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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

METAL COMPLEXES OF FERROCENECARBOXALDEHYDE 2,4-DICHLOROBENZOYLHYDRAZONE

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Published online: 15 Feb 2007.

To cite this article: Guo-sheng Huang , Qing-bao Song & Yong-xiang Ma (2001) METAL COMPLEXES OF FERROCENECARBOXALDEHYDE 2,4-DICHLOROBENZOYLHYDRAZONE, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 31:2, 297-302, DOI: 10.1081/SIM-100002048

To link to this article: http://dx.doi.org/10.1081/SIM-100002048

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SYNTH. REACT. INORG. MET.-ORG. CHEM., 31(2), 297–302 (2001)

METAL COMPLEXES OF FERROCENECARBOXALDEHYDE 2,4-DICHLOROBENZOYLHYDRAZONE

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ABSTRACT

A new chelating ligand, ferrocenecarboxaldehyde 2,4-dichlorobenzoylhydrazone (HFdcbh), and seven metal complexes, $M(Fdcbh)_2$ [M=Co(II), Ni(II), Cu(II), Hg(II)] and $Ln(HFdcbh)Cl_3 \cdot 4H_2O_2$ [Ln=La(III), Sm(III) and Er(III)], have been prepared and characterized by elemental analyses, IR and ^1H NMR spectra. The deprotonated HFdcbh ligand acts as a bidentate donor, coordinating to the metal ions *via* its nitrogen and oxygen atoms.

INTRODUCTION

Schiff bases from acylhydrazine and their complexes have strong antitumor and antivirus activities (1–5) and the presence of a ferrocenyl group can improve these properties (6). Some ferrocene derivatives are excellent nonlinear optical materials (7) owing to their strong electron donor properties and behavior as an electron-flow bridge. In view of their interesting structural characteristics and wide-ranging uses, studies of the Schiff bases and their ferrocene derivatives have

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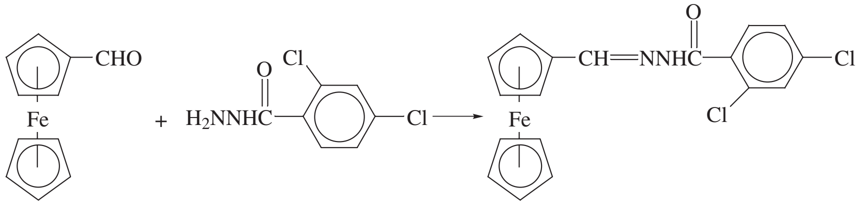

Figure 1. The structure of the ligand (HFdcbp).

attracted the attention of many investigators. In the present work, we report the synthesis and Characterization of a new ligand (HFdcbh) and its complexes with transition metals and lanthanides. The preparation and structure of the ligand showed as in Figure 1.

EXPERIMENTAL

Materials and Methods

Ferrocenecarboxaldehyde and 2,4-dichlorobenzoylhydrazine were prepared by literature methods (8,9). Other reagents were analytical grade. CHN analysis was carried out with an Elementary Vario EL elemental analyzer. The IR spectra were recorded on a Nicolet 170 SX spectrophotometer as KBr discs in the 4000–200 cm^{-1} region ^{1}H NMR spectra were measured with a FT-80A NMR spectrometer using DMSO-d_6 or $CDCl_3$ as solvent and TMS as internal standard. Molar conductances were recorded by a DDS-IIA conductometer in DMF at 15°C. Melting points were determined on a RY-1 melting point apparatus and are uncorrected.

Preparation of HFdcbh

Ferrocenecarboxaldehyde (2.14 g, 10 mmol) was dissolved in 15 mL of anhydrous ethanol, which was added dropwise into a solution of 2,4-dichlorobenzoylhydrazine (2.05 g, 10 mmol) in anhydrous ethanol (60 mL) under stirring and refluxing. A red precipitate appeared immediately and the mixture was refluxed for 2 h with stirring. The mixture was cooled to room temperature, and the product was collected on a Büchner funnel, washed twice with ethanol and diethyl ether, respectively, recrystallized in anhydrous ethanol, and dried in *vacuo*. Reddish orange crystals were obtained. Yield 4.0 g (90%), m.p. 230°C (dec.).

Table I. Yield, Elemental Analysis Data, and Physical Properties of the Complexes

No.	Formula	Formula Weight	Yield (%)	D.p. (°C)	Found (Calcd.) (%)			Color	Λ_m $(\Omega^{-1}\text{cm}^2\cdot\text{mol}^{-1})^a$
					C	H	N		
(**1**)	HFdcbh	401.06	90	230	53.8	3.5	7.0	reddish	2.1
	$C_{18}H_{14}CI_2$ Fe N_2O				(53.9)	(3.5)	(7.0)	orange	
(**2**)	Co[Fdcbh]$_2$	859.05	82	245	50.0	3.0	6.5	red	8.0
	$C_{36}H_{26}Cl_4Fe_2N_4O_2Co$				(50.3)	(3.1)	(6.5)		
(**3**)	Ni[Fdcbh]$_2$	858.83	82	245	50.3	3.1	6.5	red	8.0
	$C_{36}H_{26}Cl_4Fe_2N_4O_2Ni$				(50.3)	(3.1)	(6.5)		
(**4**)	Cu[Fdcbh]$_2$	863.66	80	240	49.9	3.0	6.4	red	5.8
	$C_{36}H_{26}CI_4Fe_2N_4O_2Cu$				(50.1)	(3.0)	(6.5)		
(**5**)	Hg[Fdcbh]$_2$	1000.71	74	252	43.1	2.6	5.5	red	4.0
	$C_{36}H_{26}CI_4Fe_2N_4O_2Hg$				(43.2)	(2.6)	(5.6)		
(**6**)	La[HFdcbh]Cl$_3\cdot 4H_20$	718.39	67	205	29.7	3.1	3.8	brown	95.4
	$C_{18}H_{22}CI_5FeN_2O_5La$				(30.1)	(3.1)	(3.9)		
(**7**)	Sm[HFdcbh]Cl$_3\cdot 4H_2O$	729.83	69	200	29.4	2.9	3.7	brown	88.6
	$C_{18}H_{22}CI_5FeN_2O_5Sm$				(29.6)	(3.0)	(3.8)		
(**8**)	Er[HFdcbh] Cl$_3\cdot 4H_2O$	746.74	74	210	29.0	2.9	3.8	brown	81.2
	$C_{18}H_{22}CI_5FeN_2O_5Er$				(29.0)	(3.0)	(3.8)		

[a] Molar contactance, concentration of the solution (in DMF) was about 1×10^{-4} mol/dm^3.

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Preparation of Co, Ni, Cu, and Hg Complexes

$M(OAc)_2.nH_2O$ (0.25 mmol) was dissolved in 25 mL of anhydrous ethanol with heating (50°C), and this solution was added dropwise into a solution of HFdcbh (0.2 g, 0.50 mmol) in 50 mL anhydrous ethanol with stirring at room temperature. Then the mixture was stirred continuously for 20 min at room temperature and for 6–8 h under reflux. A red solid was formed which was collected immediately on a Büchner funnel, washed twice with warm ethanol and diethyl ether, respectively, and dried in *vacuo.* The yield and elemental analysis results of the complexes are listed in Table I.

Preparation of Lanthanide Complexes

A solution of HFdcbh (0.4 g, 1.0 mmol) in 50 mL of anhydrous ethanol was added dropwise into a solution of $LnCI_3$ (0.5 mmol) (Ln = La, Sm and Er) in 60–70 mL of anhydrous ethanol with heating and stirring. The mixture was stirred for 12 h under reflux. Then it was concentrated under reduced pressure in a warm water bath until its volume was reduced to 1/3, cooled, filtered and the solid washed with warm ethanol and diethyl ether, and dried in *vacuo.* The yields and analytical data of the complexes are shown in Table I.

RESULTS AND DISCUSSION

HFdcbh and its complexes are colored solids that remain stable in air below 200°C. Their physical properties are shown in Table I. The elemental analyses results show that the ligand coordinates to the central metal ions in two

Table II. Some Characteristic IR Wave Numbers of the Ligand and Its Complexes [a] (cm^{-1})

Compd.	ν(N–H)	ν(C=0)	ν(C=N–H=C)	ν(C=N)	ν(N=C–O)	ν(C–O)	ν(N–N)
(**1**)	3238 s	1662 vs	—	1604 s	–	–	999 w
(**2**)	–	–	1622 m	1580 s	1523 s, 1352 s	1245 w	1007 m
(**3**)	–	–	1619 m	1587 s	1534 vs, 1352 vs	1241 w	1011 m
(**4**)	–	–	1619 m	1584 s	1510 vs, 1358 vs	1241 w	1012 m
(**5**)	–	–	1629 m	1587 s	1510 s, 1369 vs	1248 w	1001 m
(**6**)	3236 sh	1656 vs	–	1587 s	–	–	1000 m
(**7**)	3230 sh	1650 vs	–	1585 s	–	–	1002 m
(**8**)	3235 sh	1654 vs	–	1588 vs	–	–	1001 m

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

Table III. ^{1}H NMR Data (δ) ^{b} of the Ligand and Its Complexes (**5**) and (**6**)

No.	N–H	N=CH	$-C_6H_3Cl_2$	C_5H_4	C_5H_5
(**1**)	11.68 (s, 1H)	8.10 (s, 1H)	7.48–7.88 (m, 3H)	4.68 (d, 2H), 4.48 (d, 2H)	4.23 (s, 5H)
(**5**)	–	7.78 (s, 2H)	7.30–7.70 (m, 6H)	4.76 (d, 4H), 4.46 (d, 4H)	4.34 (s, 10H)
(**6**)	11.71 (br, 1H)	7.75 (s, 1H)	7.45–7.66 (m, 3H)	4.65 (d, 2H), 4.46 (d, 2H)	4.24 (s, 5H)

^{b} br = broad, s = singlet, d = doublet, m = multplet.

forms, *i.e.* M[Fdcbh]$_2$ and Ln[HFdcbh]Cl$_3 \cdot 4H_2O$. The molar conductivity data approach the reported values of a non-electrolyte for transition metal complex (2.1–8.0 $\Omega^{-1}cm^2 \cdot mol^{-1}$) or 1:1 electrolyte for the lanthanide complexes (81–96 $\Omega^{-1}cm^2 \cdot mol^{-1}$) in the literature (10).

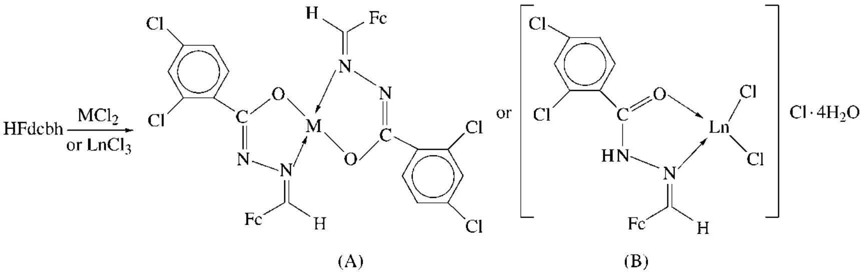
IR Spectra

The main features of the IR spectra of free HFdcbh and its complexes are shown in Table II. The bands appearing at 3228, 1662, 1604 and 999 cm^{-1} are attributed to ν(N–H), ν(C=O), ν(C=N) and ν(N–N). The IR spectra of the complexes (**2**)–(**5**) show apparent changes as compared with that of the ligand. The bands attributed to ν(N–H) and ν(C=O) had disappeared, while four new bands appeared at about 1620, 1520, 1355 and 1245 cm^{-1} arising from ν(C=N–N=C), ν(NCO) and ν(C–O). The IR spectra of the complexes (**6**)–(**8**) exhibited few changes, and only the bands due to ν(C=O) and ν(C=N) are shifted to lower frequency by 6–12 or 16–19 cm^{-1}, respectively. These results indicate that the ligand coordinates to central metal ions either in the deprotonated enol form (for transition metals) or in the neutral keto-form (for the lanthanides).

^{1}H NMR Spectra

The ^{1}H NMR data for (**1**) and its complexes (**5**) and (**6**) are listed in Table III. The proton signals at 11.68, 8.10, 7.48–7.88, 4.68 and 4.48, and 4.23 ppm for (**1**) arise from NH, N=CH, aryl ring, substituted and unsubstituted cyclopentadienyl, respectively. The proton signal due to NH disappeared for (**5**) and remained unchanged for (**6**). The proton signal due to N=CH for (**5**) and (**6**) shifted upfield by 0.3 and 0.2 ppm, respectively. These results agree with those obtained from elemental analyses and IR spectra.

Summarizing the present results, we consider that the ligand HFdcbh forms two types of complex. When using metal acetate, the ligand coordinates to the



(Fc = η^5-$C_5H_5FeC_5H_4$; **(2)-(5)** for A and **(6)-(8)** for B)

Figure 2. Proposed structure of the complexes of HFdcbh.

central ions as deprotonated enol-form (A) (11) and using metal chloride it coordinates as neutral keto-form (B) (12) as shown in Figure 2.

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Received August 17, 2000
Accepted November 29, 2000
Referee I: J. P. Jasinski
Referee II: E. Rosenberg

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