



Synthesis and Characterization of Transition Metal Complexes with 2,2'-[(Propylene-1,3-diylidioxy)bis(nitrilomethylidene)]diphenol

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In anhydrous ethanol medium, a series of transition metal complexes have been synthesized by the reaction of 2,2'-[(propylene-1,3-diylidioxy)bis(nitrilomethylidene)]diphenol (H₂L) with Cu(II), Ni(II), Co(II) and Mn(II) acetate hydrate. All these metal complexes were characterized by elemental analyses, IR spectra, UV-VIS spectra, molar conductances and TG-DTA analyses.

Key Words: Transition metal complexes, Salamo-type compound, Synthesis, Characterization.

INTRODUCTION

Transition metal complexes with salen-type or oxime-type ligands are extensively investigated, which have long been used as chelating ligands in the synthesis of transition metal complexes due to their ease of preparation and structural variety. These compounds play a seminal role in the development of modern coordination chemistry, which can accommodate several metal centers and form homo- and heteronuclear metal complexes with favourable properties¹, such as their enormous variety of structural topologies, as well as their potential applications in optoelectronics, magnetism, non-linear optical materials², biological activity³ and catalysis⁴⁻⁸. To change the structures or improve the functions of the resulted complexes, herein, a new salamo-type bisoxime ligand, 2,2'-[(propylene-1,3-diylidioxy)bis(nitrilomethylidene)]diphenol (H₂L) and its transition metal complexes have been synthesized and structurally characterized.

EXPERIMENTAL

2-Hydroxy benzaldehyde ($\geq 98\%$) and 1,3-dibromo propane was purchased from Alfa Aesar and used without further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without further purification. Elemental analyses for transition metals were detected by an IRIS ER/S-WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. FT-IR spectra were recorded on a VER-

TEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-400 cm⁻¹). UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. TG-DTA analyses were carried out at a heating rate of 5 °C/min on a ZRY-1P thermoanalyzer. Molar conductance value measurements were carried out on a model DDS-11D type conductivity bridge using 1.0 × 10⁻³ mol dm⁻³ solution in DMF at 21 °C. Melting points were obtained by use of an X4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected.

Synthesis of 2,2'-[(propylene-1,3-diylidioxy)bis(nitrilomethylidene)]diphenol (H₂L): The ligand H₂L was synthesized with a slightly modified method reported literature¹. Synthetic route to salamo-type bisoxime ligand H₂L is shown in Fig. 1.

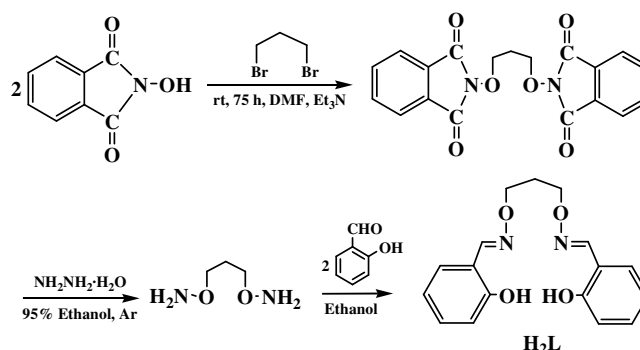


Fig. 1. Synthetic route to the salamo-type bisoxime compound

1,3-Bis(phthalimidooxy)propane was synthesized according to an analogous method reported earlier¹.

1,3-Bis(aminoxy)propane was synthesized according to an analogous method reported earlier¹. ¹H NMR(400 MHz, CDCl₃) δ: 1.88 (m, 2H), 3.77 (t, 4H), 5.00(s, 4H).

Synthesis of H₂L: To an ethanolic solution (10 mL) of 2-hydroxy benzaldehyde (366.4 mg, 3 mmol) was added an ethanolic solution (5 mL) of 1,3-bis(aminoxy)propane (159.2 mg, 1.5 mmol). The solution had been stirred at 55 °C for 4 h. When the solution cooled to room temperature, the resulting solid was filtered and washed with ethanol and ethanol/hexane (1:4), respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to obtain 385.7 mg of white crystalline solid H₂L. Yield, 81.8 %. m.p. 80-81 °C. ¹H NMR (400 MHz, CDCl₃) δ: 2.09 (t, *J* = 6.0 Hz, 2H), 4.25 (t, *J* = 6.0 Hz, 4H), 6.88 (t, *J* = 8.0 Hz, 4H), 7.11 (s, 2H), 7.18 (s, 2H), 8.13 (s, 2H), 9.76 (s, 2H).

Synthesis of Cu(II) complex: A solution of copper(II) acetate monohydrate (20 mg, 0.10 mmol) in ethanol (5 mL) was added dropwise to a solution of H₂L (31.4 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. The solution became green immediately and formed the brown flocculent precipitate, then stirred for 3.5 h at room temperature. The resulting solid was filtered off, washed with ethanol/ether (1:4) and ether, respectively. The product was dried *in vacuo* and obtained 31.8 mg of Cu(II) complex (Yield 79.7 %).

Synthesis of Ni(II) complex: To an ethanolic solution (3 mL) of H₂L (31.4 mg, 0.10 mmol) was added an ethanolic solution (6 mL) of nickel(II) acetate tetrahydrate (24.8 mg, 0.10 mmol). After the mixture solution had been stirred at 55 °C for 4 h. The formed precipitate was separated by filtration and washed successively with ethanol and ether. The product was dried under reduced pressure to obtain 27.9 mg of Ni(II) complex (Yield 66.9 %).

Synthesis of Co(II) complex: To an ethanolic solution (2 mL) of H₂L (31.4 mg, 0.10 mmol) was added an ethanolic solution (8 mL) of cobalt(II) acetate tetrahydrate (24.9 mg, 0.10 mmol). After the mixture solution had been stirred at 55 °C for 3 h. The resulting solid was filtered off, washed with ethanol and ether, respectively. The product was dried *in vacuo* and obtained 27.8 mg of Co(II) complex (Yield 66.6 %).

Synthesis of Mn(II) complex: To an ethanolic solution (2 mL) of H₂L (31.4 mg, 0.10 mmol) was added an ethanolic solution (6 mL) of manganese(II) acetate tetrahydrate (24.5 mg, 0.10 mmol). After the mixture solution had been stirred at 55 °C for 6 h, the formed precipitate was separated by filtration and washed with ethanol and ether, respectively. The product was dried under reduced pressure to obtain 26.0 mg of Mn(II) complex (Yield 63.0 %).

RESULTS AND DISCUSSION

A new salamo-type bisoxime ligand H₂L and a series of complexes have been synthesized. The composition were confirmed by elemental analyses and characterized by IR, UV-visible spectra, molar conductances and TG-DTA analyses.

Composition of H₂L and metal complexes: The colour, yields and elemental analytical results of the synthesized salamo-type bisoxime ligand and its transition metal complexes are presented in Table-1.

Their compositions agree with the formulae. The ligand is stable in air and soluble in methanol, ethanol, acetone, chloroform, dichloromethane, tetrahydrofuran, acetonitrile, ether, DMF and DMSO while insoluble in *n*-hexane. The molar conductance values of the complexes at 21 °C in 1.0 × 10⁻³ mol dm⁻³ DMF solutions are 1.67, 1.58, 1.60 and 1.72 S cm² mol⁻¹, respectively, indicating that all of these complexes are non-electrolytes⁹.

IR spectra of H₂L and complexes: The IR spectral details of the salamo-type bisoxime ligand H₂L and its corresponding transition metal complexes are given in Table-2.

The characteristic C=N stretching band of the free ligand H₂L appears at 1609 cm⁻¹, while the C=N bands of the complexes are observed at 1604, 1605, 1603 and 1603 cm⁻¹, respectively. The Ar-O stretching band occurs at 1270 cm⁻¹ for H₂L, whereas those at 1246, 1247, 1242 and 1240 cm⁻¹ for the complexes, respectively. These shifts of C=N and Ar-O stretching frequencies indicate that the M-N and M-O bonds are formed between the transition metal ions and the oxime N and the phenolic O atoms of deprotonated (L)²⁻ unit^{1a}. Meanwhile, a O-H stretching band of the free ligand H₂L at 3410 cm⁻¹ disappears in the complexes, indicating the oxygen in phenolic alcohol of the complexes has been deprotonated and

TABLE-1
COLOUR, YIELDS AND ANALYTICAL DATA OF H₂L AND ITS TRANSITION METAL COMPLEXES

Compound	m.f. (m.w.)	Colour	Yield (%)	Found (calcd.) (%)			
				C	H	N	M
H ₂ L	C ₁₇ H ₁₈ N ₂ O ₄ (314.3)	White	81.8	64.88 (64.96)	5.80 (5.77)	8.65 (8.91)	-
[CuL]·0.5CH ₃ CH ₂ OH	C ₁₈ H ₁₉ N ₂ O _{4.5} Cu (398.9)	Gray	79.7	53.97 (54.20)	5.02 (4.80)	6.94 (7.02)	15.96 (15.93)
[NiL]·CH ₃ CH ₂ OH	C ₁₉ H ₂₂ N ₂ O ₅ Ni (417.1)	Green	66.9	54.88 (54.71)	5.11 (5.32)	6.58 (6.72)	14.32 (14.07)
[CoL]·CH ₃ CH ₂ OH	C ₁₉ H ₂₂ N ₂ O ₅ Co (417.3)	Yellow	66.6	54.74 (54.68)	5.19 (5.31)	6.53 (6.71)	14.35 (14.12)
[MnL]·CH ₃ CH ₂ OH	C ₁₉ H ₂₂ N ₂ O ₅ Mn (413.3)	White	63.0	55.42 (55.21)	5.22 (5.36)	6.64 (6.78)	13.43 (13.29)

TABLE-2
IR SPECTRAL (cm⁻¹) DATA FOR H₂L AND ITS TRANSITION METAL COMPLEXES

Compound	ν(C=N)	ν(Ar-O)	ν(O-H)	ν(C=C) benzene ring skeleton
H ₂ L	1609	1270	3410	1572, 1494, 1472
[CuL]·0.5CH ₃ CH ₂ OH	1604	1246	3439	1536, 1470, 1445
[NiL]·CH ₃ CH ₂ OH	1605	1247	3429	1538, 1476, 1443
[CoL]·CH ₃ CH ₂ OH	1603	1242	3429	1543, 1470, 1441
[MnL]·CH ₃ CH ₂ OH	1603	1240	3421	1545, 1471, 1440

TABLE-3
UV-VISIBLE SPECTRA DATA OF H₂L AND ITS TRANSITION METAL COMPLEXES

Compound	C (× 10 ⁻⁴ mol L ⁻¹)	First band		Second band	
		λ _{max1} (nm)	ε ₁ (× 10 ⁴ L mol ⁻¹ cm ⁻¹)	λ _{max2} (nm)	ε ₂ (× 10 ⁴ L mol ⁻¹ cm ⁻¹)
H ₂ L	1.00	267	2.29	313	1.19
[CuL]·0.5CH ₃ CH ₂ OH	1.00	269	1.04	300	0.59
[NiL]·CH ₃ CH ₂ OH	1.00	280	1.12	289	0.40
[CoL]·CH ₃ CH ₂ OH	1.00	279	0.89	292	0.68
[MnL]·CH ₃ CH ₂ OH	1.00	275	1.09	288	0.70

coordinated to the metals. In the 1572-1440 cm⁻¹ region, the observed bands were attributed to aromatic C=C vibrations. In addition, infrared spectra of the complexes show the expected strong absorption bands due to ν(O-H) at 3439-3421 cm⁻¹, which are the evidence for the existence of ethanol molecules^{1c}.

UV-visible spectra of H₂L and complexes: The UV-visible spectra of H₂L and its corresponding complexes in diluted DMF solution are presented in Table-3. The spectra of the complexes are similar to each other, but are different from the spectrum of the ligand H₂L. The UV-visible spectrum of the free ligand H₂L exhibits two absorption peaks at 267 and 313 nm. The former absorption peak at 267 nm can be assigned to the π-π* transition of the benzene rings, while the latter one at 313 nm can be attributed to the intra-ligand π-π* transition of the C=N bonds¹⁰.

Compared with the absorption peak of the free ligand, the former absorption peaks at 269, 280, 279 and 275 nm are observed in Cu(II), Ni(II), Co(II) and Mn(II) complexes, respectively, which are bathochromically shifted by 2-13 nm. Meanwhile, the second absorption peaks at 300, 289, 292 and 288 nm are observed in Cu(II), Ni(II), Co(II) and Mn(II) complexes, respectively, which are hypsochromically shifted by 13-25 nm. These indicate that the oxime nitrogen atom is involved in coordination to the metal atom^{11,12}. In addition, the new band observed at 362 nm for the Cu(II) complex is assigned to the n-π* charge transfer transition from the filled pπ orbital of the bridging phenolic oxygen to the vacant d-orbital of the Cu(II) ion, which is characteristic of the transition metal complexes with N₂O₂ coordination spheres¹³.

Thermal properties: The thermal decomposition processes of the complexes compared with the ligand are significantly different. The ligand has a sharp endothermic peak at 83 °C in the DTA curve, with no weight loss in the TG curve and has an exothermic peak at 266 °C, weight loss occurs at 239 °C in the corresponding TG curve. The ligand decomposed completely by one step. However, the DTA curves of all the complexes have endothermic peaks in the range 78-142 °C,

with weight loss in the TG curve. The weight loss values of Cu(II), Ni(II), Co(II) and Mn(II) complexes are 5.6, 11.5, 10.7 and 11.8 %, respectively, which are close to the theoretical values (5.8, 11.1, 11.0 and 11.2 %) of losing corresponding ethanol molecule. The complexes have no sharp melting point. All of the complexes have two exothermic peaks at 300 °C, with apparent weight loss, which are staged oxidative decomposition of the complexes. On further heating, the final solid products are likely to be CuO, NiO, CoO and Mn₂O₃ with a residual value of 19.3, 17.2, 17.0 and 18.5 %, which was found to be close to the calculated values (19.9, 17.9, 17.9 and 19.1 %) when the temperature is above 800 °C.

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