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# POLYMERIC COMPLEXES OF EMBELIN WITH SOME METAL IONS

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**ABSTRACT**
The Formation and characterization of solid polymeric complexes: $[Be(C_{17}H_{24}O_4)]_n$, $[Mg(C_{17}H_{24}O_4)(H_2O)_2]_n$, $[Al(C_{17}H_{24}O_4)_{1.5}]_n$,$[Mn(C_{17}H_{24}O_4)(H_2O)_2]_n$, $[Zn(C_{17}H_{24}O_4)(H_2O)_2]_n$, $[Zr(C_{17}H_{24}O_4)_2]_n$,$[Ru(C_{17}H_{24}O_4)_{1.5}]_n$, $[Cd(C_{17}H_{24}O_4)(H_2O)_2]_n$,$[Sn(C_{17}H_{24}O_4)]_n$, $[Sb(C_{17}H_{24}O_4)_{1.5}]_n$,$[Tb(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$,$[Pb(C_{17}H_{24}O_4)]_n$ and $[Bi(C_{17}H_{24}O_4)_{1.5}]_n$ of embelin (2,5-dihydroxy-3-undecyl-p-benzoquinone) is reported. Nature and geometry of the complexes is supported by elemental analysis, electronic absorption, Infra red and thermal decomposition studies.

**KEY WORDS:** Polymeric complex, metal ions, infra red, elemental analysis etc.

## INTRODUCTION

Embelin is a biologically active benzoquinone derivative[1]. Embelia Laeta is known as a Chinese traditional herbal medicine and its active constituents have been determined [2-3]. Embelia ribes found to have antiproliferative properties[4]. Embelin shows a wide spectrum of biological activities. It shows antibacterial, antitumor, antiflammatory and analgesic activity [5-6]. Embelin can act as an antioxidant in physiological conditions[7]. H.M. Kumara Swamy has reported wound healing activity of emblin[8]. Purified embelin also shows antifertility, antioestrogenic and anthelmintic activities[9]. It gives intense color reactions with a large number of metal ions on paper chromatograms in visible and UV light[10]. Embelin cream (E 0.05%) is sold as cheap global discount cancer drug. Keeping in view the importance of embelin, synthesis of polymeric metal complexes of embelin is reported in present communication. Some complexes of embelin are already reported by us [11-12].

## MATERIALS AND METHODS

Embelin was isolated from emblia ribe seeds. It was crystallized from hot acetic acid and recrystallized as orange yellow plates from ether benzene mixture, M.P.142$^o$ C (Lit 142-143$^o$C). The complexes were prepared by mixing ethanolic solutions of the respective metal ion (taken in excess) and embelin, and then concentrating the solution. To the concentrated solution, water was added in excess which precipitated complex because of insolubility in water. The complexes were separated by filtration and excess of metal ion was removed by repeated washing with water. The complex of Sn(II) was prepared by adding embelin to molten $SnCl_2$ (taken in excess) with constant stirring followed by heating on low flame for half an hour. It was cooled, water was added, solid complex was precipitated. Solid was separated by filtration and was repeatedly washed with water. In case of antimony complex, $SbCl_3$ and embelin (1:5) were dissolved in benzene. The solution was refluxed on water bath for one hour, the solid complex which separated on cooling was washed with benzene. The complexes were finally dried under vacuum over anhydrous calcium chloride. AnalaR metal salts used were: $BeCl_2$, $MgCl_2.6H_2O$, $AlCl_3$, $MnCl_2.4H_2O$, $ZnCl_2.5H_2O$, $ZrOCl_2.8H_2O$, $RuCl_3.3H_2O$, $CdCl_2.5H_2O$, $SnCl_2.2H_2O$, $SbCl_2$, $TbCl_3$, $Pb(NO_3)_2$ and Bi $(NO_3)_3$. Carbon and hydrogen were estimated by using micro analytical combustion method. The metal content was estimated by ignition of the complexes to their respective oxides. IR spectra of the ligand and complexes were done by using KBr pellets recorded on Perkin Elmer-377 grating IR spectrophotometer. The electronic absorption spectra of the complexes were recorded as diffuse reflectance spectra on VSU2P (Carl Zeiss) spectrophotometer from 50,000 to 12500 cm$^{-1}$. The thermal decomposition of Al (III) and Zn (II) complexes was done by Paulik- Paulik MOM derivatograph (Hungary) and of Mn (II), Ru(II) and Cd (II) complexes was done by Stanton Redcraft-STA-780 thermal analyzer.

## RESULTS AND DISCUSSION

Elemental analysis results (Table-I) support to the composition of the complexes. The IR spectra (Table-II) of the benzoquinone derivative shows strong bands at 3322, 1610 and 1190 cm$^{-1}$ which are assigned to υ(O-H), υ(C=O) and υ(O-C) stretching vibrations respectively. The spectra of the complexes show significant shifts in these bands because of changes of force constants due to coordination of the ligand to the metal ion through oxygens of the Carbonyl functional group and the adjacent hydroxyl groups[13]. The υ(O-H) band at 3322cm$^{-1}$ of the ligand disappears completely in all the complexes due to coordination of the ligand to the metal ion through oxygen of the hydroxyl group with abstraction of proton. New bands appear in the region (440-700) cm$^{-1}$ as a result of the υ (M-0) stretching modes[14]. The appearance of bands at 1470cm$^{-1}$ in the complex of Tb(III) is due to coordinated ethanol. In the complexes of Mg (II), Mn (II), Zn (II) and

Cd (II), the bands at 3370cm$^{-1}$ ,3410cm$^{-1}$ and 3450 cm$^{-1}$ are assigned to stretching modes of water.

The electronic absorption spectra of the complexes are recorded in table - III. The electronic absorption bands of the complexes of Be(II), Mg(II), Cd(II), Sn(II), Sb(III), Al(III), Zn(II), Pb(II) and BI(III) are assigned as charge transfer electronic transition within the ligand, Ligand to metal and metal to ligand [15]. The electronic absorption bands at 26700 cm$^{-1}$ and 17211cm$^{-1}$ for Tb (III) complex are assigned due to $^5D_3 \leftarrow {}^7F_6$ and $^5D \leftarrow {}_2{}^7F_6$ respectively. The other bands in the complex are assigned due to $5d \rightarrow 4F$, $M \rightarrow L$ and $L \rightarrow M$ transitions[16-17]. The bands of the complex of Zr(IV) are assigned to electronic transition[18] within the ligand, $L \rightarrow M$ and $M \rightarrow L$. In case of Mn(II) complex, the bands at 13157, 16260 and 19047 are assigned to the transitions[19]: $^4T_{1g} \leftarrow {}^6A_{1g}$, $^4T_{2g} \leftarrow {}^6A_{1g}$, and $^4A_{1g} \leftarrow {}^6A_{1g}$,. The bands at 45871 and 33783 are change transfer bands. The bands in the range: 16400-17000, 20500-21000, 25000-26000 and 28000-32000 are assigned to $^2A_{2g} \leftarrow {}^2T_{2g}$ , $^2E_g \leftarrow {}^2T_{2g}$ , $^2A_{1g} \leftarrow {}^2T_{2g}$ and $\pi \leftarrow {}^2T_{2g}$ respectively in Ru(III) octahedral field[20]. The other higher region bands are charge transfer bands. The chemical composition and structures are also supported by the thermo-analytical study of the complexes:$[Al(C_{17}H_{24}O_4)_{1.5}]_n$ and $[Zn(C_{17}H_{24}O_4)(H_2O)_2]_n$ . Figure-1 shows the simultaneous DTA-TGA curves of Al(III) complex with 100mg of the sample and Zn(11) complex with 90 mg of the sample at the heating rate 10$^o$ per minute. The DTA curve of Al (III) complex shows one exothermic peak at 410$^o$C which explains the decomposition of the complex. Zn (II) complex shows one endothermic peak at 170$^o$C and two exothermic peaks (one strong at 390$^o$C and one weak at 460$^o$C).

**TABLE-I:** Elemental analysis (%) of the complexes

| S.No. | Complexes | Colour | Calculated | | | Found | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | M | C | H | M |
| 1 | $[Be(C_{17}H_{24}O_4)]_n$ | Light Yellow | 67.77 | 7.93 | 2.99 | 66.73 | 8.71 | 2.90 |
| 2 | $[Mg(C_{17}H_{24}O_4)(H_2O)_2]_n$ | Light Yellow | 64.12 | 8.19 | 6.81 | 62.31 | 7.11 | 6.38 |
| 3 | $[Al(C_{17}H_{24}O_4)_{1.5}]_n$ | Purple | 65.10 | 7.65 | 5.80 | 65.50 | 7.60 | 5.68 |
| 4 | $[Mn(C_{17}H_{24}O_4)(H_2O)_2]_n$ | Brown | 53.27 | 7.30 | 14.30 | 53.30 | 7.20 | 4.15 |
| 5 | $[Zn(C_{17}H_{24}O_4)(H_2O)_2]_n$ | Blue | 51.85 | 7.11 | 16.61 | 51.65 | 7.21 | 16.51 |
| 6 | $[Zr(C_{17}H_{24}O_4)_2]_n$ | Black | 60.42 | 7.10 | 13.50 | 60.68 | 7.14 | 13.39 |
| 7 | $[Ru(C_{17}H_{24}O_4)_{1.5}]_n$ | Dark Grey | 66.55 | 5.54 | 17.11 | 66.50 | 5.10 | 17.10 |
| 8 | $[Cd(C_{17}H_{24}O_4)(H_2O)_2]_n$ | Bluish Grey | 46.32 | 6.35 | 25.52 | 45.90 | 6.50 | 25.10 |
| 9 | $[Sn(C_{17}H_{24}O_4)]_n$ | Yellowish Green | 49.67 | 5.84 | 28.90 | 49.51 | 5.62 | 28.61 |
| 10 | $[Sb(C_{17}H_{24}O_4)_{1.5}]_n$ | Dull Green | 54.66 | 5.80 | 21.75 | 54.50 | 5.51 | 21.70 |
| 11 | $[Tb(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$ | Black | 51.38 | 6.96 | 22.06 | 51.19 | 6.48 | 23.29 |
| 12 | $[Pb(C_{17}H_{24}O_4)]_n$ | Green | 42.62 | 6.08 | 35.04 | 42.32 | 6.48 | 35.29 |
| 13 | $[Bi(C_{17}H_{24}O_4)_{1.5}]_n$ | Green | 47.29 | 5.56 | 32.30 | 47.69 | 5.38 | 32.59 |

**TABLE- II:** IR spectra of the ligands and the complexes

| S.No. | Ligand/ Complexes<br>$C_{17}H_{26}O_4$ (Ligand) | υ (0-H)<br>3322 | υ (C=O)<br>1610 | υ (O-C)<br>1190 | υ (M-0)<br>or<br>υ (M-O+C-C) |
|---|---|---|---|---|---|
| 1 | $[Be(C_{17}H_{24}O_4)]_n$ | -- | 1510 | 1220 | 450 |
| 2 | $[Mg(C_{17}H_{24}O_4)(H_2O)_2]_n$ | -- | 1480 | 1230 | 440 |
| 3 | $[Al(C_{17}H_{24}O_4)_{1.5}]_n$ | -- | 1545 | 1230 | 535 |
| 4 | $[Mn(C_{17}H_{24}O_4)(H_2O)_2]_n$ | -- | 1530 | 1230 | 450 |
| 5 | $[Zn(C_{17}H_{24}O_4)(H_2O)_2]_n$ | -- | 1520 | 1225 | 520 |
| 6 | $[Zr(C_{17}H_{24}O_4)_2]_n$ | -- | 1530 | 1230 | 480 |
| 7 | $[Ru(C_{17}H_{24}O_4)_{1.5}]_n$ | -- | 1500 | 1260 | 480 |
| 8 | $[Cd(C_{17}H_{24}O_4)(H_2O)_2]_n$ | -- | 1530 | 1200 | 700 |
| 9 | $[Sn(C_{17}H_{24}O_4)]_n$ | -- | 1610 | 1240 | 550 |
| 10 | $[Sb(C_{17}H_{24}O_4)_{1.5}]_n$ | -- | 1530 | 1250 | 560 |
| 11 | $[Tb(C_{17}H_{24}O_4)_{1.5}(C_2H_5OH)_2]_n$ | -- | 1590 | 1215 | 490 |
| 12 | $[Pb(C_{17}H_{24}O_4)]_n$ | -- | 1540 | 1230 | 458 |
| 13 | $[Bi(C_{17}H_{24}O_4)_{1.5}]_n$ | -- | 1130 | 1230 | 480 |

The first arrest in TGA curve corresponding to DTA peak of the Zn (11) complex shows a weight loss of 9.5% (Cal 9.15%) corresponds to the elimination of water molecules. The sharp endothermic peak in the complex of Al (III) and Zn (II) in the range of 420$^o$C-460$^o$C points to the loss of side chain of the ligand. The loss on pyrolysis in these complexes corresponds to the formation of their respective oxides which are $Al_2O_3$ and ZnO. Figure-II shows simultaneous DTG, DTA and TG curves of Mn (II), Ru (III) and Cd (II) complexes with 15.33 mg, 25.42 mg and 21.52 mg weight of the samples respectively, at the heating rate of 10$^0$C per minute. The DTA curve of Mn (II) complex indicates virtually no change up to 120$^0$C. At 140-155$^0$ C a loss of 11.51% is observed which

corresponds to the mass loss due to water which is fairly close to the calculated value. The loss of water molecules in the above range of temperature indicates that the water molecules are coordinated[21].

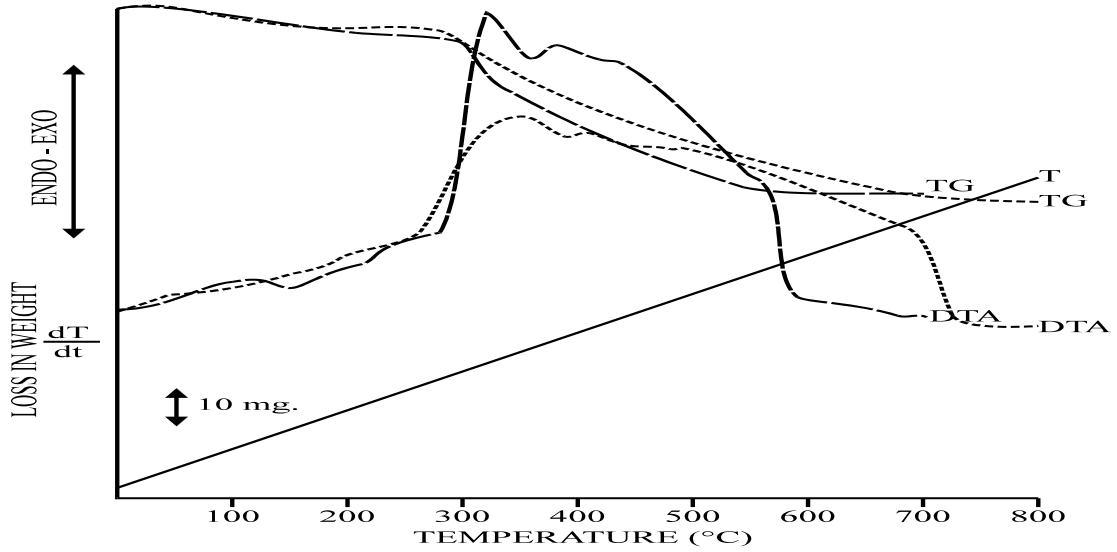


**Fig.1: SIMULTANEOUS DTA – TG CURVES OF:**
(a) $[Al(C_{17}H_{24}O_4)_{1.5}]_n$ ----- , (b) $[Zn(C_{17}H_{24}O_4)(H_2O)_2]_n$ ——

The DTA curve of Mn(II) complex shows one endothermic peak at 140-151$^0$C which corresponds to the loss of two water molecules. One exothermic peak at 355$^0$C explains the decomposition of the complex. Corresponding to this temperature there is as a sharpe decrease in the TG curve indicating a further loss of 83% by weight due to the final decomposition of the complex leaving the residue of $Mn_3O_4$, the final product formed at 700$^0$C. Similarly in case of Cd (II) complex, there is one endothermic peak at 140$^0$C in the DTA curve, corresponding to the loss of water molecules and simultaneous arrest in DTG curve showing a weight loss of 7.0% of the complex. There is one broad exothermic peak at 350$^0$C- 500$^0$C corresponding to the mass loss of 71.0% of the TG curve. The final weight of the residue corresponds to the weight of CdO. Ru (III) complex shows one broad extherm from 295$^0$C to 475$^0$C corresponding to the mass loss of 82.69% from the complex. The final weight of the compound corresponding to the formation of the oxide $Ru_2O_3$. There is no endothermic peak in the DTA curve of Ru (III) complex indicating the absence of coordinated water or ethanol molecules. On the basis of above studies, the proposed geometry of Al (III) , Mg(II), Mn(II) and Cd(II) complexes is octahedral having $sp^3d^2$ hybridization[22-24]. Pb(I1) and Sn(II) complex has trigonal pyramidal structure with $sp^3d$ hybridization[25], Bi(III) and Sb(III) complex have distorted octahedral geometry with $sp^3d^3$ hybridization[26], Zr[IV] complex has triangular faced do decahedral geometry with $sp^3d^3$ hybridization [27]. Ru (III) complex is octahedral with $d^2sp^3$ hybridization and Tb (III) complex has triangular faced dodecahedral geometry[28-29]. It is concluded that embelin (2,5.dihydroxy-3-undecyl-p-benzoquinone) has two hydroxyl and carbonyl functions in two vicinal positions at 1, 2 and 4, 5.The hydroxyl groups at positions 2 and 5 being highly acidic are expected to suffer abstraction of protons thereby giving rise to divalent $C_{17}H_{24}O_4$ anion. Embelin has two chelating sites at the opposite position. This peculiar characteristic results in the formation of polymeric complexes.

**TABLE –**III: Electronic Absorption spectra of the complexes

| S.No. | Complexes | Bands ($cm^{-1}$) |
|---|---|---|
| 1 | $[Be\ (C_{17}H_{24}O_4)]_n$ | 21598,32467,45871 |
| 2 | $[Mg\ (C_{17}H_{24}O_4)(H_2O)_2]_n$ | 21276,31250,44642 |
| 3 | $[Al\ (C_{17}H_{24}O_4)_{1.5}]_n$ | 39215(m),28571(m),16949(br) |
| 4 | $[Mn\ (C_{17}H_{24}O_4)(H_2O)_2]_n$ | 13157,16260,19047,33783,45871 |
| 5 | $[Zn\ (C_{17}H_{24}O_4)(H_2O)_2]_n$ | 41666(w),28409(s),22415(w),16666(m) |
| 6 | $[Zr\ (C_{17}H_{24}O_4)_2]_n$ | 41666(w),40000(w),29715(s),16129(s) |
| 7 | $[Ru\ (C_{17}H_{24}O_4)_{1.5}]_n$ | 16400,21052, (16400-17000), (20500-21000), (25000-26000), (28000- 32000),(31847-45871) |
| 8 | $[Cd\ (C_{17}H_{24}O_4)(H_2O)_2]_n$ | 19762,2500,34129, 47169 |
| 9 | $[Sn\ (C_{17}H_{24}O_4)]_n$ | 16760, 21276,32467,44652 |
| 10 | $[Sb\ (C_{17}H_{24}O_4)_{1.5}]_n$ | 16313,20408,21276,31847,45871 |
| 11 | $[Tb\ (C_{17}H_{24}O_4)_{1.5}\ (C_2H_5OH)_2]_n$ | 41666(w),27100(s) |
| 12 | $[Pb\ (C_{17}H_{24}O_4)]_n$ | 39062(w),25125(s0,16666(br) |
| 13 | $[Bi\ (C_{17}H_{24}O_4)_{1.5}]_n$ | 40322(w), 27100(s) |

**TABLE- IV:** TGA Loss (in Mass %) of the representative complexes

| S. No | Complexes | Calculated | | Found | |
|---|---|---|---|---|---|
| | | Ist Step | Final Product | First Step | Final Product |
| 1 | $[Al (C_{17}H_{24}O_4)_{1.5}]_n$ | -- | 80.8 | --- | 80.0 |
| 2 | $[Mn (C_{17}H_{24}O_4)(H_2O)_2]_n$ | 12.00 | 83.00 | 11.51 | 82.50 |
| 3 | $[Zn (C_{17}H_{24}O_4)(H_2O)_2]_n$ | 9.15 | 79.34 | 9.5 | 79.00 |
| 4 | $[Ru (C_{17}H_{24}O_4)_{1.5}]_n$ | --- | 83.00 | --- | 82.69 |
| 5 | $[Cd (C_{17}H_{24}O_4)(H_2O)_2]_n$ | 7.0 | 71.00 | 7.20 | 71.18 |

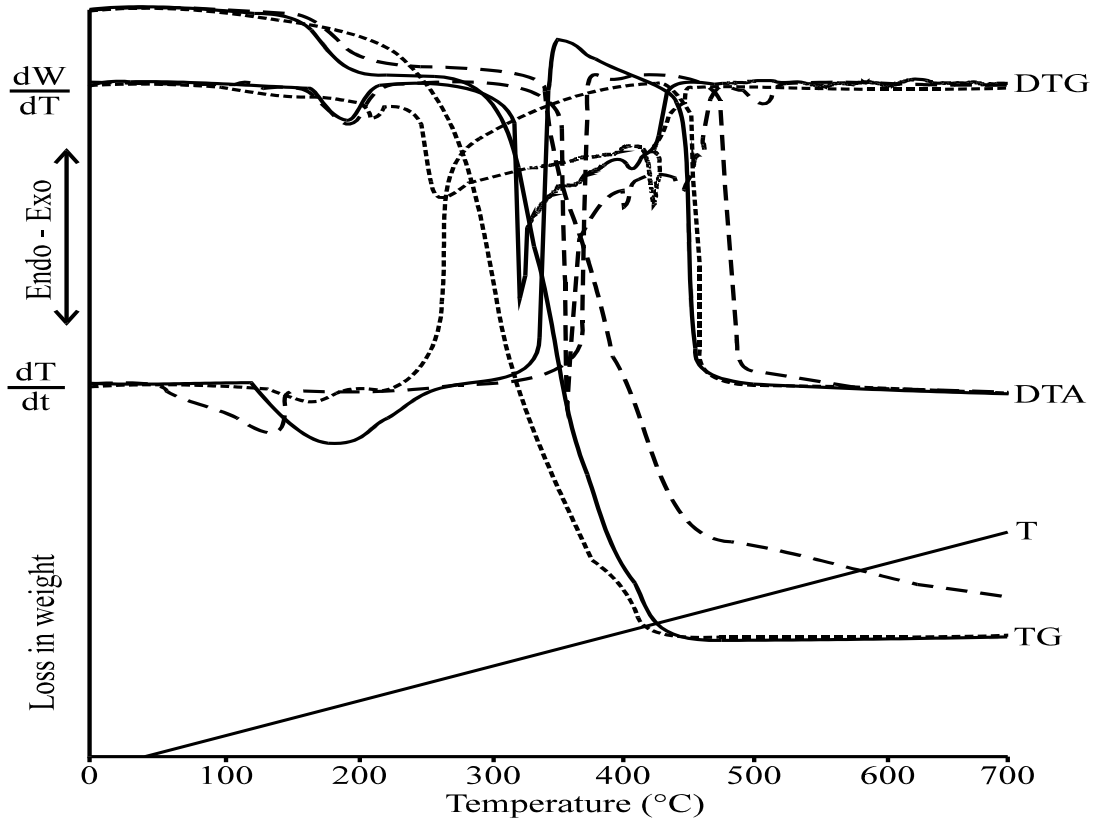


**Fig. 2: SIMULTANEOUS DTG - DTA - TG CURVES OF:**
(a) $[Mn(C_{17}H_{24}O_4)(H_2O)_2]_n$ —— ,(b) $[Ru(C_{17}H_{24}O_4)_{1.5}]_n$ - - - ,(c) $[Cd(C_{17}H_{24}O_4)(H_2O)_2]_n$ — —

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