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Note

# COMPLEXING BEHAVIOUR OF 2-HYDROXY-3-(-3-METHYL-2-BUTENYL)-1,4-NAPHTHALENEDIONESEMICARBAZONE

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The diversified utility of hydroxynaphthoquinones has attracted the attention of researchers; their complexing behaviour has been well examined by Sawhney et al. [1–5]. The missing literature on hydroxynaphthoquinone-semicarbazone has been of interest; this attempt covers the synthesis, the mass spectral study of 2-hydroxy-3-(-3-methyl-2-butenyl)-1,4-naphthalenedionesemicarbazone and its subsequent behaviour towards metals, viz. Tb(III), Gd(III) and Eu(III) in solution with a follow-up operation on the stability and thermodynamics of these systems.

## EXPERIMENTAL

All the chemicals used were of analytical grade. To synthesise 2-hydroxy-3-(-3-methyl-2-butenyl)-1,4-naphthalenedionesemicarbazone, a mixture containing equal moles of semicarbazide hydrochloride (in water) and 2-hydroxy-3-(-3-methyl-2-butenyl)-1,4-naphthalenedione (in acetone) was refluxed for 1/2 h; the yellow colour of the mix changed to brownish red, and the precipitate that appeared on cooling was filtered, washed with ice-cold water and dried at 35–40°C.

A solution study was carried out, on each of the following: Tb-, Gd- and Eu-2-hydroxy-3-(-3-methyl-2-butenyl)-1,4-naphthalenedionesemicarbazone in 50% acetone and ionic strength: 0.1 M $KNO_3$, following earlier details [6–10].

A Kratos MS-Model with DS-55 data system was employed for recording the mass spectrum of the respective compound. A filament current of 300 $\mu$A and EI mode of fragmentation at 70 eV were maintained. A direct insertion probe was used because of the solid nature of the sample. Source/probe temperature was 250/150°C; scan interval was 3 s per decade.

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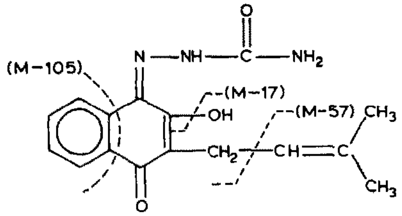
## RESULTS AND DISCUSSION

Chemical analysis conformed to the structure



### *Mass spectral study*

A careful examination of the mass spectrum of the title compound showed an odd molecular peak ($m/e$ 299); the molecular ion corresponds to the above proposed structure. The M − 17 ion peak suggests OH as the most facile group. A peak at $m/e$ 242 which is 57/56 mass less than $m/e$ 299, is due to a $C_4H_8$ or $C_4H_9$ fragment—the only possible target in the proposed structure. A peak at $m/e$ 105 is strongly indicative of Mackafferty arrangement.

### *pH study*

Formation functions: $\bar{n}_H$, $\bar{n}$ and $pL$ have been determined following Irving and Rossotti [11] and Bjerrum expressions [12]. A plot of (pH vs. $\log \bar{n}_H/(1-\bar{n}_H)$) was used to work out the value of the protonation constant of the title compound ($\log {}^{P}K^{H} = 4.75$ (35°C) and 5.75 (45°C)). The upper limit of $\bar{n}_H$ was unity, allowing the conclusion of the monoprotic nature of the compound.

Lowering of pH on the addition of a metal to the ligand solution (and so releasing more hydrogen ions into it) manifested the presence of the salt-formation group (–OH) in the ligand, and so its subsequent role in the chelation.

The whole study was performed near infinite dilution and at constant ionic strength, permitting the direct determination of the thermodynamic formation constant; under these conditions the activity coefficient of the species involved reduces to unity, equalising the formation constant determined at a specified concentration and also the thermodynamic formation constant. Formation curves ($\bar{n}$ vs. $pL$) failed to provide data to warrant the conditions necessary to apply the Bjerrum half integral method for the estimation of these constants; the graphical methods depended upon data reliability (Table 1). Stability data on these systems revealed a decreasing trend, showing the lessening of the strength of the ligand bond with reference to either of the metals with successive attachment of ligand molecules.

TABLE 1

Stability and thermodynamics [a] of Tb(III)-, Gd(III)- and Eu(III)-2-hydroxy-3-(-3-methyl-2-butenyl)-1,4-naphthalenedionesemicarbazone systems

| | Metals | | | | | |
|---|---|---|---|---|---|---|
| | Tb(III) | | Gd(III) | | Eu(III) | |
| | 35°C | 45°C | 35°C | 45°C | 35°C | 45°C |
| log $k_1$ | 5.20 | 5.48 | 5.20 | 5.90 | 4.78 | 6.40 |
| log $k_2$ | 4.05 | 4.02 | 4.10 | 3.90 | 3.92 | 4.05 |
| log $k_3$ | 3.75 | 3.70 | 3.70 | 3.65 | 3.70 | 3.74 |
| log $\beta_3$ | 13.02 | 13.20 | 13.00 | 13.45 | 12.40 | 14.19 |
| $\Delta G°$ | −18.47 | −19.33 | −18.44 | −19.70 | −17.59 | −20.78 |
| $\Delta H°$ | | +8964 | | +20169 | | +80.23 |
| $\Delta S°$ | | +88.97 | | +125.36 | | +317.63 |

[a] $\Delta G°$ and $\Delta H°$ in kcal $\mathrm{mol}^{-1}$; $\Delta S°$ in cal $\mathrm{mol}^{-1}$ $\mathrm{K}^{-1}$.

Further, the data on the Eu-2-hydroxy-3-(-3-methyl-2-butenyl)-1,4-naphthalenedionesemicarbazone system showed a decrease in logarithmic values of $^{\mathrm{P}}K^{\mathrm{H}}$, $k_1$, $k_2$ and $k_3$ with increasing temperature, making allowance for high temperatures favouring the reaction by the increase of collision rate and also the increase of the kinetic energies of the molecules involved. In other systems a regular sequence (decreasing or increasing) was absent; no reasonable explanation could be given to the observed data; $\Delta H°$ assumed positive values, indicating the endothermic nature of the reaction in support of the earlier inferences on the system; the other systems are also endothermic. All the reactions are accompanied by an increase in entropy ($\Delta S°$) and tend to be spontaneous. Negative values of $\Delta G°$, assumed by the systems, and which became more negative at higher temperature, showed conclusively their feasibility; the spontaneous nature of the reactions backs up the entropy-based inferences.

Under experimental conditions the completeness of the formation curves of the systems at both ends has been observed; with $\bar{n}$ assuming 3 as its value, the formation of 1 : 1, 1 : 2 and 1 : 3 species in solution is concluded.

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