

Synthesis of Some Transition Metal Complexes of a Novel Schiff Base Ligand Derived from 2,2'-bis(*p*-Methoxyphenylamine) and Salicylaldehyde

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Received: 25 February 2003; in revised form: 3 April 2003 / Accepted: 5 April 2003 / Published: 31 May 2003

Abstract: A novel Schiff base ligand derived from 2,2'-bis(*p*-methoxyphenylamine) and salicylaldehyde and its transition metal complexes with Cu (II), Co (II) and Mn (II) have been synthesized. Their spectral properties and electrochemical behavior were investigated.

Keywords: Schiff base; transition metal complexes; synthesis; properties.

Introduction

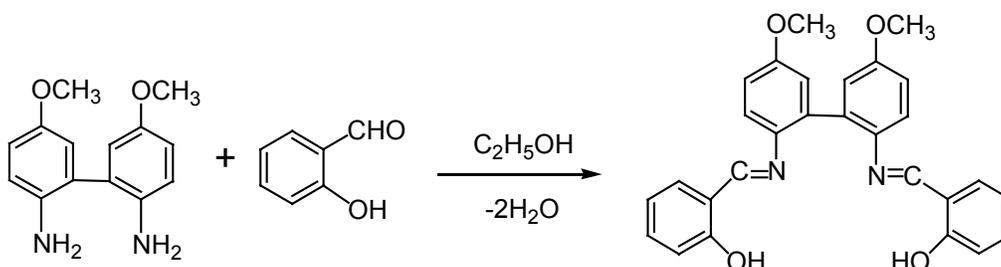
During the past two decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors [1-4]. This may be attributed to their stability, biological activity [5] and potential applications in many fields such as oxidation catalysis [6], electrochemistry [7], etc. Herein we report the synthesis of a novel Schiff base ligand (H₂L) and its Cu (II), Co (II) and Mn (II) complexes. Their spectral properties and electrochemical behavior were investigated.

Results and discussion

Ligand synthesis

The ligand (H_2L) was prepared as outlined in Figure 1.

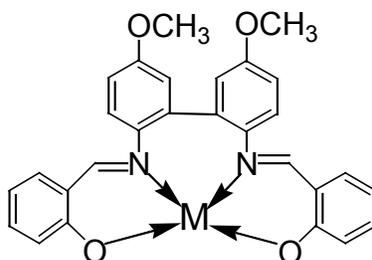
Figure 1. Synthesis of the ligand



Complexes

Elemental analyses indicate that the complexes of H_2L with Cu (II), Co (II) and Mn (II) can be formulated as $M \cdot L$. The disappearance of the OH band of the free ligand in the IR of the metal complexes indicates that the OH group is deprotonated and coordinated to the metal ion as $-O^-$. On the other hand, the C=N stretching mode is shifted to a lower frequency by about 29 cm^{-1} , compared to the free ligand. These IR results indicate that the ligand is coordinated to Cu (II), Co (II), Mn (II) *via* both N and O. The new IR bands appearing at $420 \sim 430\text{ cm}^{-1}$ and $541 \sim 560\text{ cm}^{-1}$ are assigned to $\nu(M-O)$ and $\nu(M-N)$ vibrations, respectively. In addition, no new bands at $1610 \sim 1550\text{ cm}^{-1}$ and $1420 \sim 1300\text{ cm}^{-1}$ are observed, indicating that the complexes do not contain CH_3COO^- anions, which is in accordance with the elemental analysis results for the complexes. According to the aforementioned data, we propose for the complexes prepared the structure shown in Figure 2. It is suggested that the complexes are square planar or nearly square planar, coordinated according to the common stereochemistry of this kind of compounds.

Figure 2. The proposed chemical structure for the transition metal complexes



M= Cu (II), Co (II), Mn (II)

Electrochemistry

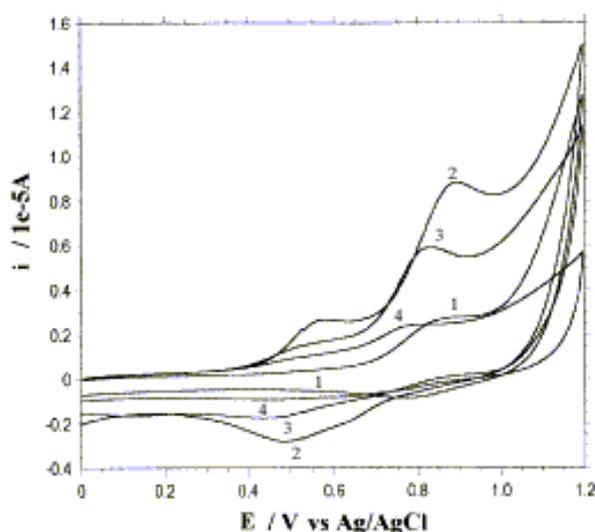
The electrochemical behaviors of the H₂L ligand and the MnL, CuL and CoL complexes were examined by means of cyclic voltammetry in CH₂Cl₂. A typical cyclic voltammogram of H₂L and its complexes is shown in Figure 3 and the results are summarized in Table 1.

Table 1 Cyclic voltammetric data for ligand and complexes in CH₂Cl₂

Ligand and Complexes	$E_{p,a1}/V$	$E_{1/2}/mV$	$\Delta E_{p1}/mV$	$E_{p,a2}/V$	$E'_{1/2}/mV$
L	0.8579	782.4	75.5	—	—
MnL	0.580	495.0	110.0	0.895	800.0
CuL	0.830	745.0	—	—	—
CoL	0.782	700.0	—	—	—

The MnL complex shows two oxidation processes at $E_{p,a} = 0.58$ and $0.895V$. The first wave is nearly reversible with $\Delta E_p = 110mV$. This process is consistent with a one-electron oxidation to form the mixed valence Mn(II, III) species. The second wave is irreversible at $0.895V$. On the other hand, the complexes of CuL and CoL only show one oxidation process at 0.83 and $0.782V$, respectively, which are irreversible. This process is attributed to the oxidation of ligand. The observed reaction voltages of the complexes of CuL and CoL are lower than that of the ligand, while the MnL one is higher.

Figure 3. Cyclic Voltammogram of the Complexes in CH₂Cl₂; Scan Rate 100mV/s



1- L, 2-MnL, 3-CuL, 4-CoL.

Acknowledgments

We thank National Natural Science Foundation of China (No. 29871014) and the Doctoral Foundation of Lanzhou University for financial support.

Experimental

General

The C, H, N data were determined using a Varian EL elemental analyzer. IR spectra was recorded on a Nicolet 170SX FT IR spectrophotometer using KBr discs in the range $\nu = 400\text{--}4000\text{ cm}^{-1}$. The cyclic voltammetry experiments were carried out using a CHI660A electrochemical workstation (Covarda, USA). All chemicals were analytical grade and used without further purification.

Preparation of the Ligand

Salicylaldehyde (20 mmol) was added to a solution of 2,2'-bi(p-methoxyphenylamine) (10 mmol) in ethanol (30 mL). The mixture was continuously stirred for 3 h at room temperature, and the resulting yellow product was collected by filtration to give pale white crystals in 94% yield. Calculated for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{O}_4$: 74.3 % C, 5.4 % H, 6.2 % N. Found: 73.9 % C, 5.6 % H, 6.1 % N. IR (in KBr pellets) cm^{-1} : 1657 (-C=N-), 3450 (-OH) cm^{-1} .

Preparation of the Complexes

A mixture of $\text{M}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$ (2 mmol) [$\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Cu}(\text{II})$], LiOH and ligand in a 1:2:1 molar ratio was stirred in ethanol (20 mL) at 50°C for 4h. The crude complexes were filtered off and then recrystallized from 1:1 water-ethanol. The products were dried in vacuo for 48 h.

CuL: brown solid, yield, 85 %; Calculated for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4\text{Cu}$: 65.4 % C, 4.3 % H, 5.5 % N. Found: 65.2 % C, 4.6 % H, 5.7 % N. IR cm^{-1} : 1628 (-C=N).

CoL: orange solid, yield, 88 %; Calculated for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4\text{C}$: 66.0 % C, 4.4 % H, 5.5 % N. Found: 65.8 % C, 4.3 % H, 5.7 % N. IR cm^{-1} : 1629 (-C=N).

MnL: dark-brown solid, yield, 88 %; Calculated for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4\text{Mn}$: 66.5 % C, 4.4 % H, 5.5 % N. Found: 66.8 % C, 4.1 % H, 5.2 % N. IR cm^{-1} : 1628 (-C=N)

Electrochemical Measurements

The cyclic voltammetry experiments were carried out with a three electrode apparatus using a CHI660A electrochemical workstation (Covarda, USA), the working electrode was a glassy carbon disc, polished with an Al₂O₃ suspension prior to every experiment. Ag/AgCl and Pt foil were used as reference and counter electrodes, respectively. The H₂L and complexes solutions ($1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) in CH₂Cl₂, with tetraethylammonium perchlorate ($0.1 \text{ mol} \cdot \text{L}^{-1}$) as supporting electrolyte were purged of oxygen by bubbling nitrogen for 15 min. and then blanketed with the same gas during the experiments. All compounds were investigated at 25 °C. The voltammograms were recorded with a potential scan of $100 \text{ mV} \cdot \text{s}^{-1}$.

References

1. Djebbar, S. S.; Benali, B. O.; Deloume, J. P. Synthesis, characterization and electrochemical behavior of copper(II) complexes with linear and tripodal tetradentate ligands derived from Schiff bases. *Polyhedron*, **1997**, *16*, 2175-2182
2. Bhattacharyya, P.; Parr, J.; Ross, A. T. First synthesis of a unique dilead Schiff base complex. *J. Chem. Soc. Dalton*. **1998**, 3149-3150
3. He, L.; Gou, S. H.; Shi, Q. F. The formation of a Schiff base intermediate: a nickel(II) complex of an asymmetric tripodal ligand. *J. Chem. Crystallogr.* **1999**, *29*, 207-210
4. Wu, J. C.; Tang, N.; Liu, W. S.; Tan, M. Y.; Chan, A. S. C. Intramolecular hydrogen bond self-template synthesis of some new Robson-type macrocyclic ligands. *Chin. Chem. Lett.* **2001**, *12*, 757-760
5. Liu, C. M.; Xiong, R. G.; You, X. Z.; Liu, Y. J.; Cheung, K. K. Crystal structure and some properties of a novel potent Cu₂Zn₂SOD model Schiff base copper(II) complex. *Polyhedron*, **1996**, *15*, 4565-4571
6. Djebbar, S. S.; Benali, B. O.; Deloume, J. P. Synthesis, characterization, electrochemical behavior and catalytic activity of manganese(II) complexes with linear and tripodal tetradentate ligands derived from Schiff bases. *Transit. Metal. Chem.* **1998**, *23*, 443-447
7. Hamada, Y. J. The development of chelate metal complexes as an organic electroluminescent material. *IEEE Trans. Electron Devices*, **1997**, *44*, 1208-1217

Sample availability: Not available.