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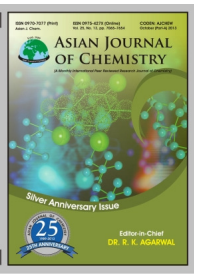

Synthesis and Characterization of Mn(II) and Zn(II) Complexes with Tetrahydroxyl Substituted Salamo-type Compound

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Two new complexes have been synthesized by the reaction of Mn(II) and Zn(II) salts with a Salamo-type chelating ligand 5,5',6,6'-tetrahydroxy-2,2'-[ethylene-1,2-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_6L) in anhydrous ethanol medium and characterized by elemental analyses, IR spectra, UV-visible spectra and molar conductances. The likely formulae of the Mn(II) and Zn(II) complexes may be suggested as $[Mn_3(HL)(CH_3COO)]\cdot EtOH$ (**1**) and $[Zn_3(HL)(CH_3COO)]\cdot EtOH$ (**2**).

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

INTRODUCTION

It is well known that the Salen and its derivatives are excellent chelating ligands in modern coordination chemistry[1-3]. In the past few years, they have also been widely applied to synthesize their transition metal complexes, mainly due to their unique properties[4], such as outstanding catalytic activity for epoxidation and aziridination[5]. In addition, they are also used as models for reaction centers in metalloenzymes[6], non-linear optical materials[7], molecular recognition and biological activity[8]. 2,2′-[Ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (Salamo) and its analogues are a kind of extensively studied Salen-type ligands. These preferable Salamo-type ligands have been reported by using an O-alkyloxime unit (CH=NO$(CH_2)_2$ON=CH) instead of the (CH=N$(CH_2)_2$N=CH) group, the large electronegativity of oxygen atoms is expected to affect strongly the electronic properties of N_2O_2 coordination sphere, which can lead to different and novel properties and structures of the resulted complexes[4,9]. Herein, a new Salamo-type chelating ligand, 5,5',6,6'-tetrahydroxy-2,2'-[ethylene-1,2-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_6L) and its Mn(II) and Zn(II) complexes have been synthesized and characterized.

EXPERIMENTAL

2,3,4-Trihydroxy benzaldehyde (≥ 98.5 %) was purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification. Zinc(II) acetate dihydrate (≥ 99 %) and manganese(II) acetate tetrahydrate (≥ 99 %) were purchased from Beijing Pinggushuangyan Reagent Factory. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without further purification. Elemental analyses for Mn(II) and Zn(II) 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 VERTEX70 FT-IR spectrophotometer, with samples prepared as KBr (4000-400 cm^{-1}). UV-visible absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. 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 25 ºC. 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 ligand H_6L: The ligand H_6L was synthesized with a slightly modified method reported literature[4]. Yield: 79.8 %. m.p. 215.5-216.5 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.31 (s, 4H), 6.33-6.37 (d, 2H), 6.80-6.83 (d, 2H), 8.30 (s, 2H), 8.45 (s, 2H), 9.30 (s, 2H), 9.49 (s, 2H).

Synthesis of complex 1: A solution of manganese(II) acetate tetrahydrate (21.3 mg, 0.10 mmol) in ethanol (8 mL) was added dropwise to a solution of H_6L (36.7 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. The mixture solution have been stirred at 55 ºC for 9 h, then concentrated under reduced pressure to 4 mL. After cool to room temperature, a large number of yellow precipitate was obtained, separated by filtration and washed successively with ethanol/ether (1:4)

TABLE-1
COLOUR, YIELDS AND ANALYTICAL DATA OF H_6L^3 AND ITS Mn(II) AND Zn(II) COMPLEXES

Compound	m.f. (m.w.)	Colour	Yield (%)	Found (calcd.) (%)				Molar conductance (S cm^2 mol^{-1})
				C	H	N	M	
H_6L	$C_{16}H_{16}N_2O_8$ (364.3)	White	79.8	53.00 (52.75)	4.39 (4.43)	7.37 (7.69)	–	–
1	$C_{20}H_{20}N_2O_{11}Mn_3$ (629.2)	Yellow	67.8	38.01 (38.18)	3.42 (3.20)	4.51 (4.45)	25.86 (26.19)	8.15
2	$C_{20}H_{20}N_2O_{11}Zn_3$ (660.5)	Yellow	34.9	36.12 (36.37)	3.21 (3.05)	4.05 (4.24)	29.48 (29.70)	8.54

and ether, respectively. The product was dried under reduced pressure and obtained 42.7 mg of yellow solid. Yield: 67.8 %.

Synthesis of complex 2: To an ethanolic solution (3 mL) of H_6L (36.5 mg, 0.10 mmol) was added an ethanol solution (10 mL) of zinc(II) acetate dihydrate (22 mg, 0.10 mmol). The mixture solution have been stirred at 55 ºC for 11 h, then concentrated under reduced pressure to 3 mL. After cool to room temperature, a large number of yellow precipitate was obtained, separated by filtration and washed successively with ethanol/ether (1:4) and ether, respectively. The product was dried under reduced pressure and obtained 36.7 mg of yellow solid (Yield: 34.9 %).

RESULTS AND DISCUSSION

A Salamo-type compound H_6L and its Mn(II) and Zn(II) complexes have been synthesized and the compositions are confirmed by elemental analyses, IR, UV-visible spectra and molar conductances.

Composition of Mn(II) and Zn(II) complexes: The colour, yields and analytical results of synthesized Mn(II) and Zn(II) complexes are given in Table-1.

Their compositions agree with the formulae $[Mn_3(HL)(CH_3COO)]\cdot EtOH$ for the complex **1** and $[Zn_3(HL)(CH_3COO)]\cdot EtOH$ for the complex **2**. The molar conductance values of Mn(II) and Zn(II) complexes in 1.0×10^{-3} mol dm^{-3} DMF solutions at 21 ºC are shown in Table-1. Compared with the molar conductance values about different types of electrolytes in organic solvents, we can consider that the formed Mn(II) and Zn(II) complexes are non-electrolytes[10], indicating the acetate anions in the Mn(II) and Zn(II) complexes are coordinated to the Mn(II) and Zn(II) ions.

IR spectra of H_6L, Mn(II) and Zn(II) complexes: The most important FT-IR spectral data for H_6L and its Mn(II) and Zn(II) complexes are listed in Table-2.

TABLE-2
THE IR SPECTRAL DATA FOR H_6L AND ITS Mn(II) AND Zn(II) COMPLEXES (cm^{-1})

Comp.	ν(C=N)	ν(Ar-O)	ν(O-H)	ν(C=C) benzene ring skeleton
H_6L	1615.7	1292.0	3453.1	1595.2, 1525.0, 1471.1
1	1596.2	1242.5	3419.7	1552.7, 1545.9, 1468.4
2	1582.9	1246.2	3397.7	1556.2, 1541.0, 1454.6

From the results of IR spectra, the free ligand H_6L and its Mn(II) and Zn(II) complexes are different, which proves that the Mn(II) and Zn(II) ions have been in coordination with the $(HL)^{5-}$ unit and new complexes formed. The characteristic C=N stretching band of the free ligand H_6L appears at 1615.7 cm^{-1}, while the C=N stretching bands of the complexes are observed at 1596.2-1582.9 cm^{-1}. The C=N stretching frequency shifted to a lower frequency by 32.8-19.5 cm^{-1} upon complexation, indicating a decrease in C=N bond order due to the coordination of the Mn(II) and Zn(II) ions with oxime nitroen[4]. The Ar-O stretching band occurs at 1292 cm^{-1} for H_6L, whereas those at 1242.5 and 1246.2 cm^{-1} for the Mn(II) and Zn(II) complexes[11]. This shifting Ar-O stretching frequency indicates that the M-O bonds are formed between the Mn(II) and Zn(II) ions and oxygen of phenolic group[4,12]. In addition, the O-H stretching band of the free H_6L ligand appears at 3453.1 cm^{-1} and broad absorption bands at 3397.7-3419.7 cm^{-1} in the Mn(II) and Zn(II) complexes are assigned to phenolic alcohol group of the $(HL)^{5-}$ unit and -OH groups of non-coordinated ethanol molecules.

UV-visible spectra of H_6L, Mn(II) and Zn(II) complexes: The absorption spectra of H_6L and its Mn(II) and Zn(II) complexes in diluted DMF solution are presented in Table-3.

TABLE-3
UV-VISIBLE SPECTRA DATA OF H_6L AND ITS Mn(II) AND Zn(II) COMPLEXES

Comp.	C ($\times 10^{-4}$ mol L^{-1})	First band		Second band	
		λ_{max1} (nm)	ε_1 ($\times 10^4$ L mol^{-1} cm^{-1})	λ_{max2} (nm)	ε_2 ($\times 10^4$ L mol^{-1} cm^{-1})
H_6L	1.00	283	13.01	–	–
1	1.00	274	3.25	318	2.10
2	1.00	271	3.18	322	2.01

The spectra of Mn(II) and Zn(II) complexes are similar to each other, but are different from the spectrum of the free ligand H_6L. The UV-visible spectrum of the free ligand H_6L exhibits one absorption peak at 283 nm. which can be assigned to the π-π* transition of the benzene rings[13]. Compared with the absorption peak of the free ligand H_6L, corresponding absorption peaks at 274 and 271 nm are observed in Mn(II) and Zn(II) complexes, which is shifted by 12-9 nm, indicating the coordination of Mn(II) and Zn(II) ions with the $(HL)^{5-}$ unit[14]. Meanwhile, new absorption peaks are observed at 318 and 322 nm in Mn(II) and Zn(II) complexes, which are 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 Mn(II) and Zn(II) ions[15,16].

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