

PREPARATION AND PROPERTIES OF SOME METAL COMPLEXES OF PLUMBAGIN

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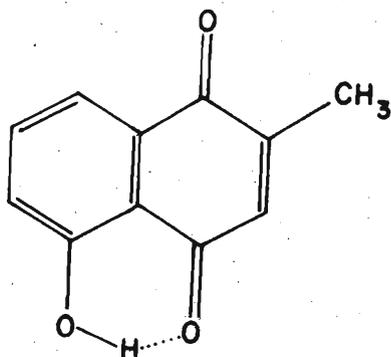
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Abstract : The preparation and the characterisation of the complexes formed by plumbagin, a naturally occurring naphthaquinone with the ions Cu(II), Ni(II), Co(II), Mn(II), Zn(II) and Hg(II) is reported. The stability constants of these complexes in solution have been determined using potentiometric titration techniques. The high values observed for the stability constants may have some relevance to support the hypothesis that certain carrier molecules are involved in the uptake of metal ions by plants.

1. Introduction

As a part of an investigation on the naturally occurring ligands we have studied the complex forming ability of plumbagin (I), a naturally occurring naphthaquinone. This paper reports the preparation, characterisation and the solution studies on several of these complexes. These studies may have some relevance to the theory² that carrier molecules which form complexes with metal ions are important in metal ion uptake and transport in plants.



2. Experimental

Plumbagin was isolated from the dried root extract of *Aristea ecklonii* as previously published.⁴ The product was crystallized as bright orange needles from hexane. The purity of plumbagin was verified by its melting point, ¹H NMR, IR and TLC data. The IR spectra were obtained in KBr discs using a Perkin-Elmer 257 spectrophotometer and the UV-VIS spectra using Pye-Unicam model SP 8000 spectrophotometer. The ¹H NMR were obtained from a Varian T60 instrument. The pH measurements during the potentiometric titrations were obtained from a Corning model 5 pH meter equipped with combination glass and calomel electrodes. The pH meter was calibrated using standard Corning buffer solutions having pH values 7.00 and 4.00 at 25 ± 1°C. The solvents and chemicals used were of reagent grade. The C-H analysis of these complexes were carried out by Ciba-Geigy Ltd., Geneva, Switzerland.

2.1 Preparation of the complexes

The Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Mg(II) complexes of plumbagin were prepared by mixing the appropriate metal acetate solutions in methanol with hot methanolic solutions of plumbagin. The resultant mixture was heated in a water bath for about 15 min and the precipitates obtained were filtered, washed with hot methanol and dried in vacuo. The yields, in most cases, were 50–60% (based on plumbagin). The analytical data and the colours of the complexes are given in Table 1. The metal analyses were carried out by standard colorimetric methods.

Complex	Colour	Found (Calc.)%		
		Metal	C	H
Cu(C ₁₁ H ₇ O ₃) ₂ ·2H ₂ O	brown red	13.83 (13.32)	55.10 (55.81)	3.60 (3.80)
Ni(C ₁₁ H ₇ O ₃) ₂ ·2H ₂ O	brown-violet	12.51 (12.52)	55.00 (56.32)	4.00 (3.84)
Co(C ₁₁ H ₇ O ₃) ₂ ·2H ₂ O	brown-red	12.00 (12.56)	56.00 (56.31)	3.80 (3.83)
Mn(C ₁₁ H ₇ O ₃) ₂ ·2H ₂ O	brown-red	12.00 (11.81)	56.30 (56.78)	3.90 (3.87)
Zn(C ₁₁ H ₇ O ₃) ₂ ·2H ₂ O	brown-red	14.00 (13.75)	55.20 (55.53)	3.80 (3.78)
Mg(C ₁₁ H ₇ O ₃) ₂ ·2H ₂ O	brown-red	5.50 (5.59)	61.00 (60.78)	3.90 (4.14)

Table 1. Analytical data and the colours of the plumbagin metal complexes.

2.2 Determination of stability constants

Solutions containing plumbagin (5.0×10^{-4} M) and metal acetates (2.5×10^{-4} M) were titrated with carbonate free 0.1 M KOH at $\mu = 0.1$ M (KCl) under an atmosphere of nitrogen and the pH recorded, after the addition of 0.2 ml aliquots of alkali.

3. Results and Discussion

All these complexes possess different shades of brown red colour. The elemental analysis (Table 1) indicate 1:2 (metal:ligand) stoichiometry for all these complexes. The copper complex is slightly soluble in chloroform while all the other complexes are insoluble in chloroform. However, all these complexes are readily soluble in DMSO and pyridine. Their melting points were found to be above 250°C .

3.1 Infrared spectra

Plumbagin has two carbonyl groups, with the hydrogen bonded one appearing at 1640 cm^{-1} and the other at 1660 cm^{-1} (Figure 1). Only the hydrogen bonded carbonyl group should be affected by complex formation and this is indeed what is observed. In the complexes, the carbonyl stretch of free plumbagin at 1640 cm^{-1} appears in the range of $1620\text{--}1630\text{ cm}^{-1}$. Such downward shifts in the carbonyl stretching frequencies of coordinated carbonyl groups have been previously observed¹ in the metal complexes of 1-hydroxyxanthone. This provides definite evidence for the participation of the carbonyl group in the bonding of these complexes. The possible structures for a typical metal complex of plumbagin are shown in Figures II

3.1.1 Electronic spectra

The UV-VIS spectrum of plumbagin in methanol shows a characteristic absorption maximum at 394 nm assigned to a $\pi \rightarrow \pi^*$ transition of the carbonyl group. All the metal complexes exhibited the presence of an additional intense charge transfer absorption band with the maximum in the range of 450–460 nm (Table 2).

3.2 Solution studies

The successive stability constants were determined by the potentiometric techniques and calculated by the method of Irving and Rosotti.³

The stability constants calculated in this manner are given in Table 3. These are in agreement with the Mellor-Maley's series⁵ for divalent metal

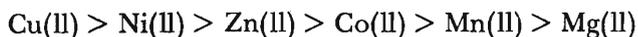
Table 2 Electronic spectral data of the plumbagin metal complexes

Complex	Absorption maximum (nm)	(Epsilon x 10 ⁶)
C ₁₁ H ₈ O ₃ (plumbagin)	394	(3.1)
Cu(C ₁₁ H ₇ O ₃) ₂ .2H ₂ O	460	(7.1)
Ni(C ₁₁ H ₇ O ₃) ₂ .2H ₂ O	452	(6.8)
Co(C ₁₁ H ₇ O ₃) ₂ .2H ₂ O	460	(5.9)
Mn(C ₁₁ H ₇ O ₃) ₂ .2H ₂ O	465	(7.3)
Zn(C ₁₁ H ₇ O ₃) ₂ .2H ₂ O	450	(6.3)
Mg(C ₁₁ H ₇ O ₃) ₂ .2H ₂ O	456	(5.7)

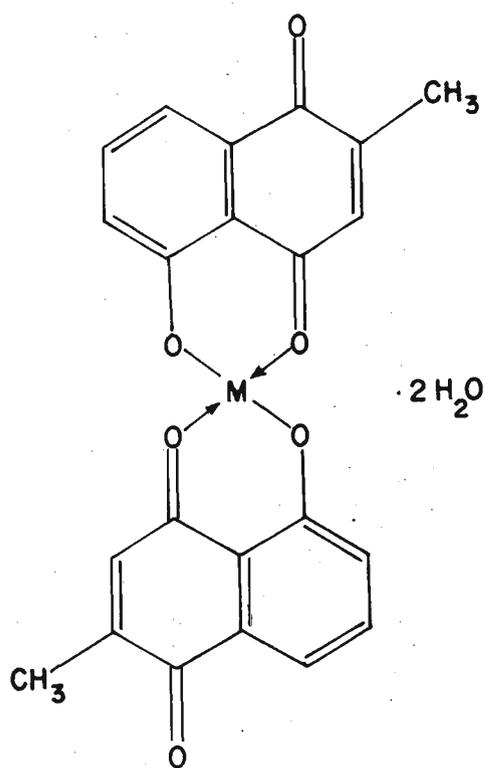
Table 3. Stability constants of plumbagin metal complexes

Metal ion	log K ₁	log K ₂
Cu(II)	5.31	4.93
Ni(II)	4.90	4.54
Co(II)	4.84	4.66
Mn(II)	4.80	4.28
Zn(II)	4.45	3.74
Mg(II)	4.32	3.73

ions for the corresponding 8-hydroxyquinoline complexes:

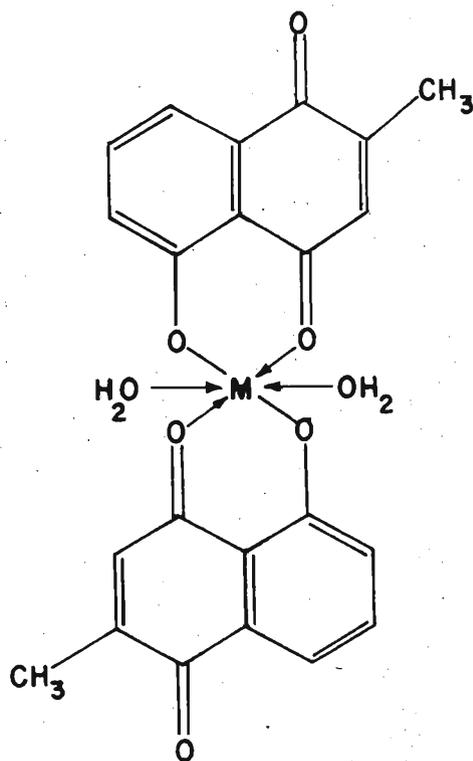


Studies on complex formation of biologically important metal ions may be important in understanding metal ion transport and storage in plants. The metal ions move against a concentration gradient in the root hairs. The exact mechanism of how the metal ions pass through the cell membrane is not well understood. It has been proposed that certain carrier molecules are involved in this type of transport,² analogous to, for example, the role of ferrichromes in the uptake of iron by certain types of bacteria.



IIa

OR



IIb

4. Conclusion

In this context, the results described above on the complex formation by a naturally occurring ligand may provide a model for the uptake, transport and the storage of nutrient metal ions by plants.

Acknowledgement

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References

1. DANGALLA, A. C. M., DIAS, H. W. & ILEPERUMA, O. A. (1986) *Indian J. Chem.*, 25A, 80.
2. DA SILVA, J. J. R. F. (1978) *New Trends in Bio-inorganic Chemistry*, 449, New York, Academic Press.
3. IRVING, H. & ROSOTTI, H. S. (1953), *J. Chem. Soc.*, 3397.
4. KUMAR, V., MEEPAGALA, K. M. & BALASUBRAMANIAM, S. (1985) *Phytochemistry*, 24(5): 1118.
5. MALEY, L. E. & MELLER, D. P. (1948) *Nature*, 161: 436.