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STUDY OF THE COORDINATION CHEMISTRY OF FERROCENE-CONTAINING PYRAZOLE DERIVATIVES WITH IIB GROUP METAL IONS

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ABSTRACT

Complexes of the type $[(3-Fc, 5-Me)Pz]_n MCl_2 [Fc = ferrocenyl, Pz = pyrazole, M = Zn(II), Cd(II) and n = 1 or 2] have been synthesized and characterized by elemental analyses, IR, ¹H NMR spectra and cyclic voltammetry. Elemental analyses reveal a ligand to metal ratio of 1 : 1 for Cd(II) and 2 : 1 for Zn(II). No satisfactory elemental analysis results were obtained for the Hg(II) complex due to possible decomposition of the ligand.$

INTRODUCTION

In the past years, many studies¹⁻⁵ on pyrazole derivatives have been focused on their significant coordination behavior. In this paper, the steric and electronic effects of 3,5-substituted pyrazoles in their coordination behavior towards IIB group metal ions were investigated.

EXPERIMENTAL

Elemental analysis for C, H, N were performed on a CHN-CORDERM 7-3 autoanalyzer. Melting points were determined on a PHMK melting point apparatus (made in Germany) and are uncorrected. ¹H NMR spectra were recorded on a JEOLFX-90QNMR, using DMSO-d₆ as solvent, and TMS as internal standard. IR spectra were determined with a NICOLET-FT-IR5-DX infrared spectrophotometer. Cyclic voltammetric experiments were performed on a BAS-100B electrochemical analyzer equipped with a three-electrode assembly with 0.1 mol/L TBAFB (Bu₄NBF₄) as support electrolyte and DMSO as solvent. The working electrode was a 1.5 mm diameter platinum disk embedded in a cobalt glass seal and was polished consecutively with polishing alumina and diamond suspensions between runs. 0.1 M AgNO₃/Ag (in 0.1 M Bu₄NBF₄-DMSO) was the reference electrode. A platinum filament was used as an auxiliary electrode. FcC(O)CH₂C(O)CH₃ and FcC(O)CH₂C(O)Ph were prepared by published methods⁷.

Synthesis of the Ligands

<u>(3-Fc,5-Me)Pz (HPz*)</u>. To FcC(O)CH₂C(O)CH₃ (27.0 g, 0.1 mol) dissolved in alcohol (80 mL) with continuous stirring was added 85% hydrazine hydrate (5.64 mL, 0.15 mol). After refluxing for 3 h, the solvent was removed *in vacuo*, and the residue was recrystallised from alcohol to give orange-yellow crystals, the yield was 25.8 g (97%).

<u>(3-Fc, 5-Ph)Pz (HPz')</u>, To FcC(O)CH₂C(O)Ph (33.2 g, 0.1 mol) dissolved in alcohol (80 mL) with continuous stirring was added 85% hydrazine hydrate (5.64 mL, 0.15 mol). After refluxing for 5 h, the solvent was removed *in vacuo*, and the residue was recrystallised from alcohol to give yellow crystals, the yield was 29.3 g (90%).

Synthesis of Metal Complexes

 $Zn(HPz^*)_2Cl_2$, To a solution of (3-Fc, 5-Me)Pz (0.266 g, 1 mmol) in 10 mL alcohol, a solution of ZnCl₂ (0.410 g, 3 mmol) in 15 mL alcohol was added and stirred at room temperature for 24 h. The orange-yellow powder obtained on

filtration was washed with alcohol and ethyl ether successively, yield 0.536 g (81%).

<u> $Cd(HPz^*)Cl_2$ </u>. To a solution of (3-Fc, 5-Me)Pz (0.266 g, 1 mmol) in 10 mL alcohol, a solution of CdCl₂ (0.550 g, 3 mmol) in 15 mL alcohol was added and stirred at room temperature for 24 h. The orange-yellow powder obtained on filtration was washed with alcohol and ethyl ether successively, yield 0.414 g (93%).

RESULTS AND DISCUSSION

The general equation for the formation of the complexes is shown below.

n Ligand + MCl₂ $\xrightarrow{\text{alcohol}}$ (Ligand)n MCl₂ M = Cd, n = 1. M = Zn, n = 2

The complexes are stable in air. They are soluble in DMSO and DMF but scarcely soluble in other common organic solvents.

Coordination Behavior Studies

Both the steric effect of the substituents on pyrazole and the properties of the metal ions affect the coordinating reaction and the stability of the complexes.

Under the same experimental conditions, HPz^* [(3-Fc, 5-Me)Pz] can coordinate with ZnCl₂ and CdCl₂ but HPz' [(3-Fc, 5-Ph)Pz] can't. Various attempts have been made by changing the solvent and the ratio of metal to ligand. Gray powders were isolated and the elemental analyses indicated that they are not the analogous complexes.

The different coordination behavior between HPz* and HPz' can be rationalized by the following tautomeric equilibrium in the free ligand⁶:

When R' = Fc, its electron donating property increases the electron density of the pyrazolyl ring. On the other hand, its steric effect makes it more difficult for the metal ion to approach the pyridine nitrogen^{1,8} in form I. As a result, ferrocene-



Fig. 1. The Tautomeric Equilibrium of Two Possible Forms of Pyrazol Ligand.

containing pyrazoles often act as pyridine-like ligands in form II. When $R = CH_3$ (the structure of the expected complex is described as (1) in Fig. 2), the σ bond of CH₃-C (ring) can rotate freely and the hydrogen atoms of CH₃ exert little hindrance on the metal ion. When R = Ph (the structure of the complex is illustrated as (2) in Fig. 2), the phenyl and the pyrazolyl rings are limited to the same plane for the π - π * conjugation. The σ bond of C(Ph)-C(Pz) can't rotate freely. Thus the 2(6)-hydrogen on the phenyl ring hinders the metal ion and the complexes of HPz' were not obtained.

In addition, many attempts at the synthesis of the Hg(II) complexes have been made, but were not successful. In all cases, gray powders are obtained which are insoluble in all of the organic solvents available (including DMSO and DMF) and the contents of C, H, and N are far lower than the calculated values according of the elemental analyses. It may be possible that the polarization effect of Hg(II) is too strong to maintain the framework of the pyrazolyl ring, and the ligand decomposed on complexation.

IR Spectra

The infrared spectra of the free ligand show one medium strong band at 3254.1 cm⁻¹, assigned to the N-H stretching vibration. The weak band at 3107.0 cm⁻¹ is attributed to the stretching vibration of C-H in the ferrocenyl ring. Pyrazolyl ring absorptions are located at 1581.2 cm⁻¹, 1540.2 cm⁻¹ and 1417.2 cm⁻¹, and some absorptions of the ferrocenyl ring are observed at 1269.5 cm⁻¹, 1056.2



Fig. 2. Different Mode of Complexation of HPz* (1) and HPz' (2) to Metal Ion.

Compound	Empirical	F . W .	Color	M.p.	Yield	Elemental Analyses (%) Found (Calc.)		
	Formula			(T)	(%)	С	Н	N
HPz•	C14H14N2Fe	266	orange- yellow	162-163	97	63.01(63.19)	5.23(5.30)	10.77(10.53)
Zn(HPz*)2Cl2	C28H28N4Cl2ZnFc2	668	orange- yellow	202.5-204.5	81	50.53 (50.30)	4.32 (4.22)	8.16 (8.38)
Cd(HPz*)Cl ₂	C14H14N2Cl2CdFe	449	orange- yellow	275-278	93	37.74 (37.41)	2.99 (3.14)	5.63 (6.23)
HPz'	C19H16N2Fe	326	yellow	267-269	90	69.78(69.53)	5.02(4.91)	8.33(8.54)

Table I. Analytical and Physical Data

Table II. IR Data

Compound	v(N-H)	v(C-H) (ferrocenyl)	υ(C=N)	υ(C=C) (pyrazolyl)	v(C=C) (ferrocenyl)
HPz*	3254.7 m	3107.0 w	1212.1	1581.2, 1417.2 w	1269.5, 1105.5
$Zn(HPz^*)_2Cl_2$	3369.5 s	3098.8 w	1203.9	1589.4, 1491.0 w	1277.7, 1105.5
	3336.7 s			1450.0	
Cd(HPz*)Cl ₂	3295.7	3098.8 w	1203.9	1597.7, 1491.0 w	1285.9, 1105.5

Table III. ¹H NMR Data

Compound	δ	δ _{m-}	δ _{C5H5}	$\delta_{H(N)}$	δ _{H(C)}	δ _{CH3}
HPz*	4.58	4.23	4.05	8.56	6.08	2.30
$Zn(HPz^*)_2Cl_2$	4.57	4.35	4.11	10.91	6.15	2.20
$Cd(HPz^*)Cl_2$	4.65	4.25	4.01	12.38	6.08	2.16

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cm⁻¹ and 752.73 cm⁻¹. There are some striking differences between the ligand and its coordinating compounds: **a**) the N-H stretching frequency shifts to a higher wave number, which is consistent with the fact that electrons of ferrocene transfer to the pyrazolyl ring after coordination, **b**) υ (C-H) (ferrocenyl ring) shifts to lower wave number due to electrons shifted away from ferrocene, **c**) υ (C=N) and υ (C=C) of pyrazole and ferrocene varied little due to the former reasons.

¹<u>H NMR Spectra</u>

In the ¹H NMR spectra, there are three signals in the region 4.00-5.00 ppm with a 2 : 2 : 5 ratio. This is characteristic of monosubstituted ferrocene derivatives. Since the pyrazolyl ring acts as an electron donating group in the free ligands, the chemical shifts of the cyclopentadienyl protons increase in the order $\delta_{\text{ortho}} > \delta_{\text{meta}} > \delta_{C5H5}$ Upon coordination, the chemical shifts of the ferrocenyl and pyrazolyl hydrogens shift downfield, which confirms the former conclusion that the ligand is a Lewis base and electrons flow from the ferrocenyl ring to the pyrazolyl ring and then to the metal ion through the pyridine nitrogen. The N-H peak at 8.56 ppm (in the free ligand HPz*) shifts to 10.91 ppm in Zn(HPz*)₂Cl₂ and 12.38 ppm in Cd(HPz*)Cl₂. A plausible explanation is that the electron density of the pyrazolyl ring tends to equalize after coordinating, and the strengthened antimagnetic ring current of the pyrazolyl ring is responsible for the downfield shifts of the N-H proton.

Based on the above discussion, the suggested structures of the complexes synthesized are illustrated in Fig. 3.

Cyclic Voltammetric Measurements

The redox reversibility of ferrocene often serves as an electron microprobe, which makes C.V. analysis of ferrocene-containing compounds possible. The \overline{Ep} ($\overline{Ep} = 1/2(Ep_a+Ep_c)$) values vary according to the properties of the substituents attached to it. Thus, by judging the change in \overline{Ep} , we can determine the direction



Fig. 3. Suggested Structures of the Complexes.

Table IV. C.V. Data*

Compound	Ep _a (V)	Ep _c (V)	Ēp (V)	$ip_a \times 10^7 (A)$	$ip_c \times 10^7 (A)$	ip _a /ip _c
Fc-H	0.148	0.070	0.109	5.78	5.90	0.98
HPz*	0.138	0.065	0.102	2.00	1.83	1.09
$Zn(HPz^*)_2Cl_2$	0.143	0.075	0.109	2.14	1.86	1.15

* Ep_a is anodic peak potential, Ep_c is cathodic peak potential, $\overline{Ep} = 1/2(Ep_a + Ep_c)$, ip_a is anodic peak current, and ip_c is cathodic peak current.

of electron transfer. In the free ligand, the pyrazolyl ring releases electrons to ferrocene which makes Fe(II) easier to be oxidized, while in the complexes \overline{Ep} emerges at higher potentials compared to the ligand. This is further evidence of the former conclusion.

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