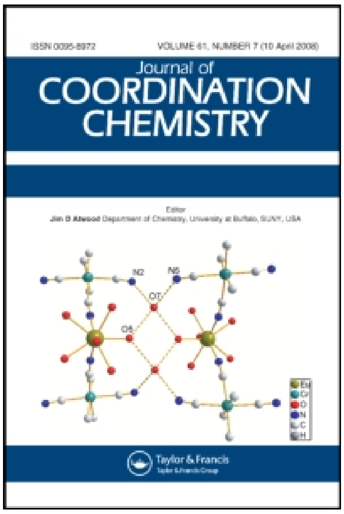

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ACETHYLFERROCENE-2-THENOYLHYDRAZONE COMPLEXES WITH TRANSITION METAL IONS

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Complexes of acetylferrocene-2-thenoylhydrazone with Cu(II), Ni(II), Co(II) and Hg(II) have been prepared and characterized by elemental analyses, IR, NMR, electronic spectra, ESR, molar conductivity and thermal analyses. All results show that the ligand coordinates to the metal ion through the enolic oxygen and the azomethine nitrogen atoms as a bidentate donor.

KEYWORDS: ferrocene, thenoylhydrazone, transition metals, complexes

INTRODUCTION

Hydrazide chelates with transition metals have been reported to be biologically active[1–4] and to have antitubercular activity. Preparation of metal complexes of hydrazides and derivatives[5–7] and factors influencing their isolation have been the subject of many reports.[6,8,9] Since 1975, many authors have reported that ferrocene derivatives exhibit biological activity and also behave as β-lactamase inhibitors.[10,11] The present article describes the isolation of acetylferrocene-2-thenoylhydrazone (HAfth) chelates with some transition metal(II) ions. Probable structures have been proposed on the basis of elemental analyses, IR, NMR, electronic spectra, ESR, molar conductivity and thermal analyses.

EXPERIMENTAL

Materials

All chemicals were of analytical grade. Solvents were used as supplied. Acetylferrocene and 2-thenoylhydrazine were prepared following literature methods.[12,13]

Preparation of the ligand

Acetylferrocene-2-thenoylhydrazone (HAfth) was prepared by refluxing an ethanolic solution of acetylferrocene and 2-thenoylhydrazine in a mol ratio of 1:1, in the

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presence of a few drops of acetic acid, for 6h. After cooling, the resulting orange red precipitate was filtered, washed with ethanol and recrystallized from acetone. Yield: 87%.

Preparation of complexes

The complexes $M(Afth)_2 \cdot nH_2O$(M=Cu(II), Ni(II), Co(II) and Hg(II)) were prepared by the following method. A solution of metal acetate in acetonitrile was mixed with an acetonitrile solution of the ligand in a 1:2 mol ratio and the mixture was refluxed for 8–10h. for Cu(II), Ni(II) and Co(II), but the mixture containing mercury was stirred for 3h at room temperature. The product was filtered, washed with hot ethanol and acetone, then dried *in vacuo.* Yield >80%.

Physical measurements

Elemental analyses were carried out in the microanalytical laboratory of Lanzhou University. IR spectra were obtained with a Nicolet-5DX spectrophotometer using KBr discs in the 200–4000 cm^{-1} region. Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer in the range 190–750 nm using a solution in DMF. ^1H NMR spectra were obtained using an FT-80A spectrometer with $CDCl_3$ and DMSO (d^6) as solvents and TMS as internal standard. Conductivity measurements were performed with a DDS-11A conductometer at 25°C in DMF at 3.2×10^{-4}M concentration. TG analyses were carried out on a DuPont 1090 thermal analyzer between room temperature and 700°C in an atmosphere of nitrogen. ESR spectra were obtained on ER 200D-SRC spectrometer.

RESULTS AND DISCUSSION

Analytical and physical data for the ligand and its complexes are listed in Table 1. The data indicate that only complexes of enolic form, $M(Afth)_2 \cdot nH_2O$, were isolated. All complexes are slightly soluble in common polar organic solvents, but soluble in DMF and DMSO. Low values of molar conductivities, 1.5–4.8$\Omega^{-1}cm^2mol^{-1}$, show that they are nonelectrolytes in DMF solution.[14] Complexes of Zn(II), Cd(II) and UO_2(II)) could not be prepared. In all cases, the ligand acts as a bidentate and coordinates to metal ion *via* one azomethine nitrogen and one enolic oxygen after deprotonation.

^1H NMR spectra

NMR data for the ligand and complex **IV** are given in Table 2. The NMR spectrum of the ligand in $CDCl_3$ shows the unsubstituted cyclopentadienyl is observed at 4.15 ppm as a singlet. The proton signal due to the 3 and 4 positions of the substituted cyclopentadienly group at 4.35 ppm and the other two proton signal at 4.7 ppm appear as two multiplets. NH appears at 9.8 ppm (1H), and is exchanged with D_2O. Martin *et al.*, have studied NMR spectra of 2-thenoyl derivatives and found that the chemical shift order of hydrogen on the thiophene ring is $\delta_a > \delta_c > \delta_b$.[15,16] This order

Table 1 Analytical and physical data for the ligand and its complexes.

	Formula	Colour	Yield (%)	Melting point (°C)	Analysis (Calc. %)			λ^{*m} (in DMF)	TG analysis		
					C	H	N		Weight loss %	Temperature range (°C)	Assignment
HAfth	$C_{17}H_{16}N_2O$ SFe	Reddish orange	87	172-173	57.78 (57.97)	4.63 (4.59)	8.21 (7.95)	2.72	8.0(8.0) 27.1(27.3)	190-265 270-360	N_2 $C_4H_4S + C$
I	$C_{34}H_{34}N_4O_4S_2Fe_2Cu$	Dark brown	81	178-181	50.75 (50.92)	3.99 (4.27)	6.85 (6.99)	4.1	4.7(4.5)	110-180	$2H_2O$
II	$C_{34}H_{34}N_4O_4S_2Fe_2Ni$	Orange yellow	83	176-178	51.4 (51.2)	4.39 (4.30)	7.32 (7.03)	4.8	4.6(4.52)	120-180	$2H_2O$
III	$C_{34}H_{36}N_4O_5S_2Fe_2Co$	Orange yellow	80	179-182	50.31 (50.1)	4.51 (4.45)	6.93 (6.87)	4.7	2.4(2.2) 4.5(4.4)	50-80 115-185	H_2O $2H_2O$
IV	$C_{34}H_{34}N_4O_4S_2Fe_2Hg$	Yellow	92	164-166	43.28 (43.47)	3.44 (3.65)	6.07 (5.97)	1.5	4.0(3.84)	100-160	$2H_2O$

* λ_m: molar conductance ($\Omega^{-1}cm^{-2}mol^{-1}$).

may qualitatively be explained as follows (only charge-separated structures are represented below),

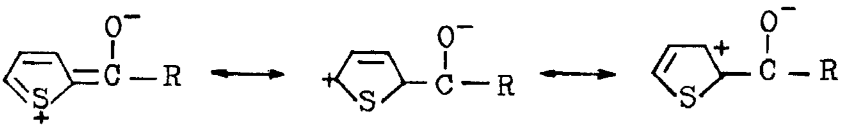

Figure 1 Resonance formulae of the 2-thenoyl group.

where R=H, CH_3, Cl, OEt, *etc.* Sulfur is electron-releasing and shows an ability to stabilize positive charge. Thus position a has a greater formal charge than position c. Position b has no positive formal charge. The order of electron density is b>c>a; therefore, the order of chemical shifts of hydrogens on the thiophene ring is $\delta_a>\delta_c>\delta_b$. According to this order, the proton signals at 7.1, 7.6 and 8.1 ppm may be attributed to H_b, H_c and H_a of the thiophene ring (stated in Table 2), respectively. CH_3 is observed at 2.15 ppm as a singlet(3H). The spectrum of complex IV in DMSO(d^6) solution shows that the signal at *ca* 9.8 ppm due to the NH disappears. Signals assignable to the methyl group and C_5H_5 appear at 2.5 (3H, s) and 4.2 ppm (5H, s), respectively. Signals of the substituted cyclopentadienyl group appear at 4.5 (2H, m) and 4.75 ppm (2H, m). Protons on the thiophene ring of complex IV are observed at 7.15 (m), 7.65 (m) and 7.95 ppm (m), assigned to H_b, H_c and H_a of the thiophene ring, respectively. Thus the ligand coordinates to the metal ion in the enolic form. In addition, all signals in the complex are shifted downfield. This maybe due to decrease of the electron density after forming the complex.[17]

IR spectra

Principal absorptions of the ligand and its complexes are given in Table 3. Bands in the ligand spectrum at 3257, 1626 and 1033 cm^{-1} are assigned to υ(N−H), υ(CO) or υ(C=N) and υ(N−N) modes, respectively.[18] Characteristic IR bands of the ferrocenyl group appear at about 3090, 1105, 820 and 490 cm^{-1} in the ligand and all complexes.[19] Bands at 1430, 1390, 1002, 730 and 557 cm^{-1} in the spectrum of HAfth are attributable to ring stretching, C−H bending, $C_{ring}-C_{exo}$ stretching, in-plane and out-of-plane ring deformation modes of the thiophene ring, respectively, and remain almost unchanged in the spectra of the complexes. This observation is commensurate with non-involvement of the sulfur of the thiophene ring in bonding.[20] In the complexes, υ(N−H) disappears and five new bands are observed at *ca* 1570, 1536, 1275, 370 and 310 cm^{-1} arising from υ(C=N−N=C),

Table 2 ^1H NMR chemical shifts of the ligand and complex IV (δ, ppm).

	NH	CH^3	Thiophene ring*			C_5H_4		C_5H_5
			Ha	Hc	Hb	3,4	2,5	
HAfth	9.8 (s,1H)	2.15 (s,3H)	8.1 (m,1H)	7.6 (m,1H)	7.1 (m,1H)	4.35 (m,2H)	4.7 (m,2H)	4.2 (s,5H)
IV		2.5 (s,3H)	8.15 (m,1H)	7.65 (m,1H)	7.19 (m,1H)	4.5 (m,2H)	4.75 (m,2H)	4.25 (s,5H)

*: S-CH_c = CH_b-CH_a = C− ; s: singlet; m: multiplet.

Table 3 Characteristic IR data for the ligand and its complexes*.

	υ(OH)	υ(NH)	υ(C=O)	υ(C=N–N =C)	υ(NCO)	υ(C–O)	υ(N–N)	υ(M–O)	υ(M–N)
HAfth		3257m	1626vs				1033m		
I	3374br			1578s	1537s	1275m	1023m	371w	318w
II	3370br			1572s	1540s	1273m	1028m	372w	319w
III	3372br			1565vs	1538vs	1276m	1023m	372w	310w
IV	3380br			1580s	1536s	1276m	1029m	370w	308w

* S: strong; vs: very strong; m: medium; w: weak; br: broad.

υ(NCO),[21] υ(C–O), υ(M–O) and υ(M–N),[22] respectively. All the above indicates ligand coordination to the metal ion *via* an azomethine nitrogen and an enolic oxygen after deprotonation. In the high frequency region, a broad band centred at 3370 cm^{-1} is attributed to the presence of coordinated water molecules.[20,23] This is further supported by thermal analyses.

Thermal analysis

TG data for the ligand and its complexes are also listed in Table 1. The ligand loses 8.0% of its weight at 190°C, which corresponds to the loss of one molecule of nitrogen (calculated value 8.0%). Then it loses 27.1% of its weight, corresponding to the loss of (C_4H_4S + C) (calculated value 27.3%). All complexes show similar thermal behaviour. For **I**, **II** and **IV**, loss of two molecules of water begins at *ca* 100–120°C; this is indicative of the presence of coordinated water and in accord with IR data and elemental analyses.[24] Complex **III** loses about 2.4% of its weight at 50°C, which corresponds to the loss of one molecule of water (calculated value 2.2%). Then it loses 4.5% of its weight at 115°C, corresponding to another two molecules of water. The former is crystal water and the latter is coordinated water.[25] Complex **III** decomposes continuously between 210 and 400°C. The above facts suggest that each complex contains two molecules of coordinated water.

Electronic spectra

Data for the ligand and its complexes in DMF are given in Table 4. Generally speaking, the ligand and its complexes show three absorption bands. That at 267 nm arising from the B band of the cyclopentadienyl group show a hypsochromic shift compared with that of the ligand.[26] Owing to slightly enhanced bonding of the

Table 4 Electronic spectra of the ligand and its complexes.*

	Characteristic absorption bands (λ_{nm})			$\varepsilon_{\lambda 1}$(x104)	$\varepsilon_{\lambda 2}$(x104)	$\varepsilon_{\lambda 3}$
	1	2	3			
HAfth	271.9	299.3	446br	1.75	1.49	271
I	266.5	333.4	†	2.66	1.44	
II	270.3	301	454hbr	2.66	2.34	306
III	266.7	345	452br	1.39	1.0	444
IV	270.6	358	448br	2.29	0.9	620

* ε_λ: molar extinction coefficient; concentration of each compound is 3 × 10^{-5}M in DMF; br, broad.
† The third band is obscured by the second broad band.

cyclopentadienyl group in the complexes, the energy difference between π and π* orbitals of the cyclopentadienyl group becomes larger. This fact leads to a hypsochromic shift of the B band of the cyclopentadienyl group in the complexes.[27] The band at 330 nm which is assigned to an intraligand π-π* transition shows a bathochromic shift. Covalent bonding should be taken into account in order to explain bathochromic shifts of π-π* transitions of complexes. In view of the large conjugated system (O−C=N−N=C−R) being formed,[28] according to FMO theory, the HOMO or LUMO of the O−C=N−N=C−R group and HOMO or LUMO of the metal ion mix with each other, (approximately, HOMO-HOMO, LUMO-LUMO) to make the energy of the new HOMO higher and the energy of the new LUMO lower. The energy difference between the new HOMO and the new LUMO is smaller than that of the O−C=N−N=C−R group. The above result in a bathochromic shift of the K band. In the visible region, the absorption at 446 nm in the ligand shifts to longer wavelength (*ca* 450 nm) in the complexes. The third band of complex **I** is obscured by the second broad band. Because d-d transitions an usually weak, absorptions of the ligand and its complexes in the visisble region may be attributed to d-d transitions of the transition metal ions.[29] One absorption of the ferrocenyl group in the visible region obscures other d-d transitions of the complexes. Information on stereochemistry is thus precluded.

ESR spectra

ESR spectra of complexes have been recorded for powdered samples and in DMF. ESR spectra of complexes, **I, II** and **III** show one broad signal at room temperature. Hyperfine splitting was not observed on changing concentration or by measuring at 223 K. Complex **IV** shows no signal and is diamagnetic as expected.

In conclusion, HAfth acts as a bidentate ligand, which coordinates to the metal ion in the enolic form through one azomethine nitrogen and one enolic oxygen after deprotonation. Each complex has two molecules of coordinated water to give a coordination number of six. Because one negative charge of Afth⁻ may be

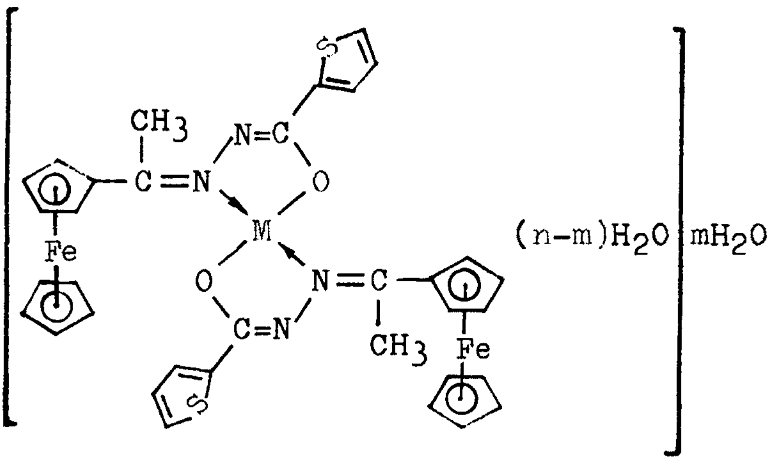

Figure 2 Proposed structure for the complexes; M = Cu, Ni, Hg, n = 2, m = 0; M = Co, n = 3, m = 1.

delocalized, Afth$^-$ is a soft base. Therefore, excellent chelating properties for mercury(II) can be explained as the result of a soft acid-soft base reaction.[25] Proposed structures for the complexes are shown in Figure 2.

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