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Synthesis and Characterization of Co(II), Ni(II) and Cd(II) Complexes with Salamo-Type Compound Bearing Multihydroxyl Substituents

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Three divalent transition metal complexes, $[M_3(HL)(CH_3COO)]\cdot EtOH$ [M = Co(II), Ni(II) and Cd(II)] have been synthesized by the reaction of 5,5',6,6'-tetrahydroxy-2,2'-[ethylene-1,2-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_6L) with Co(II), Ni(II) and Cd(II) acetate hydrates in anhydrous ethanol medium, respectively. All the complexes were characterized by elemental analyses, IR spectra, UV-visible spectra, TG-DTA analyses and molar conductance measurements.

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

INTRODUCTION

Salen-type ligands are a class of flexible compounds which can coordinate to most of the transition metal ions as versatile ligands so that they have long been used as chelating ligands in the synthesis of transition metal complexes[1]. These compounds can accommodate one, two or more metal centers and form homo- and heteronuclear metal complexes with unique properties[1,2], such as, some Salen complexes can be applied as an effective catalyst[3]. In addition, they are also used as models for reaction centers in metalloenzymes[4], non-linear optical materials[5], molecular recognition and biological activity[6]. Herein, a new Salen-type bisoxime chelating ligand, 5,5',6,6'-tetrahydroxy-2,2'-[ethylene-1,2-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_6L) and its Co(II), Ni(II) and Cd(II) comp-lexes have been synthesized and structurally characterized.

EXPERIMENTAL

2,3,4-Trihydroxy benzaldehyde (≥ 98.5 %) was purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. 1,2-*Bis*(aminooxy)ethane was synthesized according to an analogous method reported earlier[1]. Cobalt(II) acetate dihydrate (≥ 98.5 %) and nickel(II) acetate tetrahydrate (≥ 98.5 %) were purchased from Beijing Pinggushuangyan Reagent Factory. Cadmium(II) acetate dihydrate (≥ 98.5 %) was purchased from Sinopharm Chemical Reagent Co., Ltd. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory and were used without further purification. Elemental analyses for Co(II), Ni(II) and Cd(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-VIS absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. TG-DTA analyses were carried out at a heating rate of 5 ºC/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 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.

General procedure

Synthesis of ligand H_6L: The ligand H_6L was synthesized with a slightly modified method reported literature[1]. Synthetic route to Salen-type bisoxime ligand H_6L is shown in Fig. 1.

Reaction of 1,2-*bis*(aminooxy)ethane (133.5 mg, 1.45 mmol) with 2 equivalents of 2,3,4-trihydroxy benzaldehyde (462.4 mg, 3.00 mmol) in ethanol (10 mL) at 55 ºC for 6 h. After cooling to room temperature, the resulting solid was filtered and washed with ethanol and ethanol/hexane (1:4), respectively. The product was dried *in vacuo* and obtained

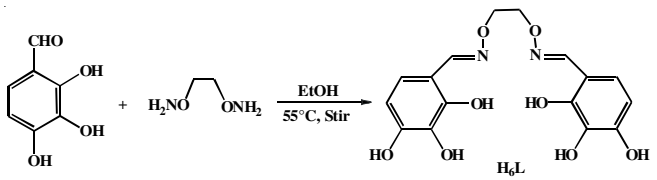

Fig. 1. Synthetic route to 5,5',6,6'-tetrahydroxy-2,2'-[ethylene-1,2-diyldioxy)*bis*(nitrilomethylidyne)]diphenol (H_6L)

483.7 mg of white microcrystal. 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 Co(II) acetate tetrahydrate (24.9 mg, 0.10 mmol) in ethanol (8 mL) was added dropwise to a solution of H_6L (36.5 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. A bright purple solution was obtained and stirred vigorously and refluxed for 12 h. The resulting solid was concentrated under reduced pressure and obtained a large number of black precipitate which was washed with ethanol/ether (1:4) and ether, respectively. The product was dried *in vacuo* and obtained 43.7 mg of black solid (Yield: 68.1 %).

Synthesis of complex 2: A solution of Ni(II) acetate tetrahydrate (19.0 mg, 0.10 mmol) in ethanol (10 mL) was added dropwise to a solution of H_6L (36.6 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. A transparent solution was obtained and stirred vigorously and refluxed for 10 h. the resulting solid was concentrated under reduced pressure to 5 mL and obtained a large number of black precipitate which was washed with ethanol/ether (1:4) and ether, respectively. The product was dried *in vacuo* and obtained 40.3 mg of brown solid (Yield: 62.8 %).

Synthesis of complex 3: To an ethanolic solution (3 mL) of H_6L (36.4 mg, 0.10 mmol) was added dropwise an ethanol solution (6 mL) of Cd(II) acetate dihydrate (20.7 mg, 0.10 mmol). A transparent solution was obtained and stirred vigorously and refluxed for 9 h. The formed precipitate was separated by filtration and washed successively with ethanol/ether (1:4) and ether, respectively. The product was dried under reduced pressure to obtain 36.7 mg of black solid (Yield: 45.7 %).

RESULTS AND DISCUSSION

A Salamo-type compound H_6L and its Co(II), Ni(II) and Cd(II) complexes have been synthesized with good yields and the compositions are confirmed by elemental analyses, IR, UV-visible spectra, TG-DTA analyses and molar conductance measurements.

Composition of Co(II), Ni(II) and Cd(II) complexes: The colour, yields and analytical results of the complexes are given in Table-1.

Their compositions agree with the formulae $[Co_3(HL)(CH_3COO)]\cdot EtOH$ for the complex **1**, $[Ni_3(HL)(CH_3COO)]\cdot EtOH$ for the complex **2**, $[Cd_3(HL)(CH_3COO)]\cdot EtOH$ for the complex **3**. The molar conductance values of the 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 Co(II), Ni(II) and Cd(II) complexes are non-electrolytes[7], indicating the acetate anions in the Co(II), Ni(II) and Cd(II) complexes are coordinated to the Co(II), Ni(II) and Cd(II) ions.

IR spectra of H_6L, Co(II), Ni(II) and Cd(II) complexes: The most important FT-IR spectral data for H_6L and its Co(II), Ni(II) and Cd(II) complexes are presented in Table-2. From the results of IR spectra, the ligand and its comp-lexes are different, which proves that the Co(II), Ni(II) and Cd(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 1599.0-1602.8 cm^{-1}. The C=N stretching frequency shifted to a lower frequency by 16.7-12.9 cm^{-1} upon complexation, indicating a decrease in C=N bond order due to the coordination of the Co(II), Ni(II) and Cd(II) ions with oxime nitroen[1].The Ar-O stretching band occur at 1292.0 cm^{-1} for H_6L, whereas those at 1254.2-1246.6 cm^{-1} for the Co(II), Ni(II) and Cd(II) comp-lexes[8]. This shifting Ar-O stretching frequency indicates that the M-O bonds are formed between the Co(II), Ni(II) and Cd(II) ions and oxygen of phenolic group[1,9]. In addition, the O-H stretching band of the free ligand H_6L appears at 3453.1 cm^{-1} and broad absorption bands at 3420.5-3395.9 cm^{-1} in the Co(II), Ni(II) and Cd(II) complexes is assigned to phenolic

TABLE-1
COLOUR AND ANALYTICAL DATA OF H_6L AND ITS Co(II), Ni(II) and Cd(II) COMPLEXES

Comp.	m.f. (m.w.)	Colour	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	53.00 (52.75)	4.39 (4.43)	7.37 (7.69)	–	–
$[Co_3(HL)(CH_3COO)]\cdot EtOH$	$C_{20}H_{20}Co_3N_2O_{11}$ (641.2)	Black	3774 (37.46)	3.02 (3.14)	4.20 (4.37)	27.73 (27.57)	7.21
$[Ni_3(HL)(CH_3COO)]\cdot EtOH$	$C_{20}H_{20}Ni_3N_2O_{11}$ (640.5)	Brown	37.24 (37.51)	3.08 (3.15)	4.69 (4.37)	27.26 (27.49)	7.42
$[Cd_3(HL)(CH_3COO)]\cdot EtOH$	$C_{20}H_{20}Cd_3N_2O_{11}$ (801.6)	Black	30.12 (29.97)	2.46 (2.51)	3.45 (3.49)	41.88 (42.07)	7.69

TABLE-2
IR SPECTRAL DATA FOR H_6L AND ITS Co(II), Ni(II) AND Cd(II) COMPLEXES (cm^{-1})

Compound	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
$[Co_3(HL)(CH_3COO)]\cdot EtOH$	1602.8	1251.3	3395.9	1591.4, 1510.8, 1457.9
$[Ni_3(HL)(CH_3COO)]\cdot EtOH$	1602.5	1254.2	3408.3	1588.0, 1515.2, 1449.5
$[Cd_3(HL)(CH_3COO)]\cdot EtOH$	1599.0	1246.6	3420.5	1589.7, 1521.6, 1444.0

TABLE-3
UV-VIS SPECTRA DATA OF H_6L AND ITS Co(II), Ni(II) AND Cd(II) COMPLEXES

Compound	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		
$[Co_3(HL)(CH_3COO)]\cdot EtOH$	1.00	279	3.45	311	2.18
$[Ni_3(HL)(CH_3COO)]\cdot EtOH$	1.00	277	3.03	318	2.19
$[Cd_3(HL)(CH_3COO)]\cdot EtOH$	1.00	272	3.11	303	1.99

TABLE-4
THERMAL ANALYSIS DATA OF H_6L AND ITS Co(II), Ni(II) AND Cd(II) COMPLEXES

Compound	Endothermic peak temperature (ºC)	Weight loss rate (%)		Exothermic peak temperature (ºC)	Residual weight rate (%)		Final product
		Found	Calcd.		Found	Calcd.	
$[Co_3(HL)(CH_3COO)]\cdot EtOH$	156	7.0	7.2	285.3, 335.2	12.1	11.7	CoO
$[Ni_3(HL)(CH_3COO)]\cdot EtOH$	158	6.8	7.2	240.7, 288.9	12.2	11.7	NiO
$[Cd_3(HL)(CH_3COO)]\cdot EtOH$	152	5.4	5.8	267.6, 330.5	16.5	16.0	CdO

alcohol group of the $(HL)^{5-}$ unit and -OH groups of non-coordinated ethanol molecules.

UV-visible spectra of H_6L and its Co(II), Ni(II) and Cd(II) complexes: The absorption data of H_6L and its Co(II), Ni(II) and Cd(II) complexes in diluted DMF solution are listed in Table-3. The absorption spectra of the complexes are similar to each other, but are different from the spectrum of the 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[10]. Compared with the absorption peak of the ligand H_6L, corresponding absorption peaks at 279-272 nm are observed in Co(II), Ni(II) and Cd(II) complexes, which are hypsochromically shifted by 4-11 nm, indicating the coordination of Co(II), Ni(II) and Cd(II) ions with the $(HL)^{5-}$ unit[11]. Meanwhile, new absorption peaks are observed at 318-303 nm in Co(II), Ni(II) and Cd(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 Co(II), Ni(II) and Cd(II) ions[12,13].

Thermal properties: Thermal analysis data of the free ligand H_6L and its Co(II), Ni(II) and Cd(II) complexes are summarized in Table-4. The free ligand H_6L has a small sharp endothermic peak at 218 ºC in DTA curve, with no weight loss in the TG curve, which is its melting point. On further heating, the free ligand H_6L has a exothermic peak at 282 ºC, with a weight loss in the TG curve and the ligand decompose completely by one step. The thermal decomposition process of complexes **1**, **2** and **3** can be divided into three stages. The initial weight loss occurs in the range 72-128 ºC for the three complexes, corresponding to an endothermic peak and the TG curve shows that the weight loss corresponding to this temperature range is 7.0, 6.8 and 5.4 % that roughly coincides with the values of 7.2, 7.2 and 5.8 %, respectively, calculated for the loss of one ethanol molecule. On further heating, one exothermic peak appears at 285.3 ºC for complex **1** (240.7 ºC for complex **2** and 267.6 ºC for complex **3**) in the DTA curve and a continued weight loss occurs in the TG curve. Then, the second strong exothermic peak at 335.2 ºC for complex **1** (at 288.9 ºC for complex **2** and 330.5 ºC for complex **3**) accompanied with further decomposition of the compounds and the final solid products are likely to CoO with a residual value of 12.1 % (theoretical value, 11.7 %) for complex **1**, NiO with a residual value of 12.2 % (theoretical value, 11.7 %) for complex **2** and CdO with a residual value of 16.5 % (theoretical value, 16.0 %) for complex **3** when the temperature is above 800 ºC.

REFERENCES

1. (a) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009); (b) W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010); (c) W.K. Dong, X.N. He, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao and X.L. Tang, *Polyhedron*, **28**, 1419 (2009); (d) W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009); (e) W.K. Dong, L. Li, C.F. Li, L. Xu and J.G. Duan, *Spectrochim. Acta A*, **71**, 650 (2008); (f) W.K. Dong, Y.X. Sun, G.H. Liu, L. Li, X.Y. Dong and X.H. Gao, *Z. Anorg. Allg. Chem.*, **638**, 1370 (2012); (g) W.K. Dong, J.G. Duan, Y.H. Guan, J.Y. Shi and C.Y. Zhao, *Inorg. Chim. Acta*, **362**, 1129 (2009).
2. Y. Sui, D.P. Li, C.H. Li, X.H. Zhou, T. Wu and X.Z. You, *Inorg. Chem.*, **49**, 1286 (2010).
3. N.S. Venkataramanan, G. Kuppuraj and S. Rajagopal, *Coord. Chem. Rev.*, **249**, 1249 (2005).
4. M.F. Summers, L.G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc.*, **106**, 4478 (1984).
5. P.G. Lacroix, *Eur. J. Inorg. Chem.*, 339 (2001).
6. S.S. Sun, C.L. Stern, S.T. Nguyen and J.T. Hupp, *J. Am. Chem. Soc.*, **126,** 6314 (2004).
7. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
8. X.Q. Song, J.R. Zheng, W.S. Liu and Z.H. Ju, *Spectrochim. Acta A*, **69**, 49 (2008).
9. M. Asadi, K.A. Jamshid and A.H. Kyanfar, *Inorg. Chim. Acta*, **360**, 1725 (2007).
10. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M.G.B. Drew, *Inorg. Chim. Acta*, **360**, 1753 (2007).
11. H.E. Smith, *Chem. Rev.*, **83**, 359 (1983).
12. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).
13. L. Gomes, E. Pereira and B. de Castro, *J. Chem. Soc. Dalton Trans.*, 1373 (2000).