Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Synthesis and Characterization of 3,3′-bis(N-Ferrocenyl methylene formylhydrazone)-2,2′-bipyridyl and its Cd(II), Hg(II), Cu(II), and Mn(II) Complexes

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To cite this article: Ben-Lai Wu, Cheng-Xiang Liu, Ming-Xing Yao, Hong-Yun Zhang, Pei-Kun Chen, Hong-Yan Mao, Xiao-Qing Shen & Shou-Chang Liu (2004) Synthesis and Characterization of 3,3′-bis(N-Ferrocenyl methylene formylhydrazone)-2,2′-bipyridyl and its Cd(II), Hg(II), Cu(II), and Mn(II) Complexes, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 34:10, 1709-1719, DOI: 10.1081/SIM-200030165

To link to this article: http://dx.doi.org/10.1081/SIM-200030165

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SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
Vol. 34, No. 10, pp. 1709–1719, 2004

Synthesis and Characterization of 3,3′-*bis*(*N*-Ferrocenyl methylene formylhydrazone)-2,2′-bipyridyl and its Cd(II), Hg(II), Cu(II), and Mn(II) Complexes

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ABSTRACT

In this article, 3,3′-*bis*(*N*-ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl and its Cd(II), Hg(II), Cu(II), and Mn(II) complexes have been synthesized and characterized by elemental analyses, IR, ^{1}H NMR spectral, thermal analyses, and molar conductances. In the complexes, 3,3′-*bis*(*N*-ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl coordinates to the transition metal ions using a methylenimine nitrogen, the amide oxygen in the enolic form, the pyridyl nitrogen, the acetate in

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DOI: 10.1081/SIM-200030165 0094-5714 (Print); 1532-2440 (Online)
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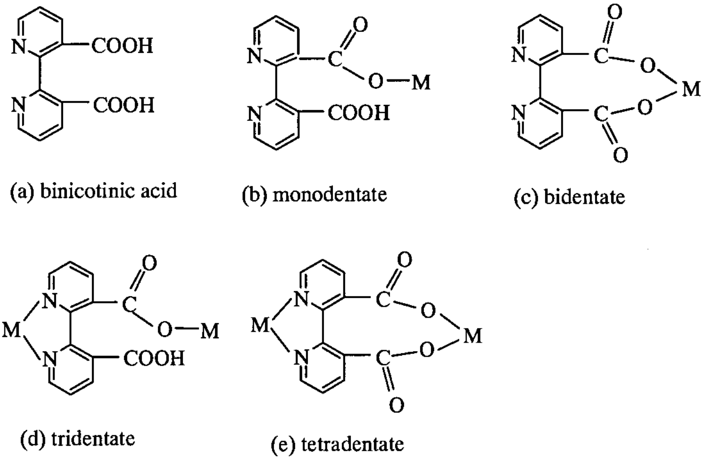
a symmetrical bidentate manner, and one water molecule, all of which participate in coordination to form a binuclear complex. The ligand and the complexes are insoluble in common organic solvents and slightly soluble in strongly polar solvents such as DMF and DMSO.

Key Words: Ferrocene; Binicotinic acid; Binuclear complex; Aroylhydrazone.

INTRODUCTION

It is reported that a replacement of aromatic groups by the ferrocenyl moiety in penicillin and cephalosporin molecules improves their antibiotic activity.[1] Ferrocenyl aroylhydrazones possess strong biological activity and can inhibit many vital enzymatic reactions catalyzed by heavy metals in cells.[2] Owing to the formation of stable and deeply colored complexes with transition metals, ferrocenylaroylhydrazones are promising as specific reagents in analytical and extractive chemistry.[3] Binicotinic acid [as shown in Fig. 1(a)] is a multidentate ligand and forms model complexes with the ligand acting as a monodentate, bidentate, tridentate, or tetradentate with metals[4,5] [as shown in Fig. 1(b)–(e)]. In recent years, research on the structure and the properties of binicotinic acid, its derivates, and its complexes have been reported.[6,7] In order to further improve the coordination ability of



(a) binicotinic acid (b) monodentate (c) bidentate (d) tridentate (e) tetradentate

Figure 1. The suggested structures of the binicotinic acid and its monodentate, bidentate, tridentate, and tetradentate coordinated forms.

binicotinic acid and to synthesize complexes with novel structures and specific optical, electrical, magnetic, and biological properties, we synthesized 3,3′-*bis*(*N*-ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl and its complexes with transition metals. The ligand and the complexes have been characterized by elemental analyses, IR, ^{1}H NMR spectral, thermal analyses, and molar conductances. The poor solubility of the complexes in many solvents prevented the application of other physico-chemical methods.

EXPERIMENTAL

Reagents and Materials

Ferrocene is an industrial product of 99% purity and was obtained from the State Operated Lanzhou 504 Factory and used as received. Formylferrocene,[8] binicotinic acid, and 3,3′-dicarbomethoxy-2,2′-bipyridyl[9] were synthesized by the literature methods. 1,10-Phenanthroline and the other reagents of analytically pure grade were obtained from the Zhengzhou First Chemical Reagent Company.

Equipment and Measurements

IR spectra were recorded on a FTS-40 spectrophotometer using KBr discs in the 4000–400 cm^{-1} regions. ^{1}H NMR spectra were obtained on a Bruker DPX-400 MHz spectrometer using deuterated dimethylsulfoxide as solvent and TMS as internal standard. Elemental analyses were obtained using a Carlo-Erba 1106 elemental analyzer. Molar conductances were measured with a ADD-11A conductometer using DMF as solvent at 25 °C. Thermal analyses were measured on NETZSCH TG209 and DSC204 instruments in nitrogen atmosphere from room temperature to 800 °C.

Synthesis of 3,3′-*bis*(*N*-Ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl

Synthesis of 3,3′-Biformylhydrazine-2,2′-bipyridyl

An 8 mL (88 mmol) hydrazine hydrate (50%) was added to a solution of 2.0 g (7.3 mmol) 3,3′-dicarbomethoxy-2,2′-bi-pyridyl dissolved in 38 mL anhydrous ethanol. The reaction mixture was heated for 8 hr with stirring under reflux, then two-thirds of its volume was evaporated in *vacuum* and a white solid appeared. The mixture was cooled to room temperature, filtered, washed three times with anhydrous ethanol and diethyl ether, respectively, and dried under *vacuum* at 50 °C, to give a white solid; yield: 1.6 g (80%); m.p. 241–242 °C.

Synthesis of 3,3′-*bis*(*N*-Ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl

A solution of 1.10 g (4.0 mmol) 3,3′-biformylhydrazine-2,2′-bipyridyl and 1.81 g (8.4 mmol) formylferrocene dissolved in 38 mL anhydrous ethanol was heated for 18 hr with stirring under reflux under nitrogen atmosphere, to yield an orange solid. Then, the solvent was evaporated to remove half of its volume, cooled to room temperature, and filtered. The crude product was dissolved in 20 mL DMF and filtered, 20 mL distilled water was added to the filtrate with stirring, again an orange solid appeared which was filtered. The residue was washed three times with anhydrous ethanol and diethyl ether, respectively, dried under *vacuum* at 50 °C, to give a brown-yellow powder; yield: 1.74 g (65%); m.p. 230 °C (decomposition).

Synthesis of the Complexes of 3,3′-*bis*(*N*-Ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl with Cd(II), Hg(II), Cu(II), and Mn(II)

A quantity of 0.199 g (0.3 mmol) of 3,3′-*bis*(*N*-ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl was dissolved in 40 mL acetonitrile with heating. A solution containing $M(OOCCH_3)_2 \cdot nH_2O$ (0.3 mmol) [M = Cd(II), Hg(II), Cu(II), or Mn(II)] in 20 mL anhydrous ethanol was added to the above solution with stirring. The reaction mixture was heated for 4 hr under reflux in a 80–85 °C water bath, then cooled to room temperature, filtered, and the residue washed three times with hot ethanol and diethyl ether, respectively. The complexes were dried under *vacuum* at 50 °C yield: 60–70%.

RESULTS AND DISCUSSION

3,3′-*bis*(*N*-Ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl is insoluble in common organic solvents and slightly soluble in strongly polar solvents such as acetonitrile, DMF, and DMSO. The structure of its complexes is shown in Fig. 2. Owing to the solubilities of the complexes being lower than that of

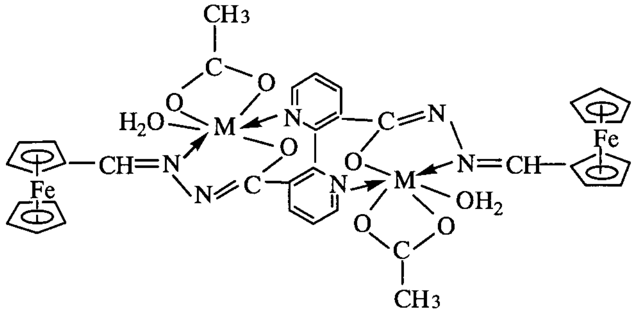
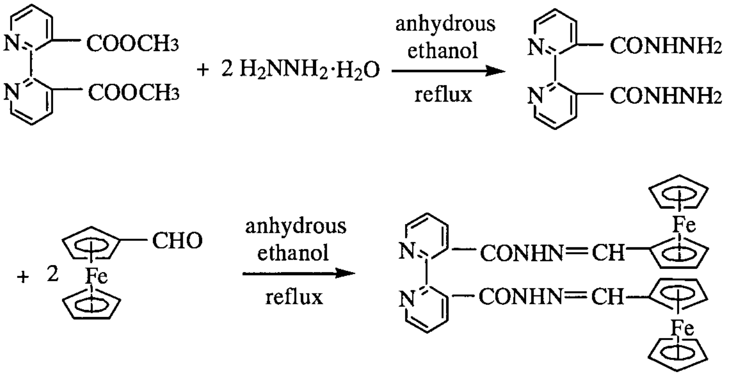


Figure 2. Suggested structural formula of the complexes [M = Cd(II), Hg(II), Cu(II), and Mn(II)].

the ligand, single crystals of the complexes could not be grown and some properties could not be determined. The elemental analyses, the molar conductances, and some physical properties of the ligand and the complexes are listed in Table 1, and their selected IR spectral absorption frequencies are listed in Table 2. It is judged from the data of the elemental analyses and IR spectra that these complexes contain binuclear structure units, with one ligand molecule and two acetates in a symmetrical bidentate manner and two water molecules coordinated to two metal centers, respectively, as shown in Fig. 2.

3,3′-*bis*(*N*-Ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl was synthesized as described in Eq. (1):



(1)

The complexes of 3,3′-*bis*(*N*-ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl with Cd(II), Hg(II), Cu(II), and Mn(II) were synthesized as shown in Eq. (2):

Table 1. Elemental analyses, molar conductances, and some physical properties of the ligand and its complexes.

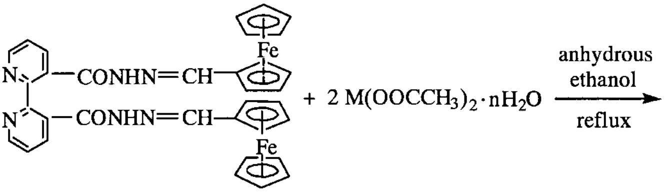
					Analysis, found (calcd) (%)			
Compound	M.W.	Yield (%)	M.p. (°C)	Color	C	H	N	Λ (Ω^{-1} cm^2 mol^{-1})
H_2L, $C_{34}H_{28}Fe_2N_6O_2$	664.3	65	230	Brownish yellow	60.95 (61.41)	4.37 (4.25)	12.43 (12.65)	13.80
$Cd_2L(OAc)_2(H_2O)_2$, $C_{38}H_{36}Cd_2Fe_2N_6O_8$	1,041.2	70	236	Brownish yellow	44.05 (43.83)	3.52 (3.48)	8.36 (8.07)	12.40
$Hg_2L(OAc)_2(H_2O)_2$, $C_{38}H_{36}Fe_2Hg_2N_6O_8$	1,217.6	60	248	Brownish red	37.77 (37.49)	2.77 (2.97)	7.23 (6.90)	14.90
$Cu_2L(OAc)_2$, $C_{38}H_{32}Cu_2Fe_2N_6O_6$	907.5	65	270	Purple red	50.10 (50.30)	3.26 (3.55)	9.50 (9.26)	4.15
$Mn_2L(OAc)_2(H_2O)_2$, $C_{38}H_{36}Fe_2Mn_2N_6O_8$	926.3	70	222	Brownish red	49.21 (49.28)	4.05 (3.91)	9.26 (9.07)	11.25

Note: H_2L, 3,3′-*bis*(*N*-ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl.

Table 2. Selected IR spectral absorption frequencies (cm^{-1}) of the ligand and its complexes.

Compound	ν(N–H)	ν(C=O)	ν(C=NN=C)	ν(C=N)	ν(C–O)	$\Delta = \nu_{as}(OAc) - \nu_s(OAc)$	Ferrocenyl
H_2L	3,190 m	1,661 m	—	1,420 s	—	—	1,103 m, 817 m, 502 w
$Cd_2L(OAc)_2(H_2O)_2$	—	—	1,567 s	1,413 s	1,039 m	130 = 1,655 − 1,519	1,105 m, 820 m, 489 w
$Hg_2L(OAc)_2(H_2O)_2$	—	—	1,568 s	1,410 s	1,039 m	136 = 1,653 − 1,523	1,105 m, 821 m, 484 w
$Cu_2L(OAc)_2$	—	—	1,569 s	1,413 s	1,041 m	120 = 1,654 − 1,534	1,105 m, 822 m, 465 w
$Mn_2L(OAc)_2(H_2O)_2$	—	—	1,569 s	1,413 s	1,040 m	121 = 1,653 − 1,532	1,103 m, 817 m, 502 w

Note: s, strong; m, middle; w, weak.



$M_2(L)(OOCCH_3)_2(H_2O)_2$ (2)

(M = Cd(II), Hg(II), Cu(II) and Mn(II); H_2L = 3,3'-Bis(N-ferrocenylmethylene formylhydrazone)-2,2'-bipyridyl

IR and ^{1}H NMR Spectra

It is seen from Table 2 that ν(N–H), ν(C=O), and ν(C=N) of the ligand appear at 3190, 1661, and 1420 cm^{-1}, respectively, which indicates that the free ligand exists in the keto form. In the IR spectra of the complexes, ν(N–H) and ν(C=O) are absent, ν(C=N–N=C) and ν(C–O) were observed in the 1567–1569 and 1039–1041 cm^{-1} regions, respectively, and ν(C=N) is shifted to lower frequency by 7–10 cm^{-1}. These changes show that the ligand coordinates to the transition metal ions by the methylenimine group nitrogen and amide oxygen in the enolic form.[10] Owing to Δ of acetate, $\nu_{as}(CH_3COO^-) - \nu_s(CH_3COO^-) = 120–136\,cm^{-1}$, being values smaller than 200 cm^{-1}, the carboxylic groups coordinate to transition metal ions in a symmetrical bidentate manner.[11] The characteristic IR spectral absorption frequencies of ferrocenyl are all observed in the IR spectra of the ligand and the complexes.

In the ^{1}H NMR spectrum of the ligand, the single peak of the unsubstituted cyclopentadiene protons and the multiplet peaks of the substituted cyclopentadiene appeared at 4.18 and 4.02–4.62 ppm, respectively, and the multiplet peaks of the bipyridyl ring protons were at 7.48–8.13 ppm. At 8.59 and 11.67 ppm, the single peaks of the methyne and the imine group proton were observed, respectively. In the ^{1}H NMR spectrum of the Cd(II) complex, the single peak of the unsubstituted cyclopentadiene protons and the multiplet peaks of the substituted cyclopentadiene were observed at 4.16 and 4.04–4.61 ppm, respectively, the single peak of the CH group at 8.58 ppm, the multiplet peaks of the bipyridyl rings protons at 7.47–7.98 ppm, and the single peak of the imine group is absent. The characteristic peaks of the Cd(II) complex are all slightly shifted to higher field compared with those of the ligand. These results suggest that the ligand coordinates to the transition metal ion in the enolic form. The conclusion obtained from the ^{1}H NMR spectra of the ligand and the Cd(II) complex is consistent with that of their IR spectra.

Thermal Analyses

The DSC–TG curves of the ligand and the complexes were recorded from room temperature to 800 °C in nitrogen atmosphere at a heating of 10 °C min^{-1}. Their data of thermal analyses are listed in Table 3. The ligand began to decompose at 230 °C with an endothermic effect, and the loss of weight was 20.5%, corresponding to the loss of two –CONHN=CH– groups (calcd 21.1%). An explosive decomposition took place at 456 °C with a strongly endothermic effect, and the loss of weight was 60.8%, which probably corresponds to two ferrocenylmethylenes and 2,2′-bipyridyl (calcd 62%). The residue was 17.7%, probably being iron (calcd 16.8%).

Table 3. Thermal decomposition of the ligand and its complexes.

Compound	*T* (°C)	Leaving group	Weight loss (%)
H_2L	215–275	2CONHN	20.5 (21.0)
	275–558	2Fc and 2,2′-bipyridyl	61.8 (62.3)
	>558	Residue Fe	17.7 (16.8)
$Cd_2L(OAc)_2(H_2O)_2$	66–164	$2H_2O$	3.9 (3.5)
	164–285	2FcCH	28.4 (27.3)
	825–420	2CONHN and $2CH_3COO$	18.8 (16.5)
	420–700	2,2′-bipyridyl	18.2 (15.0)
	>700	Residue Fe and Cd	30.7 (32.3)
$Hg_2L(OAc)_2(H_2O)_2$	74–180	$2H_2O$	3.5 (3.0)
	180–295	2FcCH	22.6 (23.3)
	295–385	2CONHN and $2CH_3COO$	20.5 (19.0)
	385–468	2,2′-bipyridyl and Hg evaporating	44.7 (45.6)
	>468	Residue Fe	8.7 (9.2)
$Cu_2L(OAc)_2$	180–385	2CONHN and $2CH_3COO$	24.7 (25.6)
	385–658	2FcCH and 2,2′-bipyridyl	50.2 (48.3)
	>658	Residue Fe and Cu	25.1 (26.3)
$Mn_2L(OAc)_2(H_2O)_2$	64–222	$2H_2O$	4.2 (3.9)
	222–440	2CONHN and $2CH_3COO$	26.8 (25.0)
	440–730	2FcCH and 2,2′-bipyridyl	45.6 (47.5)
	730	Residue Fe and Mn	23.4 (23.9)

Note: Fc, Ferrocenyl.

The loss of weight of the Cd(II) complex was 3.9% from 66 to 164 °C, corresponding to two coordinated water molecules (3.5%). At 164–285 °C, a strongly endothermic effect was observed and the loss of weight was 28.4%, corresponding to two Fc-CH groups (Fc representing ferrocene) (calcd 27.3%). A weak endothermic effect was appeared at 285–420 °C, and the loss of weight was 18.8%, corresponding to two CONHN and two CH_3COO (calcd 16.5%). At 420–700 °C, a very weak endothermic effect was observed, and the loss of weight was 18.2%, corresponding to 2,2′-bipyridyl (calcd 15.0%). The residue was 30.7%, corresponding to Fe and Cd (calcd 32.3%).

Molar Conductance

It is seen in Table 1 that the molar conductances of the ligand and the complexes are in the 4.15–14.90 $\Omega^{-1}\,cm^2\,mol^{-1}$ range in DMF at 25 °C, which is smaller than that of a 1 : 1 electrolyte (65–90 $\Omega^{-1}\,cm^2\,mol^{-1}$) under identical condition.[12] Thus, it can be deduced that 3,3′-*bis*(*N*-ferrocenylmethylene formylhydrazone)-2,2′-bipyridyl and acetate coordinate to Cd(II), Hg(II), Cu(II), or Mn(II) to form stable complexes with coordinated covalent bonds.

ACKNOWLEDGMENT

The authors thank the Natural Science Foundation of China (20271046), the Natural Science Foundation of Henan Province (0211020300), and the Natural Science Foundation of the Henan Education Department (2001500001) for the support of this work.

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Received January 2, 2003
Accepted June 3, 2004