

# Preparation and XPS studies of macromolecule mixed-valent Cu(I, II) and Fe(II, III) complexes

Bo Wang<sup>a,\*</sup>, Fengqin Gao<sup>a,b</sup>, Hongzhu Ma<sup>a</sup>

<sup>a</sup> Institute of Energy Chemistry, College of Chemistry and Materials Science, Shaanxi Normal University, Xi'an 710062, PR China

<sup>b</sup> Department of Chemistry, Xianyang Normal University, Xianyang, PR China

Received 8 August 2006; received in revised form 12 October 2006; accepted 13 October 2006

Available online 21 October 2006

## Abstract

A new macromolecule ligand and its mixed-valent Cu(I, II) and Fe(II, III) complexes have been prepared by using ethylenediamine as core and maleic anhydride as branched units and characterized by UV–vis, FT-IR, thermal analysis and X-ray photoelectron spectroscopy (XPS). The data obtained from these studies suggested that the coordinate bonds of N → M, Cl → M, Ph–OH → M and H<sub>2</sub>O → M have been formed and possible binding models are proposed for these complexes. The thermal analysis (TG-DTG) reveals that these complexes possess thermal stable property below 800 °C.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Mixed-valent; Copper complex; Iron complex; Preparation; Characterization

## 1. Introduction

The continuing interest in the field of highly branched macromolecules is evidenced by the fact that a number of reports concerning the use of these highly symmetrical molecular structures in a variety of applications have appeared recently [1–3]. The multiplicity of the structures of macromolecules brings more inspiration to the coordination chemistry of macromolecule. Usually, such ligands have multiple sites available for coordination so that a wide variety of coordination modes are possible and it is becoming more interesting to design and synthesize such metal coordination macromolecules because of their intriguing structural topologies [4–6].

Continuing to study on potential functional coordination and especially on the structure exploration by XPS spectra [7–12], a new macromolecule and its mixed-valent copper(I, II) and iron(II, III) complexes have been synthesized from a polymer ligand, which achieved by using ethylenediamine as core and maleic anhydride as branched units. The possible structures of the polymer and its complexes are defined on the basis of their UV, IR and XP spectra analysis, and the thermal stability in air has also been studied.

## 2. Experimental

### 2.1. Regents and measurements

Methanol, ethylenediamine, maleic anhydride, salicylaldehyde, NaCl, NaOH, HCl (36.5%), CuCl<sub>2</sub>·2H<sub>2</sub>O, Cu<sub>2</sub>Cl<sub>2</sub>, FeCl<sub>2</sub> and FeCl<sub>3</sub>·6H<sub>2</sub>O were AR grade and employed without further purification.

UV spectra of the complexes were recorded on a UV-75 double-beam spectrophotometer with DMSO as solvent in the range of 200–400 nm. IR spectra were obtained on a Nicolet AVATAR 360 FT-IR spectrophotometer in the range of 400–4000 cm<sup>-1</sup> as potassium bromide pellets. X-ray photoelectron spectra (XPS) were taken on a PHI-5400 apparatus, using Mg K $\alpha$  radiation and the carbon 1s peak at 284.6 eV as standard. The accuracy of the measured BE value is  $\pm 0.1$  eV. Thermal analysis (TG-DTG) measurements were carried out in nitrogen atmosphere between room temperature and 500 °C on a Thermoflex TG-DTG meter.

### 2.2. Preparation of the ligand and complexes

The 14G dendritic polymer and its ligand (L) were synthesized according to Ref. [13] and following the reaction shown in Fig. 1. The yellow powder was collected and dried at 40 °C in vacuo. Yield: 52%.

\* Corresponding author. Tel.: +86 29 85308442; fax: +86 29 85307774.  
E-mail address: [wangbo@snnu.edu.cn](mailto:wangbo@snnu.edu.cn) (B. Wang).

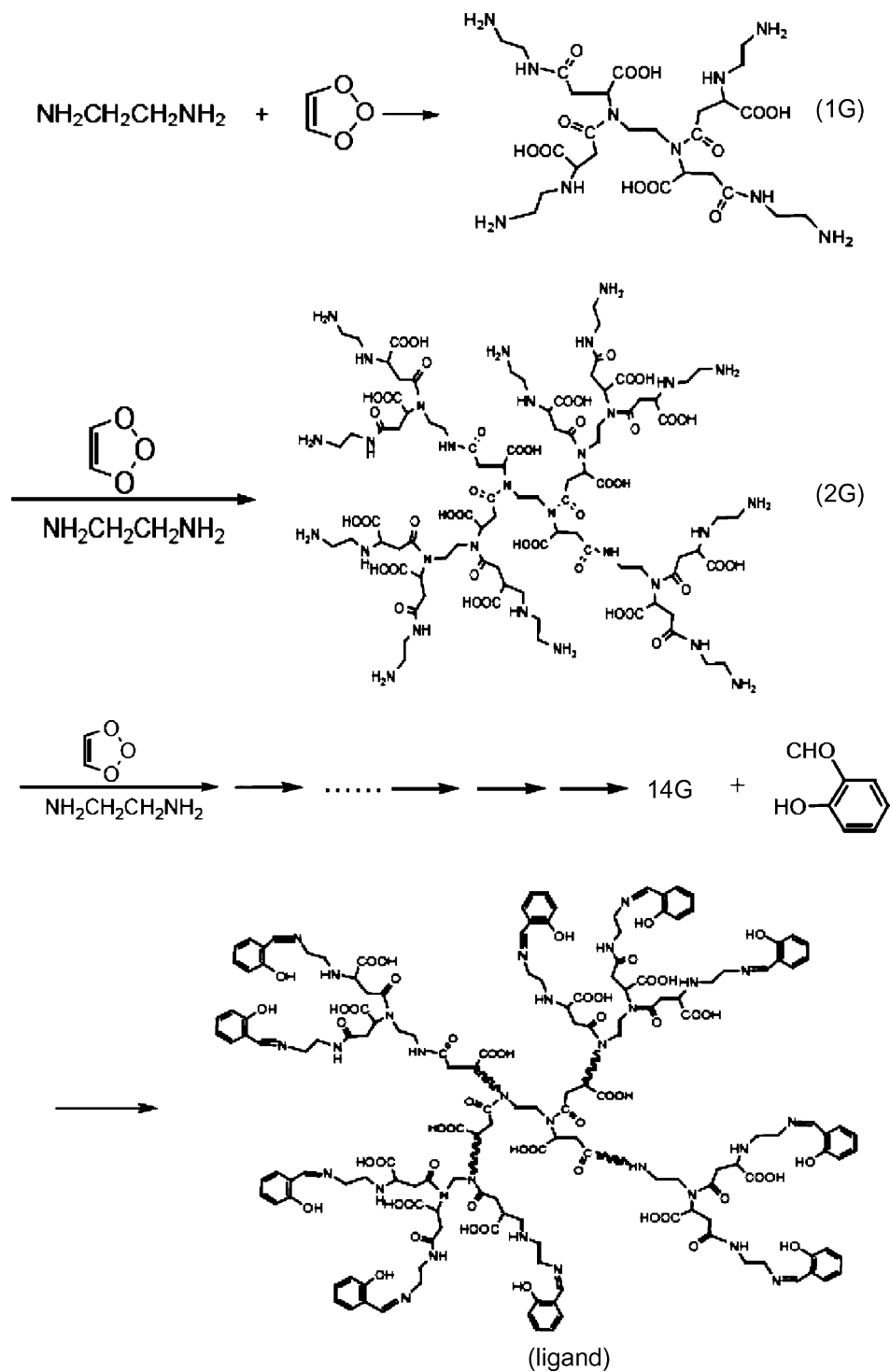


Fig. 1. The synthesis of the 14G dendritic polymer and ligand.

The complex of the Cu(I, II) (A) was obtained by the following method: to water (30 ml) solution of NaCl (51 mmol, 3.0 g),  $\text{Cu}_2\text{Cl}_2$  (5 mmol, 1.0 g) was added with stirring until the white crystal was absolutely dissolved, into it  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (6 mmol, 1.0 g) was added and adjusted the acidity of the solution by dilute HCl until pH 5 to obtain the clear solution, then the yellow ligand (0.7 g) was added with stirring for 4 h at room temperature. The resulting precipitate was separated by filtration, washed with water until the filtrate became col-

orless and finally dried overnight at  $50^\circ\text{C}$  in vacuo. Yield: 65%.

The complex of the Fe(II, III) (B) was achieved following the similar method. To a solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (3 mmol, 0.75 g) and  $\text{FeCl}_2$  (6 mmol, 0.75 g) in 25 ml of water, the yellow ligand (0.5 g) was added with stirring for 4 h at room temperature. The product was filtered off, washed with water until the filtrate became colorless and dried overnight at  $50^\circ\text{C}$  in vacuo. Yield: 60%.

Table 1  
The data of UV spectra of the ligand and its metal complexes

Compound	$\lambda$ (nm) (log $\epsilon$ )
<b>L</b> 14G dendritic ligand	237.0 (0.3) 263.6 (1.0) 335.2 (0.5)
<b>A</b> Cu (I, II) complex	237.0 (0.4) 262.8 (1.1) 322.6 (0.5)
<b>B</b> Fe (II, III) complex	237.6 (0.3) 263.0 (0.9) 324.0 (0.5)

L = 14G dendritic ligand, A = Cu (I, II) complex, B = Fe (II, III) complex.

### 3. Results and discussions

#### 3.1. UV spectra and thermal analysis

UV spectra of these complexes are similar (Table 1), which indicated that the central ion and ligands are coordinated in a similar mode. The strong bands at 263 nm are assigned to the  $\text{C}=\text{O}$  bond and the bands at 237 nm attributed to  $\pi \rightarrow \pi^*$  transitions [14] of the benzene ring, and these bands were almost unchanged after coordination. Comparing with the ligand, the bands at 322–324 nm for the complexes attributed to the absorption of  $\text{C}=\text{N}$  group show a blue shift *ca.* 11–13 nm, which related to electronic transitions based mainly on the ligand moieties and ligand-to-metal charge-transfer bands may be present.

The thermo-gravimetric analysis (Fig. 2) reveals a progressive loss of weight, a slight inflection appearing at 113 °C, which would correspond to the theoretical loss of coordinated water molecule (4.5%), indicated that water molecule coordinating to the metal ion. A mass loss about 15% for the complex was observed up to 300 °C which reverse the decomposing of the coordinated ligand and a progressive decomposing continued up to 800 °C, corresponding to the formation of Cu oxide and overall mass loss reach to 39.75% to the complex studied.

#### 3.2. IR spectra

It is obvious from infrared spectra of these compounds that there are differences between the main characteristic absorption

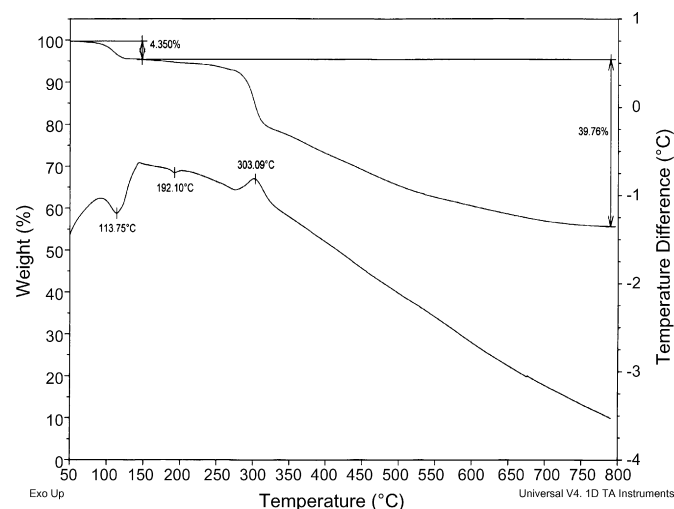


Fig. 2. TG-DTG curves of the Cu complex.

Table 2  
Some important IR frequencies of the ligand and its complexes ( $\text{cm}^{-1}$ )

Compound	$\nu_{\text{O-H}}$	$\nu_{\text{NH}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$	$\delta_{\text{C=C}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$
<b>L</b>	3442 br	3016 s	1611 s	1498 m	750 m		
<b>A</b>	3434 br	3016 m	1635 m	1537 m	758 w	568 w	408 w
<b>B</b>	3435 br	3017 m	1629 m	1531 m	766 w	601 w	401 w

br = broad, s = strong, m = medium, w = weak.

peaks of these complexes and those of the ligand. The main IR bands with their tentative assignments [15] are listed in Table 2. The band of  $\nu(\text{NH})$  in these complexes almost unshifted compared to that of the ligand, which indicated that NH in the ligand was not coordinated with metal ion. The intense peaks close to 3430–3435  $\text{cm}^{-1}$  in IR spectra of these complexes may be assigned to  $\nu(\text{OH})$ , phenolic OH or water, which appears at 3442  $\text{cm}^{-1}$  in the ligand, indicated that  $\text{OH}$  coordinated to the central metal ion. Compared with the ligand, the bands at 1635  $\text{cm}^{-1}$  can be very safely assigned to  $\nu(\text{C}=\text{N})$  shifted highly 24–28  $\text{cm}^{-1}$  in these complexes, suggesting that the azomethine group  $\text{C}=\text{N}$  in these complexes were in the coordinated form [16], which was consistent with the result of UV spectra.

Furthermore, in the spectra of these complexes, several new bands observed at about 573–601  $\text{cm}^{-1}$  and 401–408  $\text{cm}^{-1}$  region may be assigned to  $\nu(\text{M-N})$  and  $\nu(\text{M-O})$ , respectively [17,18], suggested that nitrogen atom in azomethine group and oxygen in phenolic or water coordinated to the metal ion. However, the band of  $\nu(\text{M-Cl})$  was not observed in this spectra which should lie about at 200–400  $\text{cm}^{-1}$  [17].

#### 3.3. XPS spectra analysis

In order to prove the coordinated model of the ligand and the molar ratio of the mixed-valent metal atom in the complexes, XPS data of the ligand and its complexes have been studied. The values of the metal electron binding energy (BE) in the complexes are important to analyze the coordination model of mixed-valent metal atoms. C1s, O1s, N1s and Cl1s spectra bands of two complexes are approximately the same and shown in Table 3 and Fig. 3.

The XPS Cu 2p<sub>3/2</sub> core-level spectrum of the complex in Fig. 3a has been deconvoluted into two different valences and the ratio of two different chemical environmental metal ions is 59.1:40.9 ( $\text{Cu}^{2+}:\text{Cu}^+$ ). In agreement with the literature data [19–21], the Cu(II) and Cu(I) species correspond to the peak components with BE at 935.3 and 933.2 eV, respectively, while two metal salts,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Cu}_2\text{Cl}_2$ , Cu2p 3/2 binding energy appears at 935.8 and 932.2 eV, respectively. The difference of the Cu2p 3/2 binding energy indicated that the electron density of Cu(II) increased while contrary result appeared to that of Cu(I). As a result, the electrons of the Cu(I) atom may be transfer to some atom of the ligand to form a coordination bond. On the other hand, the result of the increased electron density of Cu(II) may lie in that Cu(II) atom accepts electrons from somewhere of the ligand.

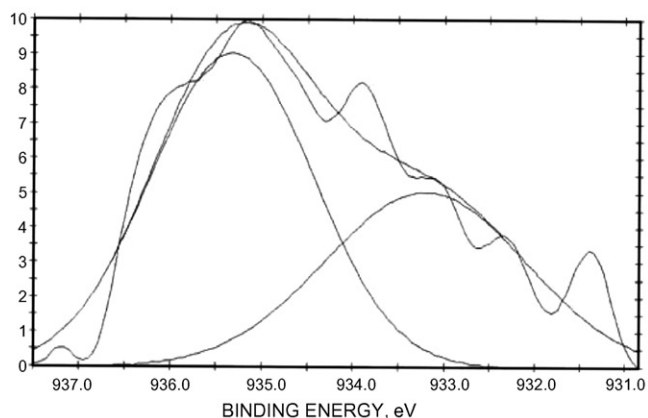
The XPS Fe 2p<sub>3/2</sub> peak (Fig. 3b) has been deconvoluted to two different valent atoms and the ratio of two atoms

Table 3  
The data of XPS spectra of the ligand and its complexes (binding energy/BE (eV))

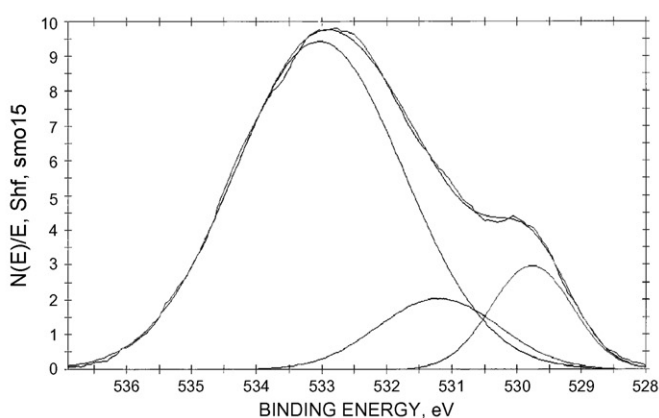
Compound	C1s	O1s	N1s	C11s	M <sub>2p<sub>3/2</sub></sub> (molar ratio)
L	285.1, 286.0	530.3, 532.2, 533.8	398.8, 400.2		
A	285.2, 286.7	529.8, 531.6, 533.8	399.2, 400.2	200.5, 199.2	935.3, 933.2 (59.1:40.9)
B	285.1, 286.5	529.7, 532.0, 533.9	399.3, 400.2	200.4, 199.3	709.4, 711.6 (73.6:26.4)

is 73.6:26.4(molar ratio). The binding energy at 711.6 eV suggests the presence of Fe(III) as expected and 709.4 eV assigned to Fe(II). The binding energy of Fe(III) atom increased 1.2 eV but that of the Fe(II) atom decreased 0.4 eV (in salts,

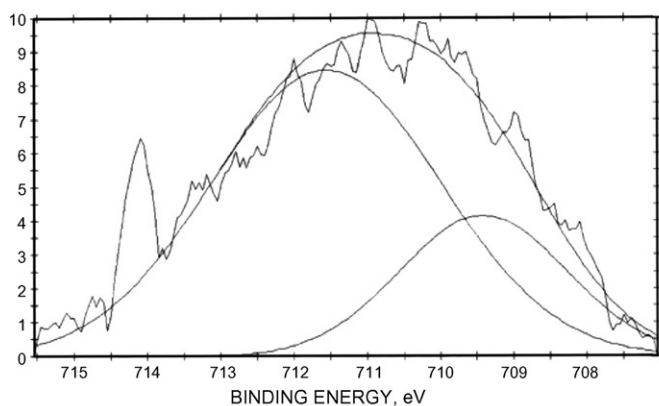
the binding energy of Fe(III) and Fe(II) were 710.4 eV and 709.8 eV, respectively), which indicate that Fe(III) atom maybe as electron-donors to the ligand while Fe(II) atom accept electrons from the ligand [19].



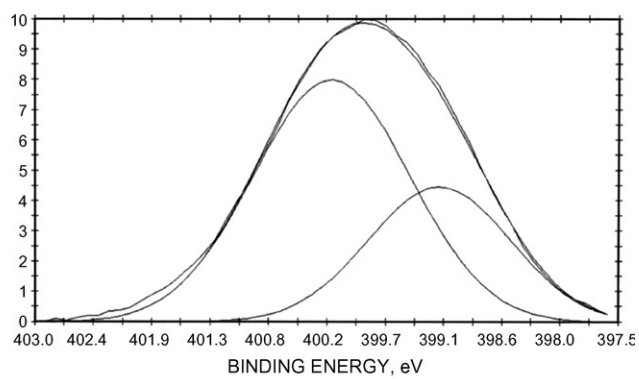
(a) The close-up Cu(2p<sub>3/2</sub>) in Cu complex



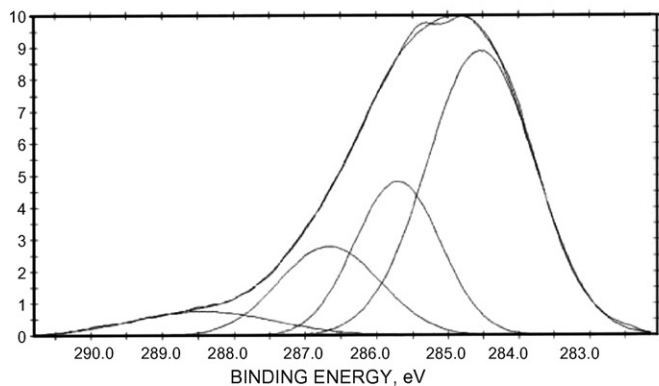
(d) The close-up O1s



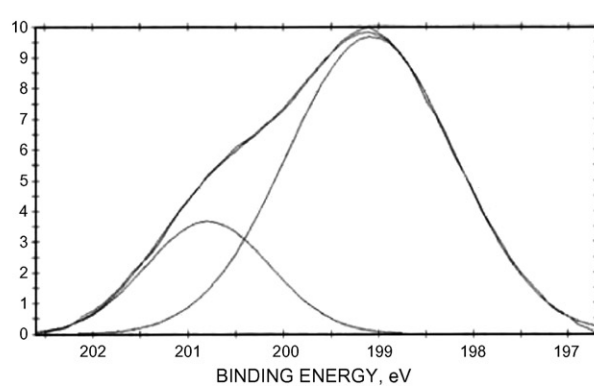
(b) The close-up Fe(2p<sub>3/2</sub>) in Fe complex



(e) The close-up N1s



(c) The close-up C1s



(f) The close-up C11s

Fig. 3. XPS spectra of the complexes (c–f in Cu complex).

It was recognized that most Cu(I) and Fe(II) ions were air sensitive. Perhaps, during the reaction process the system was contaminated with air so that the number of coordination of high-valent metal is more than that of low-valent one. Moreover, the stable  $d^{10}$  or  $d^5$  structure maybe contributes to the formation of coordination.

The C1s binding energies of backbone carbon were observed at *ca.* 285 eV (Fig. 3c), peaks at about 286.5 eV assigned to C1s of the azomethine group  $-C=N$ , shift slightly after coordination, which also supported that N atom in the azomethine group  $-C=N$  coordinated to the metal ion.

The XPS O1s peak of the Cu(I, II) complex (Fig. 3d) has been deconvoluted to several peak components at BE at 529.8, 531.6 and 533.8 eV, which may be assigned to the hydroxyl of Ph-OH,  $-C-O^-$  and  $-C=O$  species, respectively. The BE value at 533.8 eV correspond to  $C=O$  group almost unshifted, which indicated that the oxygen atom in the  $C=O$  group was not coordinated with the metal ion; while the peak at BE 529.8 eV maybe related to oxygen atom of the phenolic hydroxyl which may have undergone partial charge transfer with the ligand shifted slightly, indicating that the phenolic hydroxyl coordinated to the metal atom and the electrons in the copper atom may flow into the oxygen atom to form an O-M coordinated bond, which is in line with the data of the IR spectra. However, the  $-C-O^-$  is difficult to distinguish whether coordinate to the metal ion because of no other evidences was found and the fact should still be paid more attention to further study [22–24].

The XPS N1s peak of Cu (I, II) complex (Fig. 3e) has been deconvoluted to two peak components (Table 3). In agreement with the literature data [21], the imine and amine species correspond to the peak components with BE at 399.2 and 400.2 eV, respectively. The binding energy of amine was almost unshifted while the other shifted higher binding energy about 0.4 eV, which represents only nitrogen atom of the imine group in the ligand coordinated with the metal ion, which was consistent with UV and IR spectral data.

The Cl1s peak of Cu complex (Fig. 3f) indicated that the chlorine atom were in two different environmental, which may be coordinated to the metal ion due to that the data of chlorine atom shifted highly in the complexes compared to that of the salt (in  $Cu_2Cl_2$  was 198.2 eV and in  $FeCl_2$  and  $FeCl_3$  was 198.6 eV and 198.9 eV, respectively). Moreover, it may be concluded from the result that chloride atom in the complex may act as a electron-donor to the metal ion so that the electron density of chloride atom decreased. The binding energy of chloride atom in  $CuCl_2$  is 199.2 eV, which indicated one chloride atom was not coordinate to Cu atom, while the other chloride was in coordinated form.

#### 4. Conclusion

Based on the above studies and reports already available in the literature [11,12], two different mixed-valent metal complexes derived from this potentially highly branched multiple sites macromolecules ligand have been successfully synthesized and characterized by UV-vis, FT-IR, thermal analysis and XPS spectroscopy. It was found that the central metal ion exhibit

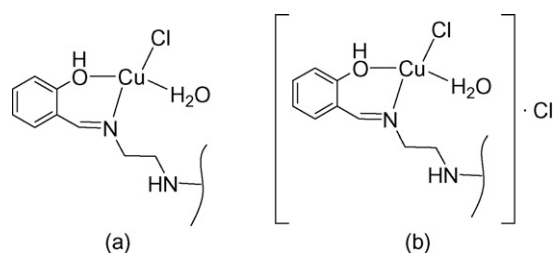


Fig. 4. Suggested structures for the Cu(I)(a)–Cu(II)(b) complex.

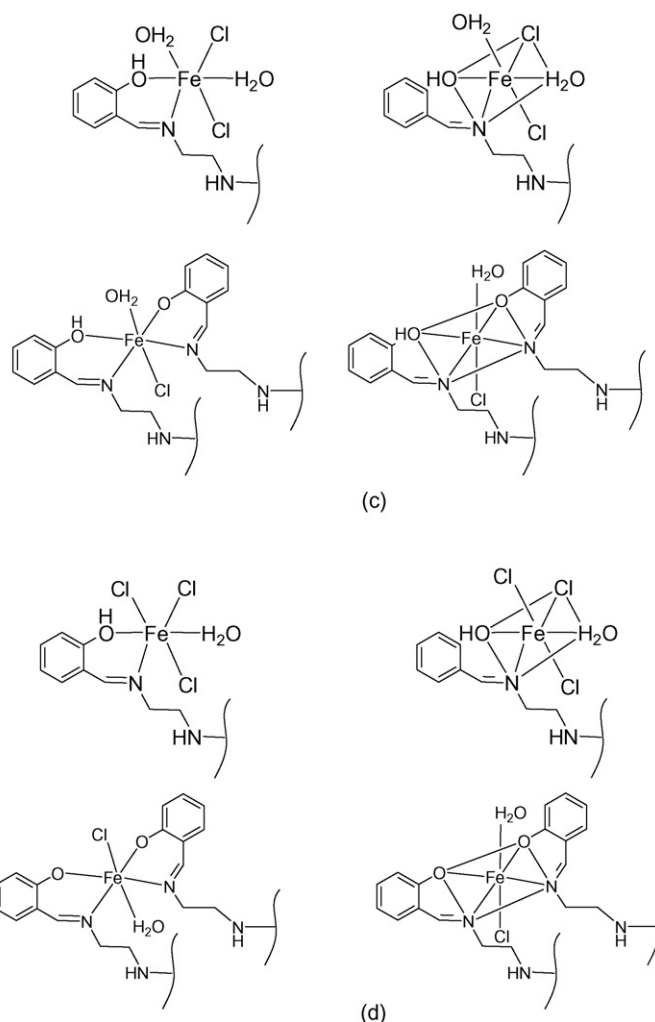


Fig. 5. Suggested structures for the Fe(II)(c)–Fe(III)(d) complex.

two different valences and several coordinate bonds  $N \rightarrow M$ ,  $Cl \rightarrow M$ ,  $Ph-OH \rightarrow M$  and  $H_2O \rightarrow M$  may have been formed. Considering the stability of the coordination style and the electron configuration of the metal, different coordination modes were proposed for Cu(I,II) and Fe(II,III) complexes [25] and the possible structures were shown in Figs. 4 and 5.

#### References

- [1] M. Jikei, M. Kakimoto, Prog. Polym. Sci. 26 (2001) 1233.
- [2] A.J. Pardey, A.D. Rojas, J.E. Yanez, P. Betancourt, C. Scott, C. China, C. Urbina, D. Moronta, C. Longo, Polyhedron 24 (2005) 511.
- [3] E. Uchida, H. Iwata, Y. Ikada, Polymer 41 (2000) 3609.

- [4] Y.P. Wang, Y. Chang, R.M. Wang, F. Zha, *J. Mol. Catal. A: Chem.* 159 (2000) 31.
- [5] Y.H. Wen, J.K. Cheng, J. Zhang, Z.J. Li, Y. Kang, Y.G. Yao, *Inorg. Chem. Commun.* 7 (2004) 1120.
- [6] M. Dasgupta, M.B. Peori, A.K. Kakkar, *Coord. Chem. Rev.* 233/234 (2002) 223.
- [7] S. Thamizharasi, A.V.R. Reddy, S. Balasubramanian, *React. Funct. Polym.* 40 (1999) 143.
- [8] A.V. Murugan, *Electrochim. Acta.* 50 (2005) 4627.
- [9] H.Z. Ma, B. Wang, Q.Zh. Shi, *Synth. React. Inorg. Met. Org. Chem.* 11 (2003) 1763.
- [10] H.-Z. Ma, B. Wang, *Spectrosc. Lett.* 3 (2003) 239.
- [11] X.P. Zhou, D. Li, S.L. Zheng, X. Zhang, T. Wu, *Inorg. Chem.* 45 (18) (2006) 7119.
- [12] L. Hou, D. Li, W.J. Shi, Y.G. Yin, S.W. Ng, *Inorg. Chem.* 44 (22) (2005) 7825.
- [13] F.Q. Gao, B. Wang, H.Z. Ma, X.N. Yan, *Chin. J. Inorg. Chem.* 21 (10) (2005) 1460.
- [14] H.Z. Ma, B. Wang, Q.Z. Shi, *Synth. React. Inorg. Met. Org. Chem.* 3 (2002) 617.
- [15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., John Wiley and Sons, 1978.
- [16] B. Wang, H.Z. Ma, *Inorg. Chem. Commun.* 3 (2000) 243.
- [17] J.R. Ferrero, *Low Frequency Vibration of Inorganic Coordination Compounds*, Plenum Press, New York, 1976.
- [18] J. Lewis, R.G. Wilins, *Modern Coordination Chemistry*, Inter-science, New York, 1960, p. 403.
- [19] S.H. Liu, D.H. Wang, C.H. Pan, *X-photo electron Spectrometric Analysis*, Science Press, Beijing, 1988.
- [20] P. Pfluger, M. Krounbi, G.B. Street, G. Weiser, *J. Chem. Phys.* 78 (1983) 3212.
- [21] E.T. Kang, K.G. Neoh, K.L. Tan, *Surf. Interface Anal.* 19 (1992) 33.
- [22] A.V. Murugan, *Electrochim. Acta.* 50 (2005) 4627.
- [23] A. Drelinkiewicz, J. Stejskal, A. Waksmundzka, J.W. Sobczak, *Synth. Met.* 140 (2004) 233.
- [24] M. Khaled, P. Srivastava, B.R. Sekhar, K.B. Garg, S.K. Agarwal, A.V. Narlikar, F. Studer, *J. Phys. Chem. Solids* 59 (1998) 777.
- [25] Y.C. Su, C.X. Cheng, *Chin. J. Appl. Chem.* 5 (1994) 31–35.