

## FIRST TRANSITION SERIES – METAL COMPLEXES OF PHTHALIC HYDRAZIDE OR ITS ANION

Mirza Arshad Ali Beg and S. Ashfaq Hussain

PCSIR Laboratories, Karachi-39 Pakistan

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The reaction of phthalic hydrazide ( $H_2PH$ ) with Cr(III), Mn(II), Fe(III) and Cu(II) salts yields corresponding mononuclear complexes of type  $[Cr(HPH)_2(H_2O)_2] \cdot 2H_2O$  (I),  $[Mn(HPH)_6] \cdot (H_2O)_2$  (II),  $[Fe(HPH)_2(H_2O)_2]$  (III) and a binuclear complex of type  $[Cu_2(HPH)_3(H_2O)_6] \cdot H_2O$  (IV). Infrared and electronic spectra and magnetic properties suggest octahedral structure for all the complexes. The ligand field parameters (wherever possible) have been calculated. The value in Cr(III) complex (I) indicates II-type delocalization of metal  $t_{2g}$  electrons. The Dq values follow the usual order of metal M(II) and M(III) ions in the spectrochemical series. The magnitude of  $\nu_{M-O}$  frequencies in metal (II) complexes shows an agreement with the Irving-Williams stability order for divalent metal ions.

**Key words:** First transition series, Metal complexes, Anion phthalic hydrazide.

## INTRODUCTION

The study of coordination properties of phthalic hydrazide ( $H_2PH$ ), towards Co (II) [1] and Ni(II) ions [2] suggest that the former behaves as a monobasic bidentate ligand in the mononuclear complexes. The present investigation is an extension of the earlier studies to some other metals of the first transition series. The infrared and electronic spectra and magnetic properties have been recorded to compare changes, if any, in the mode of linkage of phthalic hydrazide with the said metal atoms.

## EXPERIMENTAL

**Preparation of the ligand and complexes:** Phthalic hydrazide ( $H_2PH$ ) and its metal complexes were prepared and purified by the methods reported earlier [1-4]. Laboratory grade metal salts like  $CrCl_3 \cdot 6H_2O$  (10mM) or  $FeCl_3 \cdot 6H_2O$  (10mM), or  $MnCl_2 \cdot 4H_2O$  (10mM) or  $CuCl_2 \cdot 2H_2O$  (20mM) on the one hand and phthalic hydrazide (20mM) on the one hand and Phthalic hydrazide, 20mM, on the other hand were taken for preparing the corresponding complex. The pH of reaction medium was adjusted between 5.5 and 7.0.

**Physical measurements.** Recording of electronic spectra, IR spectra and room temperature magnetic susceptibility measurements were carried out by methods reported earlier [2]. Elemental analyses were carried out by the di-

gestion of the sample in concentrated nitric acid using Perkin Elmer-107 atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

Phthalic hydrazide ( $H_2PH$ ), 1-hydroxyphthalazine-4-one, forms complexes with Co(II), Ni(II), Cr(III), Mn(II), Fe(III) and Cu(II) ions in the presence of ammonium hydroxide in the pH range 5.5-7.0 as reported earlier [2]. Appearance of NH and C = O bands in the IR spectra of all complexes indicates coordination through lactim group of the ligand and suggests that the lactam-lactim structure of the ligand persists on complexation with metal ions of the first series.

The Cr(III), and Fe(III) complexes are formed on following the reaction scheme reported earlier [2] where phthalic hydrazide behaves as a monobasic bidentate chelating ligand while in the Mn(II) complex, it seems to behave as monobasic monodentate ligand. In the case of the Cu(II) complex it acts both as a monobasic bidentate chelating and a bridging ligand.

The analytical data of compounds reported in Table I correspond to the formulations  $[(Cr(HPH)_2(H_2O)_2) \cdot 2H_2O]$  (I),  $[Mn(HPH)_6]$  (II),  $[Fe(HPH)_2(H_2O)_2]$  (III) and  $[Cu_2(HPH)_3(H_2O)_6] \cdot H_2O$  (V).

The complexes are stable under laboratory conditions

Table 1. Analytical Data.

S. No.	Compound	Colour	C		H		N		M	
			Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)	Calc. (%)	Found (%)
I.	$[Cr(HPH)_2(H_2O)_2] \cdot 2H_2O$	Light Blue	43.04	42.97	4.06	3.95	12.55	12.48	11.64	11.72
II	$[Mn(HPH)_6]$	White	56.42	56.45	2.95	2.99	16.44	16.62	5.37	5.29
III	$[Fe(HPH)_2(H_2O)_2]$	Brown	46.40	46.36	3.40	3.28	13.52	13.45	13.48	13.35
IV	$[Co(HPH)_2(H_2O)_2]$	Pink	46.0	45.99	3.38	3.84	13.42	13.38	14.11	14.24
V	$[Cu_2(HPH)_3(H_2O)_6] \cdot H_2O$	Green	39.13	39.07	3.96	4.08	11.41	11.68	17.25	17.38

and as reported for the other complexes, they decompose above 350°. They are slightly soluble in methanol and ethanol and are insoluble in other organic solvents, due to poor solubility, their NMR spectra could not be recorded.

**Magnetism and electronic spectra.** The magnetic moments of complexes (I-V) are listed in Table 2. The room temperature moment of Cr(III) complex (I) is found to be slightly less than the spin-only value of 3.88 B.M. expected for three unpaired electrons in octahedral high-spin mononuclear Cr(III) complexes [5].

The Mn (II) and Fe(III) complexes (II, III) show their magnetic moments in the range of 4.89-5.70 and 5.33-5.90 B.M. respectively as expected for five unpaired electrons. This suggests that the high spin Mn(II) and Fe(III) mononuclear complexes [5,6] are octahedral in configuration.

The Co(II) complex (IV) has magnetic moment higher than the spin-only value of 3.87 B.M. expected for three unpaired electrons but lower than the value of 5.00 B.M. which is usually observed for regular octahedral Co (II)

complexes [5,6]. These changes may be associated with partial quenching of the orbital angular momentum possibly due to presence of low-symmetry ligand field components.

The Cu(II) complex (V) shows a moment below the range of 1.70-1.90 B.M. expected for mononuclear Cu(II) complexes containing one unpaired electron [5,6]. This indicates the antiferro magnetic character of the complex as has been reported in the binuclear Cu(II) complexes of schiff bases and benzoic acids[5] and suggests a binuclear structure for V.

The electronic mull spectra and their assignments listed in Table 2 are in agreement with the structure proposed above for the complexes.

The Cr(III) complex (I), like other Cr(III) complexes of oxygen and nitrogen donor ligands, such as acyclic hydrazide [6], amides [7,8], urea [9], biuret [10] and  $\beta$ -diketone [11], exhibits two spin-allowed and one spin-forbidden d-d bands. The appearance of  ${}^4A_2g \rightarrow {}^4T_2g$  and  ${}^4A_2g$

Table 2. Magnetic moments, electronic spectra and ligand field parameters.

Compound	298°K		State		Assignment	$D_q$	$B_{35}$	$B_{55}$	$B_{55}$	$B_{55}$	LFSE (Kcal/ mole)	
	$\mu$ eff B.M.	EtOH	DMF	NM								
I. [Cr(HPH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	3.80	14.30	14.28	14.28	${}^4A_2g \rightarrow {}^2E_g$	18.52	0.588	0.64	0.736	0.80	63.49	
		(1.36)	(1.73)									
		18.52	18.40	19.23		${}^4A_2g \rightarrow {}^4T_2g(F)$	—	—	—	—	—	—
		(1.42)	(1.82)									
II. [Mn(HPH) <sub>6</sub> ]	5.50	—	12.50	13.50	—	—	—	—	—	—	—	
				very								
				weak								
III. [Fe(HPH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	5.68	13.68	13.33	13.80	${}^6A_1g \rightarrow {}^4T_1g(G)$	15.00	0.82	—	—	—	—	
		(1.60)	(1.78)									
		18.20	18.18	18.87		${}^6A_1g \rightarrow {}^4T_2g(G)$	—	—	—	—	—	
		(1.73)	(1.85)									
		23.60	23.52]			${}^6A_1g \rightarrow {}^4T_1g+{}^4E$	—	—	—	—	—	
		(1.85)	(1.96)]									
IV. [Co(HPH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	4.32	8.33	8.16	8.00	${}^4T_1g \rightarrow {}^4T_2g(F)$	9.34	0.90	0.94	—	—	16.01	
		(1.45)	(1.54)									
		16.90	16.66	15.40		${}^4T_1g \rightarrow {}^4A_2g(F)$	—	—	—	—	—	
		(1.58)	(1.68)									
V. [Cu <sub>2</sub> (HPH) <sub>3</sub> (H <sub>2</sub> O) <sub>6</sub> ]H <sub>2</sub> O	1.55	12.10	11.50	12.99	—	—	—	—	—	—	—	
		(1.80)	(2.17)									
		14.50	13.80	14.50		${}^2Eg \rightarrow {}^2T_2g$	14.50	—	—	—	—	
		—	—	27.17			—	—	—	—		

Note: Band position in KK, Log  $\epsilon$  in parenthesis, etOH, ethanol; DMF, dimethyl formamide; NM, Nujol mull.

→  ${}^4T_{1g}$  transition bands in the present Cr(III) complex (I) at higher energies compared to the Cr(III) complexes of the above ligands seems to be indicative of the chelate effect [11, 12] of phthalic hydrazidato anion. The first d-d band appears to give lower intensity than the second as has been found in diaquo Cr(III) complexes of Schiff-base ligands such as those of NN'-ethylene bis-(salicylideneimine) [13]. This indicates the trans arrangement of water molecules at the axial position of the octahedron. The appearance of spin-forbidden band supports this conclusion for which further evidence is obtained by comparing the spectrum of the present complex with the spectra of bis (1-lysinate)- and bis-glycinato diaquo chromium (III) complexes [14] possessing a cis structure with respect to nitrogen or oxygen atoms. These complexes exhibit the first d-d band of higher intensity with no splitting as compared to that of the second.

Assuming the first spin-allowed band to be equal to  $10Dq$ , the values of  $B_{35}$  and  $B_{55}$  may be calculated using the standard equation [11] for  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  and  ${}^4A_{2g} \rightarrow {}^2E_g$  transitions respectively. The values are found to be reduced considerably with respect to those of the free-ion Cr(III), in the general order of  $\beta_{35} > \beta_{55}$  [12]. The  $\beta_{35}$  value seems to indicate  $\pi$  and  $\sigma$ -type delocalization, whereas  $B_{55}$  seems to suggest  $\pi$ - $\pi$  type back bonding mechanism for the delocalization of  $t_{2g}$  electrons of the metal [11]. This is possibly due to bonding through C = N group of phthalic hydrazidato anion. The  $Dq$  value seems to be consistent with  $CrN_2O_4$  chromophore [12-15].

The Mn(II) complex (II), like other octahedral Mn (II) complexes of oxygen and nitrogen donor ligands [6, 9, 12, 15, 17] exhibits a very weak absorption band near  $13500\text{ cm}^{-1}$ . Since the six coordinate octahedral structure of the complex (II) has been suggested by elemental analysis, magnetic moment as well as by its IR spectrum, it seems reasonable to suggest  $MnO_6$  chromophore for the same.

The Fe(III) complex (III) exhibits three d-d bands which have been assigned as listed in Table-2 by using the Tanabe-Sugano diagram [12, 18] and the parameters  $Dq$  and  $\beta$  have been calculated therefrom. These values have been found to be consistent with the  $FeN_2O_4$  chromophores [12, 15, 19, 20]. The  $Dq$  value, calculated by using the empirical relation  $10Dq = [f(\text{ligand})] [g(\text{metal ion})]$ , [15] where  $[f(\text{ligand})]$  of phthalic hydrazidato anion is determined by using the  $10Dq$  of Cr (III) complex (I) is directly obtained from the spectrum and seems to be consistent with the conclusion with respect to chromophore.

There seems a resemblance between the spectrum of Fe(III) complex (III) and octahedral high-spin ferric porphyrin complexes containing  $MN_4O_2$  chromophore [21, 22]. The porphyrin has been reported to occupy the equatorial plane while the oxygen-donor ligand is axially coordinated. The differences in bond energies and intensities are possibly the result of differences in chromophores and for-

mation of dimeric complexes.

Electronic spectra of the Co(II) complex (IV) have not been studied previously (I) in detail. They show three spin-allowed d-d bands. The parameters  $Dq$ ,  $B$  and  $\beta$  have been calculated by numerical method [23] by using  $\nu_1$  and  $\nu_3$  bands from the observed data. The  $Dq$  value seems to be consistent with the  $CoN_2O_4$  chromophore [12, 15, 24, 26].

The Cu(II) complex (V) shows a broad band near  $14500\text{ cm}^{-1}$  with shoulders at  $12990\text{ cm}^{-1}$  and  $27170\text{ cm}^{-1}$  and is similar to the spectra of complexes with other oxygen and nitrogen donor ligands [26-30]. The features of the spectrum seem to be consistent with an octahedral binuclear structure (31). The appearance of this band at higher energy as compared to the first d-d band of Ni (II) complex [2] and the ratio  $\nu_{Cu}/\nu_{Ni}(1.50)$  indicates a considerable Jahn-Teller distortion of  ${}^2E_g$  state [32] of Cu (II) complex (V). Assuming this band to be equivalent to  $10Dq$ , the  $Dq$  value is consistent with  $CuN_2O_4$  chromophore [12, 16, 27, 28, 32]. The resemblance of mull spectra of the complex (V) with that between Cu(II) and aroylhydrazine [30] suggest the phthalic hydrazidato anion to be occupying the equatorial plane.

The  $Dq$  and  $\beta$  values as a function of metal ions in the complexes (I, III, IV) have been found in the usual order in spectrochemical and nephelauxetic series [12] and like Ni(II) complexes [2], they have been found in the usual order in spectrochemical and nephelauxetic series [12].

Like Ni(II) complexes [2], the Cr(III), Fe(III) and Co(II) complexes (I, III and IV) of phthalic hydrazide show a lower intensity of first d-d band ( $\nu_1$ ) as compared to that of second ( $\nu_2$ ) which may suggest the trans arrangement of water molecules in the axial position of the octahedron while the equatorial positions may be suggested to be occupied by phthalic hydrazidato anion.

*Infrared spectra.* The solid state spectra of metal (II) and metal (III) complexes (I-V) (Table 3), like Ni(II) Complexes [2], exhibit the bands due to NH, C = O, C = N and C-O stretching modes indicating the persistence of lactim structure of phthalic hydrazide in all the complexes.

In Cr(III), Mn(II) and Fe(III) complexes (I-III) the NH stretching band appears in the same frequency region as the free ligand, but it is shifted to higher frequency by 25 and  $12\text{ cm}^{-1}$  in Co (II) and Cu(II) complex (IV and V) respectively. The  $\nu_{C=O}$  band of free ligand is found to remain unchanged in all the complexes (I-V). These results indicate the weakening of hydrogen bond of the type (C = O...HN) expected in free phthalic hydrazide ( $H_2PH$ ) [33, 34]. The NH in-plane deformation band of free ligand on the other hand is shifted to higher frequency in all the metal M (II) and M(III) complexes possibly due to coupling with  $\nu_{C=O}$  band as it has been noted in Ni(II) complexes [2] and metal complexes of nucleic acid bases such as those of thymine [16]. These observations suggest that the NH and C = O groups of phthalic hydrazide are not donors in all the

Table 3. IR Spectral data.

Compound	VOH Free	VOH Coord	VNH	VC=O	VC=N	$\delta$ NH in plane	Ring VC-O	VCN	$\delta$ OH in plane	$\delta$ NH out of plane	Pr (H <sub>2</sub> O)	Pw (H <sub>2</sub> O)	Ring Vib	VM-O $\leftarrow$ VM-O	VM	
I. H <sub>2</sub> PH	-	-	3125s	1658s	1598s	1550s	1450s	1370s	1300s	860s	-	-	815s 550w	-	-	
II. [Cr(HPH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]2H <sub>2</sub> O	3680w,br	3322s	3125s	1658vs	1602s	1558s	1450s	1387s	-	866s	-	645w 625w	847s 700s 560w	440w	382w	340w
III. [Mn(HPH) <sub>2</sub> ]	-	-	3125s	1658vs	1602s	1560s	1452s	-	-	866s	-	640w	815w 550w	420w	-	-
IV. [Fe(HPH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	3635w,br	3342w	3125s	1658vs	1602s	1558s	1450s	1387s	-	870s	-	640s	846w	465w	382w	3.40
V. [Co(HPH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	-	3342w br	3150s	1645vs	1602s	1570s	1450s	1370s	-	875w	-	645w 635w	835s 560s	425w	375w	320w
VI. [Cu <sub>2</sub> (HPH) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]H <sub>2</sub> O	3650w, br	3347w br	3137s	1550s	1606w	1580s	1453s	1390s	-	877w	825w	650w 630w	850w 560w	470w	390w	330w

s, strong; vs, very strong; w, weak; br, broad

metal complexes (I-V). The higher shift of  $\nu$ C-N band in all the metal complexes (I-V) by 10-5 cm<sup>-1</sup> supports this conclusion.

The C = N stretching and ring vibration bands of phthalic hydrazide, in Ni(II) complexes [2] and other metal complexes with nucleic acid bases such as those of cytosine [35], are shifted to higher frequencies. These results, therefore, may be indicative of the bonding through nitrogen of C = N group of phthalic hydrazide (HPH). The appearance of new bands in the 710-700, 415-400 and 340-330 cm<sup>-1</sup> regions may be assigned to ring stretching, deformation and  $\nu$ M-N modes respectively and seems to be consistent with the suggested mode of bonding.

The disappearance of  $\delta$ OH band observed in free phthalic hydrazide at 1300 cm<sup>-1</sup> from the spectra of the complexes and appearance of  $\nu$ M-O band in the 470-415 cm<sup>-1</sup> region as in those of Ni(II) complexes [2] and metal complexes of other oxygen donor ligands like  $\beta$ -diketones [36] and pyrazolone derivatives [37], suggest anionic coordination through the enolic carbonyl oxygen. The energy of this band in the present M (II) complexes (II,V) in comparison with those of Co (II) and Ni(II) complexes [1,2] decreases in the order Cu > Ni > Co > Mn agreeing with the Irving and William's stability order [38].

The M(II) and M(III) complexes, like other aquo complexes [2, 36, 39, 40] exhibit  $\nu$ OH and  $\rho$ w (H<sub>2</sub>O) bands in the 3342-3322 and 640-630 cm<sup>-1</sup> regions respectively. These observations indicate the presence of coordinated water in the complexes I, III, IV and V.

### CONCLUSION

Phthalic hydrazide forms high spin octahedral complexes with the metal ions of the first transition series. It seems to act as a monobasic ligand (HPH) in all the complexes (I-V). It behaves as a bidentate chelating ligand in Cr(III) and Fe(III) complexes (I,III) as a monodentate ligand in Mn(II) complex (II) and as a bidentate chelating

and bridging ligand in Cu(II) complex (V), occupying the equatorial positions of the octahedral framework.

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RESULTS AND DISCUSSION

The effect of hydrochloric acid concentrations on the corrosion of Al-Mn alloy was investigated covering the range 2 - 4.5 M. It has been found that as the concentration increase, the corrosion rate increases and the maximum temperature T<sub>max</sub> increase with decreasing the time (t) needed to reach T<sub>max</sub>. The same conclusions were reported by Table 1 at (10). The observed high corrosive action of HCl may be due to the formation of aluminum chloride complex which catalyses the dissolution process of the alloy. The results obtained are given in Table 1.

Table 1. Effect of HCl concentrations on the corrosion rate of Al-Mn alloy

Conc. M	T <sub>max</sub> °C	t, min	R.N. °C/min
2.5	75	74	0.71
3.0	92	30	3.08
3.5	97	27	3.74
4.0	98	21.24	3.81
4.5	99.2	14.24	3.62

Temperature change of the system involving Al-Mn alloy in 3.0 M HCl was followed in absence and presence of different additive concentrations. Figure 1 represents the

In this paper, the effect of KSCN, NaCN, NaCN (CH<sub>3</sub>)<sub>2</sub>SO and CH<sub>3</sub>NH<sub>2</sub> on the corrosion of Al-Mn alloy in hydrochloric acid solution was investigated.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade. The solutions were prepared in double distilled water. Experiments were carried out at 25 ± 1.0°. Duplicate runs were performed for each concentration and the mean values were recorded. Each experiment was carried out with 25 ml of the test solution and with a new test piece.

The reaction vessel used in testing the corrosion rate was basically as described by Mylius (7). The vessel was placed in a dewar flask to minimize heat losses by radiation. The test pieces of 1x10 cm surface area was bent in U-shape. The variation of the temperature of the system was measured to ± 0.5° by the thermometer. Before use, the test pieces were cleaned by recommended procedures (8, 9). The chemical composition of the alloy is 98% Al and 2% Mn.

The reaction number (R.N.) of the studied compounds in presence of 3.0M hydrochloric acid can be evaluated using Mylius formula as given in equation (1)

$$R.N. = \frac{AT_1 - AT_2}{t_1 - t_2} \quad (1)$$

where  $\Delta T = T_1 - T_2$  and  $t_1$  and  $t_2$  are the maximum and initial