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Studies on Some Binuclear Metal Complexes of Tetradentate Ligands Derived from Isonitrosoacetophenones and Benzidine

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STUDIES ON SOME BINUCLEAR METAL COMPLEXES OF TETRADENTATE LIGANDS DERIVED FROM ISONITROSOACETOPHENONES AND BENZIDINE

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ABSTRACT

Tetradentate ligands derived from some isonitrosoacetophenones and benzidine and their binuclear complexes of the type $M_2L_2.4H_2O$ {L = bis[2-hydroxyimino-1-(4-X-phenyl)-1-ethylidene]benzidine, X = H, Cl, Br, CH₃; M = Fe(II), Co(II), and Ni(II)} have been synthesized and characterised by elemental analyses, molar conductance, magnetic susceptibility, electronic, PMR and IR spectra. Substitution in the phenyl ring of the complexes produces shifts in the azomethine stretching vibration $\nu_{(C=N)}$ which are related to the Hammett's substituent parameter. The magnetic moments and electronic spectra indicate octahedral geometry for the complexes.

INTRODUCTION

Metal complexes with ligands capable of coordinating to two or more metal ions have evoked much interest in

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coordination chemistry¹⁻⁵. The metal complexes of the ligands bis(acetylacetone)benzidine⁶⁻⁸, bis(salicylalde-hyde)benzidine⁹ and bis(p-dimethylaminobenzilidene)benzidine¹⁰ are reported. In view of the interesting ligating behaviour of these systems, we have considered it worthwhile to prepare the tetradentate ligands, bis[2-hydroxyimino-(4-X-phenyl)-1-ethylidene]benzidine, hereafter abbreviated as $(p-X-HINAP)_{2}bz$ (X = H, Cl, Br and CH₃), derived from isonitrosoacetophenones and benzidine, and their metal complexes with Fe(II), Co(II) and Ni(II). The complexes have been characterized by various physico-chemical methods.

RESULTS AND DISCUSSION

Characterisation of Ligands

The condensation of various substituted isonitrosoacetophenones (*p*-X-HINAP) [I] with benzidene [II] gave the tetradentate ligands [III]. The reactions can be represented as shown in Fig. 1.

The elemental analyses, colours and melting points of the various ligands are given in Table I. The thermal stability of the ligands, as reflected in their melting points, increases in the order $(\text{HINAP})_2\text{bz} < (p-\text{Cl}-\text{HINAP})_2\text{bz}$ $< (p-\text{Br}-\text{HINAP})_2\text{bz} < (p-\text{CH}_3-\text{HINAP})_2\text{bz}.$

The IR spectra of the ligands recorded in KBr pellets do not show bands due to free or hydrogen bonded carbonyl groups, usually observed in the region around 1642-1690cm⁻¹ in HINAP and several isonitrosoketones¹¹. This indicates



Fig. 1. Preparation of (p-X-HINAP), bz.

successful replacement of the carbonyl oxygen in p-X-HINAP by azomethine nitrogen in the Schiff base formation during the preparation of the ligands. This is further supported by the appearance of an additional strong band in the region 1600-1640 cm⁻¹ due to $\nu_{(C=N)}$ of the azomethine group, in addition to the band around 1580-1610 cm-1 attributed to the $\nu_{(c=N)}$ mode of the oxime group. The N-H symmetric and asymmetric stretching vibrations observed at 3390-3320 cm⁻¹ in the spectra of benzidene¹² are not observed in the spectra of the ligands. The spectra reveal a broad band near 3200 cm⁻¹ which is assigned to the hydrogen bonded $\nu_{(O-H)}$ mode of the =NOH group. The characteristic bands due to the phenyl ring systems in the ligands are found in the region 1440-1500 cm⁻¹. The N-O stretching vibrations are observed in the form of a medium to strong intensity band at 985-990 cm⁻¹.

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TABLE I

Colour, Decomposition Temperature, Magnetic Susceptibility and Analytical Data^a of the Ligands and the Metal Compleyed

	Н\$
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	Decompo-
	Yield
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400	Empirical

Complex	Empirical formula	Colour	Yield (%)	Decompo- sition tempera-	W\$	U %	N 8	H%	μ _{•εε} (B.M.)
(1)	(2)	(3)	(4)	ture (°C) (5)	(9)	(7)	(8)	(6)	(01)
zd ₂ (HINAP)	C ₂₈ H ₂₂ N4O2	Brown	60	106 ^b		75.81 (75.31)	12.59 (12.54)	5.24 (4.96)	
(p-Cl.HINAP) ₂ bz	C ₂₈ H ₂ ,Cl ₁₂ N ₄ O ₂	Reddish Brown	65	215 ^b		64.82 (65.24)	11.23 (10.86)	4.25 (3.91)	
$(p-Br.HINAP)_{2}bz$	C ₂₈ H ₂ ,Br ₂ N ₄ O ₂	Yellow	55	230 ^b		56.24 (55.62)	9.01 (9.27)	4.02 (3.33)	
(P-CH3.HINAP)2bz	C ₃₀ H ₂₆ N4O ₂	Brown	60	280 ^b		76.1 4 (75.92)	12.02 (11.80)	5.14 (4.67)	
[Fe(INAP) ₂ bz.2H ₂ 0] ₂	Fe ₂ C ₅ eH ₄ eN ₈ O ₈	Green	40	240	10.63 10.41)	63.02 (62.69)	10.65 (10.44)	4.52 (4.51)	2.43
[Fe (Cl . INAP) 2bz .2H20] 2	Fe ₂ C ₅ ,H ₄ Cl ₄ N ₆ O	green	45	210	9.14 (9.22)	54.23 (55.55)	9.62 (9.25)	3.86 (3.66)	2.19

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[Fe(Br.INAP) ₂ bz.2H ₂ 0] ₂	Fe ₂ C ₅ 6H ₄ Br ₄ N ₆ O	green	60	185	7.98 (8.04)	47.62 (48.44)	7.98 (8.07)	2.92 (3.19)	2.49
[Fe (CH ₃ . INAP) ₂ bz. 2H ₂ 0] ₂	Fe ₂ C ₆₀ H ₅ ,N ₆ O ₈	Green	45	250	10.45 (9.89)	62.94 (65.24)	10.25 (10.86)	5.42 (3.91)	2.21
[Co (INAP) ₂ bz . 2H ₂ 0] ₂	Co₂C₅€H₄₅NgOg	Red	65	180	11.54 (10.91)	61.96 (62.28)	9.62 (10.37)	3.69 (4.48)	4.54
[Co (C1. INAP) ₂ bz. 2H ₂ 0] ₂	ຬօ [຺] ຬ຺ຩ຺຺ຬ1 ຺ ຑ ຺ ໐	s Red	60	160	10.25 (9.68)	54.26 (55.27)	8.60 (9.20)	3.92 (3.64)	4.48
[Co (Br. INAP) ₂ bz. 2H ₂ 0] ₂	Co ₂ C ₅ ,H ₄ ,Br ₄ N ₈ O	, Red	58	150	9.45 (8.45)	49.23 (48.23)	7.46 (8.03)	2.63 (3.18)	5.04
[Co (CH ₃ . INAP) ₂ bz . 2H ₂ 0] ₂	ເວ [ຼ] ເ₀,H₅,N _ຍ 0	Ređ	60	190	11.43 (10.38)	62.42 (63.49)	10.24 (9.87)	5.24 (4.96)	4.45
[Ni (INAP) ₂ bz.2H ₂ 0] ₂	Ni ₂ C ₅ eH ₄ eNeO ₈	Yellow	40	260	11.54 (10.89)	61.45 (62.36)	11.40 (10.39)	4.70 (4.49)	2.94
[Ni (Cl: INAP) _z bz.2H ₂ 0] ₂	Ni ₂ C ₅ 6H ₄₄ Cl ₄ N ₈ O	[.] Yellow	4 D	230	10.24 (9.65)	56.02 (55.29)	8.60 (9.21)	3.98 (3.64)	2.96

(Contd)

							Table	л(С	ontd).
(1)	(2)	(3)	(4)	(5)	(9)	(1)	(8)	(6)	(10)
[Ni (Br. INAP) ² bz.2H ₂ 0] ₂	Ni ₂ C56H44Br4Ng0 ₈	Yellow	50	200	9.64 (8.42)	47.93 (48.24)	7.50 (8.03)	3.62 (3.18)	2.88
[Ni (CH ₃ . INAP) ₂ bz. 2H ₂ 0] ₂	Ni ₂ C ₆ ,H ₅ N ₈ O ₉	Yellow	6 5	260	10.45 (10.34)	62.24 (63.51)	10.40 (9.87)	3.85 (4.97)	2.98
^a Calculated values	are given in pe	arenthese		1					

Melting point.

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The absence of NH₂ proton signals in the PMR spectra of the ligands in DMSO further corroborates the conclusion regarding successful Schiff base formation by replacement of the C=O group arrived at on the basis of infrared studies. The other PMR spectral data of the ligands are presented in Table II. The analytical data and spectral properties of the ligands are consistent with their structures [III] in Fig. 1.

Characterization of Metal Complexes

The analytical and physical data on the metal complexes of the ligands are presented in Table I. The complexes are brightly coloured and thermally stable at least upto 150°C. They are insoluble in water and common organic solvents but are somewhat soluble in DMF at room temperature. The analytical data of the metal complexes (Table I) indicate that the complexes have 1:1 metal-ligand stoichiometry. The values of molar conductance in DMF solution at 10⁻³ M dilution are in the range 0.14-0.40 ohm⁻¹ cm² mole⁻¹ suggesting a non-electrolyte nature of these complexes¹³. The ligands [III] have four coordination sites but involvement of all four donor atoms in bonding to the same metal in the formation of a complex is sterically not favourable. However linear dimers^{10,14} are possible and the structure of the complexes may be represented as shown in Figure 2. The analytical data of the complexes (Table I) is consistent with their formulation as [ML.2H,0], where M = Fe(II), Co(II), Ni(II) and L represents the benzidino derivatives of the deprotonated isonitrosoacetophenones, i.e. (p-X-INAP),bz.

Infrared spectra of the metal chelates are complex and it is not possible to assign all the bands without

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TABLE II

Proton Magnetic Resonance Shifts^a of Schiff Base Ligands and their Assignments

bz Assignments	Hydroxy imino proton	C-H proton of HINAP	Phenyl protons of benzidine	Phenyl protons of p-X-HINAP	CH ₃ protons	
(p-CH ₃ .HINAP) ₂	12.0	8.4	6.6-7.2	7.3-7.8	2.4	
(p-Br.HINAP) _z bz	12.2	. 8	6.6-7.2	7.6-8.0	I	
$(p-Cl.HINAP)_{2}bz$	12.2	8.4	6.6-7.2	7.6-8.0	1	
(HINAP) ₂ bz	11.7	8.6	6.6-7.2	7.4-8.0	1	

In ppm relative to TMS.

đ



(IV)

 $X = H, Cl, Br, CH_3$ $M = Fe^{II}, Ni^{II}, Co^{II}$

Fig. 2. Proposed Structures for the Fe^{II}, Ni^{II} and Co^{II} Complexes of Bis[2-hydroxyimino-1-(4-X-phenyl)-1-ethylidene]benzidine.

ambiguity. However, structurally important bands such as those due to $\nu_{_{\rm (O-H)}},\;\nu_{_{\rm (C=N)}},\;\nu_{_{\rm (C-N)}}$ and $\nu_{_{\rm (N-O)}}$ modes are distinguishable and provide unequivocal evidence regarding the structural features of the ligands and their manner of bonding with metal ions. Neutral complexes of Fe(II), Co(II) and Ni(II) of the type $[ML.2H_0]$, $\{L=(p-X-INAP), bz\}$ show strong and broad bands around 3300 cm⁻¹. These attributed to asymmetric and symmetric bands are stretching modes of water and their centre of gravity near 3300 cm⁻¹ implies coordination of water ions. In all the molecules to the metal metal complexes the $v_{(C=N)}$ vibrations undergo a shift to lower energy indicating coordination of the azomethine nitrogen and oxime nitrogen atoms of the ligand. This view is further supported by the appearance of the band corresponding to the metal-nitrogen stretching vibration at 515-523 cm⁻¹ in the complexes¹⁵. The IR bands due to phenyl ring systems between 1500-1400 cm⁻¹ are almost unaffected in the metal complexes. The (N-O) band shifts to higher frequency at 1193-1249 cm⁻¹ in the complexes indicating coordination through the nitrogen atom of the oxime group⁵. Infrared spectra also indicate that $v_{(c-N)}$ (azomethine stretch) is affected by substitution in the phenyl moiety of the parent ligand. In the metal chelates, there are both σ and π interactions and $v_{(C=N)}$ (azomethine stretch) decreases in the order Me>H>Cl>Br and this sequence is consistent with the Hammett's σ values (Me:-0.17, H: 0, Cl: 0.224, Br: 0.232). The electron releasing substituents like the methyl group tend to increase the electron density on the nitrogen of the C=N groups, thereby facilitating strong σ but poor π -interaction. The shift to lower energy observed in the complex with a chloro substituent is indicative of backbonding. For the same substituent in the phenyl ring, $v_{C=N}$ (azomethine stretch) varies as Fe>Co>Ni indicating extensive delocalization of electrons from the highly populated d-orbitals into π * orbitals of the ligand. This order is in keeping with the Irwing-Williams order of stabilities.

Magnetic Properties

The magnetic moments of the Fe(II) complexes at room temperature are in the range 2.1-2.5 B.M. which are intermediate between the range expected for spin-paired and spin free Fe(II) complexes. The possibility of the observed magnetic moments arising from the presence of Fe(III) species is ruled out on the basis of the results of repeated analysis and the fact that the preparation of

the complexes is carried out in the presence of sodium thiosulphate, a reducing agent. A possible explanation of the observed anomalous magnetic moments of these complexes could be based on a spin cross-over between ${}^{5}T_{2g}$ and ${}^{1}A_{2g}$ states¹⁶. Alternatively, the presence of the S=1 ground state can give rise to such intermediate moments¹⁷. It is interesting to note here that such intermediate magnetic moments are also observed in Fe(II) complexes of some carbonyl oximes¹⁸ and hydrazonyl derivative of isonitrosopropiophenone¹⁹.

The magnetic moments of the Co(II) and Ni(II) complexes are in the range 4.44-5.04 B.M. and 2.88-2.98 B.M., respectively, (Table I) and are suggestive of an octahedral geometry for these complexes.

Diffuse Reflectance Spectra

A distortion in the regular octahedral geometry is evidenced by the peak observed for the transitions at 13.5-17.0 kK, which, along with the intermediate¹⁹ magnetic moments obtained for the Fe(II) complexes, suggest that some mixing of the ${}^{1}A_{2g}$ state with the ${}^{5}T_{2g}$ state may be responsible for the observed spectral characteristics. The diffuse reflectance spectra of the Co(II) complexes exhibit three bands in the range of 7.14-7.16 kK, 15.00-16.13 kK and 18.5-20.00 kK, which may be ascribed to the transitions ${}^{4}T_{1g}(F) ---> {}^{4}T_{2g}(F) (v_{1})$, ${}^{4}T_{1g}(F) ---> {}^{4}A_{2g}(F) (v_{2})$ and ${}^{4}T_{1g}(F) ---> {}^{4}T_{1g}(P) (v_{3})$, respectively, characteristic of octahedral geometry. The Ni(II) complexes show the dd transition bands in the range of 8.35 - 10.60 kK, 13.50 - 18.51 kK and 23.00 - 25.00 kK, which are assigned as ${}^{3}A_{2g}(F) ---> {}^{3}T_{2g}(F) (v_{1})$, ${}^{3}A_{2g}(F) ---> {}^{3}T_{1g}(F) (v_{2})$ and ${}^{3}A_{2g}(F)$ ---> ${}^{3}T_{1g}(P)$ (v_{3}) transitions, respectively. The Dq, B, β and v_{2}/v_{1} values given in Table III are in good agreement with the proposed octahedral structure. Various spectral parameters have been calculated according to the equations of König²⁰. The B values for the complexes are lower than those for the free ion value which is an indication of orbital overlap and delocalization of d-orbitals. The present β -values are less than unity suggesting considerable covalent character of the metal-ligand bonds. From the value of Dq and B thus obtained, the transition v_{2} or v_{3} have also been calculated. The experimental values are seen to be in good agreement with the calculated ones.

Thermogravimetric Analysis

The decomposition temperatures (Table I) indicates that for various metal complexes the thermal stability increases in the order of Co(II) < Fe(II) < Ni(II). The observed order of thermal stability indicates the trend in metal-ligand bond strength in the solid state. The weight loss between 130°-200°C in the Fe(II) and Ni(II) complexes and between 120°-150°C in the Co(II) complexes corresponds to the loss of four coordinated water molecules. The observed and calculated weight loss for the metal complexes due to coordinated water molecules is presented in Table IV. The loss of coordinated water moleclues at a temperature in the range 110°-150°C has also been reported for bis(benzylidene)-benzidine complexes of Mn(II), Co(II) and Ni(II)¹⁴, and bis(p-dimethylaminobenzylidene)benzidine complexes of trivalent lanthanides¹⁰. Thus, the results of the thermal studies indicating the presence of

coordinated water molecules in the metal complexes further corroborate the assumption made on the basis of infrared spectral studies.

EXPERIMENTAL

<u>Materials</u>

All chemicals used in the present work were of AR grade. Benzidine (Renal, Hungary) was recrystallized, while the solvents were purified and double-distilled before use.

METHODS

Preparation of Ligands

Isonitrosoacetophenone (HINAP) [Ia] was prepared as per the procedure reported²¹. The *p*-substituted derivatives [Ib]-[Id] were prepared in a similar manner using appropriately substituted acetophenones and n-butyl nitrite. The ligands [III] were obtained by condensation of [I] with [II] as follows: 0.01 mole of *p*-X-isonitrosoacetophenone (1.49 g HINAP, 1.83 g *p*-Cl-HINAP, 2.28 g *p*-Br-HINAP or 1.63 g *p*-CH₃-HINAP) and 0.005 mole of benzidine (0.920 g) were dissolved separately in absolute alcohol (15 mL each) and then mixed. 0.01 mole (0.820 g) of fused sodium acetate was added and the reaction mixture was refluxed for six hours. It was cooled and poured into crushed ice, when a yellow to brown coloured compound separated out, which was filtered by suction, washed with 50% alcohol and dried in air. Downloaded by [University of Sydney] at 05:38 29 December 2014

TABLE III

Electronic Spectral Data for Co(II) and Ni(II) Complexes

Complexes	⁴ T ₁₉ (F)> ⁴ T ₂₉ (F)	⁴ T ₁₉ (F) > ⁴ A ₂₉ (F)	⁴ T _{1g} (F)> ⁴ T _{1g} (P)	Dq	а	Я	V ₂ /V ₁
[Co(INAP) ₂ bz.2H ₂ 0] ₂	7.407	15.625 (15.918)	20.000	822.1	893.6	0.920	2.109
[Co(Cl.INAP) ₂ bz.2H ₂ 0] ₂	7.142	15.151 (15.322)	18.518	800.9	816.2	0.840	2.121
[Co(Br.INAP) ₂ bz.2H ₂ 0] ₂	7.142	14.705 (15.348)	19.230	756.3	833.9	0.858	2.058
[Co(CH ₃ .INAP) ₂ bz.2H ₂ 0] ₂	7.692	16.129 (14.569)	20.000	843.7	870.2	0.896	2.096

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[Ni(INAP) ₂ bz.2H ₂ 0] ₂	10.638	18.518 (16.054)	25.000 (22.536)	1063.6	773.6	0.473	1.470
[Ni (Cl.INAP) ₂ bz.2H ₂ 0] ₂	8.695	13.513 (14.168)	23.809 (21.308)	869.5	749.1	0.719	1.584
[Ni (Br. INAP) ₂ bz.2H ₂ 0] ₂	8.695	14.705 (14.168)	23.809 (28.436)	869.5	828.6	0.795	1.691
[Ni (CH ₃ . INAP) ₂ bz. 2H ₂ 0] ₂	8.333	13.888 (13.888)	25.000 (25.055)	833.3	925.9	0.889	1.666

Calculated values are given in parentheses.

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TABLE IV

Thermal Studies for Metal Complexes

Complex	Temperature	% Weight loss d	ue to $4H_2O$
	range (°C)	Calculated	Observed
[Fe(INAP),bz.2H,0],	150-200	6.71	7.02
[Fe(Cl.INAP),bz.2Ho],	160-180	5.94	6.14
[Fe (Br.INAP),bz.2H,0],	130-150	5.18	5.45
[Fe(CH ₃ .INAP) ₂ bz.2H ₂ 0] ₂	160-180	6.37	6.50
[Co(INAP),bz.2H,O],	120-130	6.67	7.01
[Co(Cl.INAP),bz.2H,O],	120-145	5.91	6.13
[Co(Br.INAP),bz.2H,0],	120-130	5.16	5.32
[Co(CH ₃ .INAP) ² bz.2H ₂ 0] ²	130-150	6.34	6.52
[Ni (INAP) ,bz.2H,0] ,	150-190	6.67	6.80
[Ni (Cl.INAP) ,bz.2H,0] ,	140-160	5.91	6.26
[Ni (Br. INAP) , bz.2H, 0] ,	130-150	5.16	5.24
[Ni (CH ₃ . INAP) 2bz. 2H ₂ 0] 2	160-180	5.34	5.45

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Preparation of the Complexes

Equimolar quantities of metal chloride [Co(II) or Ni(II)] and $(p-X-HINAP)_{2}bz$ were dissolved separately in DMF and mixed. The reaction mixture was refluxed for half an hour. The hot solution was poured into crushed ice; the precipitate obtained was allowed to settle, filtered, washed with a water-DMF (1:1) mixture then dried in *vacuo*. For the preparation of the Fe(II) complexes, however, a freshly prepared filtered solution of ferrous sulphate in the minimum quantity of water was used. The preparation was carried out in the presence of sodium thiosulphate (0.005 mole) to prevent oxidation of Fe(II).

The amounts of reactants used for the preparation of the complexes are given in Table V.

Instrumentation

Metal contents in the complexes were determined by standard methods. Conductance was measured in dimethylformamide (DMF) (10^{-3} M solution) on an Elico digital conductivity meter model CM-180. The IR spectra was recorded in KBr discs on a Perkin Elmer model 1600 FTIR spectrophotometer. The reflectance spectra of the complexes in the visible range were taken on a Carl-Zeiss VSU-2P Jena spectrophotometer. The PMR spectra were recorded in DMSO on a VXR-300S Varian Supercon NMR spectrometer using TMS as the internal reference. Magnetic susceptibility measurements were carried out by employing the Gouy method using Hg[Co(SCN)₄] as a calibrant. The effective magnetic moments were calculated after diamagnetic correction for ligand components using Pascal's constants²². Thermogravi-

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TABLE V

Quantities of the Reactants used in Preparation of Metal Complexes

etals		Ligands		
	[IIIa]	[111]	[IIIc]	[IIId]
H₂O ble	(HINAP) ₂ bz 4.46 g 0.01 mole 20 mL DMF	(p-Cl-HINAP) ₂ bz 5.15 g 0.01 mole 20 mL DMF	(<i>p</i> -Br-HINAP) ₂ bz 6.04 g 0.01 mole 20 mL DMF	(<i>p</i> -CH ₃ -HINAP) ₂ bz 4.74 g 0.01 mole 20 mL DMF
H ₂ O ile	(HINAP) ₂ bz 4.46 g 0.01 mole 20 mL DMF	(<i>p</i> -Cl-HINAP) ₂ bz 5.15 g 0.01 mole 20 mL DMF	(<i>p</i> -Br-HINAF) ₂ bz 6.04 g 0.01 mole 20 mL DMF	(<i>p</i> -CH ₃ -HINAP) ₂ bz 4.74 g 0.01 mole 20 mL DMF
H ₂ O le MF	(HINAP) ₂ bz 4.46 g 0.01 mole 20 mL DMF	(<i>p</i> -Cl-HINAP) ₂ bz 5.15 g 0.01 mole 20 mL DMF	(<i>p</i> -Br-HINAP) ₂ bz 6.04 g 0.01 mole 20 mL DMF	(<i>p</i> -CH ₃ -HINAP) ₂ bz 4.74 g 0.01 mole 20 mL DMF

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metric studies of the complexes were made by recording the change in weight on increasing the temperature from room temperature to 300°C at a heating rate of 10°C per minute.

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