This article was downloaded by: [University of Windsor] On: 20 November 2014, At: 20:35 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsrt20</u>

Synthesis of N,N'-bis[4-(benzeneazo)salicylaldehyde] 4-methyl-1,2-Phenylenediamine and Its Transition Metal Complexes

Maryam Lashanizadegan ^a & Mina Jamshidbeigi ^a

^a Department of Chemistry, Faculty of Science, Alzahra University Vanak, Tehran, I. R. Iran Accepted author version posted online: 14 Mar 2012.Published online: 01 May 2012.

To cite this article: Maryam Lashanizadegan & Mina Jamshidbeigi (2012) Synthesis of N,N'-bis[4-(benzeneazo)salicylaldehyde] 4-methyl-1,2-Phenylenediamine and Its Transition Metal Complexes, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 42:4, 507-512, DOI: <u>10.1080/15533174.2011.613432</u>

To link to this article: http://dx.doi.org/10.1080/15533174.2011.613432

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions



Synthesis of N,N'-bis[4-(benzeneazo)salicylaldehyde] 4-methyl-1,2-Phenylenediamine and Its Transition Metal Complexes

Maryam Lashanizadegan and Mina Jamshidbeigi

4-(Benzeneazo)salicylaldehyde(HL') was synthesized with ani-

Department of Chemistry, Faculty of Science, Alzahra University Vanak, Tehran, I. R. Iran

EXPERIMENTAL

Preparation of 4-(benzeneazo)salicylaldehyde (HL')

line, sodium nitrite, and salicylaldehyde. The di-Schiff base ligand, N,N'-bis[4-(benzeneazo)salicylaldehyde]-4-methyl-1,2-phenylenediamine (H_2L) has been prepared by 2:1 molar condensation of HL' with 4-methy-l,2-phenylenediamine. Its manganese(II), copper(II), nickel(II), zinc(II), cobalt(II), and cadmium(II) transition metal complexes were prepared and characterized by their infrared spectra, electronic spectra, and elemental analysis. The ¹H NMR spectra of the ligand and its diamagnetic complexes were recorded in DMSO-d₆ solvent and obtained data confirm that the nitrogen atoms of the imino groups and oxygen atoms of phenolic groups coordinated to the metal ions. All complexes were also prepared by template method.

Keyword azo-link, salisylaldehyde, Schiff base, template

INTRODUCTION

Azo derivatives have been utilized as organic dyes,^[1] indicators,^[2] radical reaction initiators,^[3] and therapeutic agents.^[4] In addition, azo derivatives have the potential for use in electronic^[5] and drug delivery applications.^[6] The coordination chemistry of Schiff base linked to azo compound has been the subject of many studies, and the antitumor activities of some of these complexes are of considerable current interest.^[7] Our interest has been focused on synthesis and characterization of metal complexes of azo-linked compounds. We prepared the ligand N,N'-bis[4-(benzeneazo)salicylaldehyde]-4-methyl-1,2phenylenediamine (H₂L) and its Mn(II), Cu(II), Ni(II), Zn(II), Co(II), and Cd(II) metal complexes and characterized them by the spectroscopic and analytical methods.

Financial assistance from Alzahra University is acknowledged.

4-(Benzeneazo)salicylaldehyde(HL') was obtained as described elsewhere.^[8] Distilled aniline was diazotized by sodium nitrite in the presence of hydrochloric acid (1). Diazotized anilin (1) reacts with salicylaldehyde to produce 4-(benzeneazo)salicylaldehyde dye (2) in good yield (Scheme 1).

Preparation of ligand (H₂L)

4-Methyl-1,2 phenylenediamine (5 mmol) in ethanol (5 mL) and 4-(benzeneazo)salicylaldehyde (10 mmol) in ethanol (10 mL) were mixed and refluxed for 2 h. After cooling the solution, the resulting precipitate was filtered and washed with ethanol and then recrystallized from ethanol and dried at 50°C (Scheme 1).

Preparation of the complexes (ML)

Metal complexes (ML; M = Mn, Cu, Ni, Zn, Co, and Cd) were prepared by the addition of $M(CH_3COO)_2 xH_2O (1 \text{ mmol})$ in water (5–10 mL) into $H_2L (1 \text{ mmol})$ in hot ethanol (10 mL). The mixture was then refluxed for 2 h. The precipitated solids were filtered off from the ice-cooled reaction mixture. The solids were washed with ethanol and then recrystallized from ethanol and dried at 50°C.

Preparation of the Complexes (ML) by Template Method

 $M(CH_3COO)_2 xH_2O (M = Mn, Cu, Ni, Zn, Co, and Cd)$ (1 mmol) in water (5–10 mL), 4-methy 1–2 phenylenediamine (1 mmol) in ethanol (10 mL), and 4-(benzeneazo)salicylaldehyde (2 mmol) in ethanol (10 mL) were mixed and refluxed for 5 h. The precipitated solids were filtered off from the ice-cooled reaction mixture. The solids were washed with ethanol and then dried at 50°C. The complexes are air-stable colored solids, insoluble in water, partly soluble in ethanol and methanol, and soluble in DMSO and DMF.

Physical Measurements

Melting points were determined using an electrothermal melting point apparatus. FT-IR spectra were recorded using a

Received 16 August 2009; accepted 7 August 2011.

Address correspondence to Maryam Lashanizadegan, Department of Chemistry, Faculty of Science, Alzahra University, Vanak, P. O. 1993893973, Tehran, I. R. Iran. E-mail: m_lashani@alzahra.ac.ir



M= Mn(II), Cu(II), Ni(II), Zn(II), Co(II) and Cd(II)

SCH. 1.

Bruker (Madison, WI; USA) Tensor 27 spectrometer. The visible spectra were determined using a Perkin Elmer (Waltham, MA, USA) Lambda 35 UV/Vis Spectrophotometer. ¹HNMR spectra were obtained on a Bruker Avance 300 MHz spectrometer using TMS as internal standard. Elemental analyses (C, H, N) were performed using a CHN Perkin Elmer 2400 Series II.

RESULTS AND DISCUSSION

Element Analysis

Analytical data given in Table 1 elemental analysis demonstrate the validity of the chemical composition of the complexes. This data suggest that the metal-ligand stoichiometry is 1:1.

Analytical data of the ligand and its complexes Found (Calcd.) % С M.P. °C Color Yield%

TABLE 1

Formula	M.P. °C	Color	Yield%	С	Н	Ν
H ₂ L	215	Red	86	72.73	4.75	15.61
$C_{33}H_{26}N_6O_2$				(73.60)	(4.83)	(15.61)
NiL	250	Red	89	65.19	4.08	13.85
C ₃₃ H ₂₄ NiN ₆ O ₂				(66.66)	(4.04)	(14.14)
CuL	260	Brown	93	64.42	4.08	13.97
$C_{33}H_{24}CuN_6O_2$				(65.13)	(3.94)	(13.81)
ZnL,H ₂ O	290	Brown	92	65.8	4.5	5.7
$C_{33}H_{26}ZnN_6O_3$				(65.9)	(4.4)	(6.1)
CdL	280	Red	78	61	4.2	12.7
$C_{33}H_{24}CdN_6O_2$				(61.06)	(3.7)	(12.95)
CoL	265	Dark brown	86	66	4.2	14.2
$C_{33}H_{24}CoN_6O_2$				(66.6)	(4.03)	(14.11)
MnL	270	Brown	96	66.6	4.3	14.2
$C_{33}H_{24}MnN_6O_2$				(67.0)	(4.06)	(14.21)



FIG. 1. IR spectra of H₂L and NiL, MnL, and ZnL complexes (color figure available online).

IR Spectra

The IR spectra of the ligand (H_2L) shows a strong band at 1617 cm⁻¹. This band can be assigned to C=N stretching vibration. In the IR spectra of all the complexes the sharp single

band due to azomethine (C=N) group within 1617–1607 cm⁻¹ are routinely noticed (Figures 1 and 2).^[9] The lowering of the positions of the bands due to C=N stretching vibration indicates their coordination to the metal centers.^[10,11]



FIG. 2. IR spectra of CdL, CuL and CoL complexes (color figure available online).

The phenolic C-O stretching vibration appeared at 1282 cm^{-1} in the Schiff base^[12,13] under a shift toward lower frequencies in the complexes (Table 2). This shift confirms the participation of oxygen in the C–O–M bond.^[14]

¹H NMR Spectra

Assignments of the ¹H NMR spectrum are given in Table 3. The ¹H NMR spectra of the free ligand exhibit a singlet at $\delta \approx$ 2.4 ppm assigned to the methyl protons and O—H protons of the two phenolic groups are at $\delta \approx 12$ ppm. In the ¹H NMR spectra of NiL, ZnL, and CdL, the ligand peaks, assignable to the OH groups, are absent. This shows that both hydrogen atoms are lost during the synthesis, which indicates the ligand behaves as a dianionic ligand. The azomethine protons in the free ligand appear at $\delta \approx 8.6$ ppm and due to complexes the azomethine protons are shifted to $\delta \approx 9.1$, 9.2, and 8.9 ppm, in NiL, ZnL, and CdL, respectively, that confirms the bonding of imino nitrogen to metal ions. Methyl protons group and azomethine hydrogens exhibit as a doublet due to unsymmetrical azo–Schiff base complexes

TABLE 2 Important IR absorption bands (cm⁻¹) of the ligand and its complexes

comprenes				
Compound	ν (C=N)	ν(C -O)	$\nu(N=N)$	
H_2L	1617	1282	1429	
CuL	1610	1263	1412	
MnL	1608	1220	1413	
NiL	1607	1220	1412	
CoL	1607	1219	1412	
ZnL	1617	1215	1413	
CdL	1611	1214	1411	

TABLE 3¹H NMR spectra of the ligand and its complexes (ppm)

		e	1	11 /
Compound	δО−Н	δCH=N	δCH ₃	Aromatic H
H ₂ L	12	8.6	2.4	7–7.9
	(br s, 2H)	(d, 2H)	(s, 3H)	(m, 19H)
NiL		9.1	2.25	7-8.2
		(d, 2H)	(d, 3H)	(m, 19H)
ZnL		9.2	2.50	6.84-8.22
		(d, 2H)	(d, 3H)	(m, 19H)
CdL		8.9	2.45	6.7-8.1
		(d, 2H)	(d, 3H)	(m, 19H)

s = singlet, br = broad, m = multiple, d = doublet.

(Figure 3). These observations suggest that the ligand coordinates to the metal atom through the charged phenolic oxygen and the nitrogen atoms of azomethine groups of the N_2O_2 in the complex.^[15]

 TABLE 4

 Electronic spectra data of the ligand and its complexes

Compound	Band nm (log ε)		
H ₂ L (3)	369(sh), 352(5.8), 286(5.5)		
CuL	506(sh), 370(5.62), 327(5.72)		
NiL	537(sh), 378(6.02),310(5.66)		
CoL	536(sh), 391(5.59)		
MnL	525(sh), 367(5.71)		
ZnL	401(sh), 362(4.67),		
CdL	484(sh), 355(5.52)		

sh = shoulder, $\varepsilon = L \mod^{-1} \operatorname{cm}^{-1}$.

6.88 6.85 6.85

6.84

5.51

2.50 2.44 1.85

8



Edd



FIG. 3. ¹H NMR spectra of ZnL and CdL in DMSO-d₆.

Electronic Spectra

The electronic spectra data of the ligand and its complexes are summarized in Table 4. The three peaks at 286 nm, 352 nm, and 369 nm in the electronic spectrum of the ligand in chloroform were attributed to benzene Π - Π * and imino n Π^* transition.^[10] These bands in the complexes become broad with high intensity (Figure 4). Complexes CuL, NiL, and CoL show a shoulder at 506 nm, 537 nm, and 525 nm, respectively, indicating a large crystal-field splitting and consistent with the square-planar geometry of these complexes.



FIG. 4. Absorption spectra of ligand and its complexes (color figure available online).

CONCLUSIONS

On the basis of the physical and spectral data of the Schiff base and its complexes, it can be assumed that the metal ions are bonded to the ligand via phenolic oxygen and imino nitrogen. The ligand H₂L (**3**) acts as a tetradentate chelae in complexes ML leading to a square planer stereochemistry. All complexes have also been isolated employing a template route,^[16] which is fast and simple. Attempts for isolating single crystal were not successful.

REFERENCES

- Hunger, K. Industrial Dyes: Chemistry, Properties, Applications; Wiley-VCH: Weinheim, Germany, 2003.
- Anderson, R.G.; Nickless, G. Heterocyclic azo dyestuffs in analytical chemistry. Part I. The ligand properties of 2-(2-pyridylazo)-1-naphthol and its sulphonated analogues. *Analyst*, **1968**, *93*, 13–19.
- (a) Athey, R.D. Jr. Free radical initiator basics. *Eur. Coatings J.* 1998, 3, 146–149; (b) Sheppard, C.S. *Encyclopedia of Polymer Science and Technology*, 2nd Edn.; Wiley: New York, 1985, pp. 143–157.

- (a) Hoult, J.R. Pharmacological and biochemical actions of sulphasalazine. *Drugs* 1986, *32*, 18–26; (b) Sandborn, W.J. Rational selection of oral 5aminosalicylate formulations and prodrugs for the treatment of ulcerative colitis. *Am. J. Gastroenterol.* 2002, *97*, 2939–2941.
- (a)Cisnetti, F.; Ballardini, R.; Credi, A.; Gandolfi, M.T.; Masiero, S.; Negri, F.; Pieraccini, S.; Spada, G.P. *Chem. Eur. J.* **2004**, *10*, 2011–2021; (b) Tripathy, S.; Kim, D.Y.; Li, L.; Kumar, J. Recent advances in polmers for electronics and option. *Pure Appl. Chem.* **1998**, *70*, 1267–1270.
- (a) Jain, A.; Gupta, Y.; Jain, S.K. Azo-chemistry and its potential for colonic delivery. *Crit. Rev. Ther. Drug Carrier Syst.* 2006, *23*, 349–400; (b) Vanden Mooter, G.; Maris, B.; Samyn, C.; Augustijns, P.; Kinget, R. Use of azo polmers for colon-specific drug delivery. *J. Pharm. Sci.* 1997, *86*, 1321–1327.
- Zhou, Y.-S.; Zhang, I.-J.; Zeng, X.-R.; Vital, J.J.; You, X.-Z. A new structurally characterized organotin Schiff-base complex with approximately rectangular molecular boxes formed through hydrogen bonds. *J. Mol. Struct.* 2000, 553, 25–30.
- Vogel, A. A Text-Book of Practical Organic Chemistry, Longman: New York, 1956.
- Sarawat, S.; Srivastava, G.S.; Mehrotra, R.C. Schiff base complexes of organotin(IV). Reactions of trialkyltin(IV) chlorides and alkoxides with *N*-substituted salicylideneimines. *J. Organomet. Chem.* 1977, 129, 155– 161.
- Liu, J.; Wu, B.; Zhang, B.; Liu, Y.; Synthesis and characterization of metal complexes of Cu(II), Ni(II), Zn(II), Co(II), Mn(II) and Cd(II) with tetradentate Schiff base. *Turk J. Chem.* 2006, *30*, 41–48.
- Khadar, A.A.; Nejati, K. Synthesis and characterization of a series of copper(II) complexes with azo-linked salicylaldimine Schiff base ligands. Crystal structure of Cu5PHAZOSALTN.CHCl₃. *Polyhedron*, **2000**, *19*, 607–613.
- Biradar, N.S.; Kulkami, V.H. A spectroscopic study of tin(IV) complexes with multidentate Schiff bases. J. Inorg. Nucl. Chem. 1971, 33, 3781–3786.
- Ruddick, J.N. R.; Sams, J.R. Mössbauer and infrared spectroscopic studies of some organotin(IV) Schiff base complexes. J. Organomet. Chem. 1973, 60, 233–246.
- Wang, G.; Chang, J.C. Synthesis and characterization of amino acid Schiff base complexes of nickel(II). *Synth. React. Inorg. Met.-Org. Chem.* 1994, 24, 1091–1097.
- Lashanizadegan, M.; Boghaei, M.D. Synthesis and X-ray structural characterization of Unsymmetrical tetradentate complexes of Ni(II) and Cu(II). *Synth. React. Inorg. Met-Org. Chem.* 2002, *32*, 345–355.
- Nath, M.; Saini, P.K.; Eng, G.; Song, X. Synthesis and solid-state spectroscopic investigation of some novel diorganotin (IV) compexes of tetraazamacrocyclic ligands. J. Organomet. Chem. 2008, 693, 2271–2278.