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Note

STUDIES OF THE INNER SALT COMPLEX OF 2-HYDROXY-1,4-NAPHTHOQUINONE (LAWSONE) WITH Hg(II)

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The usefulness of lawsone, a natural dye extractable from *Lawsonia inermis*, in biochemistry, analytical chemistry and chelatometry is well documented [1–9]. An earlier report [10] on lawsone's role in containing pigmentary disturbances of skin added to its innovative and therapeutic value.

EXPERIMENTAL

All chemicals used were of AnalaR grade. The inner salt complex was isolated by the slow addition of 1% sodium lawsonate solution to the salt solution with constant stirring. The yellow precipitate was filtered, washed with ice-cooled water and dried at 50–60°C. Chemical analysis data (THERELEC) agreed with the formula $(C_{10}H_5O_3)_2Hg$. The isolate was recrystallised in acetone for crystallographic work. For X-ray powder diffraction studies, GR XRD-6 with the following parameters was used: radiation = Cu 50; kV = 15 ma; filter = Ni; line focus; take-off angle = 4°; collimator slit = 1°; soller slit = MR; H.T. = 780; amplifier gain = 16/0,67; $E = 8$ V; $E = 34$ V; time constant = 1 s linear; scan speed = 2° min^{-1}; chart speed = 24 inch min^{-1}.

Potentiometric titrations ($I = 0.1$ M KCl; medium = 50% acetone–water) were done on a Beckman pH meter, Model 2, duly standardised with suitable buffers. The shapes of the curves after correction following Van Uitert and Haas [11] for non-aqueous media were as usual. The IR studies were made on a Perkin–Elmer Infra Cord spectrophotometer.

RESULTS AND DISCUSSION

As revealed by the conductometric, chemical analysis and pH metric studies, the inner salt complex under study composed of one mole of Hg(II) and two moles of lawsone.

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TABLE 1

Stability constants and thermodynamic functions of the inner salt complex of lawsone with Hg(II)

Temp. (°C)	$\log k_1$	$\log k_2$	$\log k_1 k_2$	ΔF^0 (cal mol^{-1})	ΔH^0 (cal mol^{-1})	ΔS^0 (cal deg^{-1} mol^{-1})
20	3.35	2.71	6.06	−8110		
30	3.58	2.90	6.48	−9030	+499	+46

The Henderson–Hesselback equation [12] was employed to determine the proton–ligand stability constant of lawsone ($\log {}^{P}K^{H} = 4.75$, 4.60 at 20° and 30°C, respectively).

The formation functions, $\bar{n}$ and pL, were calculated following Bjerrum's concept [13]. Formation curves ($\bar{n}$ vs. pL) extended to $\bar{n} = 2$, but under experimental conditions its extension to $\bar{n} = 0.5$ was not reached; hence $\log k_1$ was determined from the following relationship

$$\log k_1 = 2 \log k_{\mathrm{av}} - \log k_2$$

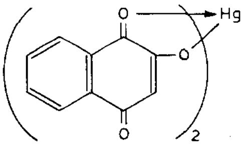
where $\log k_{\mathrm{av}}$ and $\log k_2$ could be read from formation curves at $\bar{n} = 1$ and 1.5, respectively.

Further analysis revealed a difference between $\log k_1$ and $\log k_2$ far less than 2.5, ruling out the operation of Bjerrum's half-integral method [13] for such estimation. For better results the point-wise calculation method using the following relation was employed.

$$\log k_n = \mathrm{p}L + \log \bar{n} - (n - 1)/(n - \bar{n})$$

Table 1 contains data on the stability constants of the inner salt complex.

As evidenced by the lowering of pH on the addition of Hg(II) to lawsone solution, the phenolic group behaves as a weak acid and is capable of protonation. The enolic anion liberated satisfies the valency of the metal cation, entering into coordination with the adjoining keto oxygen as a donor-forming five-membered ring.



IR studies, supporting the above conclusions, show bands at 3125 cm^{-1} and 1650 cm^{-1} attributable to O–H stretching vibration manifesting strong hydrogen bonding in lawsone, and carbonyl stretching vibration, respectively. The former band disappears whereas the latter is shifted to 1577 cm^{-1} indicating the presence of a $\rangle$C=O ··· Hg coordinate bond, on chelation.

It is seen from Table 1 that $\log k_1$ and $\log k_2$ increase with the rise of

TABLE 2

X-ray data on primitive cubic lattice of the inner salt complex of lawsone with Hg(II)

2θ	$h\,k\,l$	d(Å)		I/I_0
		Found	calc.	
11.10	1 1 1	7.9616	8.0512	15.49
12.10	2 0 0	7.3058	6.9726	39.44
14.10	2 1 0	6.2737	6.2365	12.68
15.90	2 1 1	5.5673	5.6931	5.60
17.40	2 2 0	5.0905	4.9303	5.00
20.30	3 1 0	4.3694	4.4098	7.04
22.70	3 2 0	3.9126	3.8677	11.25
24.30	3 2 1	3.6584	3.7270	6.25
26.60	4 1 0	3.3471	3.3822	100.00
27.70	4 1 1	3.2166	3.2869	16.90
30.90	4 2 2	2.8904	2.8462	8.41
34.40	4 3 2	2.6039	2.5895	14.08
43.20	6 2 2	2.0917	2.1023	4.20
48.00	7 2 1	1.8931	1.8977	4.20
55.30	8 2 0	1.6592	1.6911	4.20

temperature, favouring high temperature for complexation on account of the increase in kinetic energy due to increase in collisions.

Further, ΔH^0 is positive, pointing to the endothermic nature of the reaction and providing an explanation for the foregoing inferences. From ΔF^0 values, the spontaneous nature of the reaction is concluded. With more negative values with the rise of temperature, the feasibility of the reaction is inferred. The ΔS^0 value being positive favours complexation.

X-RAY STUDIES

Values of d (Å) calculated using the equation for a cubic system

$$d = a/\sqrt{h^2 + k^2 + l^2}$$

and different indices and experimental θ values, agreed well to the calculated values; it shows that the inner salt complex is a primitive-type lattice. Further observations from Table 2 on the absence of all possible restrictions viz. $N = 7, 15, 23, 28, 31, 39\ldots$ where $N = h^2 + k^2 + l^2$ [14] concluded the primitive cubic lattice for the inner salt complex crystal with the axial ratio a : b : c ::1 : 1 : 1 and the following values: cell dimension, a = b = c = 13.9451 Å; cell volume, 2712 Å; formula weight, 546; formula weight per cell, 1; density (g cm^{-3}), 0.3342 (X-ray).

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