

Synthesis and Characterization of Tetradentate Bissalicylaldehyde Schiff Base with Some Transition Metal Complexes

تحضير وتشخيص قاعدة شف لثنائي سلسالديهيد رباعية السن مع بعض معقدات العناصر الانتقالية

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Abstract

2,2'-[ethane-1,2-diylbis(oxy)]dibenzaldehyde (oxy) was synthesized via Williamson etherification of salicylaldehyde with dibromoethane in the presence of potassium carbonate. New tetradentate Schiff base ligand 2,2'-(((ethane1,2diylbis(oxy))bis(1,2phenelene))bis(methanylylidene))bis(azanylylidene))diphenol (L) was formed by the 1:2 molar condensation of (oxy) compound with o-aminophenol. Metal complexes of Cr(III), Co(II), Ni(II), Cu(II) and Cd(II) with Schiff base ligand were synthesized and characterized by infrared ,electronic spectra ,metal analysis, magnetic susceptibility and conductivity measurements. Tetradentate Schiff base was further identified using ^1H NMR technique; the results suggest that the metal ion is bond to the ligand through the ether oxygen and imine nitrogen.

Keywords: Williamson etherification, tetradentate Schiff base ligand, salicylaldehyde, metal complexes.

الخلاصة

تم تحضير المشتق 2,2'-[ethane-1,2-diylbis(oxy)]dibenzaldehyde (oxy) بطريقة وليمسون الايثرية من السلسالديهيد وثنائي بروموايثان بوجود كاربونات البوتاسيوم واستخدم لتحضير الليكاند قاعدة شف رباعية السن 2,2'-(((ethane1,2diylbis(oxy))bis(1,2phenelene))bis(methanylylidene))bis(azanylylidene)) diphenol(L) مع اورثوامينوفينول بنسبة 1:2 خلال تفاعل تكثيف ثم جرى تحضير معقدات مع الايونات الفلزية : الكروم الثلاثي و الكوبلت الثنائي والنيكل الثنائي و النحاس الثنائي و الكادميوم الثنائي. شخصت المعقدات المحضرة بواسطة اطياف الاشعة تحت الحمراء و الالكترونية و تحليل المحتوى الفلزي و الحساسية المغناطيسية والقياسات التوصيلية الكهربائية ,ايضا شخص الليكاند بواسطة طيف الرنين النووي المغناطيسي. لقد اثبتت النتائج اتجاه تناسق الايون الفلزي مع الليكاند من خلال ذرة الاوكسجين الايثرية و ذرة النيتروجين في مجموعة الايزوميثين. مفتاح الكلمات: تحضير الايثرات وليمسون, قاعدة شف رباعية السن, المعقدات الفلزية.

Introduction

Schiff base compounds as ligands have gained importance because of the physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordination with metal ions given complex which serve as models for biological system [1-3].The tetradentate Schiff base metal complexes are one of the most well known complexes, since the ligands can be easily synthesized. These metal complexes are stable and have many applications, such as catalysis and as O_2 -storage devices [4-5]. M. Jesmin *et al* synthesized some salicylaldehyde Schiff bases and these compounds have been studied against *Ehrlich ascites carcinoma* (EAC) cells in Swiss albino mice. These compounds enhanced life span reduced average tumour weight and inhibited tumour cell growth of EAC cell-bearing mice. They also restored the depleted hematological parameters like hemoglobin content, red blood cells (RBC) and white blood cells (WBC) counts towards normal [6-7]. Schiff bases as tetradentate ligands coordinate

predominantly in a planar arrangement to various metal ions giving trans geometries in octahedral complexes, metal complexes of tetradentate salicylaldehyde ligands had until relatively recently only been formed with trans geometry. In 1990, Floriani and co-workers reported seven coordinate acen complexes of zirconium and hafnium $[M(\text{acen})\text{Cl}_2(\text{thf})]$ with pseudo trans structure [8]. Novel two-dimensional self-assembly network formulated as $[K(\text{TSSB})]_n$ (TSSB = taurine-salicylaldehyde Schiff base) has been synthesized *via* the reaction of salicylaldehyde with taurine at the presence of potassium hydroxide in water-methanol solution, and was structurally characterized [9]. Three new metal complexes of Cr(III), Pb(II) and TiO(IV) ions with a Schiff base derived from salicylaldehyde and urea have been investigated [10].

The present work investigates the synthesis and properties of new tetradentate Schiff base ligand containing ether moiety with Cr(III), Co(II), Ni(II), Cu(II) and Cd(II) ions and characterize their geometrical structures by using different physical techniques..

Experimental part

Chemicals:

Chemical reagents and starting materials were obtained from Ajax and Sigma-Aldrich. Silica TLC plates were used with an aluminum backing (0.2 mm, 60 F₂₅₄). The reactions were monitored by TLC and visualized by development of the TLC plates with iodine vapor.

Instrumentation

Melting points were recorded by using Gallenkamp M.F.B. 600.01 of melting point apparatus . Infrared spectra were recorded using FTIR 8300 Shimadzu. UV-Visible spectra were measured using Shimadzu UV-Vis 160A Ultra-violet spectrophotometer in the range (200-1100 nm). The metal percent in the prepared complexes were determined using Shimadzu 680 cc-flame. ¹H nuclear resonance analysis spectra was using a Bruker (300 MHz spectrometer) using CDCl₃ as solvent and tetramethylsilane as internal reference. Magnetic susceptibility for the prepared complexes were obtained at room temperature using magnetic susceptibility balance Johnson Matthey catalytic system division and molar conductivity measurements were carried out at room temperature using corning conductivity meter 220.

Synthesis of 2,2'-[ethane-1,2-diylbis(oxy)]dibenzaldehyde (oxy):

Ethylene bromide (0.95 g, 5 mmol) was added drop wise to the stirred suspension of salicylaldehyde (1.46 g, 12 mmol) and K₂CO₃ (2.10 g, 15 mmol) in MeOH (50 mL). The mixture was refluxed for 24 h then the mixture was left to cool to room temperature and filtered off and diluted with water (50 mL) then extracted with ether (3x30 mL), the combined organic layers were washed successively with 5% NaOH (30 mL), 5% HCl (30 mL) then water (30 mL), dried with anhydrous Na₂SO₄, filtered and evaporated to dryness to give compound (1) (2.85 g, 88%) as a white solid.

Synthesis of 2,2'-(((ethane-1,2-diylbis(oxy))bis(1,2-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol (L):

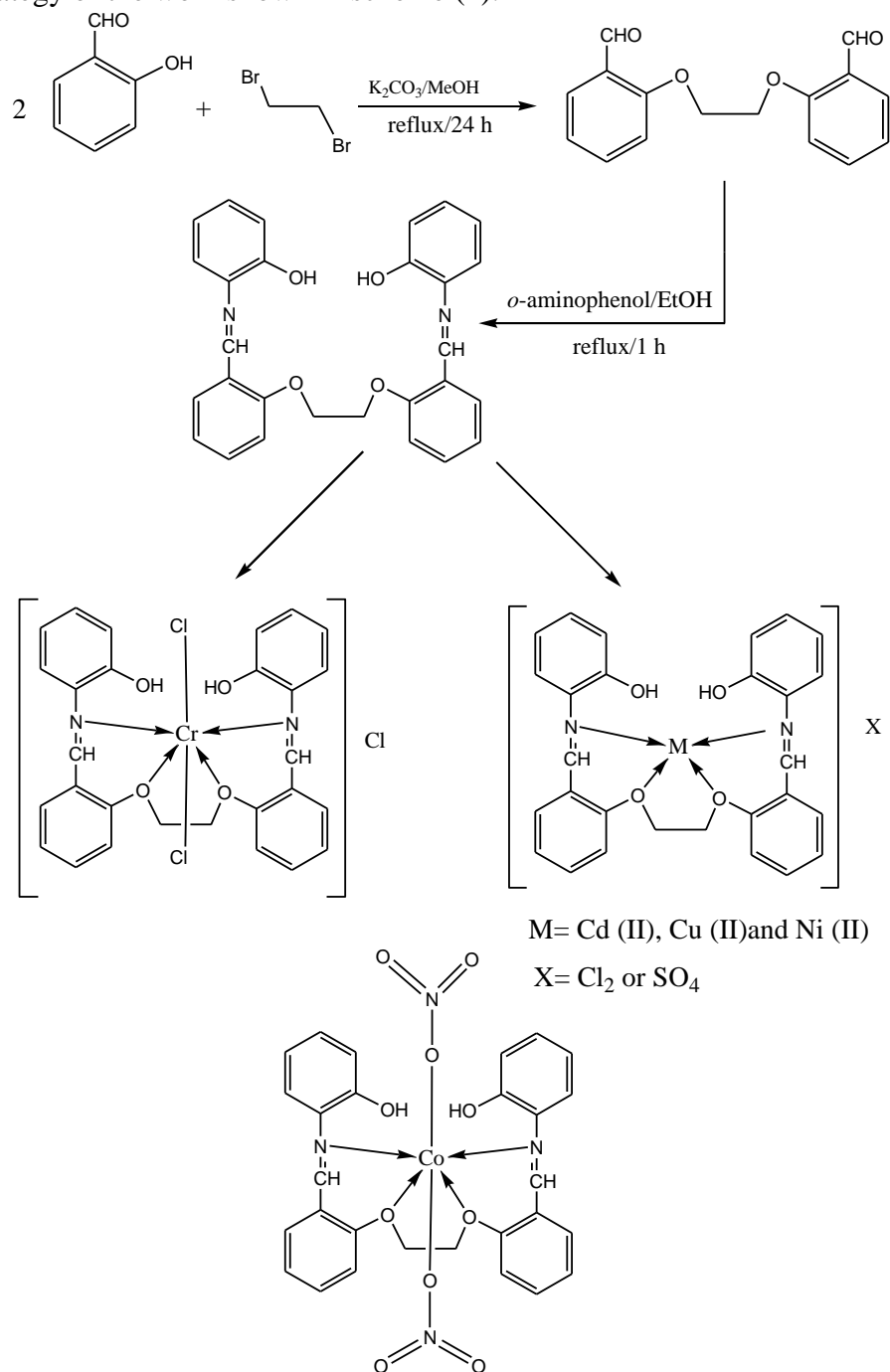
A solution of *o*-aminophenol (1.20 g, 11 mmol) in a small amount of absolute ethanol (5 mL) was added dropwise to the solution of compound (oxy) (1.35 g, 5 mmol) in absolute ethanol (20 mL). The solution was refluxed for 1 h then left to cool to room temperature, an orange solid was precipitated, the solid was collected by filtration, washed with cold ethanol, dried at 60°C and recrystallized from 50% ethanol to afford compound 2 (1.81 g, 80%) as orange needle crystals.

Synthesis of complexes:

Hot ethanolic solution of metals (CrCl₃.6H₂O, Co(NO₃)₂.6H₂O, NiCl₂.6H₂O, CuSO₄.5H₂O and CdCl₂.2H₂O) was add to hot ethanolic solution of the ligand(L) 1:1 (metal:ligand) mole ratio and refluxed for 4 hours during this time a precipitate was formed, which was filtered washed several times with hot ethanol and dried at 50 °C.

Results and discussion

The overall strategy of the work shown in scheme (1):



The physical properties and analytical data of (L) and its complexes (CrL-CdL) and molar conductivity in DMF as a solvent at concentration 10^{-3}M at room temperature 25°C are given in Table 1. The molecular formula, symbols and names of complexes are give in Table 2.

Table 1: Analytical and physical data of Schiff base ligand and complexes

Compound	Color	Melting Point,°C	Molar Conductivity $\mu\text{s}/\text{cm}$	Suggested Structure	Metal Analysis	
					Found	Calculated
L	Orange	240-242	-	-	-	-
CrL	Dark green	250-252	67.8	Octahedral	8.40	8.52
CoL	Brown	>300	29.9	Octahedral	9.10	9.28
NiL	Red	>300	133.3	Square planar	10.0	10.09
CuL	Greenish yellow	255-257	66.2	Square planar	10.30	10.39
CdL	Brown	260-262	165.5	Square planar	17.24	17.69

Table 2: Symbol, molecular formula and names of Schiff base and complexes

Symbol	Molecular Formula	Name of Complexes
L	$\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_4$	2,2'(((ethane-1,2-diylbis(oxy))bis(1,2-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol
CrL	$[\text{CrLCl}_2].\text{Cl}$	Dichloro 2,2'(((ethane-1,2-diylbis(oxy))bis(1,2-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol chromium(III).chloride
CoL	$\text{CoL}(\text{NO}_3)_2$	Dinitrito 2,2'(((ethane-1,2-diylbis(oxy))bis(1,2-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol cobalt(II)
NiL	$[\text{NiL}].\text{Cl}_2$	2,2'(((ethane-1,2-diylbis(oxy))bis(1,2-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol nickel(II).chloride
CuL	$[\text{CuL}].\text{SO}_4$	2,2'(((ethane-1,2-diylbis(oxy))bis(1,2-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol copper(II).sulphate
CdL	$[\text{CdL}].\text{Cl}_2$	2,2'(((ethane-1,2-diylbis(oxy))bis(1,2-phenylene))bis(methanylylidene))bis(azanylylidene))diphenol cadimium(II).chloride

Infrared spectra of compound (oxy) and ligand(L):

Compound (oxy) have been prepared via Williamson etherification of salicylaldehyde with dibromoethane in the presence of K_2CO_3 , FT-IR spectrum of compound (oxy) showed the following bands cm^{-1} : 2962 and 2825 ν (C-H aliphatic), 2742 ν (C-H aldehydic), 1693 ν (C=O aldehydic), 1600 and 1537 ν (C=C aromatic), 1250 and 1200 ν (C-O phenolic and ether), 881-651 (C-H aromatic) bending oop. The condensation of compound (oxy) with 2-aminophenol in absolute EtOH afforded Schiff base (L) FT-IR spectrum of compound (L) exhibited the following bands cm^{-1} : 3500 and 3310 ν (O-H phenolic), 2937 ν (C-H aliphatic), 1637 ν (C=N imine), 1590 and 1543 ν (C=C aromatic), 1262 and 1210 ν (C-O phenolic and ether), 932-665 (C-H aromatic) bending oop.¹HNMR(300 MHz, $CDCl_3$) δ ppm:4.45(s,4H,CH₂),5.46(broad s,2H,OH),7.46-7.99(m,16H,aromatic),8.57(s,2H,N=CH).

Infrared spectra of complexes:

A strong band found at 1637 cm^{-1} was assigned to the C=N stretch of the free Schiff base,this band was shifted to lower frequencies in the spectra of the complexes indicating the involvement of azomethine nitrogen in coordination[11] shown in Table 3.

There are no changes in ν (O-H), ν (C-O) groups in the spectra of all complexes ,this mean that the oxygen of the phenolic group is not entered in coordination.

ν (C-O-C) appear around 1210 cm^{-1} in the free ligand,this band in complexes is observed around (1125-1157) cm^{-1} indicating the coordination of ether oxygen atom[12-14].

The infrared of prepared complexes have shown weak bands in the range of (426-505) cm^{-1} and (525-569) cm^{-1} which was attributed to the ν (M-O) and ν (M-N) ,respectively.

Table 3: The characteristic bands of infrared spectra of the ligand and complexes

Compound	ν (O-H)	ν (C-O-C)	ν (C=N)	ν (C=C)	ν (M-O)	ν (M-N)	Other
L	3500, 3310	1210	1637	1590,1543	-	-	-
CrL	3400	1157	1604	1537,1467	505	550	ν (Cr-Cl) 432
CoL	3452	1150	1610	1533,1517	462	525	ν_a (NO ₂)1434 ν_s (NO ₂)1298 ν (N=O) 940
NiL	3400	1125	1630	1514,1465	489	569	-
CuL	3435	1151	1610	1589,1533	488	538	-
CdL	3421	1125	1602	1517,1463	426	550	-

Ultraviolet-Visible spectroscopy:

The ultraviolet-visible electronic spectra of the prepared ligand (L) and its complexes are summarized in Table 4. The spectrum of the Schiff base exhibit two bands at 284 nm and 400 nm .The first band was attributed to $\pi \rightarrow \pi^*$ electronic transition and the second was assigned to $n \rightarrow \pi^*$ electronic transition . The second band was shifted to a longer wavelength a long with increase in its intensity in the spectra of (CrL-CdL)complexes . The shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the ligand to the metal ion (N→M). Three absorption bands were present with the greatest band occurring at $\lambda_{max} = 456$ nm ,a secondary peak at 383 nm and a small peak at approximately 358 nm. These bands are consistent with the octahedral geometry of Cr(III) [10,15].Electronic spectrum of CoL complex showed three bands,two in the 459 - 443 nm regions and the other band at 407 nm indicating a high spin octahedral configuration.The NiL complex was found to be spin paired type. Bands at 436 and 414 nm have been assigned due to ($^1A_{1g} \rightarrow ^1B_{1g}$) transition, the band at 362 nm has been assigned to the $n \rightarrow \pi^*$ transition. These bands were suggested the planar geometry of Ni(II) [16].The electronic spectrum of CuL complex showed bands at 456 and 412 nm assigned to the transitions $^2B_{1g} \rightarrow ^2E_g$, $^2B_{1g} \rightarrow ^2A_{1g}$, respectively for square planar geometry[11,17].

Table 4: Electronic spectra and magnetic moment

Compound	Bond,nm	Assignment	$\mu_{eff},B.M.$
L	284 400	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-
CrL	456 383,358 211	$^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	3.9
CoL	459 443 407 260	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ $\pi \rightarrow \pi^*$	4.9
NiL	436,414 362 327,282	$^1A_{1g} \rightarrow ^1B_{1g}$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	0
CuL	456 431 412 313,265	$^2B_{1g} \rightarrow ^2E_g$ $^2B_{1g} \rightarrow ^2B_{2g}$ $^2B_{1g} \rightarrow ^2A_{1g}$ $\pi \rightarrow \pi^*$	1.92
CdL	435	-	0

Magnetic susceptibility of complexes:

The experimental magnetic moment for each complex is listed in Table 4. The magnetic moment of $\text{Cr}^{+3}(\text{d}^3)$ 3.9 B.M. supports the existence of three odd electrons and $\text{Co}^{+2}(\text{d}^7)$ was found to be 4.9 B.M.

The value of $\text{Cu}^{+2}(\text{d}^9)$ approximately 1.92 B.M., the μ_{eff} value for $\text{Ni}^{+2}(\text{d}^8)$ and $\text{Cd}^{+2}(\text{d}^{10})$ were found to be zero led to suggest the square planar structure [11, 17].

Conclusion:

New linear tetradentate Schiff base with complexes were synthesized and characterized. The molar conductivity of the Cr(III), Ni(II), Cu(II), Cd(II) complexes have electrolytic nature and Co(II) has nonelectrolytic nature. Octahedral configuration is suggested of CrL and CoL complexes, NiL, CuL and CdL complexes have square planar configuration.

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