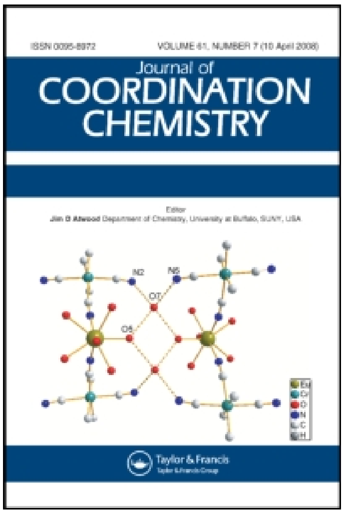

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CHELATE COMPLEXES OF FORMYLFERROCENE AND ACETYLFERROCENE SALICYLHYDRAZONE WITH TRANSITION METALS

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CHELATE COMPLEXES OF FORMYLFERROCENE AND ACETYLFERROCENE SALICYLHYDRAZONE WITH TRANSITION METALS

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Two new ligands, formylferrocene salicylhydrazone (H_2L^I), acetylferrocene salicylhydrazone (H_2L^{II}) and 12 transition metal(II) complexes, $M(HL)_2\cdot 0\text{–}1H_2O$ [M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), UO_2(II) and Mn(II)] have been prepared by the reaction of H_2L with metal(II) acetate in EtOH-DMF. Elemental analyses, IR, UV, NMR and molar conductance show that the ligands coordinate to metal ions in the enol form. The ligands act as bidentates and their complexes in DMF are non-electrolytes.

KEYWORDS: ferrocenes, aroylhydrazones, transition metals, complexes

INTRODUCTION

Due to their biological activity, especially as potent inhibitors for many enzymes, coordination complexes of arylhydrazines and related compounds have been a subject of extensive investigation.[1,2] Edwards and co-workers[3] have shown that replacement of aromatic groups by the ferrocenyl moiety in penicillins and cephalosporins improves their antibiotic activity. Recently we have reported the preparation and properties of some ferrocenyl hydrazones and their complexes with transition elements and lanthanides.[4–8] In the present paper, we describe the synthesis of formylferrocene salicylhydrazone ($FcCH = NNHCOC_6H_4OH\text{-}o$, H_2L^I); acetylferrocene salicylhydrazone ($FcC(CH_3) = NNHCOC_6H_4OH\text{-}o$, $H_2{}^{II}$) and their complexes with transition metal(II) acetates.

EXPERIMENTAL

Physical Measurements

Infrared spectra were measured with an FT - 170 SX spectrometer in KBr discs in the 400–4000 cm^{-1} range. ^{1}H NMR spectra were obtained on an FT - 80A spectrometer using DMSO(d^6) as solvent and TMS as internal reference. UV spectra

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were recorded on a UV - 240 spectrophotometer in the 190 - 700 nm range using solutions in DMF. Conductance measurements were made with a DDS - II A conductometer in DMF at 25°C.

Materials

Transition metal(II) acetates were of analytic reagent grade. Formylferrocene, acetylferrocene, salicylhydrazine were prepared by methods described in the literature.[9 - 11]

Syntheses of the Ligands

Some 5 mmol of formylferrocene (or acetylferrocene) in ethanol were added to 5 mmol of salicylhydrazine in warm ethanol (30 cm^3). The reaction mixture was heated under reflux for 2 h. The precipitated crystals were collected on a filter, and recrystallized from EtOH-DMF (1:1). Elemental analyses, yields and melting points of the two ligands obtained by this method are listed in Table 1.

Table 1 Elemental analysis and physical properties of the ligands and their complexes.

	Compound[a]	yield(%)	Colour	D.T.(°C)	Elemental analysis(%)[b]		
					C	H	N
	H_2L^I	75	Reddish orange	238	61.86 (62.00)	4.64 (4.63)	8.00 (8.05)
I	$Co(HL^I)_2$	80	orange	270	58.08 (57.59)	4.16 (4.01)	7.52 (7.43)
II	$Ni(HL^I)_2 \cdot H_2O$	76	dull yellow	273	56.24 (56.08)	3.99 (4.19)	7.12) (7.27)
III	$Cu(HL^I)_2$	85	dull brown	273	56.99 (57.05)	4.07 (3.99)	7.27 (7.39)
IV	$Zn(HL^I)_2 \cdot H_2O$	84	red	260	55.58 (55.61)	3.94 (4.15)	6.88 (7.20)
V	$Cd(HL^I)_2$	84	red	290	54.01 (53.59)	3.96 (3.75)	6.99 (6.94)
IV	$UO_2(HL^I)_2 \cdot H_2O$	70	brown	245	44.07 (44.03)	3.45 (3.28)	6.13 (5.71)
	$(HL_2^{II}$	80	Reddish orange	239	62.59 (63.00)	4.93 (5.01)	7.74 (7.74)
VII	$Mn(HL^{II})_2 \cdot H_2O$	73	orange	250	57.75 (57.38)	4.29 (4.59)	6.98 (7.05)
VIII	$Co(HL^{II})_2 \cdot H_2O$	75	red	273	57.06 (57.08)	4.35 (4.54)	6.83 (7.01)
IX	$Ni(HL^{II})_2 \cdot H_2O$	80	greenish yellow	262	57.19 (57.11)	4.51 (4.54)	7.51 (7.01)
X	$Cu(HL^{II})_2 \cdot H_2O$	85	dull brown	280	56.36 (56.77)	4.14 (4.51)	6.86 (6.97)
XI	$Zn(HL^{II})_2$	74	red	271	57.54 (57.93)	4.22 (4.35)	7.09 (7.11)
XII	$Cd(HL^{II})_2$	72	red	281	54.60 (54.67)	4.16 (4.11)	6.63 (6.71)

[a] H_2L^I = FcCH = $NNHCOC_6H_4OH$-*o*($C_{18}H_{16}N_2O_2Fe$);
H_2L^{II} = $FcC(CH_3)$ = $NNHCOC_6H_4OH$-*o*($C_{19}H_{18}N_2O_2Fe$); Fc = $C_5H_5FeC_5H_4$- [b] Calculated values are given in parentheses.

Syntheses of Complexes

All complexes were prepared by mixing metal(II) acetate (0.25 mmol) and the ligands, H_2L^I or H_2L^{II} (0.5 mmol) in 20 cm^3 of EtOH-DMF (9:1) and refluxing for 6 h. The precipitate so produced was collected on a filter, washed several times with warm ethanol and dried under vacuum. These complexes along with elemental analyses, colours, decomposition temperatures and yields are also listed in Table 1.

RESULTS AND DISCUSSION

The ligands are insoluble in weakly polar or non-polar solvents such as ether, benzene and alkanes, dissolve to some extent in polar solvents such as methanol, ethanol and acetonitrile, and dissolve in DMF and DMSO. The complexes are soluble in DMF and DMSO. Elemental analyses show that complexes conform to the formula $M(HL)_2 \cdot nH_2O$.

IR Spectra

Important IR frequencies of ligands and complexes along with relative assignments are given in Table 2. Characteristics bands of ligands due to ν(O–H), ν(N–H), ν(C = O), ν(C = N), δ(N–H), ν(C–N) and ν(N–N) appear at about 3440, 3270, 1650, 1610, 1540, 1235 and 910 cm^{-1}. IR spectra of these complexes show significant changes as compared with those of their ligands. The bands due to ν(N–H), ν(C = O), δ(N–H) and ν(C–N) disappear, but a new band is observed around 1255 cm^{-1}, which is attributed to ν(C–O).[12,13] It is also found that the ν(C = N) bands at 1611 cm^{-1} for H_2L^I and 1605 cm^{-1} for H_2L^{II} are shifted to lower frequency by *ca* 12–22 cm^{-1} after forming complexes, while ν(N–N) bands are shifted to a higher frequency by 5 - 25 cm^{-1}. A shift of the ν(C = N) band to lower frequency is attributed to conjugation of the *p* - orbital of the double bond with the *d* - orbitals of the metal atom with reduction of force constant. The ν(N–N) shift to higher frequency is attributed to the electron-attracting inductive effect when

Table 2 Significant IR absorption bands (cm^{-1}) for the ligands and complexes*

	ν(O–H)	ν(N–H)	ν(C–O)	ν(C–N)	δ(N–H)	Amide III ν(C–N)	ν(C–O)	ν(N–N)
H_2L^I	3430br,m	3292 m	1650vs	1611vs	1541vs	1237s	—	902w
I	3431br,m	–	–	1589vs	–	–	1255s	930w
II	3420br,m	–	–	1595vs	–	–	1257s	917w
III	3411br,m	–	–	1595vs	–	–	1257s	919w
IV	3407br,m	–	–	1590vs	–	–	1255s	929w
V	3433br,m	–	–	1592vs	–	–	1254s	926w
VI	3408br,m	–	–	1603vs	–	–	1249s	910m
H_2L^{II}	3448br,m	3251m	1662s	1605vs	1539vs	1233s	–	916m
VII	3413br,m	–	–	1591vs	–	–	1254s	919w
VIII	3361br,m	–	–	1587vs	–	–	1255vs	921m
IX	3424br,m	–	–	1588vs	–	–	1253s	922m
X	3406br,m	–	–	1593s	–	–	1257s	925w
XI	3437br,m	–	–	1592vs	–	–	1255s	921m
XII	3408br,m	–	–	1593vs	–	–	1254s	919m

* vs = very strong s = strong w = weak m = medium br = broad.

forming the conjugate system. The results show clearly that the nitrogen atom in the azomethine participates in coordination to the metal ions.[14] The hydroxyl group does not participate in coordination.

In addition, characteristics IR bands of the ferrocenyl group appear at about 3080, 1445, 1102, 800 and 485 cm^{-1} in the ligand and all complexes,[15] and those of *ortho*-substituted benzene appear at 1490 and 750 cm^{-1}. The IR spectra of H_2L^I and $Co(HL^I)_2$ are given in Figures 1 and 2.

UV Spectra

UV data for the ligands and their complexes in DMF are given in Table 3. Absorption bands at *ca* 200 nm may be due to the E_2 band of the benzene ring. The peaks at 275 nm for H_2L^I and 265 nm for H_2L^{II} arise from the *B* band of the cyclopentadienyl ring (a small hypsochromic shift).[16] The bands at 312 nm for H_2L^I and 320 nm for H_2L^{II}, which are assigned to the *K* band (π–π^* transition), undergo a bathochromic shift of about 6 - 12 nm in the complexes. This is because the double bond of the $^R{>}C = N-$ group and the double bond of the $^O{>}C = N-$ group form a conjugate system.[12] According to FMO theory, the HOMO or LUMO of the $^O{>}C = N-N = C{<}^R$ group and the HOMO or LUMO of the metal ions mix with each other, respectively (approximately, HOMO–HOMO, LUMO–LUMO), so that the energy gap between the new HOMO and LUMO is smaller than that of the $^O{>}C = N - NC{<}^R$ group. The above factors lead to the red shift of the π–π^* transition.

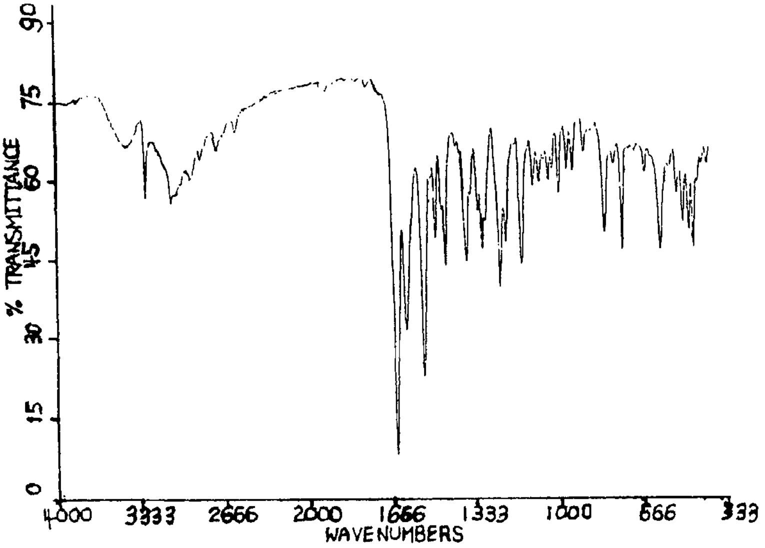

Figure 1 IR spectrum of H_2L^I

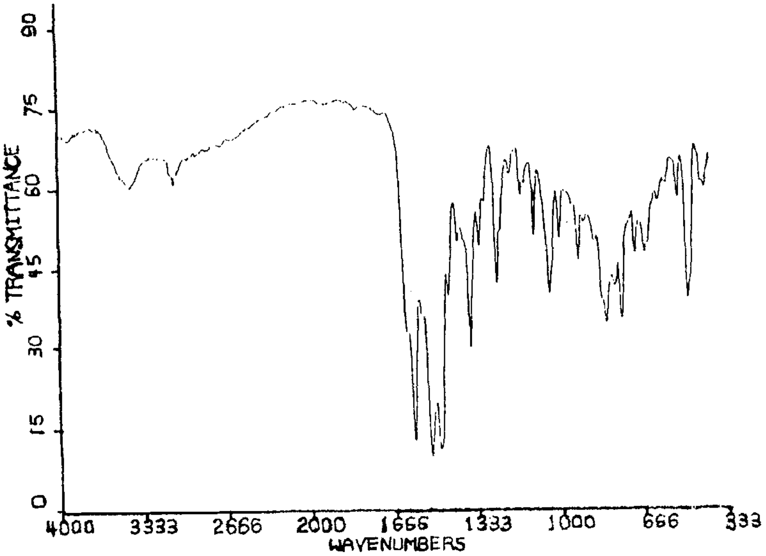

Figure 2 IR spectrum of $Co(H_2L^I)_2$.

Table 3 UV data for the ligands and their complexes (nm, λ_{max}^{DMF})

	1	2	3
H_2L^I	199	275	312
I	202	270	318
II	202	272	317
III	202	270	319
IV	202	270	318
V	202	269	318
VI	202	270	317
H_2L^{II}	199	265	320
VII	202	260	340
VIII	202	261	332
IX	202	260	336
X	202	257	332
XI	202	259	333
XII	202	261	332

^{1}HNMR Spectra

^{1}H NMR data for the ligands and the complexes $Zn(HL^I)_2 \cdot H_2O$ and $Cd(HL^{II})_2$ are listed in Table 4. It can be seen that in addition to the proton signals on aromatic and unsubstituted cyclopentadienyl rings, other proton signals in the complexes IV and XII occur with varying degrees of shifts as compared with the ligand; the nitrogen proton signal disappears. These results show the ligands coordinate to central ions in the enol form. The phenol hydroxyl proton signals are shifted downfield by 2–3 ppm, due to forming hydrogen bonds between hydrogen atoms on the hydroxyl and the uncoordinated nitrogen atom. When a DMSO(d^6) solution of

Table 4 ^1H NMR chemical shift (δ, ppm) of the ligands and their complexes

No.	Ferrocenyl group			CH = N	$-CH_3$	aromatic ring	-NH	-OH
	C_5H_5	C_5H_4						
H_2L^I	4.25[a]	4.47[b]	4.67[c]	8.30		6.81-7.92	11.58	12.05
	(5H,s)	(2H,m)	(2H,m)	(1H,s)		(4H,m)	(1H,br)	(br)
IV	4.17	4.56	4.94	8.51		6.81-7.93		14.12
	(5H,s)	(2H,m)	(2H,m)	(1H,s)		(4H,m)		(br)
H_2L^{II}	4.08	4.29	4.59		2.15	6.83-7.88	11.00	11.60
	(5H,s)	(2H,m)	(2H,m)		(3H,s)	(4H,m)	(br)	(br)
XII	4.13	4.58	4.92		2.35	6.79-7.91		14.72
	(5H,s)	(2H,m)	(2H,m)		(3H,s)	(4H,m)		(br)

[a,b,c] Signals of unsubstituted cyclopentadienyl protons and substituted cyclopentadienyl 3,4- and 2,5-protons, respectively.

Table 5 Molar conductivities (λm) of the comlexes in DMF at 25°C

	Conc. (10^{-3}mol)	λm (Ω^{-1} cm^2 mol^{-1})	Complexes	Conc. (10^{-3} mol)	λm (Ω^{-1} cm^2 mol^{-1})
I	1.01	3.1	VII	1.13	10.0
II	0.99	2.4	VIII	1.02	6.7
III	1.40	2.1	IX	1.14	7.2
IV	1.31	3.3	X	1.00	11.4
V	1.12	2.4	XI	0.99	5.3
VI	1.03	1.5	XII	1.31	6.9

$Cd(HL^{II})_2$ is diluted twice, four and eight times with tetrachloromethane, the -OH signals barely shift (*ca* 14.7 ppm).

Molar Conductance

The complexes in DMF afford deep brown solutions. Molar conductance values (Table 5) of the complexes in DMF lie in the range 2.4–11.7 ohm^{-1} cm^2 mol^{-1}, which indicates that the DMF solutions of the complexes are non-ionic in nature.[17] Thus we propose a plausible structure for these complexes as shown in Figure 3.

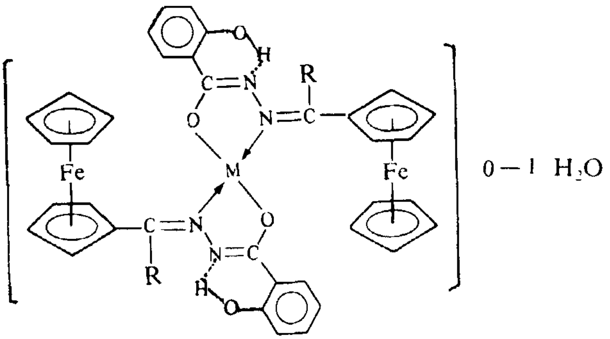

Figure 3 Proposed structure for the complexes R = H, M = Co, Ni, Cu, Zn, Cd and UO_2; R = CH_3, M = Mn, Co, Ni, Cu, Zn and Cd.

Acknowledgements

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