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Note

KINETICS AND X-RAY POWDER DIFFRACTION STUDIES ON DIHYDRATED BIS(2-HYDROXY-1,4-NAPHTHOQUINONATO) COBALT(II) AND NICKEL(II) COMPLEXES

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The literature concerning the applications of 2-hydroxy-1,4-naphthoquinone (lawsone) [1–7] make no reference to the kinetics of non-isothermal decomposition or X-ray powder diffraction studies on dihydrated bis(2-hydroxy-1,4-naphthoquinonato) cobalt(II) and nickel(II) complexes: this note concerns studies undertaken on these lines.

EXPERIMENTAL

All the chemicals used were of Analar quality. Ni(II) and Co(II) 2-hydroxy-1,4-naphthoquinone chelates were isolated according to the method of Bottei and McEachern [8] and recrystallised for X-ray studies in EtOH. Chemical analysis (THERELEK) of the chelates tallied with $M(C_{10}H_5O_3)_2 \cdot 2H_2O$ where M = Ni(II) and Co(II), in agreement with Bottei and McEachern.

A duPont instrument was used for pyrolysis using the parameters: range, = 2 mV cm^{-1}; time constant, = 5 s; atmosphere, = N_2; flow rate, = 50 ml min^{-1}; time axis, progress rate = 5°C min^{-1}, range = 25°C min^{-1}.

For X-ray analysis, a GE XRD-6 was used with the following parameters: radiation = Cu 50, kV = 15 ma; filter = Ni; line focus; take-off angle = 4°; coll. slit = 1°; soller slit = MR; H.T. = 780; amp. gain = 16/0.67; E = 8 V; ΔE = 34 V; time constant = 1 sec; linear; scan speed = 2° min^{-1}; chart speed = 24 inch min^{-1}.

RESULTS AND DISCUSSION

The pyrolysis data on Ni(II) and Co(II) 2-hydroxy-1,4-naphthoquinone chelates, tallied with the inferences drawn by Bottei and McEachern. Sigmoids appearing in thermogravimetric curves, correspond to the desolva-

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tion/decomposition of chelates.

$$ML_2 \cdot 2\,H_2O \rightarrow ML_2 + 2\,H_2O \quad (1)$$

$$ML_2 \rightarrow \text{Metal oxide} + \text{Volatile products} \quad (2)$$

where M = Ni(II) or Co(II) and L = $C_{10}H_5O_3$.

The kinetics of reactions (1) and (2) have been probed following the methods of Dave and Chopra [9]. For $n = 1$

$$k = \frac{(-dx/dt)}{(A-a)} \quad (3)$$

$$\frac{-E/2.303R(T^{-1})}{\log(A-a)} = -n + \frac{\log(dx/dt)}{\log(A-a)} \quad (4)$$

This method yielded dependable kinetic data for E (activation energy), n (order of reaction) and Z (collision number) under conditions which, if applied to other slope-dependent procedures [10,11], lead to errors in data.

Values of A, a and dx/dt were worked out from the derivative thermogravimetric (DTG) curves derived differentially from the thermogravimetric (TG) curves. A plot of log k vs. $1/T$ gave a straight line in each case, showing that the desolvation/ decomposition follows first-order kinetics. The slope ($E/2.303R$) and intercept gave the values of the E and Z, respectively.

Using eqn. (4), a linear plot of $\log(dx/dt)/\log(A-a)$ vs. $T^{-1} \times 10^3/\log(A-a)$, with a slope equal to $-E/2.303R$ and intercept equal to n was observed for each reaction.

The Coats and Redfern [12] procedure, viz.

$$-\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = -\log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] + \frac{E}{2.303RT} \quad (5)$$

where α (fraction of substance at time t) $= (W_0 - W_t)/(W_0 - W_f)$; W_0 = initial weight, W_f = final weight and W_t = weight lost at time t; A = the frequency factor; E = activation energy; a = linear heating rate.

On plotting $-\log[-\log(1-\alpha)/T^2]$ vs. $1/T$, a straight line relationship was obtained, in support of the foregoing inferences. The value of E was obtained from the slope which is equal to $E/2.303R$. The value of $\log AR[1 - 2RT/E]/aE$ as per Coats and Redfern is constant.

Table 1 gives the kinetic data obtained using eqns. (3)–(5). Low values of Z (collision number) indicate that the reactions are slow processes.

X-Ray studies

X-Ray powder diffraction studies on Ni(II) and Co(II) 2-hydroxy-1,4-naphthoquinone chelates could give an idea about their molecular arrangement within the lattice. The X-ray powder diffraction data shown in Table 2,

TABLE 1

Kinetic data on dihydrated bis(2-hydroxy-1,4-naphthoquinonato) cobalt(II) and nickel(II) inner salt complexes

Reaction [a]	Temp. range (°C)	Method					
		Eqn. (3)			Eqn. (4)		Eqn. (5)
		n	E (kcal mole^{-1})	Z	n	E (kcal mole^{-1})	E (kcal mole^{-1})
$NiL_2 \cdot 2\,H_2O \rightarrow NiL_2 + 2\,H_2O$	200–315	1	26.54	0.45	0.74	36.61	24.11
$NiL_2 \rightarrow NiO + D.P.$	345–400	1	28.98	0.56			29.10
$CoL_2 \cdot 2\,H_2O \rightarrow CoL_2 + 2\,H_2O$	200–268	1	25.42	0.40	1.00	68.64	33.18
$CoL_2 \rightarrow Co_3O_4 + D.P.$	310–400	1	28.60	1.99	0.67	68.64	28.14

[a] $L = C_{10}H_5O_3$; D.P. = dissociation products.

TABLE 2

X-Ray powder diffraction data on dihydrated bis(2-hydroxy-1,4-naphthoquinonato) cobalt(II) and nickel(II) complexes

2θ		hkl		d(Å)				I/I_t	
Ni	Co	Ni	Co	Found		Calcd.		Ni	Co
				Ni	Co	Ni	Co		
10.10	10.15	111	111	8.75	8.63	8.82	8.48	100.00	100
13.88	16.90	210	220	6.38	5.24	6.24	5.19	5.81	43.88
16.67	17.75	220	221	5.32	4.99	5.39	4.89	16.28	58.16
17.50	18.45	221	300	5.06	4.81	5.08	4.89	27.91	70.40
18.00	20.50	300	311	4.93	4.33	5.08	4.43	33.72	43.88
19.25	22.13	311	320	4.61	4.01	4.60	4.07	11.05	42.86
20.00	27.60	322	421	4.44	3.23	4.41	3.20	12.20	67.35
21.83	34.25	321	440	4.07	2.62	4.08	2.60	13.95	26.53
23.00	39.66	400	621	3.86	2.27	3.82	2.29	6.97	15.51
23.83		410		3.73		3.71		9.88	
24.83		411		3.58		3.59		7.26	
27.25		421		3.27		3.33		4.18	
28.75		422		3.10		3.11		9.30	
31.33		520		2.85		2.84		4.65	
34.00		522		2.64		2.65		8.14	
39.75		631		2.27		2.25		5.81	
43.25		721		2.09		2.08		4.65	
48.75		652		1.87		1.89		3.48	

led to the proposal that both metal chelates assume cubic(P)-type lattice structures with the absence of reflections *hkl*, that is, $N = h^2 + k^2 + l^2 = 7$, 15, 23, 28. The morphology of both complexes is given by: system, cubic(P); axial ratio, $a : b : c :: 1 : 1 : 1$.

X-Ray powder diffraction data

	Lawsone chelates	
	Ni(II)	Co(II)
Cell dimension, $a = b = c$	15.27 Å	14.68 Å
Formula weight	440.69	440.94
Formula weight per unit cell	1	1
Density (g cm^{-3})	0.2056	0.2312

Fusion behaviour

The metal chelates decompose in the range 190–200°C. The melt does not recrystallise on cooling.

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