

Formation constants of Mn(II), Cu(II), Co(II), Zn(II), Fe(II), Ni(II) and Pd(II) complexes of peonolphenylhydrazone

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Thermal and solution stabilities of peonolphenylhydrazone chelates of Mn(II), Cu(II), Co(II), Zn(II), Fe(II), Ni(II) and Pd(II) have been measured. Thermodynamic parameters of complex formation and kinetic parameters of complex decomposition have also been evaluated. The solution stabilities determined pH-metrically in 75% dioxane-water, acetone-water and ethoxyethanol-water mixtures are in fair agreement with the Irving-Williams series of stability. The results obtained are compared with the data available in the literature for structurally similar ligand complexes. Amongst the solvents employed, acetone-water shows abnormal behaviour. The order of solution stabilities is found to be: $Fe > Cu > Pd > Ni > Co > Zn > Mn$ while that for thermal stabilities, on the other hand, is: $Mn > Ni > Pd > Cu > Fe$.

In view of the biochemical^{1,2} and analytical importance³⁻⁸ of phenylhydrazones, it was thought worthwhile to study the thermal and solution stabilities of the metal chelates of peonolphenylhydrazone (2-hydroxy-4-methoxyacetophenonephenylhydrazone).

Materials and Methods

The proton-ligand and metal-ligand formation constants were determined at different temperatures using Irving-Rossotti^{9,10} pH titration technique. The titrations were performed using a double-walled beaker thermostated at $20 \pm 0.5^\circ\text{C}$, $30 \pm 0.5^\circ\text{C}$ and $40 \pm 0.5^\circ\text{C}$.

Peonolphenylhydrazone (m.p. 108°C) was prepared according to the literature method^{11,12}. Its solutions (0.1 M) were prepared in various organic solvents. The metal salt solutions were prepared in doubly distilled water and standardised by appropriate standard methods¹³. Acetone, dioxane and ethoxyethanol were purified before use by usual procedures¹².

Cu(II), Ni(II), Pd(II), Fe(II) and Mn(II) complexes were prepared by adding to the metal ion solution (containing about 60 mg of the metal ion) at pH 5.0-6.0; 3.5-4.5; 4.5-6.0 and 7.5-8.5 respectively a slight excess of the ligand solution (1% in methanol) and precipitates were washed with hot water followed by methanol and dried *in vacuo*.

An Elico digital (LI-120-A) pH meter was used for pH-measurements. The experimental procedure involved the titrations of the following solutions (total volume 50 ml) against carbonate free standard sodium hydroxide (0.1 M) solution. The ionic strength of the solution was kept at 0.05 M (KNO_3).

- (a) 5 ml of nitric acid (0.01 M)
+ 37.5 ml of organic solvent
+ 5 ml of KNO_3 solution (0.05 M)
+ 2.5 ml of water.
- (b) 5 ml of nitric acid (0.01 M)
+ 36.5 ml of organic solvent
+ 5 ml of KNO_3 solution (0.05 M)
+ 2.5 ml of water
+ 1 ml of ligand solution (0.002 M).
- (c) 5 ml of nitric acid (0.01 M)
+ 36.5 ml of organic solvent
+ 5 ml of KNO_3 solution (0.05 M)
+ 2 ml of water
+ 1 ml of ligand solution (0.002 M)
+ 0.5 ml of metal salt solution (0.01 M).

Thermal analysis was carried out at the Institute of Chemistry, KISHINEV, USSR with a MOM (Budapest, Hungary) derivatograph at a heating rate of $5^\circ/\text{min}$.

The pH meter readings were corrected for the non-aqueous medium following the procedure of Van-Uitert and Hass and others. The activity coefficient ($1/\gamma$) for the ionic strength (0.05 M) was calculated by interpolation from the data of Debye-Huckel¹⁴ and Harned-Owen¹⁵. The values for $\log U_H$, $\log 1/\gamma$ and $\log U_H^\circ$ at different temperatures and for different solvents are given in Table 1.

The dissociation constant of the ligand was obtained from the formation curve of the proton-li-

gand system (Table 1). The proton-ligand formation curve was obtained by plotting pH versus \bar{n}_A . Metal-ligand formation curves were obtained by plotting $p\bar{L}$ versus \bar{n} values. From the formation curve (\bar{n} versus $p\bar{L}$) it was found that the $\log K_1$ and K_2

values did not show any substantial difference; the values were corrected by the least squares method¹¹.

The thermodynamic parameters ΔG , ΔH , and ΔS were evaluated from the stability constants of the metal complexes determined at three different

Table 1A— Stepwise and overall stability constants of Fe, Co, Cu, Mn, Ni, Zn and Pd chelates of peonolphenylhydrazone in different aqueous organic solvents

Temp.		[Temps. = 20°, 30°, 40°C; $\mu = 0.05 M (KNO_3)$]						
		Cu(II)	Pd(II)	Co(II)	Fe(II)	Zn(II)	Ni(II)	Mn(II)
<i>75% 1,4-Dioxane-water</i>								
20°C	$\log K_1$	13.43	13.27	12.78	13.58	12.18	12.93	11.43
	$\log \beta_2$	26.25	26.05	23.96	26.76	23.10	24.74	21.26
	$\log K_2$	12.82	12.78	11.18	13.18	10.92	11.81	9.83
30°C	$\log K_1$	13.16	13.08	12.54	13.28	11.91	12.73	11.12
	$\log \beta_2$	25.94	25.50	23.51	26.20	22.65	24.45	20.83
	$\log K_2$	12.78	12.42	10.97	12.92	10.74	11.72	9.71
40°C	$\log K_1$	13.02	12.92	12.32	13.15	11.73	12.62	10.92
	$\log \beta_2$	25.39	25.30	23.01	25.68	22.11	24.09	20.05
	$\log K_2$	12.37	12.38	10.69	12.53	10.38	11.47	9.12
<i>75% Acetone-water</i>								
20°C	$\log K_1$	12.98	12.48	11.73	13.16	10.93	12.18	10.87
	$\log \beta_2$	25.10	24.19	22.56	25.44	20.99	23.46	20.75
	$\log K_2$	12.12	11.71	10.83	12.28	10.06	12.28	9.88
30°C	$\log K_1$	12.71	12.03	11.17	12.89	10.89	11.74	10.18
	$\log \beta_2$	24.25	23.48	21.38	25.01	20.44	22.72	19.30
	$\log K_2$	11.83	11.45	10.21	12.12	9.51	10.98	9.12
40°C	$\log K_1$	12.36	11.82	11.10	12.57	10.31	11.62	10.27
	$\log \beta_2$	23.83	22.85	21.27	24.24	19.74	22.30	19.32
	$\log K_2$	11.47	11.03	10.17	11.67	9.43	10.68	9.25
<i>75% 2-Ethoxyethanol-water</i>								
20°C	$\log K_1$	12.21	11.89	10.83	12.58	10.47	11.18	10.03
	$\log \beta_2$	23.54	23.05	20.91	24.56	19.80	21.84	18.90
	$\log K_2$	11.33	11.16	10.08	11.98	9.33	10.66	8.87
30°C	$\log K_1$	12.02	11.52	10.58	12.23	10.24	10.83	9.87
	$\log \beta_2$	23.11	22.34	20.32	23.70	19.16	21.01	18.20
	$\log K_2$	11.09	10.82	9.74	11.47	8.92	10.18	8.33
40°C	$\log K_1$	11.81	11.40	10.18	12.10	9.98	10.58	9.63
	$\log \beta_2$	22.69	22.02	19.51	23.58	18.81	20.59	18.00
	$\log K_2$	10.88	10.62	9.33	11.48	8.83	10.01	8.37

Values corrected to $\pm 0.05 \log K$ units using least squares method.

Table 1B—Ligand formation constants of peonolphenylhydrazone and $\log U_{II}$, $\log U_H$ and $\log 1/\gamma$ values in organic media at different temperatures ($^{\circ}\text{C}$)

Value of	Dioxane-water			Acetone-water			Ethoxyethanol-water		
	20 $^{\circ}$	30 $^{\circ}$	40 $^{\circ}$	20 $^{\circ}$	30 $^{\circ}$	40 $^{\circ}$	20 $^{\circ}$	30 $^{\circ}$	40 $^{\circ}$
Ligand formation constant	12.70	12.65	12.60	12.15	12.05	11.90	11.55	11.45	11.30
$\log U_{II}$	0.3898	0.4341	0.4609	0.3029	0.3338	0.3596	0.2191	0.2509	0.2713
$\log U_H$	0.16	0.18	0.19	0.13	0.15	0.16	0.08	0.10	0.11
$\log 1/\gamma$	0.2298	0.2541	0.2709	0.1729	0.1838	0.1996	0.1391	0.1509	0.1613

Table 2—Thermodynamic parameters of Co, Ni, Mn, Cu, Pd, Zn and Fe chelates of peonolphenylhydrazone in different aqueous organic solvents

[$\mu = 0.05 \text{ M} (\text{KNO}_3)$]

$\text{M}(\text{C}_{15}\text{H}_{15}\text{O}_2\text{N}_2)_2 \cdot 2\text{H}_2\text{O}$ $\text{M} =$	Dioxane-water medium			Acetone-water medium			Ethoxyethanol-water medium		
	$-\Delta G$	$-\Delta H$	$+\Delta S$	$-\Delta G$	$-\Delta H$	$+\Delta S$	$-\Delta G$	$-\Delta H$	$+\Delta S$
Cu(II)	35.195	18.045	58.522	33.653	26.647	23.910	30.903	17.725	45.312
Pd(II)	34.926	17.835	58.331	32.432	28.115	14.733	31.560	21.611	33.955
Fe(II)	35.878	22.660	45.112	34.108	25.178	30.479	32.928	20.562	42.204
Zn(II)	30.971	20.772	34.809	28.142	26.227	6.435	26.546	20.772	19.706
Co(II)	32.124	20.143	40.890	30.247	27.067	10.852	28.061	26.727	4.603
Ni(II)	33.170	13.639	66.661	31.453	24.348	24.279	29.281	26.227	10.423
Mn(II)	28.235	21.191	24.036	27.820	25.808	6.868	25.339	18.892	22.003

temperatures using the usual thermodynamic relationships¹⁶. From the thermal analysis data, the kinetic parameters associated with the complex decomposition reaction were evaluated using the Coats-Redfern¹⁷ equation. Coats-Redfern equation (integral method) may be written in the form

$$\log \left[\ln \frac{W_a/W_a - W}{T^2} \right] = \log \frac{ZR}{\phi E^*} (1 - 2RT/E^*) - \frac{E^*}{2.303 RT}$$

where W_a = mass loss at the completion of the reaction, W = mass loss at time, t , Z = frequency factor, ϕ = linear rate of heating and E^* = activation energy of the reaction.

A plot of $\log \left(\ln \frac{W_a}{W_a - W} / T^2 \right)$ versus $1/T$

showed a linear relationship with a slope of $-E^*/2.303 RT$ from which the activation energy was calculated. The pre-exponential factor was found out from the intercept. The activation entropy ΔS^* was obtained by the relation,

$$\Delta S^* = 2.303 R \log \frac{Zh}{k T_s}$$

where h is Planck's constant, k is Boltzmann constant and T_s is the peak temperature from DTG. The free energy of activation G^* and the specific reaction rate constant K_r were calculated using the following equations,

$$G^* = E^* - T_s \Delta S^*$$

$$K_r = Z \exp(-E^*/RT_s)$$

Results and Discussion

Solution stabilities

Peonolphenylhydrazone showed a maximum at $\bar{n}_A = 1.0$ in the dioxane-water, 2-ethoxyethanol-water and acetone-water media indicating that the hydrazone behaves as a monobasic acid. The acid dissociation constant found in different solvent media followed the order, 2-ethoxyethanol < acetone < dioxane. A plot of pK_L versus $1/D$ was found to be linear (where D is the dielectric constant). However, in acetone-water medium, the dissociation constant of the ligand is lower than the expected value and it may be attributed to the non-ideal behaviour of acetone-water solvent. The order of stabilities (Table 1) of the metal chelates observed in all the three solvents was: $\text{Fe} > \text{Cu} > \text{Pd} > \text{Ni} > \text{Co} > \text{Zn} > \text{Mn}$. This almost follows [except Fe(II)] the Irving-Williams order¹⁸.

Table 3—Analytical data of metal complexes

Complex	Found (Calc., %)			
	M	C	H	N
[Cu(C ₁₅ H ₁₅ O ₂ N ₂) ₂ ·2H ₂ O]	10.59 (10.47)	59.18 (59.06)	5.62 (5.58)	9.09 (9.18)
[Ni(C ₁₅ H ₁₅ O ₂ N ₂) ₂ ·2H ₂ O]	9.72 (9.68)	59.74 (59.68)	5.83 (5.80)	9.18 (9.25)
[Fe(C ₁₅ H ₁₅ O ₂ N ₂) ₂ ·2H ₂ O]	9.30 (9.27)	60.06 (59.95)	5.58 (5.49)	9.36 (9.31)
[Pd(C ₁₅ H ₁₅ O ₂ N ₂) ₂ ·2H ₂ O]	16.29 (16.20)	55.18 (55.09)	5.28 (5.19)	8.65 (8.56)
[Mn(C ₁₅ H ₁₅ O ₂ N ₂) ₂ ·2H ₂ O]	9.17 (9.13)	59.98 (59.83)	5.69 (5.64)	9.38 (9.30)

Hence, the nature of chelation and the type of bonding may be similar in all the chelates. The higher values for Fe(II) chelates (Table 1) may be due to the resonance stabilities in the system^{19,20}. The order of stabilities of the complexes with respect to the solvents is: dioxane > acetone > ethoxyethanol (Table 1). The dielectric constants for the pure as well as the mixed solvents are in the order: acetone > ethoxyethanol > dioxane. This also shows the abnormal behaviour of acetone-water mixture. Similar abnormalities were reported in the literature²¹⁻²³. The enhanced stability of the metal chelates in acetone-water may be due to the weak interacting behaviour of acetone. A plot of $\log \beta_2$ versus ionization potentials shows that the stabilities of the complexes can be better correlated with the second ionization potential rather than the first.

In general, for a given metal ion, if $\log K_1$ is greater than $\log K_2$ and the difference between them is large, then considerable steric hindrance would be expected during the addition of second ligand molecule. However, the data given in Table 1 show that the difference in the $\log K_1$ and K_2 values is small and the ratio of $\log K_1/K_2$ is positive in all the cases which indicate that there is no steric hindrance to the addition of second ligand molecule and the tendencies for the formation of complex species ML_2 and ML^+ are almost equal. Further, the maximum values obtained for \bar{n} are < 2 confirming 1 : 2 metal-ligand stoichiometry.

A comparison of the data of the overall stability constants ($\log \beta_2$) of peonolphenylhydrazone complexes with those of peonoloxime and 2-hydroxy-1-naphthaldoxime reveals that solution stabilities of peonolphenylhydrazone chelates are higher than those of peonoloxime²¹ and 2-hydroxy-1-naphthaldoxime²⁴ chelates. This may be attributed to the introduction of =N-NH-C₆H₅ group in place of

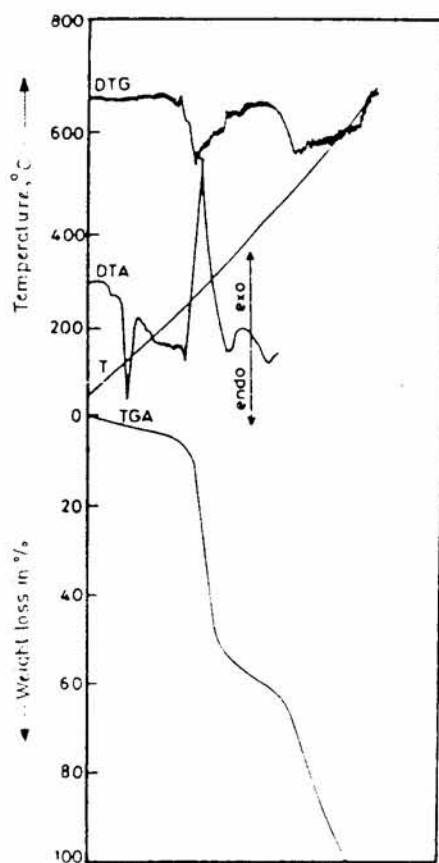


Fig. 1—TGA, DTA and DTG curves of peonolphenylhydrazone

=N-OH group which tends to increase the stabilities of the complexes, due to increase in basic character of the ligand as well as electron density at reactive centre.

The thermodynamic parameters ΔG (Gibbs energy), ΔH (enthalpy) and ΔS (entropy) of peonolphenylhydrazone complexes (Table 2) and $\log \beta_2$ values show decrease in stabilities with increase in temperature suggesting that the interaction of metal ions with the ligand is exothermic in nature²⁵. Further, ΔH_1 values are found to be greater than ΔH_2 (values are not given in Table) indicating that the metal ion progressively loses water molecules²⁶ with the formation of ML_2 complexes.

Thermal behaviour of solid complexes

The copper(II), nickel(II), palladium(II), iron(II) and manganese(II) complexes are coloured powders, non-hygroscopic in nature and stable in air. None of the complexes sublimed upon heating. Elemental analysis data indicate that the complexes are dihydrated and show 1 : 2 (metal : ligand) stoichiometry (Table 3).

Peonolphenylhydrazone is stable upto 115°C (Fig. 1) whereas its metal chelates with Fe(II), Cu(II),

Table 4—Kinetic parameters of peonolphenylhydrazone complexes

Complex	Activation energy, E^* (kcal mol ⁻¹)	Frequency factor, Z (sec ⁻¹)	Activation entropy, ΔS^* (e.u.)	Free energy of activation, G^* (kcal mol ⁻¹)	Specific reaction rate constant, K_r (S U ⁻¹)
[Cu(PPH) ₂ ·2H ₂ O]	+21.842	3.901 × 10 ³	-43.839	+53.009	3.961 × 10 ³
[Ni(PPH) ₂ ·2H ₂ O]	+14.640	4.933 × 10	-57.105	+54.213	4.985 × 10
[Fe(PPH) ₂ ·2H ₂ O]	+28.273	6.380 × 10 ⁵	-33.711	+51.635	6.512 × 10 ⁵
[Pd(PPH) ₂ ·2H ₂ O]	+14.928	1.093 × 10 ³	-46.069	+43.168	1.106 × 10 ³
[Mn(PPH) ₂ ·2H ₂ O]	+11.440	2.125 × 10	-58.988	+58.217	2.140 × 10

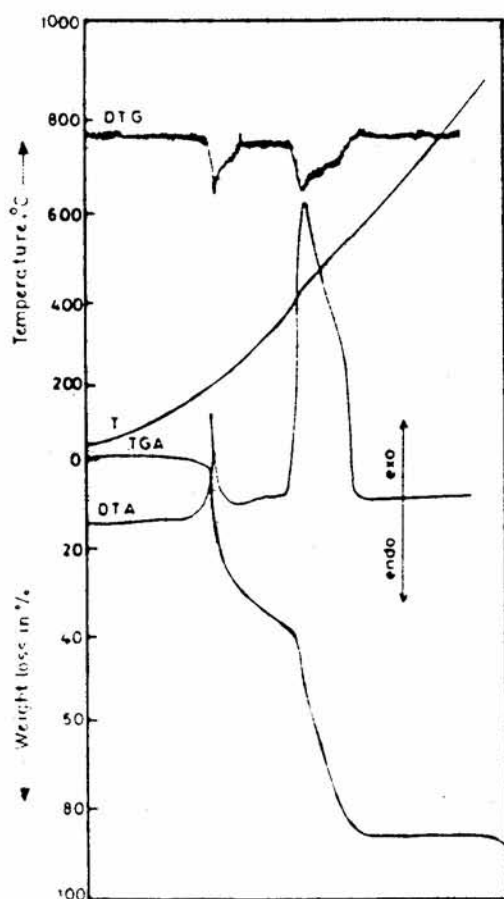


Fig. 2—TGA, DTA and DTG curves of Cu(II) peonolphenylhydrazone chelate

Pd(II), Ni(II) and Mn(II) are found to be stable upto 150°, 155°, 180° and 195°C respectively. The thermograms (Fig. 2) of these chelates indicate that they are dihydrated which is confirmed by infrared spectral data of the chelates (bands at 3480-3450, 850-835 & 790-755 cm⁻¹). The pyrolysis curves of the chelates show two distinct regions of decomposition, the first stage showing the loss of two water molecules and part of organic material (-NHC₆H₅) and the second stage indicating the loss of remaining organic material.

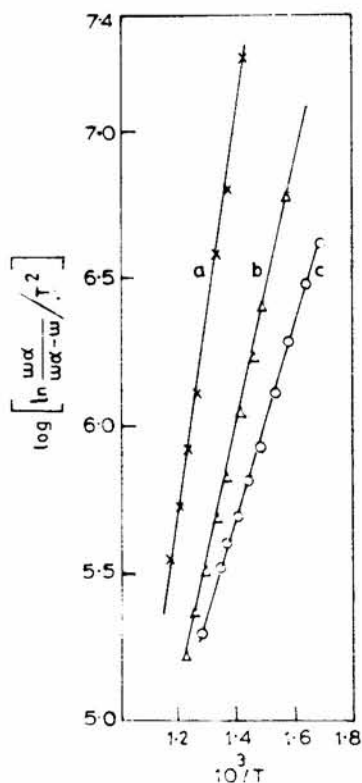
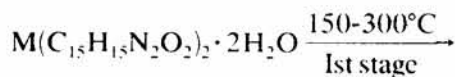
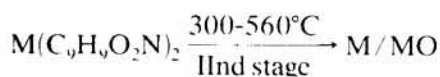


Fig. 3—Coats-Redfern plots of (a) peonolphenylhydrazone; (b) copper chelate and (c) nickel chelate

First stage:



Second stage:



The DTG curves of the complexes also indicate two distinct peaks corresponding to the two maximum slopes observed in the TGA curves confirming

the two stages of decomposition of the complexes. The final pyrolysis product in palladium chelate is the metal, while metal oxides are the end products in all the other cases. The order of thermal stabilities is found to be $Mn > Ni > Pd > Cu > Fe$. Extrapolation of the fairly linear portions of the pyrolysis curves at high and low temperatures and taking the point of intersection as the decomposition temperature leads to the following thermal stability order: $Mn > Ni > Pd > Cu > Fe$.

The kinetic parameters of complex decomposition process evaluated by using Coats-Redfern equation (Fig. 3, Table 4) reveal that the activation energy values of the complexes are in the order: $Fe > Cu > Pd > Ni > Mn$. This trend in kinetic parameters is different from the trend in thermal stability. The negative values of entropy of activation (ΔS^*) for all the chelates suggest that the activated complex has a more ordered structure than the reactants and the low Z values indicate that the reactions are slower than normal.

A comparison of the initial decomposition temperatures and the overall stability constants indicates that the thermal stabilities of chelates are in the order: $Mn > Ni > Pd > Cu > Fe$ while the solution stabilities are in the order: $Fe > Cu > Pd > Ni > Mn$. Iron complex was found to be more stable in solution than Cu, Ni, Pd and Mn chelates. The manganese chelate which is least stable in solution, on the other hand, decomposed at a much higher temperature than the copper, palladium, nickel and iron chelates. The solution and thermal stabilities of these complexes are opposed to each other^{22,24,26}. The increase in strength of metal-ligand bond results, therefore, in a decrease in the thermal stability of the complexes. This may be explained by the fact that the thermal decomposition of the chelates investigated does not begin by the scission of the metal-ligand bond but by the cleavage of another bond in the chelate ring. An increase in strength of the coordinating metal-ligand bond results in a weakening of that bond of the chelate ring, which is first ruptured on heating^{23,24,27,28}.

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