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PYRAZOLE AROYL HYDRAZONES AS LIGANDS: COMPLEXES OF 1,3-DIPHENYLPYRAZOLE -4-CARBOXALDEHYDE 2-CHLOROBENZOYLHYDRAZONE WITH Fe(III), Co(II), Ni(II), Cu(II), Zn (II), Cd(II), Hg(II), Sn(II), Bi(III) AND Pb(II)

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The complex formation process of 1,3-diphenylpyrazole -4-carboxaldehyde -2-chlorobenzoyl-hydrazone with different transition and non transition metals were investigated and complexes have been characterized through their metal analysis and by applying spectrophotometric techniques. Job's continuous variation method has been used to calculate the stability constant and stoichiometry of the complexes. The mode of complexation has been studied with the help of infra-red technique. A proposed structure of the complexes involving co-ordination through nitrogen and oxygen of the hydrazone moiety with different metals has been represented.

Key words: Pyrazole, Carboxaldehyde, Chlorobenzoyl hydrazone, Metal complexes, Spectrophotometric techniques.

Introduction

In literature various aroyl hydrazones have been reported being used in the field of medicines (Buu-Hoi *et al* 1953; Ma and Tien 1953), agriculture (Shani 1977) and basic sciences (Katyal and Dutty 1975) due to formation of stable chelates with metals present in the cell (Albert 1953). Due to the presence of several potential co-ordination sites hydrazones also exhibit interesting ligational properties (Maleeque and Chaudhry 1992). Although substituted benzoyl hydrazones have been used as ligands but hydrazone derivatives of pyrazole aldehyde has little reference in the literature as chelating agents. Our findings on the co-ordination behavior of 1,3-diphenylpyrazole-4-carboxaldehyde-2-chlorobenzoyl-hydrazone are reported here.

Materials and Methods

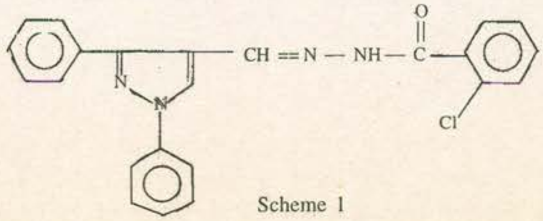
Synthesis of ligand. 1,3-diphenylpyrazole.4-carboxaldehyde (Kira and Abdul Rehman 1969) was condensed with 2-chlorobenzhydrazide in ethanol in the presence of a few drops of phosphoric acid. After heating under reflux for thirty minutes, the desired hydrazone was collected on cooling. It was purified by crystallization in ethanol to give light yellow crystals m.p. 110 °C. The structural formula of the ligand is represented in Scheme 1.

General method for preparation of metal complexes. An ethanolic solution of a metal salt (0.005 mol) was added to an ethanolic solution of the ligand (0.005 mol). The mixture was heated under reflux for 0.5 to an hour. The precipitate obtained on pouring the reaction mixture in distilled water was filtered and washed with cold ethanol, dried and stored in desiccator over anhydrous magnesium sulphate. The results are presented in Table 1.

Metal analysis. The percentage composition of the metals in the complexes presented in Table 1 were carried out by atomic absorption method. The results of these analysis are given in Table 2.

Infra-red spectral measurements. The infra-red spectra of the complexes were taken as KBr discs on Perkin Elmer Infra-red Spectrometer. The important assigned absorption bands are presented in Table 3.

Stability constant calculations. The stability constants (Job 1925; Shirif and Awad 1962) of various complexes of Table I were calculated by applying the spectrophotometric Job's continuous variation method. The stock solutions of ligand and metals ($1x10^{-4}$M) in ethanol were prepared according to the requirement of Job's method. In series of flasks the sum of the number of moles of ligand and the



Scheme 1

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Table 1

Formula, colour, percentage yield and decomposition temperature of complexes

Complex No.	Formula L:M	Colour	Yield(%)	Decomp. point °C
I	$(C_{23}H_{19}N_4OCl)_2Fe$	Black	80	230
II	$(C_{23}H_{19}N_4OCl)_2Co$	Reddish brown	70	240
III	$(C_{23}H_{19}N_4OCl)_2Ni$	Bright orange	45	250
IV	$(C_{23}H_{19}N_4OCl)_2Cu$	Gray	70	250
V	$(C_{23}H_{19}N_4OCl)_2Zn$	Off white	65	230
VI	$(C_{23}H_{19}N_4OCl)_2Cd$	Off white	50	225
VII	$(C_{23}H_{19}N_4OCl)_2Hg$	Off white	50	220
VIII	$(C_{23}H_{19}N_4OCl)_2Sn$	Off white	40	250
IX	$(C_{23}H_{19}N_4OCl)_2Bi$	Off white	65	250
X	$(C_{23}H_{19}N_4OCl)_2Pb$	Off white	80	250

number of moles of metal were kept constant. The pH values were adjusted and their absorbance was measured at λmax. The stoichiometry of various complexes was determined by plotting absorbance against various concentrations of the ligand and metal. These graphs were used to determine the stability constants of various complexes by using the following formula:

$$K_f = \frac{\dfrac{A}{Aex}Cm}{(Cm - A/AexCm)(C_l - A/AexCm)}$$

Where A= Observed absorbance, Aex = Extrapolated absorbance, Cm = Concentration of metal, Cl = Concentration of ligand and K_f = Stability constant/formation constant:

The results obtained by this method are reported in Table 4.

Table 2

Amount of metals in complexes of 1, 3-iphenylpyrazole 4-carboxaldehyde 2-chlorobenzoylhydrazone.$[C_{23}H_{19}N_4OCl]_2M$

Complex no.	Metal	Found (%)	Calculated (%)
I	Iron	7.75	6.54
II	Cobalt	7.05	6.87
III	Nickel	7.20	6.87
IV	Copper	8.90	7.30
V	Zinc	7.85	7.50
VI	Cadmium	13.50	12.28
VII	Mercury	21.45	20.22
VIII	Tin	14.75	12.85
IX	Bismuth	25.50	20.70
X	Lead	23.56	20.56

Results and Discussion

The percentage of metals present in the complexes was determined with the help of atomic absorption and the comparison of found percentages of metals with the calculated ones indicate that ligand forms complexes with the metals in the ratio of L:M::2:1 as indicated in the Table 1 and 2.

Assignment of the important infra-red absorption bands of the free ligand which help in understanding of the behaviour of bonding in complexes by showing displacement of respective absorption bands are represented in Table 5.

The study of infra-red absorption bands (Table 5) reveal that absorption bands due to C=O and C=N of the free ligand at 1650 and 1595 cm^{-1} respectively show displacement. The N-H absorption band at 3180 cm^{-1} remains unaffected, while C=O absorption band appears between 1610 to 1645 cm^{-1} on complexation representing a displacement of 5 to 40 cm^{-1} and C=N also shows a displacement of 5 cm^{-1} on complexation.

Stability constant and stoichiometry of complexes have been determined by using spectrophotometric Job's continuous variation method . The results reveal that in these complexes ligand to metal ratio is 2:1. The values of stability constants represented in Table 4 except complex III are in agreement with the general order of stability of complexes Fe < Co < Ni < Cu > Zn which has been already established (Grinberg and Yatsimerski 1952; Irving and Williams 1953; Mustafa and Wafa 1990).

The spectrophotometric calculation of the complexes carried out by atomic absorption and spectrophotometric Job's continuous variation method reveal that complexes are formed by the ratio of M:L::1:2. The ligand can form complex with the metal by co-ordinating through either the ketonic or enolic form. Investigation of characteristic absorption bands in the infra-red spectra are of great help in deciding the mode of co-ordination. It is well known that N-H gives a broad absorption band which shifts to lower frequency on co-ordination involving nitrogen as observed in the case of ammonium, amine, hydrazones and acidhydrazides etc. metal complexes (Narang and Agarwal 1975; Mustafa and Wafa 1990). The ligand gives a very strong absorption band at 3180 cm^{-1} in the N-H stretching frequency region which remains unaffected showing non participation of this group in complexation. The literature indicates that the carbonyl absorption band of ligand totally disappears only when it is enolized, it appears at lower frequency when it is involved in complexation. In the present case carbonyl absorption band of free ligand shows only a displacement of 5 to 40 cm^{-1}, which indicates that it is not enolized (Narang and Agarwal 1975; Yong Xiang 1489). A strong absorption band of C=O appears (Dutta and Sarkar 1981) at 1595 cm^{-1}, which on complexation exhibits a negative displacement of 5 cm^{-1} in most of the cases. The displacement on complexation confirms the co-ordination through nitrogen.

Based on the above evidence it is inferred that ligand forms complexes with the transition and non transition metals. On complexation C=O and C=N give absorption bands at lower

Table 3

Infrared spectra of 1,3-diphenynpyrazole 4-carboxaldehyde 2'-chlorobenzoylhydrozone and its complexes

Complex .No	Bands (cm^{-1}) and Intensity
Ligand	3180s 3040s 1650vs 1595s 1560s 1530s 1495s 1440w 1410vw 1375m 1350m 1300s 1270m 1210s 1160w 1120vw 1060m 1045s 1015s 950m 910m
I	3170m 3040m 1640vs 1590s 1560m 1530m 1500s 1440w 1350m 1300m 1210s 1150w 1045s 950s
II	3040w 1610m 1590s 1525s 1490vs 1430m 1360s 1205s 1150m 1045m 1010m 950m 900m 800w 750s
III	3175w 3040m 1610m 1590m 1520s 1510vs 1500s 1460s 1440m 1410m 1360s 1330vs 1275m 1210vs 1175w 1140w
IV	3180w 3040w 1610m 1590m 1565m 1490vs 1410m 1360s 1340s 1210s 1150w 1040s 1005s 950m 910w.
V	3180w 3040m 1635vs 1590s 1560m 1495vs 1440w 1430vw 1410m 1360s 1350s 1300s 1210s 1050w 1045s.
VI	3180m 3050m 1640vs 1590s 1560s 1530m 1495w 1490w 1385m 1350m 1300s 1210m 1160w 1065w 1040s 950m.
VII	3180s 3040s 1645vs 1590s 1530s 1495s 1440m 1390m 1380m 1340m 1300s 1210s 1150m 1120w 1045s 1010w
VIII	3180s 3040s 1640vs 1595vs 1560s 1530s 1500vs 1440m 1410w 1375s 1350s 1300vs 1210vs 1160m 1120m 1060s
IX	3180s 3040s 1645vs 1595s 1560s 1530m 1495m 1380vs 1350s 1300s 1210m 1065m 1045m 720m 715m 685m.
X	3180m 3040s 1640vs 1590s 1560m 1530s 1495s 1440m 1390m 1380m 1335m 1300s 1210s 1160w 1120vw 1065w

Table 4

Stability constants of 1,3-diphenylpyrazole 4-carboxaldehyde 2- chlorobenzoyl-hydrazone (10-4 M) with metal salts

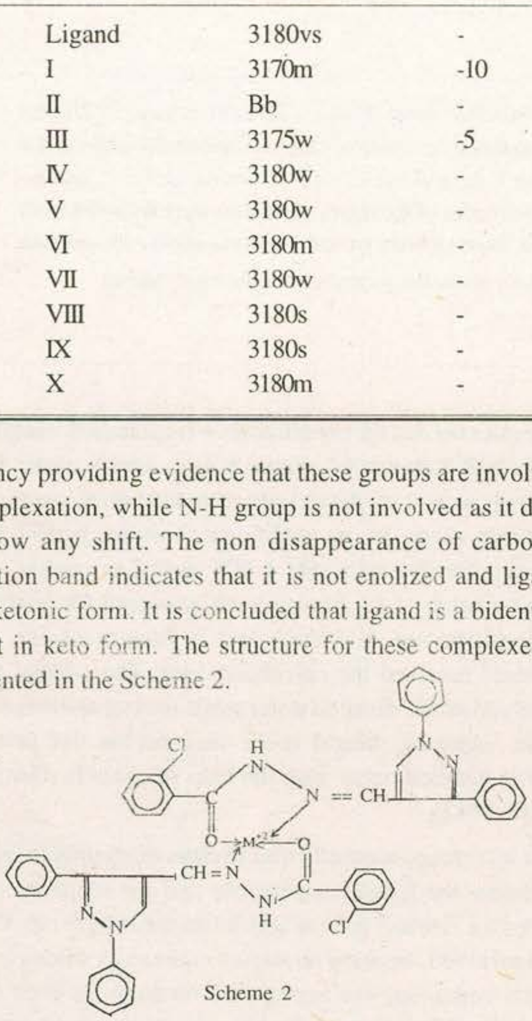
Complex No.	Metal (10^{-4}M)	A	Aex	K_f	M:L	log K_f
I	Iron (III) Chloride	2.75	2.78	8.48×10^7	1:2	7.92
II	Cobalt (II) Chloride	1.71	1.75	2.85×10^8	1:2	8.45
III	Nickel (II) Chloride	3.09	3.12	1.07×10^8	1:2	8.03
IV	Copper (II) Chloride	2.83	2.84	7.68×10^8	1:2	8.88
V	Zinc (II) Chloride	2.30	2.34	3.36×10^8	1:2	7.53
VI	Cadmium (II) Chloride	2.87	2.89	2.02×10^8	1:2	8.30
X	Lead (II) Acetate	2.75	2.76	7.77×10^8	1:2	8.89

Table 5

Important Infra-red spectral bands (cm^{-1}) of 1,3-diphenylpyrazole 4-carboxaldehyde 2-'chlorobenzoylhydrazone and its complexes

S.No	COMP. No	<-NH	SFT in <-NH	<-C=O	SFT in C=O	<-C=N	SFT in C=N
1	Ligand	3180vs	-	1650vs	-	1595s	-
2	I	3170m	-10	1640vs	-10	1590s	-5
3	II	Bb	-	1610m	-40	1590m	-5
4	III	3175w	-5	1610m	-40	1590m	-5
5	IV	3180w	-	1610m	-40	1590m	-5
6	V	3180w	-	1625vs	-15	1590s	-5
7	VI	3180m	-	1640vs	-10	1590s	-5
8	VII	3180w	-	1645s	-5	1590s	-5
9	VIII	3180s	-	1640s	-10	1590vs	-
10	IX	3180s	-	1645s	-5	1595s	-
11	X	3180m	-	1640vs	-10	1590s	-5

frequency providing evidence that these groups are involved in complexation, while N-H group is not involved as it does not show any shift. The non disappearance of carbonyl absorption band indicates that it is not enolized and ligand act in ketonic form. It is concluded that ligand is a bidentate and act in keto form. The structure for these complexes is represented in the Scheme 2.



Scheme 2

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