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Preparation of some Ferrocenylcarbonylhydrazones and their Coordination Compounds

MA YONGXIANG, LI FENG, SUN HONGSUI
Department Chemistry, Lanzhou University, Lanzhou, China
and XIE JISHAN
Lanzhou Institute of Chemical Physics, Academia Sinica, Lanzhou, China

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Abstract

Some new acylhydrazones(HL) containing the ferrocenyl group FcCONHN=CHR [Fc = η^5-C_5H_5-FeC_5H_4; R = *p*-$C_6H_4NO_2$ (I), *p*-C_6H_4OH (II), *o*-C_6H_4Cl (III), *o*-$C_6H_4NO_2$ (IV), 2-furyl (V), 2-hydroxy-1-naphthyl (VI), *o*-C_6H_4OH (VII) and Fc (VIII)], have been synthesized by the condensing reaction of ferrocenylcarbonylhydrazine with some aldehydes. Nickel(II) chelates of these organometallic compounds, NiL_2 have been prepared and characterized.

Introduction

Due to their ability to form stable complexes with transition metal ions, acylhydrazones can be used as analytic reagents [1, 2] and inhibitors of many transition metal catalyzed vital enzymatic reactions [3, 4]. In recent years, acylhydrazones including ferrocenyl and its coordination complexes have been investigated extensively [5–8]. Edwards and coworkers [9] have shown that the replacement of aromatic groups by the ferrocenyl moiety in penicillins and cephalosporins improves their antibiotic activity. In this communication we wish to report the preparation of eight new ferrocenylcarbonylhydrazones and their chelates with nickel(II) ions

Experimental

Nickel(II) acetate of analytic reagent grade is used. *p*-Nitrobenzaldehyde, *p*-hydroxybenzaldehyde, *o*-chlorobenzaldehyde, *o*-nitrobenzaldehyde, 2-furaldehyde, 2-hydroxynaphthyl aldehyde, *o*-hydroxybenzaldehyde are chemical agents and formylferrocene is prepared by the method given in the literature [10].

Preparation of Ferrocenylcarbonylhydrazine [11]

Acetylferrocene was oxidized to ferrocenecarboxylic acid with iodine by the method described in the literature [12]. Then the ferrocenecarboxylic acid was converted into ferrocenecarbonyl chloride by treating with PCl_5. The solution of ferrocenecarbonyl chloride in THF was added into a solution of hydrazine hydrate in anhydrous ethanol. Ferrocenylcarbonylhydrazine is obtained as red crystals after recrystallization in ethanol. Melting point (m.p.) 157–160 ℃. Yield 61%.

Preparation of Ferrocenylcarbonylhydrazones

5 mmol of the respective aldehyde in ethanol are added to 1.22 g (5 mmol) of ferrocenylcarbonylhydrazine in warm anhydrous ethanol (20 cm^3). The reaction mixture is heated under reflux for 20 min. The crystals that precipitated are collected on a filter, and recrystallized from anhydrous ethanol. The elemental analyses, yields and melting points of substituted phenylidene and furylidene ferrocenylcarbonylhydrazides obtained by this method are listed in Table I.

Preparation of Nickel(II) Complexes

A hot solution of $Ni(OAc)_2\cdot 2H_2O$ (0.25 mmol) in anhydrous ethanol (10 cm^3) is added dropwise with stirring to a solution of the respective ferrocenylcarbonylhydrazide in warm anhydrous ethanol. The mixture is heated under refluxing and stirring for 30 min until the precipitates separated. The isolated complexes are filtered, washed with warm ethanol and dried under vacuum. Yield above 85%. These complexes, NiL_2 along with their elemental analyses are listed in Table II.

Spectral Measurements

IR spectra are measured with a NIC-5DX spectrophotometer using KBr discs and sodium chloride optics. PMR spectra are recorded on a PMX-60 spectrophotometer using deuterodimethyl sulphoxide as solvent and tetramethylsilane as internal standard.

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TABLE I. Elemental Analysis, Yield and Melting Point of Acylhydrazones

Compound	Formula	Yield (%)	Melting point (°C)	Elemental analysis (%)[a]		
				C	H	N
I	$C_{18}H_{15}N_3O_3Fe$	96	210(dec)	57.58 (57.30)	3.87 (4.00)	11.19 (11.14)
II	$C_{18}H_{16}N_2O_2Fe$	91	230(dec)	61.61 (62.09)	4.86 (4.63)	7.89 (8.04)
III	$C_{18}H_{15}N_2OClFe$	82	215(dec)	57.81 (58.96)	4.15 (4.12)	7.42 (7.63)
IV	$C_{18}H_{15}N_3O_3Fe$	62	188–190	57.52 (57.30)	4.09 (4.00)	11.07 (11.14)
V	$C_{16}H_{14}N_2O_2Fe$	79	207(dec)	59.03 (59.65)	4.35 (4.38)	8.69 (8.70)
VI	$C_{22}H_{18}N_2O_2Fe$	94	220–221	66.34 (66.35)	4.35 (4.56)	7.03 (7.03)
VII	$C_{18}H_{16}N_2O_2Fe$	84	211–212	62.03 (62.09)	4.79 (4.63)	7.77 (8.04)
VIII	$C_{22}H_{20}N_2OFe$	89	230(dec)	60.09 (60.04)	4.63 (4.58)	6.68 (6.36)

[a]Calculated values are given in parentheses

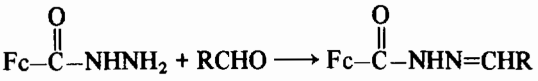
TABLE II The Elemental Analysis of Complexes NiL$_2^{I-VIII}$

No.	Complex	Formula	Decomposition temperature (°C)	Elemental analysis (%)[a]		
				C	H	N
IX	NiL$_2^{I}$	$C_{36}H_{28}N_6O_6Fe_2Ni$		53.57 (53.31)	4.08 (3.73)	10.86 (10.36)
X	NiL$_2^{II}$	$C_{36}H_{30}N_4O_4Fe_2Ni$		56.39 (57.42)	4.55 (4.02)	6.68 (7.44)
XI	NiL$_2^{III}$	$C_{36}H_{28}N_4O_2Cl_2Fe_2Ni$		53.40 (54.74	3.66 (3.57)	6.88 (7.09)
XII	NiL$_2^{IV}$	$C_{36}H_{28}N_6O_6Fe_2Ni$	263	53.64 (53.31)	3.63 (3.73)	10.20 (10.36)
XIII	NiL$_2^{V}$	$C_{32}H_{26}N_4O_4Fe_2Ni$	261	54.94 (54.83)	3.97 (3.74)	8.05 (7.99)
XIV	NiL$_2^{VI}$	$C_{44}H_{34}N_4O_4Fe_2Ni$		61.11 (61.94)	4.28 (4.02)	6.56 (6.57)
XV	NiL$_2^{VII}$	$C_{36}H_{30}N_4O_4Fe_2Ni$	270	57.20 (57.42)	4.27 (4.02)	7.42 (7.44)
XVI	NiL$_2^{VIII}$	$C_{44}H_{38}N_4O_2Fe_2Ni$	250	55.82 (56.41)	3.84 (4.30)	5.84 (5.98)

[a]Calculated values are given in parentheses

Results and Discussion

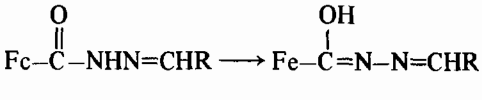
The elemental analysis (Table I) shows that the reaction of ferrocenylcarbonylhydrazine with various aldehydes forms ferrocenylcarbonylhydrazones according to the following equation



$$\mathrm{Fc{-}\overset{O}{\overset{\|}{C}}{-}NHNH_2 + RCHO \longrightarrow Fc{-}\overset{O}{\overset{\|}{C}}{-}NHN{=}CHR}$$

Fc = η^5-$C_5H_5FeC_5H_4$; R = *p*-$C_6H_4NO_2$ (I), *p*-C_6H_4OH (II), *o*-C_6H_4Cl (III), *o*-$C_6H_4NO_2$ (IV), 2-C_4H_3O (V), 1-$C_{10}H_7O$ (VI), *o*-C_6H_4OH (VII) and Fc (VIII)

These acylhydrazones can undergo enolization as shown below



$$\mathrm{Fc{-}\overset{O}{\overset{\|}{C}}{-}NHN{=}CHR \longrightarrow Fe{-}\overset{OH}{\overset{|}{C}}{=}N{-}N{=}CHR}$$

1 **2**

The hydrazones (**1**) convert into the enol form (**2**), when reacting with nickel(II) acetate, and form chelate complexes (**3**) with Ni(II) ion as shown in Fig. 1.

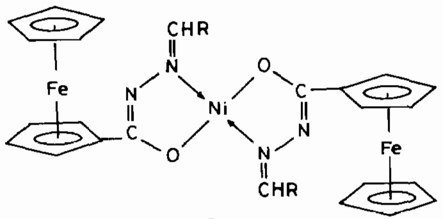


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Fig. 1. Proposed structure for the complexes.

IR Spectra

The IR frequencies of **1** along with their relative assignments are given in Table III. It can be seen that their bands characteristic of the stretching vibrations of ν(N–H), ν(C=O)(amide I), ν(C=N) and ν(N–N) appear at about 3200, 1650, 1600 and 950 cm^{-1} [13, 14]. The band at *ca.* 1550 cm^{-1} is attributed to amide II. The characteristic bands of the ferrocenyl group exhibit at *ca.* 3065, 1411, 1105, 820 and 503 cm^{-1}. The ν(N$\overset{\cdots}{-}$O) band of **I** and **IV** are observed at 1336 and 1344 cm^{-1} respectively. The absorption frequencies appearing at 3282, 3228 and 3222 cm^{-1} for **II**, **VI** and **VII**, respectively, arise from ν(O–H) of the phenol group, and the band due to ν(C–O–C) in the furyl ring of **V** appears at 1021 cm^{-1}. The bands observed at about 3065, 1450, 1105, 500 and 410 cm^{-1} can be assigned for the ferrocenyl group as ν(C–H), ν(C–C), δ(C–H), π(C–H) and Fe-ring. The presence of the bands characteristic of ν(N–H) and ν(C=O) in all the compounds shows that they exist in the keto form predominantly in the solid state.

The IR spectra of acylhydrazone complexes with the Ni(II) ion are given in Table IV. It appears that their IR spectra show significant changes as compared with those of the parent compounds. The bands due to the stretching vibrations of N–H and C=O are absent in these complexes, whereas two new bands are observed around 1600 and 1300 cm^{-1}, which are attributed to ν(C=N–N=C) and ν(C–O). It is also found that the band of amide II is shifted to a lower frequency by 10–30 cm^{-1}, while the ν(N–N) band is

TABLE III. IR Spectra[a] of Acylhydrazones (cm^{-1})

Compound	ν(N–H)	ν(C=O)	Amide II	ν(N–N)	Other	
I	3162w	1643s	1517s	943w	ν(N$\overset{\cdots}{-}$O)	1336vs
II	3196m	1643s	1546vs	940m	ν(O–H)	3282m
III	3222m	1648vs	1554s	944w		
IV	3182m	1651vs	1548s	942m	ν(N$\overset{\cdots}{-}$O)	1344s
V	3222s	1640vs	1542s	946m	ν(C–O–C)	1021m
VI	3138w	1638vs	1550vs	953m	ν(O–H)	3228s
VII	3169m	1640vs	1555s	946w	ν(O–H)	3222m
VIII	3220m	1637s	1549s	951w		

[a]vs = very strong, s = strong m = medium, w = weak

TABLE IV IR Spectra[a] of Complexes IX–XVI (cm^{-1})

Complex	ν(C=N–N=C)	Amide II	ν(C$\overset{\cdots}{-}$C) phenyl	ν(C–O)	ν(N–N)	Other	
IX	1597m	1514vs	1476vs	1293m	943w	ν(N$\overset{\cdots}{-}$O)	1340vs
X	1598s	1509s	1473vs	1280m	951w	ν(O–H)	3150br
XI	1600w	1514vs	1470vs	1285m	950m		
XII	1604w	1514vs	1470vs	1302m	951w	ν(N$\overset{\cdots}{-}$O)	1336s
XIII	1613m	1516vs	1470vs	1334s	953w	ν(C–O–C)	1029w
XIV	1590vs	1538vs	1457s	1298s	967m	ν(O–H)	3072br
XV	1593vs	1538s	1465s	1309s	951w	ν(O–H)	3050br
XVI	1609w	1516vs	1474vs	1332s	952w		

[a]vs = very strong s = strong m = medium, w = weak br = broad.

TABLE V. PMR Chemical Shifts (δ, ppm) of Acylhydrazones **I**–**VIII**

Compound	Ferrocenyl group			Azomethine proton 1H	N–H proton	Aromatic group
	C_5H_5 [a]	C_5H_4				
		2H(3, 4)	2H(2, 5) [b]			
I	4.23s	4.45t	5.0t	8.53s	11.34s	7.93, 8.27
II	4.13s	4.37t	4.88t	8.13s	10.77s	6.70–7.5
III	4.16s	4.20t	4.90t	8.60s	11.2s	7.5–7.9m
IV	4.15s	4.40t	4.90t	8.70s	11.4s	7.5–8.0m
V	4.17s	4.40t	4.90t	8.20s	11.0s	6.5, 6.8, 7.9 [c]
VI	4.20s	4.40t	4.90t	9.25s	11.3s	7.0–8.1m
VII	4.17s	4.45t	4.90t	8.50s	11.2s	6.8–7.5m
VIII	4.22s (10H)	4.45(4H),	4.65(2H) 4.94(2H)	8.20s	10.8s	

[a] Unsubstituted cyclopentadienyl ring proton signals. [b] Values in parentheses indicate proton positions on the substituted cyclopentadienyl ring. [c] The signals result from three protons of the furyl ring.

shifted to a higher frequency by 5–10 cm^{-1}. The frequency changes of amide II and ν(N–N) support the coordination through the azomethine nitrogen atom. In addition, the band at *ca.* 1470 cm^{-1} due to $\nu(\mathrm{C}\overset{\cdot\cdot\cdot}{-}\mathrm{C})$ for the aromatic ring is very weak and sometimes is not observed. When forming a complex it changes into the strongest band in the IR spectra of all the complexes, because the whole molecule of these ligands turns into a large conjugate system after enolization and coordination. It can be seen from the above-mentioned that these acylhydrazones easily undergo enolization in solution and then react with nickel ions to form the Ni(II) complexes, accompanied by the release of acetate ions.

PMR Spectra

The ^{1}H NMR spectra of acylhydrazones **I**–**VIII** in DMSO are listed in Table V. It can be seen that the chemical shift of five protons on the unsubstituted cyclopentadienyl ring is observed at 4.13–4.23 ppm as a singlet. The proton signal due to the 3 and 4 positions of the substituted cyclopentadienyl ring appears at 4.20–4.45 ppm and the other two proton signals at 4.88–5.0 ppm as a triplet [15]. In compound **VIII**, because of the presence of two ferrocenyl groups, the protons of two unsubstituted cyclopentadienyl rings and four protons on the 3,3′,4,4′-positions in two substituted cyclopentadienyl rings are equivalent protons and their signals appear at 4.22(10H) and 4.45(4H) ppm respectively, but the two protons on the 2 and 5 positions of η^5-$C_5H_4CH{=}N$– and the other two protons on 2′ and 5′ of η^5-C_5H_4CO are non-equivalent protons and their signals appear at 4.65(2H) and 4.94(2H) ppm respectively. The azomethine proton signal appears at 8.1–9.3 ppm as a singlet and that of the N–H at 10.8–11.4 ppm as a singlet, but the N–H proton signal disappears on deuteration. The aromatic protons of compound **I** exhibit typical *para*-substituted proton signals at 7.9 and 8.3 ppm, but the aromatic proton signals of **II**, **VI** and **VII** along with hydroxy protons appear at 7.2, 7.6 and 7.1 ppm respectively. The proton signals on the 3, 4 and 5 positions of the furyl ring appear at 6.8, 6.5 and 7.8 ppm respectively.

The ^{1}H NMR spectra of complexes **IX**–**XVI** in DMSO do not exhibit any signals; perhaps, they are paramagnetic.

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