

METAL COMPLEXES OF THE ALKALOID 4-FORMYL-8-HYDROXY-QUINOLINE OCCURRING IN THE TIMBER OF *BROUSSONETIA ZEYLANICA* (THW.) CORNER

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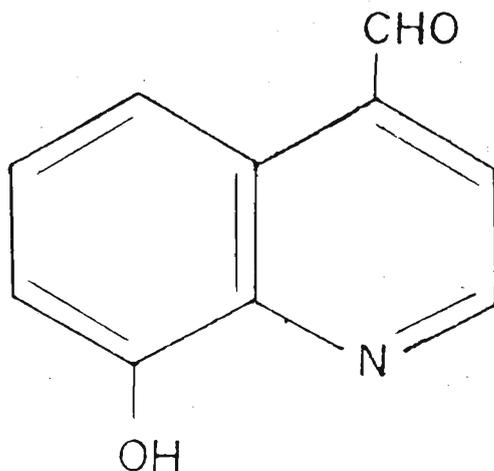
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Abstract: Several complexes of the ligand 4-formyl-8-hydroxyquinoline with the metal ions, Ni^{2+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Mn^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} and MoO_2^{2+} have been synthesized. Their compositions have been characterised from elemental analyses and spectroscopic data. These studies may bear some relevance to the role of naturally occurring ligands in the metal ion translocation in plants.

1. Introduction

Chelating ligands from plants and their metal complexes have received some attention as possible models for metal ion translocation in plants.¹ The role of carrier molecules⁴ in metal ion absorption and transport is attractive to explain the mechanism of the movement of metal ions into plants. In the case of bacteria, water soluble ligands such as ferrichromes and siderochromes fulfill this role.⁷ The presence of several classes of natural products with chelating ability prompted our investigations in this area.^{2,3}

Broussonetia zeylanica is an endemic plant to Sri Lanka belonging to the Moraceae family. The first naturally occurring 8-hydroxyquinoline derivative was isolated⁵ from the timber extracts of this plant (I).



(I)

On account of the well known complexing ability of 8-hydroxyquinoline, we have investigated the complexes of this ligand (I) with some biologically important metal ions.

2. Experimental

The isolation of the ligand 4-formyl-8-hydroxyquinoline is reported elsewhere⁵ and a sample was kindly provided by Prof. A. A. L. Gunatilaka of this Department. The complexes of Fe^{3+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Mn^{2+} , Al^{3+} , Cu^{2+} and Mg^{2+} were prepared by the following procedure. A solution of the metal chloride (0.5 m mole) in 5 ml of water, 1 ml of 5N acetic acid and 0.5 g of sodium acetate was warmed to 70–80°C. A solution of the ligand (in the appropriate molar ratio) in 10 ml of ethanol was then added and the reaction mixture was boiled. In the case of the molybdenum complex, molybdic acid was used in place of the metal chloride. The resultant dark coloured solution was cooled and the precipitate obtained was filtered, washed with ethanol, ether and dried in vacuo. The yields obtained were in the range of 50–80% (based on the metal). The yields were in general lower than in the case of 8-hydroxyquinoline complexes since the complexes appear to be more soluble in aqueous media. The colours of the complexes persisted in solution and in the case of the iron complex, further evaporation was necessary to separate the complex as a precipitate.

Infrared spectra were obtained in KBr discs using a Perkin-Elmer 257 spectrophotometer. The UV-VIS spectra were recorded on a Pye-Unicam model SP 8000 spectrophotometer. The complexes were analyzed for the oxine by the standard titration technique⁹ with KBrO_3 and the metal by standard gravimetric techniques. During gravimetry it was necessary to remove the ligand in some cases by extracting it into chloroform.

3. Results and Discussion

3.1 Composition of the complexes

From the analytical data it was possible to derive the composition of these complexes. Table 1 summarizes the analytical data and the formulae of the complexes obtained.

Analysis of the oxine content in these complexes also confirm the stoichiometries proposed for them in Table 1.

Table 1. Analytical data and the composition of the complexes of 4-formyl-8-hydroxyquinoline

| Complex | % of Metal observed | (calculated) |
|-------------------------------------|---------------------|--------------|
| NiL ₂ .2H ₂ O | 13.39 | (13.30) |
| ZnL ₂ | 15.66 | (15.95) |
| FeL ₃ | 9.96 | (9.79) |
| cis-MoO ₂ L ₂ | 20.41 | (20.33) |
| CdL ₂ .H ₂ O | 23.21 | (23.66) |
| MgL ₂ | 6.47 | (6.59) |
| MnL ₂ .2H ₂ O | 12.61 | (12.61) |
| CuL ₂ .2H ₂ O | 13.75 | (14.31) |
| AlL ₃ | 4.72 | (4.97) |

3.2 Infrared Spectra

The IR spectrum of the free ligand showed the presence of a broad band at ca. 3200 cm⁻¹ due to the OH group and a band at 1690 cm⁻¹ due to the -CHO group. The IR spectra of the metal complexes showed the disappearance of the broad band at 3200 cm⁻¹ indicative of coordination via the hydroxyl group. Since the ¹H NMR spectrum of the free ligand in CDCl₃ showed the appearance of an acetal proton upon addition of CD₃OD, the IR spectra of metal complexes were closely examined for the presence of the -CHO group. All complexes showed the presence of the -CHO group intact with the $\nu_{C=O}$ shifted⁶ to ca. 1710 cm⁻¹. The IR spectrum of the molybdenum complex showed two strong absorption bands around 900 cm⁻¹ and 925 cm⁻¹ indicating the presence of a cis-MoO₂ group.

3.3 Electronic Spectra

All complexes are intensely coloured and distinctly more so than the analogous 8-hydroxyquinoline complexes (Table 2). The increased intensity of colours can be attributed to the extended conjugation of the ligand through the -CHO. The ligand shows absorption maxima in the UV-VIS spectrum at 206, 243, 261, 322(w) and 372(w,sh) nm. The weak absorption at 372 gets shifted to 483 upon the addition of a base and can be assigned to a $n \rightarrow \pi^*$ transition. The complexes retain the positions of the first two absorption maxima of the free ligand but showed distinct downward shifts of the other three bands to lower energies (higher λ values). Thus the complexes showed absorption bands in the regions, 290-300, 335-340 and 385-390 nm, regions. Similar downward shifts of absorption bands have been observed in the case of 8-hydroxyquinoline complexes.⁸

Table 2. Comparison of the colours of metal complexes of 4-formyl-8-hydroxyquinoline with those of 8-hydroxyquinoline.

| Metal ion | Colour of the 8-hydroxyquinoline complex | Colour of the 4-formyl-8hydroxyquinoline complex |
|--------------------------------|--|--|
| Fe ³⁺ | black | black |
| MoO ₂ ²⁺ | yellow | yellowish-orange |
| Ni ²⁺ | greenish yellow | red |
| Zn ²⁺ | yellow | orange-red |
| Al ³⁺ | yellow | orange |
| Cd ²⁺ | yellow | red |
| Cu ²⁺ | green | brown |
| Mg ²⁺ | yellow | orange |
| Mn ²⁺ | yellow | brown |

4. Conclusion

Chemical analysis and spectroscopic data confirm the composition and the nature of these complexes. These complexes are more soluble in aqueous media than the corresponding 8-hydroxyquinoline complexes. They remain in ethanol/water solution at physiological pH values. This feature is important in assessing the role of naturally occurring ligands in the metal ion translocation in plants.

The enhanced activity of some drugs as their metal complexes is well documented.¹⁰ The antibacterial action of 8-hydroxyquinoline has been explained on the transport and subsequent release of Fe³⁺ in the medium across the cell membranes of certain types of bacteria.¹⁰ Thus the metal chelates studied above may also have some relevance in explaining the observed antibacterial activity of 4-formyl-8-hydroxyquinoline.

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References

1. ALBERT, A., (1958) "Metal binding agents in chemotherapy" 8th Symposium of the society of General Microbiology, The Univ. Press, Cambridge.

2. DANGALLA, A.C.M., DIAS, H.W. & ILEPERUMA, O.A. (1986), *Indian J. Chem.*, 25A, 80.
3. DANGALLA, A.C.M. & ILEPERUMA, O.A. (1985) *J. Natn. Sci. Coun. Sri Lanka*, 13(2), 141.
4. DA SILVA, J.J.R.F. (1978) "New Trends in Bio-inorganic chemistry" 449, New York, Acad. Press.
5. GUNATILAKA, A.A.L., PERERA, J.S.H.Q., SULTANBAWA, M.U.S., BROWN, P.M., & THOMSON, R.H. (1979) *J. Chem. Research (S)*, 61.
6. NAKAMOTO, K. (1963), "Infrared spectra of Inorganic and Coordination compounds", Wiley, New York.
7. RAYMOND, K.N. & CARRANO, C.J. (1979), *Acc. Chem Res.* 12, 183.
8. TOMKINSON, J.C., & WILLIAMS, R.J.P. (1958) *J. Chem. Soc.* 1153.
9. VOGEL, A.I. (1961) "A Text book of Quantitative Inorganic Analysis" 3rd edition, Longmans, London, p. 536.
10. WILLIAMS, D.R. (1972) *Chem. Rev.*, 72 ; 203.