

Synthetic, Spectral and Antibacterial Studies of Co(III) and Mn(III) Metal Chelates of 2,5-Dihydroxy undecyl 1,4-Benzoquinone and its Azo Derivatives

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Embelin (2,5 dihydroxy undecyl 1,4-benzoquinone), an orange pigment extracted from the berries of *Embelia ribes*, an Indian medicinal shrub, is a well known bioactive compound. Antiinflammatory, antibiotic and analgesic activities of embelin were reported. Embelin, having two hydroxyl groups and ketonic oxygen atoms could function as a better chelating agent. Azo derivatives of embelin, with their azo, hydroxyl and ketonic groups would possess enhanced ligational properties. With this idea, an attempt has been made to prepare Mn(III) and Co(III) complexes of embelin (EM), 3-(4'-azo-antipyrine)embelin (AAPE) and 3-(2'-hydroxyl phenyl-azo)embelin (OAPE) and were characterised by elemental analysis, molar conductance, magnetic susceptibility measurements, thermal and various spectral studies. Chemical and spectral studies indicate that embelin complexes of Mn(III) and Co(III) were polymeric in nature. In Mn(III) and Co(III) complexes, AAPE behaves as neutral tridentate while OAPE acts as monovalent tridentate having O_h or D_{4h} geometry with composition $[M(AAPE)X_3]$ and $[M(OAPE)X_2(H_2O)]$ where $M = Co(III)$ and $Mn(III)$ and $X = Cl, Br, NO_3, OAc, ClO_4$. Ligands and their few metal complexes were screened for their antibacterial activity.

Key Words: Co(III), Mn(III), Chelates, 2,5-Dihydroxy undecyl 1,4-benzoquinone, Azo derivatives.

INTRODUCTION

Embelin (EM), the bioactive principal extract of *Embelia ribes*, an Indian medicinal shrub, is of interest as it possesses antifertility, antibacterial and antihelminthic activities¹. It has been reported that metal chelates of embelin could function as a possible basis for anthelmintic drugs². Structural modifications of this bioactive compound were attempted earlier to get various pharmacological profiles³. In view of the above reports, it was of interest to study the coordinating ability of embelin and its derivatives with metal ions and expected enhanced biological activities for these complexes. Complexes of embelin with divalent metal ions, Mn(II), Ni(II), Cu(II) and Zn(II) have already been reported⁴. However, literature

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survey reveals that no attempt has been made for the synthesis and characterization of complexes of trivalent metal ions. The present report includes the preparation, characterisation and bioactivity of few complexes of Co(III) and Mn(III) with embelin (AAPE) and its azo derivatives, viz., 3-(4'-azo antipyrine) embelin (AAPE) and 3-(2'-hydroxyl phenyl azo) embelin (OAPE).

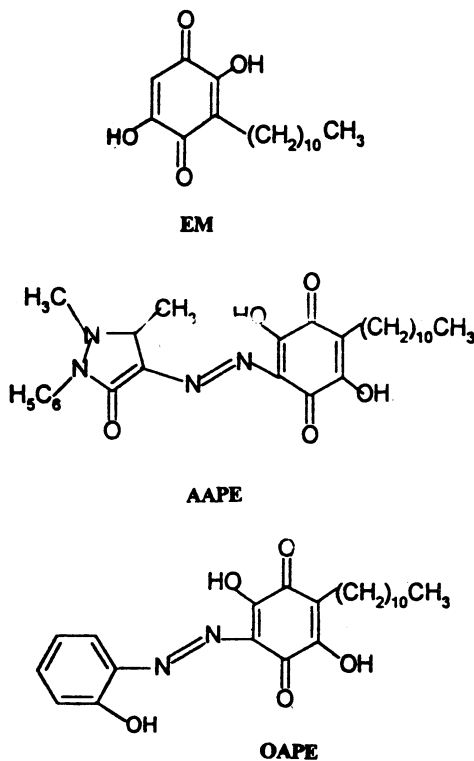


Fig. 1. (1) Embelin (2) 3-(4'-azo antipyrine) embelin (3) 3-(2'-hydroxyl phenyl azo) embelin.

EXPERIMENTAL

4-Aminoantipyrine and *o*-aminophenol (Fluka) were used as supplied. All other chemicals and metal salts were of AR grade. Embelin was obtained by extracting dried powdered berries of *Embelia ribes* with ether in a soxhlet apparatus. The extracted product was digested with petroleum ether and recrystallised from absolute alcohol⁵; m.p. 142°C.

Preparation of AAPE and OAPE: AAPE was prepared by diazotizing about 10 g (0.05 mol) of 4-aminoantipyrine in 100 mL of 1 : 1 HCl and the resulting diazonium salt solution was added slowly with stirring to an ice-cold alkaline solution of embelin. This mixture was kept in an ice bath for 30 min with occasional stirring. Bright red crystals separated were suction filtered, washed with small amounts of alcohol and then with petroleum ether and recrystallised from alcohol. (m.p. 110°C). OAPE was prepared by the same procedure using *o*-aminophenol (5 g, 0.05 mol) instead of 4-aminoantipyrine. (m.p. 120°C).

Preparation of complexes

Complexes were prepared by refluxing ethanolic solutions of metal salts and ethanolic solutions of ligands in 1 : 1 molar ratio with slight excess of ligand for 1 h. Complex precipitated was filtered, washed with hot alcohol to remove excess ligand and dried over P_4O_{10} in vacuum.

Metal contents were estimated by usual procedure after digesting the complexes with conc. H_2SO_4 and the results were further confirmed by atomic absorption spectroscopy. Chloride and bromide in the complexes were estimated by Volhard's method⁶. Perchlorate was determined by Kurtz method⁷. The electronic spectra of complexes were recorded using Shimadzu UV-1601 spectrophotometer and the IR spectra on a Perkin-Elmer RX FTIR spectrophotometer using KBr pellet disc. Magnetic moments of all the complexes were determined in Gouy balance calibrated using $[HgCo(NCS)_4]$ at room temperature. Molar conductances were measured using Elico digital conductivity meter. Thermogravimetric analyses of few complexes were carried out in air at the rate of $10^\circ C/min$ up to $700^\circ C$.

RESULTS AND DISCUSSION

All complexes are coloured ranging from brown to black. Analytical data are in agreement with composition proposed for the complexes as in Table-1.

The $\nu(O-H)$ frequency observed as a strong band at 3300 cm^{-1} for embelin is absent in the spectra of complexes indicating the coordination of phenolic oxygen to metal ion *via* deprotonation. A positive shift in $\nu(C-O)$ frequency further confirms this observation. The shift in the $\nu(C=O)$ band of the ligand observed at 1615 cm^{-1} by $30-40\text{ cm}^{-1}$ in complexes suggests the coordination through carbonyl oxygen. The new band around 520 cm^{-1} assignable to $\nu(M-O)$ in the complexes supports the coordination of carbonyl and phenolic oxygen atoms to metal ion⁸. Thus IR spectra reveal that embelin acts as a monodentate bivalent ligand in these complexes. The broad medium intense band occurring between 3400 and 3300 cm^{-1} in the spectra of Mn(III) and Co(III) complexes may be attributed to the $\nu(O-H)$ frequency of coordinated water⁹. The $\nu(O-H)$ bending frequency is observed as a weak band at 1650 cm^{-1} in the present metal-complexes. The band around 750 cm^{-1} in the complexes of embelin is characteristic of the rocking mode of coordinated water¹⁰. The presence of coordinated water molecule in the complexes is further confirmed by thermal decomposition studies and Karl-Fisher method⁶.

The $\nu(C=O)$ frequency observed at 1653 cm^{-1} in the ligand spectrum is shifted to $1620-1610\text{ cm}^{-1}$ in AAPE complexes suggesting the coordination of pyrazolone carbonyl group. The $\nu(C=O)$ vibration of embelin ring observed at 1613 cm^{-1} is shifted to lower frequency by 20 cm^{-1} in all metal-complexes confirming its coordination to metal ion. The azo group vibration $\nu(N=N)$ in the free ligand at 1487 cm^{-1} shows a downward shift of around 20 cm^{-1} in all these metal-complexes. The frequency corresponding to $\nu(O-H)$ band remains unchanged in complexes. In addition to these bands the spectrum of the AAPE complexes show non-ligand bands at around $550-540$, $520-510$ and $340-330$

cm^{-1} assignable to stretching frequencies of $\nu(\text{M}-\text{N})$, $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{Cl})$ bands respectively^{8, 9}. Thus AAPE acts as a neutral tridentate ligand.

TABLE-I
PHYSICAL AND ANALYTICAL DATA OF Mn(III) AND Co(III) COMPLEXES

Complexes	Colour	Yield (%)	% Metal Obsd. (Calcd.)	μ_{eff} (B.M.)
1. $[\text{Mn}(\text{EM})_2(\text{H}_2\text{O})\text{Cl}]$	dark brown	75	8.46 (8.45)	4.90
2. $[\text{Co}(\text{EM})_2(\text{H}_2\text{O})\text{Cl}]$	dark green	72	8.26 (8.30)	—
3. $[\text{Mn}(\text{EM})_2(\text{H}_2\text{O})\text{Br}]$	black	65	7.95 (7.94)	4.88
4. $[\text{Mn}(\text{EM})_2(\text{H}_2\text{O})(\text{OAc})]$	dark brown	62	8.16 (8.18)	4.91
5. $[\text{Co}(\text{EM})_2(\text{H}_2\text{O})\text{Br}]$	brown	72	7.89 (7.90)	—
6. $[\text{Co}(\text{EM})_2(\text{H}_2\text{O})(\text{OAc})]$	dark brown	78	8.10 (8.13)	—
7. $[\text{Mn}(\text{EM})_2(\text{H}_2\text{O})\text{NO}_3]$	dark brown	68	8.12 (8.14)	4.83
8. $[\text{Co}(\text{EM})_2(\text{H}_2\text{O})\text{NO}_3]$	dark green	70	8.12 (8.10)	—
9. $[\text{Mn}(\text{EM})_2(\text{H}_2\text{O})\text{ClO}_4]$	black	71	7.75 (7.74)	4.87
10. $[\text{Co}(\text{EM})_2(\text{H}_2\text{O})\text{ClO}_4]$	brown	70	7.68 (7.70)	—
11. $[\text{Mn}(\text{AAPE})\text{Cl}_3]$	brown	65	8.25 (8.20)	4.88
12. $[\text{Co}(\text{AAPE})\text{Cl}_3]$	dark brown	73	8.73 (8.75)	—
13. $[\text{Mn}(\text{AAPE})\text{Br}_3]$	black	80	6.81 (6.83)	4.92
14. $[\text{Mn}(\text{AAPE})(\text{OAc})_3]$	black	78	7.30 (7.29)	4.89
15. $[\text{Co}(\text{AAPE})\text{Br}_3]$	dark green	69	7.31 (7.33)	—
16. $[\text{Co}(\text{AAPE})(\text{OAc})_3]$	dark brown	78	7.80 (7.82)	—
17. $[\text{Mn}(\text{AAPE})(\text{NO}_3)_3]$	brown	75	7.42 (7.41)	4.90
18. $[\text{Co}(\text{AAPE})(\text{NO}_3)_3]$	black	62	7.92 (7.93)	—
19. $[\text{Mn}(\text{AAPE})(\text{ClO}_4)_3]$	black	67	6.35 (6.37)	4.82
20. $[\text{Co}(\text{AAPE})(\text{ClO}_4)_3]$	dark brown	68	6.83 (6.81)	—
21. $[\text{Mn}(\text{OAPE})(\text{H}_2\text{O})\text{Cl}_2]$	brown	76	9.78 (9.80)	4.88
22. $[\text{Co}(\text{OAPE})(\text{H}_2\text{O})\text{Cl}_2]$	dark brown	78	10.44 (10.48)	—
23. $[\text{Mn}(\text{OAPE})(\text{H}_2\text{O})\text{Br}_2]$	black	71	8.48 (8.50)	4.9
24. $[\text{Mn}(\text{OAPE})(\text{H}_2\text{O})(\text{OAc})_2]$	black	70	9.04 (9.02)	4.87
25. $[\text{Co}(\text{OAPE})(\text{H}_2\text{O})\text{Br}_2]$	dark brown	69	9.10 (9.07)	—
26. $[\text{Co}(\text{OAPE})(\text{H}_2\text{O})(\text{OAc})_2]$	dark green	67	9.68 (9.67)	—
27. $[\text{Mn}(\text{OAPE})(\text{H}_2\text{O})(\text{NO}_3)_2]$	brown	77	8.96 (8.98)	4.92
28. $[\text{Co}(\text{OAPE})(\text{H}_2\text{O})(\text{NO}_3)_2]$	brown	68	9.55 (9.57)	—
29. $[\text{Mn}(\text{OAPE})(\text{H}_2\text{O})(\text{ClO}_4)_2]$	dark brown	71	8.09 (8.00)	4.88
30. $[\text{Co}(\text{OAPE})(\text{H}_2\text{O})(\text{ClO}_4)_2]$	dark brown	72	8.50 (8.53)	—

The lowering of $\nu(\text{N}=\text{N})$ frequency by 30–40 cm^{-1} in OAPE complexes of Mn(III) and Co(III) may tentatively be due to $(\text{M}-\text{N})$ bond formation as evident from the appearance of new $\nu(\text{M}-\text{N})$ bands around 540 cm^{-1} . The $\nu(\text{C}-\text{O})$ (phenolic) stretching mode which occurs at 1540 cm^{-1} in OAPE is shifted to

higher energy by 10–15 cm^{-1} in complexes indicating the involvement of phenolic oxygen in coordination *via* deprotonation. The carbonyl frequency observed at 1620 cm^{-1} in the spectra of the ligand OAPE is shifted to 1600 cm^{-1} in complexes revealing its coordination to metal ion which is further supported by the appearance of new $\nu(\text{M—O})$ bands around 520 cm^{-1} in spectra of complexes of OAPE¹¹. Thus in these complexes the ligand OAPE functions as monovalent tridentate ONO donor. Appearance of new bands around 1650 cm^{-1} and 800 cm^{-1} are attributed to bending and rocking mode of vibration of coordinated water^{9,10}. Thermal studies are also inconsistent with the above conclusion which is further confirmed by Karl-Fisher Method⁶.

Apart from the above vibrational modes, there are four additional bands in the spectra of the perchlorate complexes at 1150, 1080, 660 and 610 cm^{-1} assignable respectively to ν_4 , ν_1 , ν_3 and ν_5 vibrational modes of unidentately coordinated perchlorate group¹². Since the separation between ν_4 and ν_1 observed at 1440 and 1300 cm^{-1} in the spectra of nitrate complexes is 140 cm^{-1} , it is reasonable to consider that nitrate group is coordinated monodentately^{9,13}. In the spectra of acetate complexes asymmetric stretching and symmetric stretching of $\nu(\text{OCO})$ group appear at 1580 cm^{-1} and 1392 cm^{-1} respectively. Separation between the two bands in the complexes is higher than that in the free ion, suggesting monodentate coordination for the acetate group^{9,14}.

Electronic spectra of Co(III) complexes show three bands in the regions 28000–25000 cm^{-1} , 23000–20000 cm^{-1} and 18000–16000 cm^{-1} . First band may be assigned due to ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{2g}$ transition. The other two bands are due to split components of ${}^1\text{A}_{1g} \rightarrow {}^1\text{T}_{1g}$ transition¹⁰. In Mn(III) complexes three bands are observed at 16880 cm^{-1} , 18350 cm^{-1} and 20830 cm^{-1} assignable to the transitions ${}^5\text{B}_{1g} \rightarrow {}^5\text{A}_{1g}$, ${}^5\text{B}_{1g} \rightarrow {}^5\text{B}_{2g}$ and ${}^5\text{B}_{1g} \rightarrow {}^5\text{E}_g$ respectively¹⁵. Molar conductance measurements reveal that the complexes are non-electrolytes. The room temperature magnetic moment values found for Mn(III) complexes are in favour of high spin O_h or D_{4h} symmetry. Co(III) complexes are diamagnetic with O_h or D_{4h} stereochemistry.

On the basis of the above physico-chemical studies complexes reported here are suggested to have the formulae $[\text{M}(\text{EM})_2(\text{H}_2\text{O})\text{X}]$, $[\text{M}(\text{AAPE})\text{X}_3]$ and $[\text{M}(\text{OAPE})(\text{H}_2\text{O})\text{X}_2]$ where $\text{M} = \text{Co(III)}$ and Mn(III) , $\text{X} = \text{Cl}$, Br , OAc , NO_3 , ClO_4 .

Thermal studies: Thermal studies of few complexes were carried out in static air conditions. The thermogram of embelin and OAPE complexes of Co(III) and Mn(III) indicates two clear cut stages, first corresponding to the dehydration of coordinated water and second to the decomposition process⁴. In the case of Mn(III) complexes, dehydration step is seen to merge with decomposition process resulting in a single extended stage. The temperature range for the dehydration step, in this case, has therefore been deduced from the DTG curve and the % mass loss of this stage corresponds to loss of a water molecule. Mn(III) and

Co(III) complexes of AAPE exhibit only single step decomposition. Final residues of the complexes at 900°C are found to be their metal oxides. Thermoanalytical data are presented in Table-2.

TABLE-2
THERMOANALYTICAL DATA

Complex	Dehydration temp. maxima (°C)	Decomposition temp. maxima (°C)	% mass loss after dehydration
[Co(EM) ₂ (H ₂ O)NO ₃]	140	430	2.47
[Mn(OAPE)(H ₂ O)Cl ₂]	160	525	3.10
[Co(OAPE)(H ₂ O)Cl ₂]	150	425	2.95
[Mn(AAPE)Cl ₃]	—	550	—
[Mn(AAPE)(NO ₃) ₃]	—	480	—

Antimicrobial Screening: The *in vitro* biological screening effects of few ligands and their metal-complexes were tested against Gram positive bacteria, *Staphylococcus aureus* and three Gram negative bacteria, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa* and *Escherichia coli* by disc diffusion method using agar nutrient as medium and utilizing gentamycin as control¹⁶. For disc assays, paper (6 mm) containing the compounds was placed on the surface of the nutrient agar plates previously spread with 0.1 mL of overnight cultures of microorganisms. After 36 h of inhibition, diameter of the inhibition zones was measured and listed in Table-3¹⁷. Activity of the ligands was found enhanced on complexation with metal ions^{18, 19}. [Mn(AAPE)Cl₃] shows significant activity against *S. aureus*.

TABLE-3
ANTIBACTERIAL ACTIVITY OF COMPOUNDS AT 100 µg/DISC,
ZONE FORMATION IN mms

Complex, Ligand	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>E. coli</i>	<i>K. pneumoniae</i>
Control	22	20	15	18
Embelin	8	7	7	8
[Co(EM) ₂ (H ₂ O)Cl]	12	9	8	10
[Mn(EM) ₂ (H ₂ O)Cl]	14	12	8	12
OAPE	12	10	8	10
[Co(OAPE)(H ₂ O)Cl ₂]	14	11	9	12
[Mn(OAPE)(H ₂ O)Cl ₂]	16	12	10	14
AAPE	18	12	8	10
[Mn(AAPE)Cl ₃]	22	16	12	11
[Co(AAPE)Cl ₃]	20	14	10	11

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