Asian Journal of Chemistry; Vol. 25, No. 16 (2013), 9359-9361

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15626

Synthesis and Structure Characterization of Copper(II) Complexes with 5,5'-Dihydroxy-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol

YU-HUA YANG, LI-SHA ZHANG, GANG LI*, MENG-MENG ZHAO, ZHENG-KUN WANG, XIN-YING ZHANG and JIAO-LONG MENG

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, P.R. China

*Corresponding author: E-mail: li_gang78@126.com

(*Received*: 12 April 2013; *Accepted*: 25 September 2013) AJC-14178

A new tetradentate *bis*-oxime chelating ligand, 5,5'-dihydroxy-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_4L) and its two Cu(II) complexes **1** and **2** have been synthesized by the reaction of H_4L with copper(II) acetate monohydrate and copper(II) picrate tetrahydrate, respectively. The complexes have been characterized by elemental analyses, IR spectra, UV-visible spectra, TG-DTA and molar conductances. The salen-type bisoxime chelating ligand is a good tetradentate N_2O_2-donating ligand and the likely formulae of the Cu(II) complexes may be suggested as $[Cu(H_2L)]\cdot CH_3CH_2OH\cdot 2H_2O$ (**1**) and $[Cu_2(H_2L)(picrate)_2]\cdot H_2O$ (**2**).

Key Words: Cu(II) complex, Salen-type bisoxime compound, Synthesis, Characterization.

INTRODUCTION

In recent years, transition metal complexes bearing an N,N-disalicylideneethylenediamine (Salen) ligand or its analogues are extensively studied because these complexes are used as catalysts in various organic reactions[1], non-linear optical materials[2] and exhibit interesting magnetic properties[3]. The oxime-type ligands should be stable enough to resist the metathesis of the C=N bonds[4]. Linear derivatives bearing two salicylaldoxime moieties at both ends have been reported. In this paper, a new Salen-type chelating ligand based on O-alkyloxime instead of the imine moiety, 5,5'-dihydroxy-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_4L) (Fig. 1) and the corresponding copper(II) complexes were synthesized and characterized.

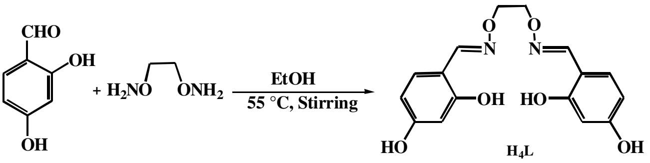

Fig. 1. Synthetic route to salen-type bisoxime compound

EXPERIMENTAL

2,4-Dihydroxybenzaldehyde (≥ 99.0 %) was purchased from Alfa Aesar and was used without further purification. 1,2-*Bis*(aminooxy)ethane was synthesized according to an analogous method reported earlier[5-9]. Elemental analysis for Cu was 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. Melting points were obtained by use of an X4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company and were uncorrected. 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 °C.

Synthesis of ligand H_4L: A solution of 1,2-*bis*(aminooxy)ethane (92.5 mg, 1.00 mmol) in ethanol (8 mL) was added to a solution of 2,4-dihydroxybenzaldehyde (290.1 mg, 2.10 mmol) in ethanol (8 mL) and the mixture solution was heated to 55 ºC under stirring for 6 h. After cooling to room temperature, the precipitate was filtered and washed successively with ethanol and ethanol/*n*-hexane (1:4), respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to yield 277.6 mg of pale-pink crystalline solid. Yield 83.6 %. m.p. 219-220 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ: 4.28 (s, 4H), 6.29 (d, $J = 7.6$, 1.4 Hz, 4H), 7.30 (d, $J = 8.0$ Hz, 2H), 8.27(s, 2H), 9.80 (s, 2H), 9.94 (s, 2H).

Synthesis of Cu(II) complex 1: A solution of copper(II) acetate monohydrate (20.1 mg, 0.10 mmol) in ethanol (3 mL) was added dropwise to a solution of H_4L (33.2 mg, 0.10 mmol) in ethanol (3 mL) at room temperature. The colour of the mixing solution turned to black and then continuing stirring for 10 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 33.5 mg of black solid. Yield 70.6 %.

Synthesis of Cu(II) complex 2: To an ethanol solution (5 mL) of H_4L (33.2 mg, 0.10 mmol) was added an ethanol solution (5 mL) of copper(II) picrate tetrahydrate (59.5 mg, 0.10 mmol). After the mixture solution had been stirred at room temperature for 10 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 71.2 mg of yellow solid. Yield 76.6 %.

RESULTS AND DISCUSSION

5,5'-Dihydroxy-2,2'-[ethylenedioxy*bis*(nitrilomethylidyne)]diphenol (H_4L) and its two Cu(II) complexes **1** and **2** have been synthesized and the composition are confirmed by elemental analyses, IR, UV-visible spectra and TG-DTA analyses.

The colour, yields, melting points and elemental analytical, molar conductance results of the synthesized salamo-type bisoxime compounds H_4L and its two Cu(II) complexes **1** and **2** are presented in Table-1.

The elemental analysis data of H_4L and its two Cu(II) complexes **1** and **2** are very close to the theoretical values, to prove the accuracy of analytical results. Copper(II) acetate monohydrate forms a 1:1 type (M:L) complex with the ligand H_4L which contains one ethanol and two water molecules in the complex **1** molecule, whereas the copper(II) picrate tetrahydrate forms a 2:1 type (M:L) complex in the complex **2** molecule which contains two picrate and one water molecules. The molar conductance values of complexes **1** and **2** in 1.0×10^{-3} mol dm^{-3} DMF solutions are 7.81 and 8.87 S cm^2 mol^{-1} at 21 ºC, respectively, indicating that both are non-electrolytes[10]. Both Cu(II) complexes aren't easy to absorb moisture and have a fairly good stability in air. The ligand H_4L can be dissolved in most solvents. The complex **1** is soluble in strongly polar solvents such as DMF and DMSO, but insoluble in weakly polar and non-polar organic solvent; the complex **2** have a good solubility, not only soluble in strongly polar solvents such as DMF and DMSO but also soluble in methanol, ethanol, *etc*. weakly polar solvents, but insoluble in *n*-hexane, benzene and acetonitrile.

The most important FT-IR spectral data for H_4L and its corresponding Cu(II) complexes are given in Table-2. The characteristic C=N stretching band of the free ligand H_4L appears at 1608 cm^{-1}, while the C=N bands of Cu(II) complexes **1** and **2** are observed at 1617 and 1610 cm^{-1}, blue shift of 2-9 cm^{-1}, respectively. The Ar-O stretching band occurs at 1246 cm^{-1} for H_4L, whereas those at 1215 and 1217 cm^{-1} for complexes **1** and **2**, red shift of 29-31 cm^{-1}, respectively. These shifts of C=N and Ar-O stretching frequencies indicate that the Cu-N and Cu-O bonds are formed between the Cu(II) ions and the oxime N and the phenolic O atoms of deprotonated $(L)^{2-}$ unit[8]. Meanwhile, the OH out-of-plane bending vibration of the free HPic at 1148 cm^{-1} appears in the spectrum of complex **2**, indicating that the H-atom of the OH group existed in complex **2**[11]. The free HPic has $\nu_{as}(-NO_2)$ and $\nu_s(-NO_2)$ at 1555 and 1342 cm^{-1}, respectively, which split into two bands at 1577, 1543, 1372 and 1332 cm^{-1}. This indicates that some of the nitryl O atoms take part in coordination[12,13]. In addition, the infrared spectra of the complexes **1** and **2** show the expected absorptions due to the stretching and bending modes of water at 3226 and 1630 cm^{-1}, respectively, indicating the presence of a water molecule[8f].

The absorption spectra data of H_4L and its corresponding Cu(II) complexes **1** and **2** (Table-3), in diluted DMF solution show that the spectra of complexes **1** and **2** are similar to each other, but are different from the spectrum of the ligand H_4L. The UV-visible spectrum of the free ligand H_4L exhibits two absorption peaks at 276 and 311 nm. The former absorption peak at 276 nm can be assigned to the π-π* transition of the benzene rings and the latter one at 311 nm can be attributed to the intra-ligand π-π* transition of the C=N bonds[14].

TABLE-1
COLOUR, YIELDS AND ANALYTICAL DATA OF H_4L AND ITS COPPER(II) COMPLEXES

Compound	m.f. (m.w.)	Colour	Yield (%)	Found (calcd.) (%)				Molar conductance (S cm^2 mol^{-1})
				C	H	N	Cu	
H_4L	$C_{10}H_{10}N_2O_6$ (332.1)	Pale-pink	83.6	58.03 (57.83)	5.08 (4.85)	7.96 (8.43)	–	–
1	$C_{18}H_{24}CuN_2O_9$ (475.1)	Black	70.6	45.24 (45.42)	4.89 (5.08)	6.02 (5.89)	13.56 (13.35)	7.81
2	$C_{28}H_{20}Cu_2N_8O_{21}$ (929.9)	Yellow	76.6	36.25 (36.10)	2.11 (2.16)	11.88 (12.02)	13.42 13.64)	8.87

TABLE-2
MOST IMPORTANT FT-IR BANDS FOR H_4L AND ITS COPPER(II) COMPLEXES (cm^{-1})

Compound	ν(C=N)	ν(Ar-O)	ν(O-H)	δ(H_2O)	ν(C=C) benzene ring skeleton
H_4L	1631	1209	3356	1627	1517, 1467, 1430
1	1617	1215	3226	1630	1543, 1443, 1341
2	1610	1270	3371	1632	1610, 1437, 1340

TABLE-3
UV-VIS SPECTRAL DATA OF H_4L AND ITS COPPER(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_4L	1.00	276	2.54	311	2.09
1	1.00	296	3.72	356	2.03
2	1.00	299	2.78	372	4.71

TABLE-4
THERMAL ANALYSIS DATA OF H_4L AND ITS COPPER(II) COMPLEXES

Compound	Endothermic peak temp. (ºC)	Weight loss rate (%)		Exothermic peak temp. (ºC)	Residual weight rate (%)		Final product
		Found	Calcd.		Found	Calcd.	
H_4L	220	25.1	24.8	241	–	–	–
1	85, 154	9.4, 7.7	9.7, 7.6	284, 336	16.5	16.7	CuO
2	128, 206	2.1, 49.1	1.9, 49.3	278, 342	16.9	17.1	CuO

Compared with the absorption peak of the free ligand, a corresponding absorption peak at 296 and 299 nm is observed in complexes **1** and **2**, respectively, which is hypsochromically shifted by 12-15 nm, indicating the coordination of Cu(II) ions with deprotonated $(H_2L)^{2-}$ unit[8]. In addition, the new bands observed at 356 and 372 nm for complexes **1** and **2** are assigned to the n-π* charge transfer transition from the filled p-π orbital of the bridging phenolic oxygen to the vacant *d*-orbital of the Cu(II) ions, which are characteristic of the transition metal complexes with N_2O_2 coordination spheres[15].

Thermal properties: The experimental results show that the thermal behaviour of the free ligand H_4L is significantly different from the Cu(II) complexes. The free ligand H_4L has a small sharp endothermic peak at 220 ºC in DTA curve, with no weight loss in the TG curve, which is its melting point. On further heating, the free ligand H_4L has a exothermic peak at 241 ºC, with a weight loss in the TG curve and the ligand decompose completely by one step. Thermal analysis data of H_4L and its copper complexes are given in Table-4.

Compared to the free ligand H_4L, the endothermic peaks of complex **1** appear at 85 and 154 ºC in DTA curve and the TG curve shows that the weight loss corresponding to this temperature range is 9.4 and 7.7 % that roughly coincides with the values of 9.7 and 7.6 %, respectively, calculated for the loss of one coordinated ethanol and two coordinated water molecules of complex **1**, which is consistent with the results of infrared spectroscopy. The DTA curve of complex **2** shows two endothermic peaks at 128 and 206 ºC with the weight losses of 2.1 and 49.1 %, respectively, which are agreement with the losses of one water (1.93 %) and two picric acid (49.3 %) molecules. On further heating, two exothermic peaks successively at 284 and 336 ºC for complex **1** (278 and 342 ºC for complex **2**) in the DTA curve and a continued weight loss occurs in the TG curve. Then, the second strong exothermic peak at 336 ºC for complex **1** (at 342 ºC for complex **2**) accompanied with further decomposition of the complex and the final solid product is likely to CuO with a residual value of 16.5 % (theoretical value, 16.7 %) for complex **1** and 16.9 % (theoretical value, 17.1 %) for complex **2** when the temperature is above 800 ºC.

REFERENCES

1. T. Katsuki, *Coord. Chem. Rev.*, **140**, 189 (2009).
2. P.G. Lacroix, *Eur. J. Inorg. Chem.*, **14**, 339 (2001).
3. J.-P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, **39**, 165 (2000).
4. K. Koehler, W. Sandstrom and E.H. Cordes, *J. Am. Chem. Soc.*, **86**, 2413 (1964).
5. M. Maneiro, M.R. Bermejo, M. Fondo, A.M. González, J. Sanmartin, J.C. Garcia-Monteagudo, R.G. Pritchard and A.M. Tyryshkin, *Polyhedron*, **20**, 711 (2001).
6. H.-B. Zhu, Z.-Y. Dai, W. Huang, K. Cui, Sh.-H. Gou and Ch.-J. Zhu, *Polyhedron*, **23**, 1131 (2004).
7. S. Akine, T. Matsumoto, S. Sairenjia and T. Nabeshima, *Supramol. Chem.*, **23**, 106 (2011).
8. (a) 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); (b) 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); (c) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012); (d) W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012); (e) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009); (f) W.K. Dong and J.G. Duan, *J. Coord. Chem.*, **61**, 781 (2008).
9. D.K. Aliakbar, A. Mehdi and T. Smail. *Inorg. Chim. Acta*, **362**, 587 (2009).
10. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
11. X.Q. Song, J.R. Zheng, W.S. Liu and Z.H. Ju, *Spectrochim. Acta A*, **69**, 49 (2008).
12. S.X. Liu, W.S. Liu, M.Y. Tan and K.B. Yu, *J. Coord. Chem.*, **10**, 391 (1996).
13. X.Q. Song, W.S. Liu, W. Dou, Y.W. Wang, J.R. Zheng and Z.P. Zang, *Eur. J. Inorg. Chem.*, 1901 (2008).
14. T. Ghosh, B. Mondal, T. Ghosh, M. Sutradhar, G. Mukherjee and M.G.B. Drew, *Inorg. Chim. Acta*, **360**, 1753 (2007).
15. L. Gomes, E. Pereira and B. Castro, *J. Chem. Soc. Dalton Trans.*, 1373 (2000).