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Some Ferrocenyl Aroyl Hydrazones and their Copper(II) Complexes*

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Ferrocenylidene derivatives of benzoyl-, p-chlorobenzoyl-, o-nitrobenzoyl-, salicyloyl- and isonicotinoyl hydrazines have been synthesised by condensing acetylferrocene and/or formylferrocene with the respective aroyl hydrazine. These organometallic compounds act as ligands for metal complexation and copper(II) complexes of some of these have been isolated and characterized.

Introduction

The tuberculostatic activity of acid hydrazides, $RCONHNH_2$ and their corresponding aroyl hydrazones, RCONHN=CHR′, is attributed to their ability to form stable chelates with transition metal ions in the cell and thereby inhibit many transition metal catalysed vital enzymatic reactions [1, 2]. Having come across reports [3, 4] that the introduction of ferrocene molecule in penicillins and cephalosphorins changes the antibiotic activities and β-lactamic susceptibility, we became interested in synthesizing some ferrocene molecule in penicillins and cephalosporins studying their chelating ability with metal ions. In this communication we wish to report the syntheses of ferrocenylidene derivatives of some N-aroylhydrazines and copper(II) complexes of some of these ligands.

Experimental

Benzoyl-, salicyloyl- and isonicotinoyl hydrazines were prepared by the method given by Struve [5]. These compounds were recrystallized from ethanol. *p*-Chlorobenzoyl- and *o*-nitrobenzoyl hydrazines were obtained from Fluka A.G., Switzerland. Acetylferrocene was prepared according to known procedure [6]. Formylferrocene was also from Fluka A.G.. All solvents were purified and dried by standard procedures. Metal salts of analytical reagent grade were used.

Spectral Measurements

The infrared spectra were recorded on a Perkin-Elmer spectrophotometer model No. 283, calibrated with polystyrene film. Solid samples were examined as Nujol or HCB mull using cesium iodide optics. PMR spectra were recorded on a Varian Associates Model T-60 spectrometer using tetramethylsilane as an internal standard. The molecular weights were determined using CEC 21-110B (U.S.A.) Double Focusing Mass Spectrometer.

Syntheses of Ferrocenyl Hydrazones

All the ferrocenylidene derivatives of α-N-aroylhydrazines were prepared using a general procedure of refluxing equimolar quantities of formyl- or acetylferrocene and N-aroylhydrazine in ethanol for 4 hours. Concentration of the solutions to the appropriate volumes and cooling at 5 °C yielded the desired compounds which were further purified by repeated recrystallisation from ethanol. The compounds thus prepared are listed in Table I along with their melting points and elemental analyses.

Syntheses of Copper(II) Complexes

Copper(II) complexes of the hydrazone ligands were prepared by mixing a solution of the respective ligand (0.001 mol) in ethanol with a hot ethanolic solution of cupric acetate dihydrate (0.0005 mol) and heating the solution for half an hour under reflux. The solid that separated out was collected on a filter, washed several times with alcohol, and dried. The compounds thus prepared are given in Table II.

Results and Discussion

The condensation reaction of formylferrocene and acetylferrocene with N-aroylhydrazines in ethanol

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TABLE I. Analytical Data of Ferrocenyl Hydrazones.

S. No.	Compound[a]	Formula	Yield (%)	M.P. (°C)	Mol. wt.	Elemental analysis (%)[b]		
						C	H	N
1.	I	Fe($C_{18}H_{16}N_2O$)	88	158	332	65.66 (65.13)	5.20 (4.86)	8.56 (8.44)
2.	II	Fe($C_{18}H_{15}N_2OCl$)	80	220	366	57.29 (58.96)	4.38 (4.12)	7.53 (7.63)
3.	III	Fe($C_{18}H_{15}N_3O_3$)	85	235	377	56.90 (57.30)	4.41 (4.00)	10.46 (11.14)
4.	IV	Fe($C_{17}H_{15}N_3O$)	90	213	333	62.85 (61.28)	5.03 (4.54)	12.58 (12.61)
5.	V	Fe($C_{18}H_{16}N_2O_2$)	85	210	348	62.66 (62.09)	5.01 (4.63)	8.01 (8.04)
6.	VI	Fe($C_{19}H_{18}N_2O$)	65	165	346	67.18 (65.94)	5.59 (5.24)	8.59 (8.09)
7.	VII	Fe($C_{18}H_{17}N_3O$)	80	140	347	63.35 (62.26)	5.35 (4.93)	11.47 (12.10)
8.	VIII	Fe($C_{19}H_{18}N_2O_2$)	70	226	363	62.21 (63.00)	5.65 (5.05)	7.98 (7.73)

[a] See Fig. 1. [b] Calculated values are given in parentheses.

TABLE II. Elemental Analysis of Copper(II) Complexes of Ferrocenyl Hydrazones.

S. No.	Complex[a]	Formula	Yield (%)	Elemental analysis (%)[b]		
				C	H	N
1.	I	$C_{36}H_{30}N_4O_2Fe_2Cu$	90	59.92 (59.56)	4.90 (4.16)	8.22 (7.72)
2.	II	$C_{34}H_{28}N_6O_2Fe_2Cu$	65	55.29 (56.10)	3.84 (3.88)	10.56 (11.54)
3.	III	$C_{36}H_{30}N_4O_4Fe_2Cu$	85	57.81 (57.23)	4.41 (3.71)	6.67 (7.47)
4.	IV	$C_{38}H_{34}N_4O_2Fe_2Cu$	88	61.67 (60.52)	4.91 (4.54)	7.29 (7.42)
5.	V	$C_{38}H_{34}N_4O_4Fe_2Cu$	85	59.33 (58.07)	4.72 (4.36)	6.62 (7.12)

[a] See Fig. 3. [b] Calculated values are given in parentheses.

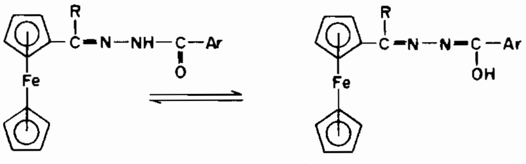

Fig. 1. (a) 'Keto' form; (b) 'enol' form.
Where

Compound	R	Ar
I	H	C_6H_5
II	H	p-C_6H_4Cl
III	H	o-$C_6H_4NO_2$
IV	H	C_5H_4N
V	H	o-C_6H_4OH
VI	CH_3	C_6H_5
VII	CH_3	C_5H_4N
VIII	CH_3	o-C_6H_4OH

gives stable crystalline compounds. Elemental analyses (Table I) of these compounds suggest the general formula as shown in Fig. 1.

The infrared spectra of these compounds exhibit bands characteristic of the stretching vibrations [7] of N–H and C=O (amide-I), besides amide II band (Table III). The presence of these bands suggests that these compounds predominantly exist in 'keto' form in the solid state. The strong intensity bands around 940 cm^{-1} can be attributed to the N–N stretching vibrations [8]. The bands observed at *ca.* 3085, 1410, 1105, 830, 500 and 400 cm^{-1} can be assigned for ferrocenyl group as νCH, νC–C, δC–H, π-CH and g(Fe–ring) respectively [9].

TABLE III. Important I.r. Frequencies (cm^{-1}) of Ferrocenyl Hydrazones.

S. No.	Compound[a]	N–H	(Amide-I)	(Amide-II)	N–N
1.	I	3160(br,m)	1630(s)	1545(s)	950(m)
2.	II	3200(br,s)	1640(vs)	1550(sh)	940(s)
3.	III	3160(br,m)	1650(s)	1550(m)	940(m)
4.	IV	3120(m)	1655(vs)	1445(s)	935(w)
5.	V	3260(vs)	1660(br,s)	1550(sh)	940(s)
6.	VI	3230(br,m)	1640(br,s)	1525(br,s)	920(s)
7.	VII	3180(br,m)	1640(s)	1540(br,s)	920(s)
8.	VIII	3260(br,m)	1625(br,s)	1535(br,s)	920(s)

[a] See Fig. 1.

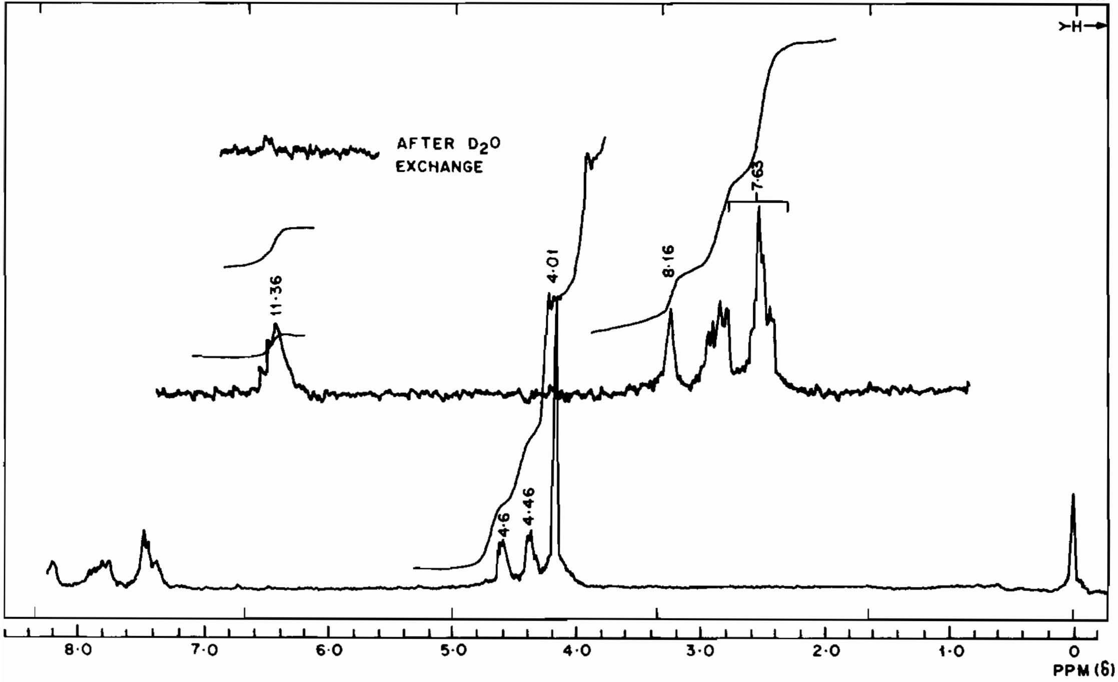

Fig. 2. NMR spectrum of α-N-benzoyl-β-N-ferrocenylidenehydrazide in DMSO.

In the spectra of compounds V and VIII (Table I) an additional broad and medium intensity band centred around ~2900 cm^{-1}, superimposed on C–H stretching vibrations is observed in hexachlorobutadiene. This band may be associated with an inter/intramolecularly bonded OH vibration [10]. The nature of hydrogen bonding in these compounds could not be studied because of their limited solubilities in carbon tetrachloride or chloroform.

The PMR spectrum of the compound I (Table I) has been studied with DMSO as solvent due to its limited solubility in CCl_4 or $CHCl_3$. The spectrum of the compound exhibits the unsubstituted cyclopentadienyl ring proton signals at around 4.01 ppm as a singlet while protons from substituted cyclopentadienyl ring appear around 4.4 and 4.6 ppm as broad peaks (triplets) (Fig. 2). This broadening of peaks can be interpreted in terms of the slowing down of the motions of cyclopentadienyl rings resulting from substitution [11]. Aromatic proton signals appear around 7.63 ppm and azomethine proton at 8.16 ppm. A broad signal due to N–H proton is observed at 11.4 ppm, which disappears on deuteration.

TABLE IV. Important I.r. Frequencies (in cm^{-1}) of Copper(II) Complexes of Ferrocenyl Hydrazones.

S. No.	Complex[a]	>C=N–N=C<	C=N (Amide-II)	(C–O)	(N–N)	(Cu–O)	(Cu–N)
1.	I	1615(s)	1510(sh)	1240(s)	930(w)	285(w)	405(s)
2.	II	1590(br,s)	1515(s)	1260(m)	950(m)	270(m)	425(m)
3.	III	1620(m)	1525(m)	1260(s)	955(w)	290(w)	430(w)
4.	IV	1600(sh)	1525(s)	1280(m)	990(m)	295(br,w)	470(s)
5.	V	1620(w)	1505(br,s)	1260(vs)	955(w)	290(w)	440(m)

[a]See Fig. 3.

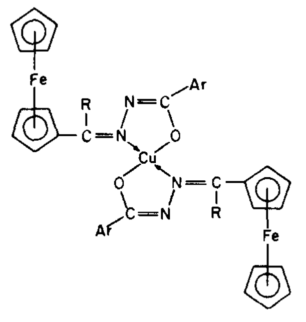

Fig. 3. Where

Compound	R	Ar
I	H	C_6H_5
II	H	C_5H_4N
III	H	o-C_6H_4OH
IV	CH_3	C_6H_5
V	CH_3	o-C_6H_4OH

Copper(II) Complexes

The complexes are stable and red in colour, insoluble in common organic solvents, and only sparingly soluble in DMF and DMSO. The elemental analyses (Table II) show that the complexes have 1:2 (metal: ligand) stoichiometry.

Infrared Spectra

The infrared spectra of copper(II) complexes show significant changes as compared with those of the parent ligands. The important i.r. frequencies along with their assignments are listed in Table IV. The bands due to ν(N–H) stretching and amide-I are absent in these complexes. Amide-II band is found to shift to a lower frequency, whereas the ν(N–N) band moves to a higher frequency. These changes clearly indicate that ligands get enolized in solution and chelation takes place through the azomethine nitrogen atom and the amide oxygen atom of the ligand as shown in Fig. 3. This is further supported by the appearance of a new medium to strong intense band in the 1280– 1220 cm^{-1} region which can be assigned to ν(C–O) vibration [12] and a sharp band in the range 1620–1600 cm^{-1} which can be attributed to the stretching mode of the conjugate –C=N–N=C– group [13].

In the far infrared region two strong-to-medium intensity bands around 425 cm^{-1} and 280 cm^{-1} are observed, which are not seen in the spectra of ligands. These can be assigned to ν(Cu–N) and ν(Cu–O) vibrations [14, 15].

The broad, weak band centred around ~2900 cm^{-1} (presumably due to the intramolecular H-bonded OH) is observed in the spectra of the compounds III and V (Table II). This suggests that phenolic OH group is not involved in the chelation. The i.r. spectra of all these compounds show bands at 3085, 1411, 1108, 1102, 834, 492 and 478 cm^{-1}, assigned to the ferrocenyl group [9].

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