Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2010, 2(5):89-95
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Physico-chemical characterization of Dichlorobis (Embelinate)Zinc(II) complex

V. Usha Rani[1], M. S. Prasada Rao[1], D. Venkata Rao[2] and B. B. V. Sailaja[1*]

[1]*Department of Inorganic and Analytical Chemistry, Andhra University, Visakhapatnam, India*
[2] *University college of Pharmaceutical sciences, Andhra University, Visakhapatnam, India*

ABSTRACT

Dichlorobis(embelinate)zinc(II) complex was obtained by the reaction of zinc chloride with embelin in 1:2 molar proportion. The thermal decomposition behaviour of the complex was studied using thermogravimetric analysis. IR analysis of the complex showed that the metal ions were coordinated through the carbonyl and the hydroxyl oxygen atoms. Elemental, Atomic absorption spectrophotometric and X-ray diffraction analyses of the complexes gave values that are consistent with six co-ordinate octahedral geometry of the metal ions. Based on data from these physico-chemical investigations the molecular formula of the complex was proposed as $Zn(C_{17}H_{25}O_4)_2Cl_2$

Key words : Zn(II) complex, Embelin, Thermal analysis, X-ray diffraction, IR, AAS.

INTRODUCTION

Embelin is a plant metabolite that was first reported from the berries of Embelia ribes of Myrsinaceae. The family myrsinaceae consists of nearly 1000 species of trees and shrubs spread over 33 genera[1] including four genera namely Myrsine, Maesa, Rapanea and Embelia, which are widely used in herbal medicines[2]. Myrsine africana L. is globally distributed in Africa, Arabia, Afghanistan, India, Pakistan, Cenrtal Nepal and China[3]. The fruit is used as an anthelmintic, especially in the treatment of tapeworm[4,5]. It is also a laxative and is used in the treatment of dropsy and colic. A gum obtained from the plant is used as a warming remedy in the treatment of dysmenorrhoea. Decoction of the leaves is used as a blood purifier[6]. Dried berries of this plant have a traditional reputation for showing anti-fertility activity[7]. Embelin is used in Ayurveda, Siddha as well as in Unani medicine system as anthelmintic and to cure skin

diseases[8,9]. Embelin also shows analgesic, anti-inflammatory[10], antibacterial[11], antitumor[12] and free radical scavenging activities[13]. The decoction of the dried fruits was noted to be useful in the treatment of fevers and diseases of chest and skin and infusion of roots was given for cough and diarrhoea[14]. Hartwell[15] reported that the extracts of E.ribes were useful in the treatment of abdominal tumours and cystic tumours. It was reported[16] that the methanol extract of the berries showed anti-plaque activity and anti-enzymatic action.The seeds of embelia were used in mordant dyeing[17]. It has also been used as an analytical reagent[18-20]. Synthesis and characterization of copper(II) complexes of embelin in the cavities of zeolite Y have been conducted[21] and found to display fairly good catalytic activity for the reduction of molecular oxygen. The derivatives of embelin showed the anticancer activity through microtubule disassembly[22]. Embelin complexes of different metals were also described[23,24]. The authors have synthesizedand characterizedthe Zn(II) complex of embelin in 1:2 molar proportion.

MATERIALS AND METHODS

Materials

Zinc chloride was purchased from Qualigens. Embelin was isolated from embelia ribe seeds. The seeds were dried and cleaned, powdered and subjected to extraction by petroleum ether in a soxhlet assembly. It was separated from the petroleum extract and it was recrystallized from hot acetic acid as orange yellow plates from an ether- benzene mixture. The melting point was observed to be 142^0C[25]. All reagents were of analytical grade.

Apparatus

Hewlett Packard CHN 185 analyzer was used to perform the elemental analysis. The metal analysis was obtained on a Chem Tech 2000 Instrument Atomic Absorption Spectrophotometer. Thermal analysis was performed on SEIKO combined thermal analysis system (TG/DTA 32), temperature programmable thermal balance and platinum crucible as container was used for taking thermograms in air. The rate of heating was fixed at 5^0C/min and sensitivity of the instrument was 0.01mg. Alumina(Al_2O_3) (recalcined at 1200^0C) was used as the reference material. The IR spectra using KBr discs were recorded on a Bruker (optic GmbH) ALPHA-T, FTIR Spectophotometer. X-ray diffraction data were collected using X-ray diffractometer of Ultima IV attached to a microprocessor. X-ray diffraction results were obtained using Cu K-α1 (Wavelength(λ)-1.54059 Á).

Preparation of the Dichlorobis(embelinate)Zinc(II)

Anhydrous zinc chloride (5mmol) and embelin(10mmol) were dissolved in ethanol ($20cm^3$) separately and mixed. Acetone ($10cm^3$) was added to the solution and it was stirred for 30min. The precipitated complex was filtered, washed with ethanol and was dried under vacuum at room temperature.

RESULTS AND DISCUSSION

Elemental analysis of Dichlorobis(embelinate)Zn(II)

The complex was soluble in 1,4-dioxan on heating, partially soluble in DMSO and insoluble in acetone, chloroform, DMF, methanol and water. In the elemental analysis chloride was estimated argentometrically and the oxygen content of the sample was computed by the difference of complex with CHN percentages. The probable formula and the composition of the complex are given in Table1

Table 1 : Elemental analysis of Dichlorobis(embelinate)Zn(II)

Method	C	H	O	Cl (Argentometry)	Zinc(AAS)	Probable Formula
Exper. %	57.13	6.98	17.79	9.85	8.25	$Zn(emb)_2Cl_2$
Calc.%	56.47	6.96	17.73	9.82	9.02	

3.2 Thermal analysis of Dichlorobis(embelinate)Zn(II)

Thermogravimetric analysis (TGA) : The pyrolysis curve of Dichloro bis embelinate zinc(II) is shown in Fig. 1 and the corresponding data in Table 2. By the TG curve it can be seen that the complex is stable up to 255^0C.

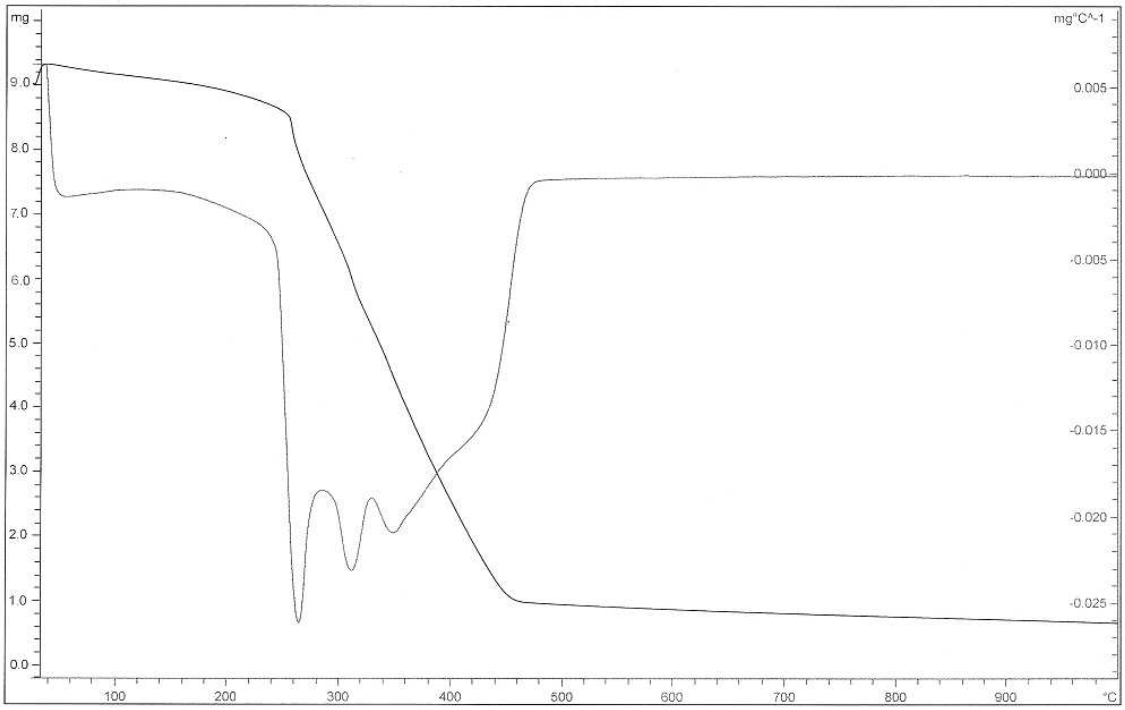

Fig. 1 TG-DTA curve of Dichlorobis(embelinate)zinc(II)

Table 2: Thermal Decomposition data of Dichlorobis(embelinate)zinc(II)

Wt. of Complex.(mg)	Step No.	Temperature		Loss in weight		Possible decomposition products
		Start ^{0}C	End ^{0}C	Obs. %	Cal. %	
9.35	0	44.05	255.05	-	-	$Zn(emb)_2Cl_2$
1.60	1	255.05	432.00	81.17	81.20	$ZnCl_2$
1.06	2	432.00	462.00	88.66	88.77	ZnO

The possible intermediates for zinc embelinate complex in the observed weight loss of 81.17% at 432^{0}C against the calculated value of 81.20% indicates the loss of embelin. The subsequent weight loss of 88.66% at 462^{0}C against the calculated value 88.77% confirms the conversion of zinc chloride to zinc oxide.

Differential Thermal Analysis (DTA) : The DTA results of the complex are also shown in Fig. 1. From the DTA curve it is evident that the first peak corresponds the decomposition of the complex and the two endothermic peaks at 312^{0}C and 350^{0}C indicate the phase changes in zinc chloride.

3.3 Infrared spectra of Dichlorobis(embelinate)zinc(II)

Embelin is expected to act as bidentate, with carbonyl and the hydroxyl oxygen atoms as coordination sites. The C=O and the O-H bands in embelin appear at 1610 cm^{-1} and 3300 cm^{-1} respectively as shown in the following Fig.2. The O-H stretching frequency is observed as a strong band at 3300cm^{-1} for embelin. The disappearance of this band in the Dichlorobis(embelinate)Zinc(II) complex indicates the loss of phenolic hydrogen on chelation.

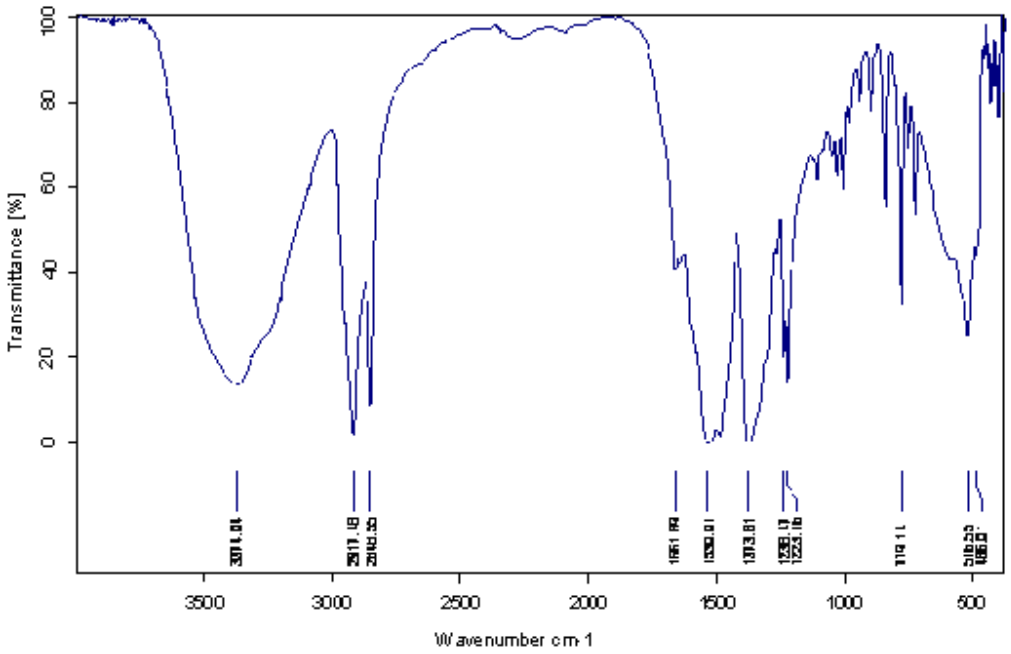

Fig. 2 Infrared Spectrum of Dichlorobis(embelinate)zinc(II)

The IR spectrum of the complex showed a shift of the carbonyl peak from 1610 to 1530 cm^{-1}. This indicates a decrease in the stretching frequency ν(C=O) as a consequence of coordination through the carbonyl oxygen atom[26]. The absorption attributed to the hydroxyl group appeared as a broad peak in the region 3550 to 3170 cm^{-1} with a maximum at 3374 cm^{-1}. Similar changes have been associated with hydrogen bonding in enols and chelates[27]. The strong signal in the region 1400 – 1300 cm^{-1} with a maximum at 1373 cm^{-1} in the complex is assigned to co-ordinated chloride. In the IR spectrum of complex, there is a considerable shift of the carbonyl absorption from 1610 to 1530 cm^{-1} and of the sharp hydroxyl peak at 3374 cm^{-1}. The rest of IR bands are associated with the embelin molecule. The overall IR evidence suggests that the embelin residue acts as a bidentate molecule and coordinates through the carbonyl and the hydroxyl oxygen atoms to form five-membered chelate rings[28].

3.4 X-ray diffraction data

The X-ray diffraction of embelin and the synthesized complex is analyzed using a X-ray diffractometer, Ultima IV with Cu K-α1 (Wavelength(λ)=1.54059 Å) in a 1 - 80^0 2θ range with a scan rate of 10^0/min. The particle lattice parameters were obtained by using Bragg's law, 2dsinθ = λ. The X-ray diffraction data of Embelin and Dichlorobis(embelinate)zinc(II) are given in Table 3. The maximum peak is sharp and observed at a 2θ value of 22.639^0 for the complex. The d-spacing has been calculated to be 4.0023 Å in the complex. The maximum peak of embelin is sharp and observed at a 2θ value of 11.698^0. The d- spacings have been calculated to be 7.5983 Å in the embelin. These parameters of the complex are not comparable with either zinc chloride or embelin diffractograms; hence it may be attributed to the formation of the complex.

Table 3 Comparison of X-Ray Diffraction Data of Dichlorobis(embelinate)zinc(II) and embelin

Dichlorobis(embelinate)zinc(II)			Embelin		
d-spacing (Å)	**Relative Int.(%)**	**Angle (2θ)**	**d-spacing (Å)**	**Relative Int.(%)**	**Angle (2θ)**
4.0023	100.0	22.639	7.5983	100.0	11.698
3.5103	16.0	26.032	6.0958	42.2	14.639
3.3479	19.3	27.398	5.1012	54.7	17.578
3.1382	16.1	29.401	4.4489	17.6	20.260
2.7279	20.4	34.385	4.3232	8.7	20.876
2.4198	16.5	39.543	4.0980	10.6	20.082
2.2264	16.7	43.786	4.0090	26.3	22.599
2.1891	19.4	44.729	3.7611	12.6	24.180
2.1717	17.6	45.184	3.3747	9.1	27.162
2.1134	17.4	46.797	3.2103	8.0	28.678

CONCLUSION

On the basis of the above thermal data, the compound was represented by the structural formula $Zn[(C_{17}H_{25}O_4)_2Cl_2]$ is shown in Fig. 3.

Based on the results of these investigations the following thermal decomposition mechanism is proposed:

$$3\ Zn(emb)_2Cl_2 \xrightarrow{44.05^0\,C - 432.00^0\,C} 3\ ZnCl_2 + 3\ emb$$

$$2\ ZnCl_2 + O_2 \xrightarrow{432.00^0\,C - 462.00^0\,C} 2\ ZnO + 2\ Cl_2$$

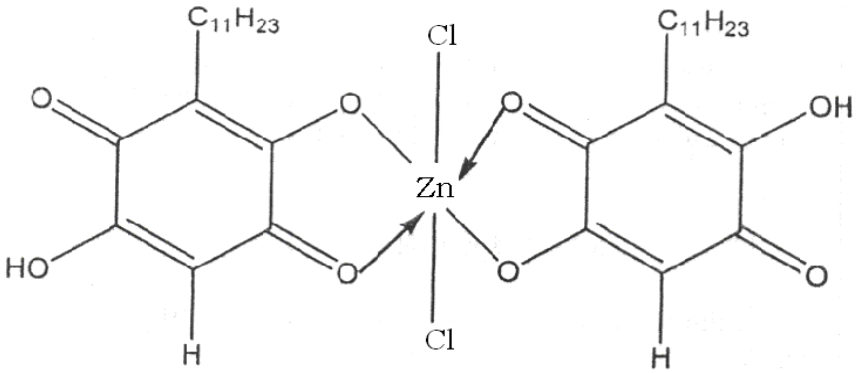

Fig. 3. Structure of Dichlorobis(embelinate)zinc(II).

REFERENCES

[1] A.H, Januaro, D. M, Fatima, F. De Silva, P.C Viera, J. B Fernanades *Phytochem* **1992**, 14,1251.
[2] J.O. Kokwara, Medicinal Plants of East Africa, East Africa Literature Bureau, Nairobi, Kenya. **1976**.
[3] K. Ravikumar, D. K Ved. Illustrated field guide: 100 Red Listed Medicinal Plants of Conservation concern in southern India, foundation for Revitalisation of Local Health Traditions, Banglore, **2000**, 467.
[4] J. S**.** Gamble, A Manual of Indian Timbers; an account of the growth, distribution and uses of the trees and shrubs of India and Ceylon, with descriptions of their wood-structure, Bishen Singh Mahendra Pal Singh, Dehra Dun, **1972.**
[5] B. L**.** Gupta, Forest Flora of Chakrata, Dehra Dun and Saharanpur, Forest Research Institute Press, **1945.**
[6] R.N. Chopra, S.L. Nayar, I. C. Chopra, Glossary of Indian Medicinal Plants, Council of Scientific and Industrial Research, New Delhi.**1992.**
[7] H. K. Kakrani, V. Kakrani, *Fitoterapia*, **1982,** 53,99.
[8] J. B. Githiori, J. Hoglund, P. J. Waller, L. R. Baker, *Vet Parasitol* **2003**,118,215.
[9] K.H.M. Swamy, V. Krishna, K. Shankarmurthy, A.B Rahiman, K. L. Manikani, K. M Mahadevan, B.G. Harish, R.H. Naika, *J Ethnopharmacol*. **2007**,109, 529.
[10] M. Chitra, E. Sukumar, V. Suja, C.S. Devi, *Chemotherapy* ,**1994**,40,109.
[11] M. Chitra, C. S. Devi, Sukumar, *E. Fitoterapia***, 2003**,74,401.
[12] M. Chitra, C.S. Devi, E. Sukumar, *J Nat Remedies* 2004, 4,80.
[13] R. Joshi, J. P. Kamat, T. Mukhrjee, *Chem-Biol Interact* **2007**,167,125.
[14] R. N. Chopra, S. L. Nayar, J. C. Chopra, Glossary of Indian Medicinal Plants, CSIR, New Delhi, 106, **1956.**
[15] J. L. Harwell, Lloydia, **1970**, 33,288.

[16] Namba et al**.** *J. of Medicinal and Aromatic plant* abstr, **1986**,8, 581.
[17] K. Venkataraman, The Chemistry of synthetic dyes, 2nd Ed., Academic Press, Inc., New York, **1952**,969**.**
[18] CH. Bheemasankara Rao, V. Venkateswarlu, *Z Anal.Chem* **1961**,178,227**.**
[19] CH.Bheemasankara Rao, V. Venkateswarlu, *Z Anal.Chem* **1962**,185,216**.**
[20] CH. Bheemasankara Rao, V. Venkateswarlu, *Z Anal.Chem* **1963**,192,183**.**
[21] R. Abraham, K.K.M. Yusuff, *J Mol Cat* **2003**; 198:175.
[22] M. Xu, J. Cui, H. Fu, P. Proksch W. Lin, M. Li, *Planta Medica***, 2005**,71,944.
[23] K. K. Abdul Rashid, Jacob Chacko, P.N.K. Nambisan, *Inorg Chim Acta*, **1987,** 151, 1.
[24] M. L. Dhar, Onkar Singh, *Inorg Chim Acta*, **1986,** 117,187.
[25] CH. Bheemasankara Rao, V. Venkateswarlu, *Indian J Pharm*, **1962**, 24: 263.
[26] R .K. Agarwal, H. Agarwal, *Bull Chem Soc Ethiop*, **2000**, 14,143.
[27] W. Kemp, Organic Spectroscopy, 3rd ed, ELBS: London, **1991**,75.
[28] J.K. Cherutoi, L.L. Cheruiyot, C. Kiprono, *Bull Chem Soc Ethiop*, **2005**,19, 295.