

PYRAZOLE AROYL HYDRAZONES AS LIGANDS-I 1,3-DIPHENYLPYRAZOLE-4-CARBOXALDEHYDE BENZOYL HYDRAZONE AS LIGAND FOR METAL COMPLEXES

Irshad Ahmad^a, Misbahul Ain Khan^b and Makshoof Athar^b

^aDepartment of Chemistry, Government Gordon College Rawalpindi, Pakistan

^bDepartment of Chemistry, Islamia University, Bahawalpur, Pakistan

(Received 9 December 1999; accepted 12 April 2001)

The 1, 3-diphenylpyrazole-4-carboxaldehyde benzoyl hydrazone on reaction with various metals gave corresponding complexes which were characterized through their metal analysis and by applying spectrophotometric techniques. Stability constants of these complexes were also calculated by spectrophotometric Job's continuous variation method. A tentative structure of complexes involving co-ordination through nitrogen and oxygen of the hydrazone moiety with the metals is suggested.

Key words: Pyrazole, Carboxaldehyde, Benzoylhydrazone, Metal complexes, Spectrophotometric techniques, Stability constant.

Introduction

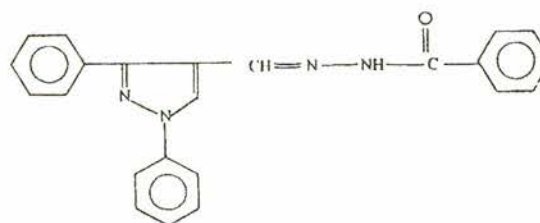
Since Sacconi's (Sacconi 1953) work on aroyl and acyl hydrazones several chemicals have studied behaviour of hydrazones as chelating agent for transition and non-transition metals (Sayed and Iskander 1971; Teotia *et al* 1980; Dutta and Sarkar 1981; Dutta and Kuntala 1989; Bhagi *et al* 1989).

Literature reveals hydrazones are used as herbicides, insecticides, nematocides, rodenticide, plant growth regulators. Plasticizers, stabilizers for polymer, polymerization initiators and antioxidants (Katyal and Dutt 1975). Recently aroyl hydrazones have been studied extensively from the analytical point of view. (Dey *et al* 1991; Dey *et al* 1992; Malik and Chaudhry 1992; Dey and Nandi, 1994).

Although both transition and non-transition metal complexes of aroyl hydrazone ligands have been studied in recent years. No such work on the metal complexes of the aroyl hydrazone derived from condensation of benzoyl hydrazide with 1, 3-diphenyl pyrazole-4-carboxaldehyde have been described in the literature. Presently, we would like to report our results on the chelating potential of benzoyl hydrazone of 1, 3-diphenylpyrazole-4-carboxaldehyde.

Experimental

Synthesis of organic ligand. The ligand 1, 3-diphenylpyrazole-4-carboxaldehyde benzoyl hydrazide was synthesized by refluxing 1, 3-diphenylpyrazole-4-carboxaldehyde (Kira *et al* 1969) with benzoyl hydrazide for thirty minutes. The hydrazone was obtained by cooling and was recrystallized in ethanol to give light yellow crystals m.p. 110°C.



General method for preparation of metal complexes. Solution (0.005 mol) of the metal salts in ethanol were refluxed with the ethanolic solution (0.005 mol) of ligand for a period of thirty to sixty minutes. The complexes were obtained by pouring the reaction mixture in distilled water. They were purified by recrystallization in ethanol 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.

Infrared spectral measurements. The infrared 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 were calculated by applying the spectrophotometric Job's continuous variation method. The stock solution of ligands and metals (1×10^{-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 plus sum of the number of

*Author for correspondence

moles of metal were kept constant. The pH values were adjusted and their absorbance was measured at a λ_{\max} . 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.

$$K_f = \frac{\frac{A}{A_{ex}} C_m}{(C_m - A/A_{ex} C_m)(C_l - A/A_{ex} C_l)}$$

A = Observed absorbance

A_{ex} = Extrapolated absorbance

C_m = Concentration of metal

C_l = Concentration of ligand

K_f = Stability constant/formation constant:

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

Results and Discussion

1, 3-Diphenylpyrazole-4-carboxaldehyde benzoyl hydrazone is found to form complexes with metals in ratio L : M :: 2 : 1 as indicated in Table 1 and 2.

The infrared spectra values of 1, 3-diphenylpyrazole-4-carboxaldehyde benzoyl hydrazone and complexes with different metals are given in Table 3. While relevant bands under consideration and their shift on complexation are shown in Table 5.

The free ligand exhibits characteristic bands in the spectrum but the bands belonging to N-H, C=O and C=N modes of stretching (Dyer 1974; Bellamy 1980) appearing at 3160, 1634 and 1590 cm⁻¹ respectively are of interest being diagnostic in complexation process. The strong band at 1590 cm⁻¹ of the ligand is due to C=N stretching frequency (Dutta and Sarkar 1981). In complex No. I, II, III, IV, VI, VIII, IX and X this band is shifted to lower frequency by 5 to 20 cm⁻¹ and appears as a strong band thus confirming the coordination with metal through azomethine nitrogen (Mustafa and Wafa 1990). The weaker N-H absorption band at 3160 cm⁻¹ of the ligand broad-

Table 2
Amount of metals in complexes of 1, 3-diphenylpyrazole 4-carboxaldehyde benzoylhydrazone.
[C₂₃H₁₈N₄O]₂m

S.No.	Complex no.	Metal	Found (%)	Calculated (%)
1	I	Iron	7.35	7.11
2	II	Cobalt	6.15	7.40
3	III	Nickel	6.58	7.46
4	IV	Copper	8.67	7.92
5	V	Zinc	8.50	8.16
6	VI	Cadmium	14.57	13.27
7	VII	Mercury	17.95	21.40
8	VIII	Tin	16.46	13.87
9	IX	Bismuth	20.85	22.20
10	X	Lead	20.56	22.20

Table 1
Formula, colour, percentage yield and decomposition temperature of complexes

Complex No	Formula L : M	Colour	Yield (%)	Decomp. temp°C
I	(C ₂₃ H ₁₈ N ₄ O) ₂ Fe	Black	40	225
II	(C ₂₃ H ₁₈ N ₄ O) ₂ Co	Light Orange	45	250
III	(C ₂₃ H ₁₈ N ₄ O) ₂ Ni	Dark Orange	65	250
IV	(C ₂₃ H ₁₈ N ₄ O) ₂ Cu	Gray	70	250
V	(C ₂₃ H ₁₈ N ₄ O) ₂ Zn	Yellow	45	282
VI	(C ₂₃ H ₁₈ N ₄ O) ₂ Cd	Off white	45	210
VII	(C ₂₃ H ₁₈ N ₄ O) ₂ Hg	Off white	48	230
VIII	(C ₂₃ H ₁₈ N ₄ O) ₂ Sn	Light Green	48	250
IX	(C ₂₃ H ₁₈ N ₄ O) ₂ Bi	Off white	47	250
X	(C ₂₃ H ₁₈ N ₄ O) ₂ Pb	Off white	48	250

Table 3

Infrared spectra of 1, 3-diphenylpyrazole 4-carboxaldehyde benzoyl hydrazone and its complexes

S.No.	Complex No.	Bands (cm ⁻¹) and Intensity
1.	Ligand	3160w 3000s 1635vs 1590s 1545s 1530s 1500m 1440w 1410w 1370m 1350s 1285vs 1210s 1140w 1070m 1050s 950m 900w 830w 750s 690vs.
2.	I	3020w 1625w 1580vs 1500vs 1490s 1430w 1360s 1300w 1210s 1130w 1040m 1010m 950w 830w 760s 695vs.
3.	II	3040w 1630s 1585m 1490s 1350s 1200m 10140m 750m 690s.
4.	III	3010w 1600vw 1570s 1490vs 1410w 1340vs 1275w 1190s 1030s 950m 940w 750s 700vs.
5.	IV	3025w 1585s 1560w 1480vs 1430w 1360s 1205vs 1040s 1010m 945m 830s 745s 680vs.
6.	V	3150m 3050m 1590s 1555m 1500m 1485vs 1425m 1380w 1355vs 1300w 1240m 1200s 1188w 1040s 1020w 950m 810s 750s 685vs 560w.
7.	VI	3490w 3150m 3034m 1620s 1580m 1535s 1490s 1430w 1400w 1370w 1345s 1285vs 1210s 1065m 1045s 950m 825m 750s 685vs.
8.	VII	3040w 1590s 1505vs 1380s 1220s 1050w 850m 830m 770m 750m 705s.
9.	VIII	3465w 3025w 1600w 1585m 1480vs 1420s 1340s 1195s 1040m 1005m.
10.	IX	1630vs 1580s 1540s 1490m 1290s 1215w 1140w 1045w 945w 825m 750.
11.	X	3021w 1580s 1475vs 1425s 1325vs 1200s 1040s 1000vs 820w 750s 720s

ens on complexation with Fe(III), Co(II), Ni(II), Cu(II), Hg(II), Sn(II), Bi(III) and Pb(II) metals and suffers displacement of 30 cm⁻¹ and 10 cm⁻¹ with Zn(II) and Cd(II) metals respectively. The very strong absorption band of C=O at 1635 cm⁻¹ totally disappears on complexation with Cu(II), Zn(II), Hg(II) and Pb(II) metals while it shows a negative displacement of 5 to 35 cm⁻¹ on complexation with Fe(III), Co(II), Ni(II), Cd(II), Sn(II) and Bi(III). This shifting and broadening of absorption bands are due to involvement of the oxygen of C=C and nitrogen of the N-H in complex formation.

Stability constant of the complexes has been calculated using spectrophotometric Job's continuous variation method. Stoichiometry of the complexes has also been determined. The results reveal that in these complexes metal to ligand ratio is 1:2. The values of stability constants reported in Table 4 are in agreement except that of complex No. III with the general order of stability of complexes Fe < Co < Ni < Cu > Z which has been established before (Grinberg and Yatsimerski 1952, Irring and Williams 1953; Mustafa and Wafa 1990).

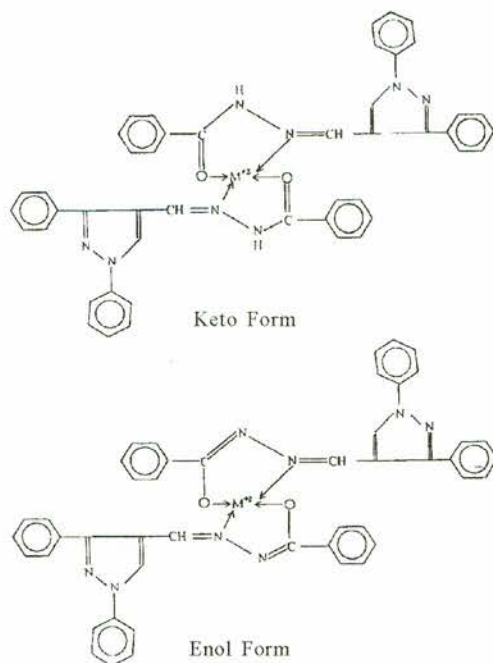
Atomic absorption studies and stoichiometric studies by Job's continuous variation method reveal that complexes formed have the metal to ligand ratio 1:2. The ligand could form complex with metal coordinating through either the ketonic or enolic form; the infrared studies are of great help in deciding the mode of coordination. It is well known that N-H gives an absorption band. When it is involved in coordination it shifts to lower frequency or broadens as is observed in the case of ammonium, amine, hydrazones and hydrazides etc. metal complexes (Narang and Agarwal 1975). The ligand gives a weak absorption band of N-H stretching frequency at 3160 cm⁻¹ which on chelation broadens in majority of cases except in complex No. V and VI. The broadening or shifting of this band is due to the involvement of the N-H of hydrazone in complexation or its enolization. The literature indicates that the carbonyl absorption band of the hydrazones does not totally

Table 4

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

Complex No.	Metal (10 ⁻⁴ M)	A	A _{ex}	K _f = $\frac{A/A_{ex} C_m}{(C_m - A/A_{ex} C_m)(Cl - A/A_{ex} C_m)}$		
				K _f	M:L	log K _f
I	Iron(III) chloride	3.23	3.25	2.58x10 ⁸	1:2	8.41
II	Cobalt(II) chloride	3.41	3.43	2.95x10 ⁸	1:2	8.47
III	Nickel(II) chloride	3.02	3.06	5.75x10 ⁷	1:2	7.76
IV	Copper(II) chloride	2.79	2.80	7.68x10 ⁸	1:2	8.89
V	Zinc(II) chloride	2.19	2.01	1.91x10 ⁸	1:2	8.07
VI	Cadmium(II) chloride	3.05	3.07	2.35x10 ⁸	1:2	8.73
X	Lead(II) acetate	2.97	2.99	2.21x10 ⁸	1:2	8.34

Based on the given evidence the structure for these complexes is represented as



disappear unless it is enolized. When it is involved in complexation, the carbonyl absorption band appears at a lower frequency. Total disappearance of the carbonyl absorption band in the complex No. III, V, VII and X supports the idea of enolization and strongly indicates that the N-H group is involved in bonding and consequently enol is deprotonated in the coordination process (Narang and Agarwal 1975; Dey *et al* 1992; Dey and Nandi 1994). The very strong carbonyl absorption band of free ligand at 1635 cm^{-1} shows a negative displacement of 5 to 35 cm^{-1} in complex No. I, II, III, V, VIII and XI. This behaviour of negative shift indicates that carbonyl absorption band is not enolized and the ligand coordinates

with metals in keto form (Syed and Iskander 1971). The free ligand shows a strong band at 1590 cm^{-1} which is attributed to C=N stretching frequency (Dutta and Sarkar 1981). On complexation this absorption band shifts to lower frequency (Table 5). This confirms the coordination through nitrogen of N-H group (Teotia *et al* 1980). The negative shift in the C=N and C=O bands shows that ligand is a bidentate and coordinates with metals in keto form. But in some cases total disappearance of carbonyl absorption band indicates the enolic behaviour of ligand (Teotia *et al* 1980; Moustafa and Wafa 1990).

References

Bhagi A K, Tyagi S B, Singh B, Kapoor R M 1989 Complexes of alkyl pyruvate benzoyl hydrazones with Ti(IV), Zr(IV) and Hf(IV) Chlorides. *Ind J Schem* **28A** 995-997.

Dey K, Bandyopadhyay D, Mandal K 1991 Complexes of copper (II) with the hydrazones derived by the condensation of 4-methoxy benzoyl hydrazide with salicylaldehydes. O-hydroxy acetophenone and diacetyl oxime. *Ind J Chem* **30A** 872-876.

Dey K, Mandal K, Bandyopadhyay 1992 Hydrazones derived by the condensation of 4-methoxy benzoyl hydrazide with salicylaldehyde. O-hydroxyacetophenone and diacetyl monoxime as ligands for cobalt (II and III). *Ind J Chem* **31A** 937-942.

Dey K, Nandi K K 1994 Synthesis and Characterization of Copper (II), nickel (II), cobalt (II), Zinc II, tin (IV) and cadmium (II) complexes with ferrocenyl morpholine N-thiohydrazone. *Ind J Chem* **33A** 633-637.

Dutta R L, Sarkar A K 1981 A study of some transition metal complexes of salicylindene-2-Picoloyl Hydrazane schiff base and related ligands. *J Inorg Nucl Chem* **43** 57-67.

Dutta R L, Kuntala D 1989 Complexes of 2-benzoyl pyridine anthraniloyl hydrazone and bis (2-benzoyl Pyridine) benzil hydrazone with some transition metals. *Ind J Chem* **28A** 807-808.

Grinberg A A, Yatsimerski K B 1952 The periodic law of Mendeleev and the stability of complex compounds. *Bull Acad Sci URSS Div Chem Sci* 239.

Irring H, Williams J P 1953 The stability of transition metal complex. *J Chem Soc* **3** 3192.

Job P 1925 Some applications of spectrographic method for a study of complexes in solution. *C R Acad Sci Paris* **180** 928.

Katyal M, Dutt Y 1975 Analytical Application of Hydrazones. *Talanta* **22** 151-166.

Kira M A, Abdel Rehman M O, Godalla K Z 1969 The Vismier-Haak reaction-III Cyclization of Hydrazones to Pyrazoles.

Table 5

Important infrared spectral bands (cm^{-1}) of 1, 3-diphenylpyrazole 4-carboxaldehyde benzoylhydrazone 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	3160w		1635vs	-	1590s	-
2	I	Bb		1625w	-10	1580s	-10
3	II	Bb		1630s	-5	1585vs	-5
4	III	Bb		1600vw	-35	1570s	-20
5	IV	Bb		-	-	1585s	-5
6	V	3130m	-30	-	-	1590s	-
7	VI	3150m	-10	1620s	-15	1580m	-10
8	VII	Bb		-	-	1590s	-
9	VIII	Bb		1600	-35	1585m	-5
10	IX	Bb		1630vs	-5	1580s	-10
11	X	Bb		-	-	1580	-10

Tetrahedron Letters 109-110.

- Maleaque A, Chaudhry A K 1992 Binary complexes in solution of schiff base ligands, o-hydroxynaphthalidenebenzoyl and salicyloyl hydrazone with thorium. Uranyl and vanadyl ions and ternary complexes of thorium with aminopolycarboxylic acids as primary ligands. *Ind J Chem* **31A** 764-769.
- Mustafa HM, Aboual-El-Wafa 1990 Cobalt, (II) nickel (II) and copper (II) chelates of N-isonicotinamido salicylaldehyde. *Pak J Sci Ind Res* **33** 469-473.
- Sacconi L 1953 Acylhydrazones of o-oxy and o-ami-

noaldehydes and ketones as tridentate complexing agents. *J Am Chem Soc* **75** 5434-5435.

- Sayed L E, Iskander M F 1971 Coordination compounds of hydrazine derivatives with transition metals. *J Inorg Nucl Chem* **33** 435-443.
- Shirif F G, Awad A M 1962 Reevaluation of the continuous variation method as applied to the uranylazide complexes. *J Inorg Nucl Chem* **24** 179-182.
- Teotia MP, Gurtu J N, Rana V B 1980 Dimeric 5 and 6 coordinate complexes of tri and tetradentate ligand. *J Inorg Nucl Chem* **42** 821-831.