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## Structural and Crystallographical Studies on the Polymetallic Chelates of Naphthazarin with Cobalt (II), Nickel (II) and Copper (II)

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### ABSTRACT

Pyrolysis has shown that the polymetallic chelates of naphthazarin with Co(II), Ni(II) and Cu(II) assumed compositionally defined structures as  $[(C_{10}H_6O_4)(M)_2xH_2O]yH_2O$  where M stands for Co(II)/Ni(II)/Cu(II),  $x = 04, 04, 00$ , (coordinated water),  $y = 3, 1\frac{1}{2},$  and 4, (lattice water) respectively satisfying the metal ligancy. Each crystal of polymetal chelate assumed cubic symmetry with forbidden number 7, 15, 23 etc being absent. The inter planer spacing  $d$  ( $\text{\AA}^0$ ),  $a$  ( $\text{\AA}^0$  (cell unit), of  $\rho$  g/cc and molecular weights of the polymetal chelates have been determined and reported. The calculated formula weight showed correspondence to the found molecule weight of each of the polymetal chelate.

**Keywords;** Pyrolysis, Naphthazarin, Cubic, Crystallographics, X-ray

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## INTRODUCTION

The advances on the composition, stability and thermodynamics of the metal complexes of the hydroxynaphthoquinones and their indicator properties have been well documented (1-10). The crystallographics thereon are equally important and are medically, analytically, geologically required to solve some of insoluble issues of chemistry, biotechnology, microbiology, and physics etc.

The determination of the crystallographics of an organic, inorganic molecule is an active area of current research. The X-ray analysis of the polymetallic chelates of naphthazarin with Co(II), Ni(II), Cu(II) has been focused here.

## MATERIALS AND METHODS

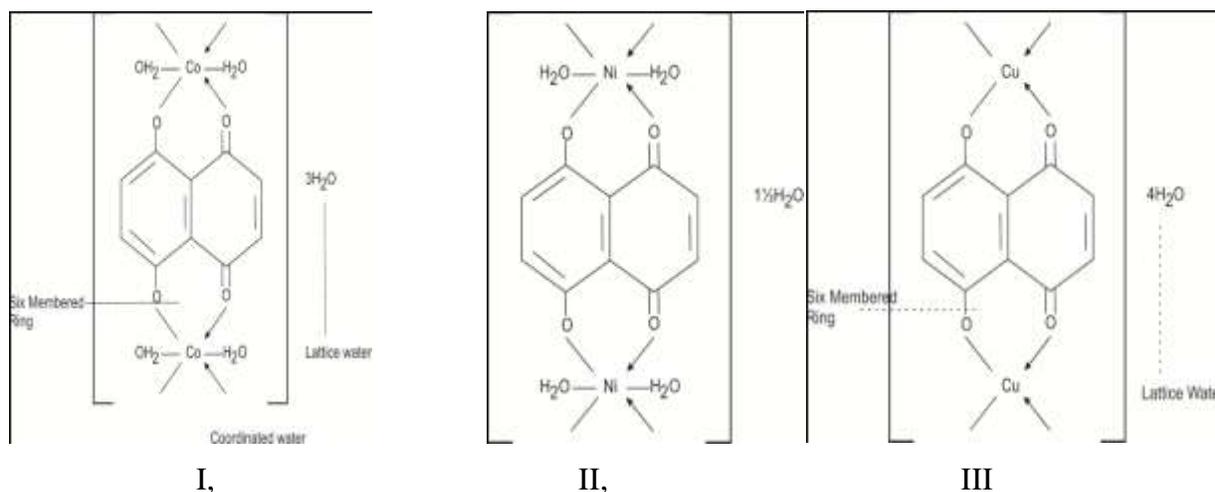
The chemicals used in the study were of pure grade. The naphthazarin (5, 8- dihydroxy-1,4-naphthoquinone) was sourced to Aldrich Chemical Co (USA).

The synthesis of polymetallic chelates was carried out by mixing equal moles of metal and naphthazarin (in 50% ethanol in water by volume), and the resulting solutions were kept overnight. The crystals so obtained were filtered, washed with 50% ethanol in water solvent and shade dried. The crystals of polychelates were re-crystallized in 50% ethanol and subjected to TG/DTG/DTA analysis and X-ray analyses.

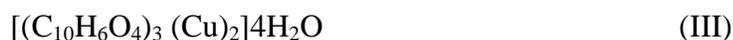
For Pyrolysis study, the EXSTAR TG/DTA 6300 in nitrogen atmosphere was used, whereas for the crystallographics study, the D 8 – ADVANCE BRUKER was depended upon.

## RESULTS AND DISCUSSION

The pyrolytically defined spectrum of each of the polymetal chelates described the chelates compositionally and structurally as



Polymetallic chelates of naphthazarin with Co (II), Ni (II), and Cu (II).



The decompositional routes traced by the polymetallic chelates (I-III) showed the plateaus of definite compositions, and the sigmoids- the representative of the departures from the parent polymetal chelate. The analytical data on these metal chelates gave us the leads on their compositions and structures as described above. (Table 1-3)

**Table; 1: Analytical Data on Non-isothermal decomposition of  $[(C_{10}H_6O_4)_3 (Co)_2 4H_2O]3H_2O$**

Reaction	Loss	Composition	Found	Calc.
Plateau I Ambient-100 <sup>0</sup> C	-	$[(C_{10}H_6O_4)_3 (Co)_2 4H_2O]3H_2O$	-	-
Sigmoid I 100 <sup>0</sup> C-169 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to $[(C_{10}H_6O_4)_3 (Co)_2$	7H <sub>2</sub> O		100 169 15.17	- - 15.46
Plateau II 169 <sup>0</sup> -200 <sup>0</sup> C		$[(C_{10}H_6O_4)_3 (Co)_2$		
Sigmoid II 200 <sup>0</sup> -363 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to $3/2(C_{10}H_6O_4) (Co)_2$	$3/2(C_{10}H_6O_4$		200 363 49.08	49.26
Plateau III 363 <sup>0</sup> -500 <sup>0</sup> C		$3/2(C_{10}H_6O_4) (Co)_2$		
Sigmoid II 200 <sup>0</sup> -363 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to Co <sub>3</sub> O <sub>8</sub>	$3/2(C_{10}H_6O_4)$		500 600 83.56	87.78
Co <sub>3</sub> O <sub>8</sub>			16.44	12.19

**Table; 2 : Analytical Data on Non-isothermal decomposition of  $[(C_{10}H_6O_4)_3 (Ni)_2 4H_2O]1 \frac{1}{2} H_2O$**

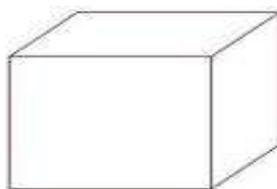
Reaction	Loss	Composition	Found	Calc.
Plateau I Ambient-99.9 <sup>0</sup> C	-	$[(C_{10}H_6O_4)_3 (Ni)_2 4H_2O]1 \frac{1}{2} H_2O$	-	-
Sigmoid I 99.9 <sup>0</sup> C-139 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C	$5 \frac{1}{2} H_2O$		99.9 136	

Loss to (C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Ni) <sub>2</sub>			12.98	12.60
Plateau II 136 <sup>0</sup> -300 <sup>0</sup> C		(C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Ni) <sub>2</sub>		
Sigmoid II 300 <sup>0</sup> -365 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to 7/4(C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) (Ni) <sub>2</sub>	1 ¼ C <sub>10</sub> H <sub>6</sub> O <sub>4</sub>		300 365 43.28	42.84
Plateau III 365 <sup>0</sup> -500 <sup>0</sup> C		7/4(C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) (Ni) <sub>2</sub>		
Sigmoid II 500 <sup>0</sup> -600 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to NiO	7/4(C <sub>10</sub> H 6O <sub>4</sub> )		500 600 77.73	81.17
NiO 600 <sup>0</sup> C on words			22.27	18.83

**Table 3: Analytical Data on Non-isothermal decomposition of [(C<sub>10</sub>H<sub>6</sub>O<sub>4</sub>)<sub>3</sub> (Cu)<sub>2</sub>] 4H<sub>2</sub>O**

Reaction	Loss	Composition	Found	Calc.
Plateau I Ambient-26.5 <sup>0</sup> C	-	[(C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Cu) <sub>2</sub> ] 4H <sub>2</sub> O	-	-
Sigmoid I 26.5 <sup>0</sup> C-71 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to (C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Cu) <sub>2</sub>	4H <sub>2</sub> O		26.5 71 9.52	9.38
Plateau II 71 <sup>0</sup> -300 <sup>0</sup> C		(C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Cu) <sub>2</sub>		
Sigmoid II 300 <sup>0</sup> -400 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to (C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Cu) <sub>2</sub>	C <sub>10</sub> H <sub>6</sub> O <sub>4</sub>		300 400 35.64	34.11
Plateau III 400 <sup>0</sup> -500 <sup>0</sup> C		(C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Cu) <sub>2</sub>		
Sigmoid II 500 <sup>0</sup> -545 <sup>0</sup> C Ti <sup>0</sup> C Tf <sup>0</sup> C Loss to 1/2(C <sub>10</sub> H <sub>6</sub> O <sub>4</sub> ) <sub>3</sub> (Cu) <sub>2</sub>	3/2(C <sub>10</sub> H 6O <sub>4</sub> )		500 545 68.63	70.57

Examination of the crystallographics data on these polymetal chelates showed that each of the crystal assumed cubic P symmetry with  $a = b = c$  and  $\alpha = \beta = \gamma = 90^\circ$  as described below.



Cubic P symmetry

$$a=b=c, \alpha = \beta = \gamma = 90^\circ$$

The absence of the forbidden number ( $N = h^2 + k^2 + l^2$ ); 7, 15, 23 etc and the evidences on the mixed odd and even values of h k l had been the contributing facts to the above conclusion on the crystallographics of each of the polymetal chelates. The cubic F and cubic I symmetries were ruled out as the crystals could not conform to the basic crystallographic conditions (odd or even values of h k l, and even values of (h+k+l) respectively).

The polymetal chelates of naphthazarin with Co(II), Ni(II), and Cu(II) assumed the density order as Co(II) ( $\rho$ ) > Ni(II) ( $\rho$ ) > Cu(II) ( $\rho$ ). The formula weight of each of (I-III) structures were in full agreement to the one determined experimentally (Table 7). The  $a^\circ$  values followed the order as that of density values. The crystallographics data on these metal chelates have been shown in tables 4,5,6,7.

**Table; 4 X-Ray data on polymetallic chelate of naphthazarin with Cobalt (II) [(C<sub>10</sub>H<sub>6</sub>O<sub>4</sub>)<sub>3</sub>(Co)<sub>2</sub>4H<sub>2</sub>O]3H<sub>2</sub>O**

Common Factor (C.F): 0.0130

$\rho = 1.10$  g/cc

$a = 10.4018^\circ \text{A}$

2 $\theta$	$\Theta$	$\text{Sin}^2 \theta$	$\text{Sin}^2 \theta/\text{C F.}$	N ( $h_2 + k_2 + l_2$ )	h k l	h + k + l	$d^\circ \text{A}$	
							found	cal.
16.50	8.25	0.0260	2.00	2	110	2	7.36	7.35
22.00	11.00	0.0364	2.80	3	111	3	6.01	6.00
30.20	15.10	0.0670	5.15	5	210	3	4.65	4.65
42.00	21.00	0.1284	9.88	10	310	4	3.29	3.28

**Table; 5 X-Ray data on polymetallic chelate of naphthazarin with Nickel (II) [(C<sub>10</sub>H<sub>6</sub>O<sub>4</sub>)<sub>3</sub>(Ni)<sub>2</sub>4H<sub>2</sub>O]1/2H<sub>2</sub>O**

Common Factor (C.F): 0.0192

$\rho = 1.92$  g/cc

$a = 8.5586^\circ \text{A}$

2 $\theta$	$\Theta$	$\text{Sin}^2 \theta$	$\text{Sin}^2 \theta/\text{C F.}$	N ( $h_2 + k_2 + l_2$ )	h k l	h + k + l	$d^\circ \text{A}$	
							found	cal.
12.00	6.00	0.01092	1.00	1	110	1	8.56	8.55
22.00	11.00	0.03600	3.29	3	111	3	4.94	4.94
30.00	15.10	0.06690	6.12	6	211	4	4.28	3.49
40.00	20.00	0.11690	10.71	11	311	5	3.83	2.58

**Table 6: X-Ray data on polymetallic chelate of naphthazarin with Copper (II) [(C<sub>10</sub>H<sub>6</sub>O<sub>4</sub>)<sub>3</sub>(Cu)<sub>2</sub>]4H<sub>2</sub>O**

Common Factor (C.F): 0.02185

 $\rho = 2.28$  g/cc $a = 8.0230^{\circ}$ A

2 $\theta$	$\Theta$	Sin <sup>2</sup> $\theta$	Sin <sup>2</sup> $\theta$ /C F.	N (h <sub>2</sub> + k <sub>2</sub> + l <sub>2</sub> )	h k l	h + k + l	d <sup>0</sup> A	
							found	cal.
17.00	8.50	0.02185	1.00	1	100	1	8.02	8.02
24.00	12.00	0.04323	1.98	2	110	2	5.67	5.67
31.20	15.50	0.07142	3.26	3	111	3	4.63	4.63
41.00	20.50	0.12265	5.61	16	211	4	4.01	3.27

**Table 7: Molecular weights of polymetallic chelate of naphthazarin**

Metal Chelates	Molecular weights	
	Calculated	Found
Co(II)	814	813.70
Ni(II)	787	784.99
Cu(II)	768	767.89

## CONCLUSION

The transition metals Co(II), Ni(II) and Cu(II) on chelation with naphthazarin form polymetal chelates combining 02 moles of metal and 03 moles of the chelator in each case. These polymetal chelates have been thermally characterized. The X-ray analysis of each of the polymetal chelates show that the crystals assume cubic P lattice. The density and molecular weight of each polymetal chelate have been calculated.

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