolved in to 10-15 mL dried methanol or (ethanol), in 50 ml flask and then the solution was added to *N*,*N*[']-bis-(2-hydroxybenzaldehyde-5-yl)-benzene-1,3-diazene (0.583 g, 1.5 mmol) and stirred for one day in room temperature, the light brown solid was precipitated and filtered ($R_f = 0.083$) (40/60) ethyl acetate/cyclohexane, yield =52%, ¹H NMR (400 MHz, DMSO- d_6): δ 9.01 (s, 4H, OH), 8.30 (d, 4H, CH = N), 7.48 (m, 28H, aromatic H); Anal. Calcd. for C₅₂H₃₆N₁₂O₄.2 H₂O: C, 67.23; H, 4.34; N, 18.09. Found: C, 66.91; H, 4.37; N, 17.94. MALDI-mass: m/z = 892.3(M+H+). UV–vis (DMSO- d_6) $\lambda_{max} = 259$ nm. IR (KBr): $\nu = 3326$, 1624, 1602, 1491, 1262 cm⁻¹.

Macrocycle metal complexation. Typical procedure: Benzene-1, 2-diamine (0.220 g, 1.5 mmol); *N*,*N*'-bis-(2-hydroxybenzaldehyde-5-yl)-benzene-1,3-diazene (0.583 g, 1.5 mmol) were dissolved in dried methanol or ethanol(10-15 mL), followed by Zn(OAc)₂.2H₂O (0.328 g, 1.5 mmol). Reaction was stirred for 6 h. A light yellow solid was precipitated .The mixture was filtered and washed with ethanol. ($R_f = 0.166$) yield = 78%.¹H NMR (400 MHz, DMSO- d_6): δ 8.97 (*s*, 4H, CH = N), 7.85 (*q*, 4H, Ar), 7.35 (*m*, 8H, Ar), 7.20 (*m*, 8H, Ar), 6.67 (*d*, 4H, Ar), 6.47(*t*, 4H, Ar); UV–vis (DMSO- d_6) $\lambda_{max} = 293,258$ nm. IR (KBr): $\nu = 1614, 1585, 1569, 1537, 1462, 1441, 1391, 1299$ cm⁻¹; Anal. Calcd. for C₅₂H₃₆N₁₂O₄Zn ₂.2 H₂O: C, 59.16; H, 3.44; N, 15.92. Found: C, 58.93; H, 3.47; N, 15.85.

The macrocycle-2 was synthesized in 91% yield by reaction of macrocycle 1 with 2 equiv of $Zn(OAc)_2.2H_2O$ in MeOH for 15 min, at room temperature.

Macrocycle Cu (II) complexation. Yield = 76%, UV–vis (DMSO- d_6) λ_{max} = 259,307 nm. IR (KBr) ν : 1607, 1577, 1522, 1487, 1458, 1375, 1186 cm⁻¹; Anal. Calcd. for C₅₂H₃₆N₁₂O₄₂Cu₂.2 H₂O: C, 59.37; H, 3.45; N, 15.98. Found: C, 59.33; H, 3.51; N, 15.37.

Macrocycle Ni (II) complexation. Yield = 65%, UV–vis (DMSO- d_6) λ_{max} = 261,376 nm. IR (KBr) ν : 1605, 1576, 1520, 1490, 1456, 1372, 1194 cm⁻¹; Anal. Calcd. for C₅₂H₃₆N₁₂O₄Ni₂.2 H₂O: C, 59.92; H, 3.48; N, 16.13. Found: C, 59.85; H, 3.56; N, 16.07.

Macrocycle Mn (II) complexation. Yield = 53%, UV–vis (DMSO- d_6) λ_{max} = 319, 291, 256 nm. IR (KBr) v: 1624, 1602, 1562, 1537, 1479, 1446, 1258 cm⁻¹; Anal. Calcd. for C₅₂H₃₆N₁₂O₄Mn₂.2 H₂O: C, 60.36; H, 3.51; N, 16.24. Found: C, 20.29; H, 3.66; N, 16.20.

2. Results and discussions

Scheme 1 shows the sequence of reactions used to obtain the macrocycles. We investigated the condensation of the N,N'-bis-(2-hydroxybenzaldehyde-5-yl)-benzene-1,3-diazene in an effort to obtain conjugated Schiff base macrocycle. Reactions to form macrocycles are typically performed in mixtures of organic solvents selected to precipitate the macrocycles as they form. We expected the reaction of N,N'-bis-(2-hydroxybenzaldehyde-5-yl)-benzene-1,3-diazene with 1,2-diaminobenzene to cause [2 + 2] Schiff base macrocycle 1 (Scheme 1).

The ¹H NMR spectra of the product showed that multiple species were formed, and it appears that the major product is the 1:1 dialdehyde: diamine condensation species. Matrix-assisted laser desorption ionization time-of-flight (MALDI–TOF) mass spectrometry of the solid showed the presence of macrocycle **1** as the dominant high molecular weight component (Fig. 1).

Spectroscopic evidence suggests that the macrocycles are strongly aggregated in noncoordinating solvents, but disassemble in the presence of a coordinating ligand. The aggregation, which is very strong, could be mediated by any number of possible intermolecular interactions— π -stacking between aromatic groups. Hydrogen bondings between



Scheme 1. Synthesis of macrocycle 1.

(hypothetical) water coordinated to Zn^{2+} , or Zn^{2+} interacting with phenolic oxygen atoms. Zinc (II) is notorious for adopting a 5-coordinate ligand environment, even in salen-type complexes, and is not likely to be in a square planar geometry [18]. Metalation of the macrocycles was investigated to demonstrate that this macrocycle can coordinate multiple transition metals in its salen-type pockets. When the macrocycle was titrated with Ni²⁺, Cu²⁺ the fluorescence was quenched (Fig. 2).

The quenching is essentially completed when 2 equiv of Ni (II) are added, giving the stoichiometry of the final product. On the other hand, upon titration with Zn^{2+} , the macrocycle undergoes significant changes in fluorescence. A large positive deviation from linearity in the Stern–Volmer analysis indicates that the quenching is static, likely due to a metal-ligand charge-transfer band near 550 nm that facilitates energy transfer through a nonradiative pathway [19].



Fig. 1. MALDI-TOF mass spectral evidence for the formation of macrocycle 1.



Fig. 2. Fluorescence spectra of macrocycle + metals (in DMSO).

Acknowledgment

This research was sponsored by Isfahan University of technology (IUT).

References

- [1] P. Suresh, S. Srimurugan, H.N. Pati, Chem. Lett. 36 (2007) 1332.
- [2] S. Srimurugan, P. Suresh, H.N. Pati, J. Incl. Phen. Mac. Chem. 59 (2007) 383.
- [3] S. Srimurugan, B. Viswanathan, T.K. Varadarajan, Org. Biomol. Chem. 4 (2006) 3044.
- [4] W. Zhang, J.S. Moore, Angew. Chem. Int. Ed. 45 (2006) 4416.
- [5] J.K. Hui, M.J. MacLachlan, Chem. Commun. 23 (2006) 2480.
- [6] M.J. MacLachlan, Pur. Appl. Chem. 78 (2006) 873.
- [7] J. Gawronski, K. Gawronska, J. Grajewski, Chem. Eur. J. 12 (2006) 1807.
- [8] J. Gregoliski, J. Lisowski, T. Lis, J. Org. Biomol. Chem. 3 (2005) 3161.
- [9] S. Srimurugan, B. Viswanathan, T.K. Varadarajan, et al. Tetrahedron Lett. 46 (2005) 3151.
- [10] P.A. Vigato, S. Tamburini, Coord. Chem. Rev. 248 (2004) 1717-2128.
- [11] J. Gawroński, H. Kołbon, M. Kwit, A. Katrusiak, J. Org. Chem. 65 (2000) 5768.
- [12] D. Zhao, J.S. Moore, J. Org. Chem. 67 (2002) 3548.
- [13] G. Givaja, A.J. Blake, C. Wilson, et al. Chem. Commun. (2003) 2508.
- [14] U. Beckmann, S. Brooker, Coord. Chem. Rev. 245 (2003) 17.
- [15] J. Gao, J.H. Reibenspies, A.E. Martell, Angew. Chem. Int. Ed. 42 (2003) 6008.
- [16] E.N. Jacobsen, W. Zhang, A.R. Muci, et al. J. Am. Chem. Soc. 113 (1991) 7063.
- [17] C. Ma, A. Lo, A. Abdolmaleki, M.J. MacLachlan, Org. Lett. 6 (2004) 3841.
- [18] J. Reglinski, S. Morris, D.E. Stevenson, Polyhedron 21 (2001) 2175.
- [19] C.B. Murphy, Y. Zhang, T. Troxler, et al. J. Phys. Chem. B 108 (2004) 1537.