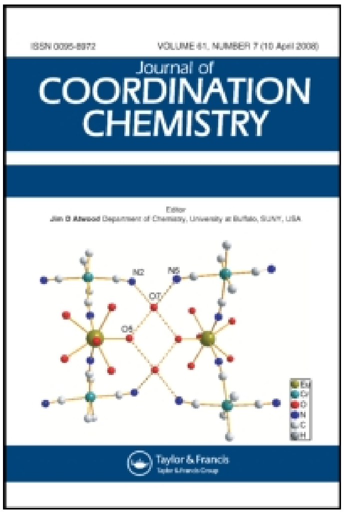

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ACETYLFERROCENE-5-PHENYL-1,3-OXAZOL-2-YLCARBONYLHYDRAZONE AND ITS COMPLEXES

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A new heterocyclic ferrocene derivative, acetylferrocene-5-phenyl-1,3-oxazol-2-ylcarbonylhydrazone (HAfoh) and its transition metal complexes, [M (Afoh)(OAc)] · nH_2O (M=Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Mn^{2+} or UO_2^{2+}) were prepared by reacting HAfoh with metal acetates. HAfoh appears to act as a bidentate, coordinating to the metal through the azomethine nitrogen and enolic oxygen atoms. The OAc^- ion coordinates to the metals as a bidentate ligand.

Keywords: aroylhydrazone; bidentate ligand; complexes; acetate

INTRODUCTION

Numerous complexes of aroylhydrazones containing ferrocenyl groups have been studied,[1-4] owing to the rich coordination chemistry of aroylhydrazones and the fact that azomethine ligands are models for metal-ligand binding sites in several enzymes.[5-6] Many reports[7-8] have shown that the replacement of an aromatic group in penicillins and cephalosporins by the ferrocenyl group improves their antibiotic activity. Considering the importance of the oxazole group in pharmacological and biological areas,[9-10] in this paper we report the synthesis and properties of complexes of a hydrazone containing substituted oxazole and ferrocene groups, acetylferrocene-5-phenyl-1,3-oxazol-2-ylcarbonylhydrazone (HAfoh).

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EXPERIMENTAL

Materials

All solvents were dried and distilled before use. Acetylferrocene was obtained by a literature method.[11] Ethyl oxalyl chloride was prepared according to the literature.[12] Metal(II) acetates and other chemicals were of analytical grade.

Preparation of HAfoh

A solution of α-aminoacetophenone (0.1 mol) and $ClCOCO_2Et$ (0.12 mol) in anhydrous benzene (50 cm^3) was refluxed until no HCl gas was evolved. The resulting solution was washed with water, 10% $NaHCO_3$ and water in succession, then dried over anhydrous Na_2SO_4. After benzene was distilled off, solid $PhCOCH_2NHCOCO_2Et$ was obtained, yield 78%. $PhCOCH_2NHCOCO_2Et$ (0.1 mol) and $POCl_3$ (40 cm^3) in anhydrous benzene (80 cm^3) was refluxed until no more HCl was evolved and the solution was treated as above, giving $Ph(C_3HNO)CO_2Et$ in 70% yield. A solution of $Ph(C_3HNO)CO_2Et$ and $NH_2NH_2{\cdot}H_2O$ (1:1.2 mol) in EtOH was refluxed for 4–6 h to give 90% of 5-phenyl-2-oxazolecarbonylhydrazine.[13]

HAfoh was prepared by refluxing a mixture of acetylferrocene and $Ph(C_3HNO)CONHNH_2$ (mol ratio = 1:1) in anhydrous EtOH for 8 h, in the presence of several drops of glacial AcOH. The yellow precipitate was filtered off, washed with EtOH and recrystallized from benzene and DMF (2:1, v/v). Yield 82%, m.p. 142–144°C.

Preparation of complexes

A solution of HAfoh (0.5 mmol) in absolute EtOH (20 cm^3) was added to a solution of 0.5 mmol of $M(OAc)_2{\cdot}nH_2O$ (M = Cu, Ni, Co, Zn, Cd, Hg, Pb, Mn and UO_2) in EtOH (10 cm^3) and the mixture was refluxed for 8–10 h. The product was separated by filteration, washed with acetone, followed by Et_2O, and dried *in vacuo*. Yields > 78%.

Measurements

IR spectra were recorded on a Nicolet-5DX spectrophotometer using KBr discs in the range 4000-400 cm^{-1}. ^1H NMR spectra were measured with a Varian FT—80A spectrometer at 80 MHz using $CDCl_3$ and DMSO-d_6 as solvents and TMS as internal standard. Electronic spectra were recorded on a Shimadzu

260 spectrophotometer, using DMF solution in the range 190–700 nm. Conductivity measurements were performed with a DDS—II A conductometer, made in the Shanghai Second Apparatus Factory, using DMF as solvent at room temperature. Thermal studies were carried out with a Du Pont 1090 thermal analyser at room temperature to 800°C for TGA under a nitrogen atmosphere.

RESULTS AND DISCUSSION

HAfoh is insoluble in low polarity solvents such as alkanes and ether, but soluble in methanol, ethanol, chloroform, acetone, benzene, DMF and DMSO. All of the complexes are insoluble in water and common organic solvents, but sparingly soluble in DMF and DMSO. Elemental analyses and some physical properties of HAfoh and its complexes are given in Table I. TGA data, show that water is lost between 20–100°C, being lattice water. HAfoh coordinates to metal ions through azomethine nitrogen and enolic oxygen atoms after deprotonation. The ligand and acetate both bond to the metal as bidentates to give [M(Afoh) · OAc] · nH_2O in high yield.

IR spectra

Important IR data of free HAfoh and its complexes are shown in Table II. In addition to the bands given in the table, characteristic bands of ferrocenyl groups appear at 3063, 1484, 1106, 825 and 489 cm^{-1}, respectively.[14] No υ(O—H) band is observed. These results show that the acylhydrazonyl group exists in the keto form in the solid state. IR spectra of the complexes show significant changes compared with that of the ligand. Characteristic bands υ(N—H), υ(C—O) and δ(N—H) at 3220, 1692 and 1532 cm^{-1}, respectively, disappear and new bands are observed at *ca* 1604 and 1265 cm^{-1} which can be attributed to stretching vibrations of C=N and C—O groups.[14] The medium intensity band due to υ(N—N) at *ca* 940 cm^{-1} in the complexes is slightly shifted to higher wavenumbers compared with free HAfoh. These changes suggests that the azomethine nitrogen and deprotonated enolic oxygen coordinate to the metal ion.[1–4] The υ(O—H) stretch of water appears above 3300 cm^{-1} in complexes (1), (3), (5) and (6) in agreement with results of elemental analyses.

New bands in the spectra of the complexes at *ca* 1410 and 1520 cm^{-1} should be assigned to υ_s(O—C—O) and υ_s(O—C—O), respectively. It is noted that the difference, $\Delta\upsilon$, between υ_{as}(O—C—O) and υ_{as}(O—C—O) is important, because these frequencies can be used for characterizing the bonding type between metal and carboxyl.[14–17] When $\Delta\nu$ is smaller than 200 cm^{-1}, the carboxyl group is

TABLE I Elemental analyses and some physical properties of HAfoh and its complexes

No.	*Compound*		*Yield*	*m.p.*	*Found (Calcd.) %*			Λ^a
		Colour	*(%)*	*(C)*	*C*	*H*	*N*	$(\Omega^{-1}cm^2mol^{-1})$
	Hafoh	Yellow	82	142–144	63.9(63.9)	4.6(4.6)	10.2(10.2)	2.18
(1)	[Cu(Afoh) · OAc] · H_2O	Brown	85	208–210	52.5(52.1)	3.9(4.2)	7.7 (7.6)	1.92
(2)	Ni(Afoh) · OAc	Yellow	88	240(dec.)	54.5(54.4)	4.2(4.0)	8.1(7.9)	1.33
(3)	[Co(Afoh) · OAc]H_2O	Red	87	235(dec.)	52.8(52.6)	4.5(4.2)	7.9(7.7)	2.02
(4)	Zn(Afoh) · OAc	Red	78	220–222	54.0(53.7)	4.2(3.9)	8.0 (7.8)	3.17
(5)	[Cd(Afoh) · OAc] · $2H_2O$	Red	80	240–242	47.0(46.5)	4.1(4.1)	7. 1(6.8)	2.87
(6)	[Hg(Afoh) · OAc] · $2H_2O$	Pale Red	84	256–258	41.0(40.7)	3.7(3.6)	6.4(5.9)	1.56
(7)	UO_2(Afoh) · OAc	Brown	84	282(dec.)	39.3(38.9)	3.1(2.9)	5.7(5.7)	24.2
(8)	Pb(Afoh) · OAc	Red	80	198–200	43.0(42.5)	3.5(3.1)	6.4(6.2)	3.48
(9)	Mn(Afoh) · OAc	Yellow	88	308–310	55.1(54.8)	4.2(4.0)	7.6(8.0)	1.22

[a] Molar conductivities in DMF solution at room temperature.

TABLE II Some characteristic IR data for free HAfoh and its complexes[a]

Compound	$\upsilon(O{-}H)$	$\upsilon(N{-}H)$	$\upsilon(C{=}O)$	$\delta(N{-}H)$	$\upsilon(C{=}N{-}N{=}C)$	$\upsilon(C{-}O)$	*Oxazole*	*Acetate*		
							$\upsilon(C{-}O)$	$\upsilon_s(CO_2)$	$\upsilon_{as}(CO_2)$	$\Delta\upsilon$
HAfoh		3320m	1692vs	1532vs			1217s			
(1)	3395w, sh				1603vs	1268s	1226s	1418s	1520s	102
(2)	-				1609vs	1266s	1220s	1411s	1523s	112
(3)	3408w, sh				1608vs	1263s	1215s	1411s	1523s	112
(4)	-				1608vs	1269s	1223s	1416s	1520s	104
(5)	3425w, sh				1604vs	1265s	1216s	1410s	1521s	111
(6)	3436w, sh				1623vs	1264s	1220s	1410s	1517s	107
(7)					1608vs	1261s	1215s	1415s	1522s	107
(8)					1604vs	1262s	1215s	1410s	1518s	108
(9)					1607vs	1263s	1213s	1416s	1521s	105

[a] Vs = very strong; s = strong; m = medium; w = weak; sh = shoulder.

TABLE III ^1H NMR data for free HAfoh and [Cd(Afoh) · OAc] · $2H_2O$(δ, ppm)^a

Compound	*N—H*	*Oxazole ring*	*C_5H_4-*	*C_5H_5*	*C_6H_5*	*$CH_3CO_2^-$*	*-CH_3*
HAfoh	10.98 (s,1H)	4.40 7.48 (s,1H)	(m,2H) 4.70 (m,2H)	4.18 (s,5H)	7.40–7.75 (m,5H)		2.30 (s,3H)
[Cd(Afoh) · OAc] · $2H_2O$		7.52 (s,1H)	4.49 (m,2H) 4.75 (m,2H)	4.17 (s,5H)	7.44–7.80 (m,5H)	1.81 (s,3H)	2.37 (s,3H)

^{a}S = singlet; m = multiplet

coordinated to central ion as a bidentate, but when $\Delta\upsilon$ is greater than 200 cm^{-1}, it acts as a unidentate.[15] In the complexes, $\Delta\upsilon$ is about 102–112 cm^{-1}, so the carboxyl coordinates as a bidentate.

^1H NMR spectra

^1H NMR data for free HAfoh (in $CDCl_3$) and complex (5) (in DMSO-d_6) are listed in Table III. In the free ligand, the proton signal of the oxazole ring is overlapped with the multiple peaks of the phenyl protons, but a sharp singlet at 7.48 ppm.[18] The NH signal of the HAfoh at 10.98 ppm disappears on deuteration with D_2O, but in the complexes is not observed, *i.e.*, the ligand is enolized and coordinated to the metal ion. The proton signal of CH_3 in acetate appears at 1.81 ppm (s, 3H). All signals are shifted downfield by 0.01–0.09 ppm in the complexes.

Electronic spectra

Electronic spectroscopic data for free HAfoh and its complexes are listed in Table IV. Band I and band II correspond to the *B* band (π-π^* transition) of cyclopentadienyl ring and the *d* — MO* transition between the iron atom and cyclopentadienyl,[19–20] respectively. Band III is assigned to the *K* band (π-π^* transition) of the compounds.[21] Compared to the ligand, bands II and III exhibit significant bathochromic shifts of 5–23 and 2–20 cm, respectively. It is possible that the *d*- or *f*-orbital of the metal atom and p-orbital of the ligand overlap to form a large conjugated system after enolization and complexing. The conjugated system makes the energy level difference between the π and π^* orbitals decrease. These factors lead to a greater bathochromic shift of bands II and III in the complexes. A broad and weak absorption at *ca* 410–450 nm is assigned to a

TABLE IV Electronic spectroscopy data for free HAfoh and its complexes[a]

Compound	*λ(nm)*			
	I	*II*	*III*	*IV*
HAfoh	262m	285m,sh	316s	444w,br
(1)	265m	305s	333s	414w,br
(2)	265m	293s	335s	455w,br
(3)	264m	291s	331s	456w,br
(4)	264m	289s	336s	429w,br
(5)	263m	290s	335s	442w,br
(6)	265m	290s	331s,sh	427w,br
(7)	264m	308s		447w,br
(8)	264m	304s		440w,br
(9)	264m	294s	318s	451w,br

[a] Spectra recorded in DMF; s = strong; m = medium; w = weak; sh = shoulder; br = broad.

transition of the 3*d* electrons on iron to either non-bonding or antibonding orbitals of the cyclopentadienyl ring.[19-20]

Thermal analyses

TGA data for free HAfoh and complexes (2) and (3) are listed in Table V. TGA data for complex (3) show that the molecular water is lost below 100°C, suggesting that the water is in the lattice. Data are consistent with the proposed formula of the complexes. The complexes show significantly higher thermal stabilities than free HAfoh.

Molar conductivities

Molar conductivity data for free HAfoh and the complexes are given in Table I. The data show that HAfoh and the complexes are all non-electrolytes.[22] This is consistent with coordination of bidentate acetate groups, as suggested by the spectroscopic data.

Analytical data, IR and ^{1}H NMR spectra show that the acetate ion also participates in coordination to the metal ions as a bidentate ligand along with HAfoh, as has been confirmed by previous work.[23-26] We recently found that anologous ligands, *e.g.* formylferrocene-5-phenyl-1,3-oxazol-2-ylcarbonyl-hydrazone and 1,1′-diacetylferrocene-*bis*(5-phenyl-1,3-oxazol-2-ylcarbonyl) hydrazone react with transition metal(II) acetates to form complexes in the same manner; the acetate also acts as a bidentate ligand. A plausible structure for our complexes is shown in Figure 1.

TABLE V Thermal analysis data for Hafoh and some of its complexes

Compound	*D.T. (°C)*	*Leaving group*	*Weight loss (%)*[a]
HAfoh	142–143 (m.p.)		
	180–280	—NHN═CMe	12(14)
	280–410	oxazole ring and carbonyl	18(17)
	410–470	phenyl and two cyclopentadienyl rings	50(50)
	up to 800	residual Fe_2O_3	20(19)
Ni(Afoh) · OAc	245–295	oxazole ring, —O—C═N—N═C—Me and AcO^-	32(32)[b]
	295–380	phenyl and two cyclopentadienyl rings	39(39)
	up to 800	residual Fe_2O_3 and NiO (1:2)	29(29)
[Co(Afoh) · OAc] · H_2O	20–100	H_2O	3(3)
	240–340	oxazole ring, —O—C═N—N═C—CH_3 and AcO^-	29(31)[b]
	340–420	phenyl and two cyclopentadienyl rings	39(38)
	up to 800	residual Fe_2O_3 and CoO (1 : 2)	29(28)

[a] Calculated values are given in parentheses. [b] Some oxygen is transformed to metal oxide.

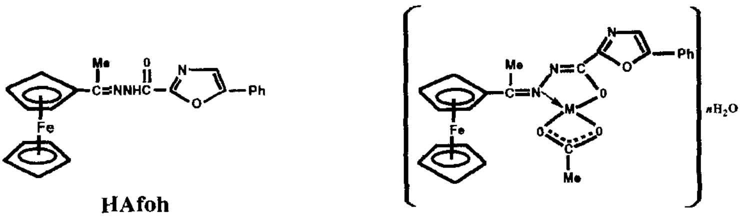

FIGURE 1 Suggested structure for HAfoh and its complexes, n=0–2.

Acknowledgments

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