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# Synthesis and Characterization of Copper(II), Iron(II), Cobalt(II), Nickel(II) and Manganese(II) Complexes of Azido-1, 4-Bis(Imidazol-1-Yl-Methyl)Benzene (Bix) Or 1, 4-Bis(Imidazol-L-Yl-Methyl)-2, 5-Dimethyl-Benzene) (Mebix)

# Hao-Yu Shen , Dai-Zheng Liao , Zong-Hui Jiang , Shi-Ping Yan & Geng-Lin Wang

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# SYNTHESIS AND CHARACTERIZATION OF COPPER(II), IRON(II), COBALT(II), NICKEL(II) AND MANGANESE(II) COMPLEXES OF AZIDO-1,4-BIS(IMIDAZOL-1-YL-METHYL)BENZENE (BIX) OR 1,4-BIS(IMIDAZOL-1-YL-METHYL)-2,5-DIMETHYL-BENZENE) (MEBIX)

Hao-Yu Shen, Dai-Zheng Liao, <sup>\*</sup>Zong-Hui Jiang, Shi-Ping Yan and Geng-Lin Wang Department of Chemistry, Nankai University, Tianjin, 300071, P. R. China

### ABSTRACT

Cu(II), Fe(II), Co(II), Ni(II), Mn(II) complexes of azido-1,4-bis(imidazol-1-ylmethyl)benzene (bix) or 1,4-bis(imidazol-1-yl-methyl)-2,5-dimethyl-benzene) (Mebix) were synthesized by the spontaneous self-assembly method. The compounds  $[Cu_2(bix)_3(N_3)_4\cdot 2H_2O, Ni_2(bix)_3(N_3)_4\cdot 6H_2O, Co_2(bix)_3(N_3)_4\cdot 6H_2O, Cu_2(Mebix)_3(N_3)_4\cdot 4H_2O]$  were characterized by element analyses, infrared and electronic spectra.  $Cu_2(bix)_3(N_3)_4\cdot 2H_2O$  was further characterized by ESR. It is suggested that all the complexes have 1D structures, in which bix or Mebix functions as bridging ligand and  $N_3^-$  as terminal ligand. The coordination environment is distorted octahedral for each metal ion.

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#### **INTRODUCTION**

The construction of solid state architectures and crystal engineering has become an area of increasing interest over the recent years.<sup>1,2</sup> Much study has been centered upon the use of supramolecular contacts and in particular hydrogen-bonding between suitable organic molecules to generate multi-dimensional arrays and networks. The design of inorganic networks is less well developed but recent examples have helped to extend the understanding of this developing area.<sup>3-6</sup> Recently, Robson *et al.* have reported two 2D polyrotaxanes derived from Zn(II) and Ag(I) with bix.<sup>7,8</sup> However, In both examples, Zn(II) and Ag(I) have d<sup>10</sup> configuration. In this paper, we present the synthesis and characterization of the Cu(II), Fe(II), Co(II), Ni(II), Mn(II) complexes of azido-, bix or Mebix. The structures of bix and Mebix are shown in Fig. 1.

### **RESULTS AND DISCUSSION**

The reactions of bix and Mebix with the corresponding metal salt may be represented as follows:

 $2 M(OAc)_2 + 3 L \cdot 2 H_2O + 4 NaN_3 + (n-6) H_2O \xrightarrow{\text{methanol }/H_2O}$  $M_2(L)_3(N_3)_4 \cdot nH_2O + 4 NaOAc$ 

$$\begin{split} M &= Cu(II), \ L = bix, \ n = 2; \ L = Mebix, \ n = 4; \quad M = Ni(II), \ L = bix, \ n = 6, \ L = Mebix, \\ n &= 4; \ M = Co(II), \ L = bix, \ n = 6; \ M = Mn(II), \ L = Mebix, \ n = 6. \end{split}$$

All of the synthesized compounds are colored solids. The compounds are stable in air, poorly soluble in common solvent, including DMSO and DMF. The elemental analyses (see Table I) are in agreement with the chemical formula of the compounds. All of the melting points of the complexes are  $>300^{\circ}$  C (the maximum temperature of the apparatus).

#### Infrared Spectra

The infrared spectra of the ligands and their complexes can provide an insight into the mode of bonding of the ligand to the metal ions. Assignments were made



Fig. 1. Structures of the Ligands

Table I. Analytica	l Data and Some Physical	Properties of Compoun	ds
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No.	Compound	Color	Formula	Yield	Found (Calcd.) %			%
	(Empirical Formula)		Weight	(%)	С	Н	N	М
1	Cu <sub>2</sub> (bix) <sub>3</sub> (N <sub>3</sub> ) <sub>4</sub> ·2H <sub>2</sub> O	deep	1046.08	46.7	48.33	4.57	32.52	11.98
	Cu <sub>2</sub> C <sub>42</sub> H <sub>46</sub> N <sub>24</sub> O <sub>2</sub>	green			(48.22)	(4.43)	(32.14)	(12.15)
2	Ni <sub>2</sub> (bix) <sub>3</sub> (N <sub>3</sub> ) <sub>4</sub> .6H <sub>2</sub> O	green	1108.43	56.8	45.54	5.13	29.98	10.78
	Ni <sub>2</sub> C <sub>42</sub> H <sub>54</sub> N <sub>24</sub> O <sub>6</sub>				(45.49)	(4.91)	(30.33)	(10.59)
3	Co <sub>2</sub> (bix) <sub>3</sub> (N <sub>3</sub> ) <sub>4</sub> .6H <sub>2</sub> O	light	1108.91	66.2	45.26	4.91	30.35	10.32
	C02C42H54N24O6	green			(45.49)	(4.58)	(30.31)	(10.63)
4	Cu <sub>2</sub> (Mebix) <sub>3</sub> (N <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	deep	1166.27	45.8	49.52	5.72	28.65	11.22
	Cu <sub>2</sub> C <sub>48</sub> H <sub>62</sub> N <sub>24</sub> O <sub>4</sub>	green			(49.43)	(5.36)	(28.82)	(10.90)
5	Mn <sub>2</sub> (Mebix) <sub>3</sub> (N <sub>3</sub> ) <sub>4</sub> ·6H <sub>2</sub> O	yellow	1185.09	56.7	48.64	5.66	28.45	9.58
Ĺ	Mn <sub>2</sub> C <sub>48</sub> H <sub>66</sub> N <sub>24</sub> O <sub>6</sub>				(48.65)	(5.61)	(28.37)	(9.27)
6	Ni <sub>2</sub> (Mebix) <sub>3</sub> (N <sub>3</sub> ) <sub>4</sub> ·4H <sub>2</sub> O	green	1156.56	63.8	49.91	5.58	28.85	10.36
1	Ni <sub>2</sub> C <sub>48</sub> H <sub>62</sub> N <sub>24</sub> O <sub>4</sub>				(49.85)	(5.40)	(29.07)	(10.15)

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	bix	Mebix	l <sup>a</sup>	2 <sup>a</sup>	3ª	4 <sup>a</sup>	5ª	6ª
$\nu(H_2O)$	3300 s	3200 s	3330 s	3350 s	3340 s	3330 s	3330 s	3240 s
$\nu(N_3)$			2080 s	2120 s	2050 s	2110 s	2080 s	2115 s
v(C∸N	1670 s	1640 s	1600 s	1620 %	1625 s	1600 s	1600 6	1610 .
imidazol)	1610 s	1620 s	1000 3	10203	10253	1000 3	1000 5	10103
v(imidazol and benzene ring)	1520 s 1450 m 1390 s	1510 s 1450 m 1405 w 1390 s	1520 s 1425 m 1400 s	1565 s 1510 m 1420 m	1515 s 1450 m 1430 m 1395 s	1520 s 1450 m 1400 s	1520 s 1460 m 1400 s	1520 s 1500 m 1450 m 1410 s
N(-CH)	1290 m	1270 m	1290 m	1295 m	1295 m	1285 m	1285 m	1280 m
	1240 s	1230 s	1240 s	1240 s	1245 s	1218 s	1225 s	1200 s
u(C=C ring)	1110 m	1105 m	1105 m	1105 m	1115 m	1102 m	1105 m	1100 m
V(C=C IIng)	1090 w	1070w	1095w	1095 w	1095 w	1080 w	1095 w	1080 w
v(C-H, benzene)	840 s	910 s	845 s	840 s	820 s	900 s	920 s	925 s
v(ring, wag)	770 m 750 s 720 w	750 s	750 s 720 w	740 s	750 s	760 m 750 s	750 s	760 m 750 s

Table II. IR Spectral Data of Complexes (cm<sup>-1</sup>)

<sup>a</sup>  $1 = Cu_2(bix)_3(N_3)_4 \cdot 2H_2O$ ,  $2 = Ni_2(bix)_3(N_3)_4 \cdot 6H_2O$ ,  $3 = Co_2(bix)_3(N_3)_4 \cdot 6H_2O$ ,

 $4 = Cu_2(Mebix)_3(N_3)_4 \cdot 4H_2O, 5 = Mn_2(Mebix)_3(N_3)_4 \cdot 6H_2O,$ 

 $6 = Ni_2(Mebix)_3(N_3)_4 \cdot 4H_2O$ 

based on typical group frequencies. The strong and broad absorption (see Table II) in the region 3600-3000 cm<sup>-1</sup> of all the complexes can be assigned to the presence of water. The new sharp and strong absoptions at ~2100 cm<sup>-1</sup> of all the complexes indicate that the N<sub>3</sub><sup>-</sup> group is present in all the complexes, and coordinates to the metal ions as terminal ligand<sup>9</sup>. The coordination of the metal ion to the imidazol nitrogen can be inferred from the broading of v(C=N) at 1700-1600 cm<sup>-1</sup>. The absorptions in the region 1540-1430 cm<sup>-1</sup> of all the complexes are assignable to the stretch of the benzene and imidazol rings<sup>10</sup>.

### Electronic Spectra

The electronic spectral data for the ligands and their complexes are shown in Table III. In the spectrum of the ligands, the band at ~415 nm may be attributed to the

Compound	$\lambda \max(nm)$							
	d-d	π-π*						
bix		415.20		280.00				
Mebix		417.30		285.20				
1 <sup>a</sup>	724.00 ( $^{2}T_{2g} \leftarrow ^{2}E_{g}$ )	401.10		267.20				
2 <sup>a</sup>	$654.00 ({}^{3}T_{1g} \leftarrow {}^{3}A_{2g})$	387.50	294.40 (sh)					
3ª	$600.00 (^{1}T_{2g} \leftarrow ^{1}A_{g})$	361.10						
4 <sup>a</sup>	$660.50 (^{2}T_{2g} \leftarrow ^{2}E_{g})$	408.20		273.10				
5 ª		434.80		271.50				
6 <sup>a</sup>	$655.50 ({}^{3}T_{1g} \leftarrow {}^{3}A_{2g})$	397.40 (sh)	305.50 (sh)	270.00				

Table III. Electronic Spectral Data (in Solid State)

<sup>a</sup> 1 =  $Cu_2(bix)_3(N_3)_4 \cdot 2H_2O$ , 2 =  $Ni_2(bix)_3(N_3)_4 \cdot 6H_2O$ , 3 =  $Co_2(bix)_3(N_3)_4 \cdot 6H_2O$ ,

$$4 = Cu_2(Mebix)_3(N_3)_4 \cdot 4H_2O, 5 = Mn_2(Mebix)_3(N_3)_4 \cdot 6H_2O,$$

 $6 = Ni_2(Mebix)_3(N_3)_4 \cdot 4H_2O$ 

imidazol (C=N) chromophore  $\pi$ - $\pi^*$  transitions. The bands at ~285 nm are associated with the imidazol and benzene rings  $\pi$ - $\pi^*$  transitions. In the spectra of the complexes, the band of the C=N chromophore  $\pi$ - $\pi^*$  transition is shifted to about 400 nm indicating that the imidazol nitrogen (N(3), see Fig. 1) is coordinated to the metal ion. The absorption frequencies ascribed to the imidazol and benzene ring  $\pi$ - $\pi^*$  transitions are shifted compared to the ligand. The bands in the region of 600-730 nm may be attributed to the d-d transition of the metal ions<sup>11-13</sup>.

# ESR of Cu<sub>2</sub>(bix)<sub>3</sub>(N<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O

The ESR spectrum of  $Cu_2(bix)_3(N_3)_4 \cdot 2H_2O$  was obtained at room temperature and 110 K,  $g_{1/} = 2.146$ ,  $g_{\perp} = 2.059$ ,  $g_{av} = 2.088$ . The result shows that  $Cu_2(bix)_3(N_3)_4 \cdot 2H_2O$  has a pseudo-octahedral structure <sup>14, 15</sup> (see Fig. 2).

From the above discussion, it is seen that the metal ions in the complexes are bonded to the ligand through the imidazol nitrogen (N(3)),  $N_3^-$ , and water. Their presumed structures are shown in Fig. 2.



L = bix or Mebix

Fig. 2. Proposed Structure of the Complexes

#### **EXPERIMENTAL**

All chemicals used in this work were of reagent grade.  $\alpha_{,\alpha}$ '-Dibromo-*p*-xylene was obtained in the following way: A stirred mixture of *p*-xylene (10.6 g, 0.1 mol), N-bromosuccinimide (NBS) (0.39 g, 2.2 mmol). azobis(isobutyronitrile) (AIBN) (~50 mg), and freshly distilled HCOOCH<sub>3</sub> (100 mL) was refluxed under illumination (500 W incandescent bulb) for 14 h. The resulting white solid was separated by filtration, washed with freshly distilled HCOOCH<sub>3</sub>, water and recrystallized from CHCl<sub>3</sub>; yield, 18 g (74%); m. p.: 142-143° C.

Bix was obtained as described in ref. 8 except using  $\alpha, \alpha'$ -dibromo-*p*-xylene instead of  $\alpha, \alpha'$ -dichloro-*p*-xylene; yield, 20.9 g (85%); m. p.: 128-131° C. 2.5-Dimethyl-1,4-dichloro-*p*-xylene was obtained in the following way: A stirred mixture of *p*-xylene (106 g, 1 mol), concentrated hydrochloric acid (530 mL), and 40% aqueous formaldehyde solution (200 mL, 2.6 mol) was refluxed at 60-70° C in HCl atmosphere for 15 h. The resulting white product was separated by filtration, and washed with water. Then another 200 mL (2.6 mol) of 40% aqueous formaldehyde solution was added to the filtrate. The mixture was refluxed at 60-70° C in HCl atmosphere for another 15 h. Upon cooling, another portion of the product was filtered off, and washed with water. The product was recrystallized from CHCl<sub>3</sub>; yield, 211.2 g (80.2%); m. p.: 128-130° C. Mebix was obtained in a similar method as described for bix except for using 2,5-dimethyl-1,4-dichloro-*p*-xylene instead of  $\alpha,\alpha$ '-dibromo-*p*-xylene; yield, 21 g (79.8%); m. p.: 166-168° C

# Synthesis of the Complexes

The synthesis of all of the complexes of the ligands bix or Mebix was similar. A methanol solution (50 mL) of the ligand (0.3 mmol) was mixed with the metal acetate (0.2 mmol) dissolved in 2 mL water, then NaN<sub>3</sub> (0.4 mmol, 26 mg in 2 mL water) was added. The mixture was stirred at room temperature for ten minutes when precipitates formed, and the reaction mixture was stirred continually for six hours. The resulting precipitates were collected by filtration, washed with water, methol, and ether. dried in a vacuum.

### Physical Measurements

C, H, N analyses were obtained with a Perkin-Elmer 240 elemental analysis instrument. Metal ions were determined by EDTA titration. Melting points were obtained using a Yanaco microscopic melting point apparatus. Infrared spectra were measured in KBr pellets on a Shimadzu IR-408 spectrometer. Electronic spectra were obtained on a Shimazu UV-Vis scanning spectrophotometer. X-band ESR spectra were obtained on a JES-FEIXG spectrometer.

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