

SHORT COMMUNICATION

SYNTHESIS AND CHARACTERIZATION OF ZINC(II) AND COPPER(II) COMPLEXES OF EMBELIN

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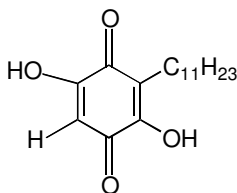
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ABSTRACT. The synthesis and characterization of zinc(II) and copper(II) complexes of embelin (1), C₁₇H₂₆O₄, are described. Zinc(II) and copper(II) ions reacted with (1) (an orange compound) in a 1:2 ratio to yield purple and green complexes, respectively. IR analysis of the two complexes showed that the metal ions were co-ordinated through the carbonyl and the hydroxyl oxygen atoms. Elemental analyses (AAS and C, H, N) of the complexes gave values that are consistent with six co-ordinate octahedral geometry about the metal ions. Molecular formulae, ZnC₃₄H₅₀N₂O₁₄ and CuC₃₄H₅₄O₁₀, for the zinc(II) and copper(II) complexes are proposed.

KEY WORDS: Zinc(II) complex, Copper(II) complex, Embelin

INTRODUCTION

Embelin (1) is produced by plants of the family Myrsinaceae. The myrsinaceae are shrubs or climbers comprising about 30 genera and 1000 species, with high ethnomedical application in the East and Central African geographical region and the Asian Continent. In Kenya, the myrsinaceae are represented by four species: *Myrsine africana*, *L. Rapanea melanphloes*, *Embelia schimperi* Vatke and *Maesa lanceolata* Forsk. The myrsinaceae are chemotaxonomically associated with long alkyl side chain benzoquinones which are found to constitute 10 % of the dry weight of their berries and 7 % of the root bark [1]. The powdered berries of the plants are used in indigenous medicine and are reported to exhibit anthelmintic (i.e. de-worming) properties on oral administration [2, 3]. Embelin (1) is probably the active anthelmintic agent and is non-toxic to mammals [4]. Synthesis and characterization of copper(II) complexes of embelin in the cavities of zeolite Y have been conducted [5] and found to display fairly good catalytic activity for the reduction of molecular oxygen. In this paper we describe embelin derivatives of zinc and copper, the first complexes of this natural product to be described.



Embelin molecule (1)

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EXPERIMENTAL

Extraction of embelin molecule. Embelin (**1**) (from the dried, ground stem bark of *Embelia schimperi*) was extracted and purified, following the procedure in ref 6. Anal. calcd. for $C_{17}H_{26}O_4$, (**1**): % C, 69.39; % H, 8.84. Found: % C, 69.13; % H, 8.55.

*Preparation of the zinc(II)-embelin complex, $[ZnC_{34}H_{50}N_2O_{14}]$, (**2**).* Zinc(II) nitrate, $Zn(NO_3)_2 \cdot 6H_2O$, (0.050 g, 0.17 mmol) was dissolved in 100 mL methanol. Embelin (**1**), ($C_{17}H_{26}O_4$), (0.100 g, 0.34 mmol) was dissolved in 150 mL methanol to give an orange solution. The two solutions were then mixed, and the purple solution that resulted was stirred for 2 h. The solution was concentrated to about 100 mL by rotary evaporation, filtered and allowed to stand for 3 h. The purple product that precipitated was filtered and washed with 150 mL methanol, followed by 100 mL acetone and finally 50 mL diethyl ether. The resulting complex (0.079 g, 60 %) was air-dried for 6 h and weighed. Anal. calcd. for $[ZnC_{34}H_{50}N_2O_{14}]$, (**2**): % Zn, 8.39; % C, 52.65; % H, 6.45; % N, 3.61. Found: % Zn, 8.65; % C, 52.33; % H, 6.80; % N, 3.43.

*Preparation of the copper(II)-embelin complex, $[CuC_{34}H_{54}O_{10}]$, (**3**).* Copper(II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$, (0.041 g, 0.17 mmol), was dissolved in 50 mL methanol. The solution was added to embelin (**1**), ($C_{17}H_{26}O_4$), (0.100 g, 0.34 mmols), which had been dissolved in 150 mL methanol. The green solution that resulted was stirred for 2 h. The volume was reduced to approximately 50 mL using a rotary evaporator, and the solution was filtered and allowed to stand for 6 h. The green product that precipitated was filtered off and washed with 150 mL methanol, followed by 100 mL acetone and finally 50 mL diethyl ether. The complex was air-dried for 8 h and weighed. The yield was 0.069 g (59 %). Anal. calcd. for $[CuC_{34}H_{54}O_{10}]$, (**3**): % Cu, 9.26; % C, 59.52; % H, 7.88. Found: % Cu, 9.65; % C, 59.23; % H, 7.61.

Physical measurements. Infrared spectra from KBr disks were recorded on a Shimadzu Model 408 spectrophotometer at the Analytical Chemistry Laboratory of Moi University.

Elemental analyses. These were performed at the Analytical Chemistry Laboratory of Egerton University. Metal analyses were obtained on a Chem Tech 2000 Instrument Atomic Absorption Spectrometer. Carbon, hydrogen and nitrogen analyses were recorded on an EAI-CE-440 Elemental Analyzer.

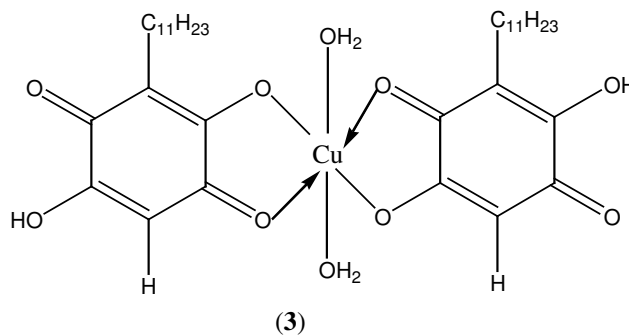
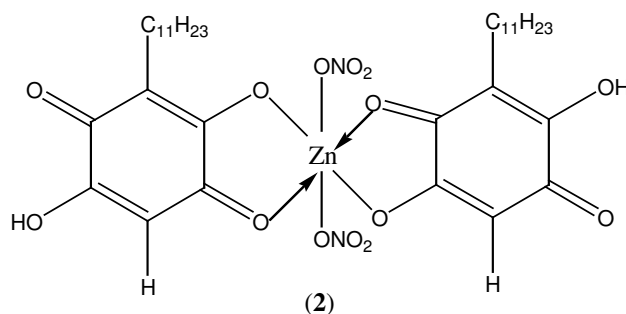
RESULTS AND DISCUSSION

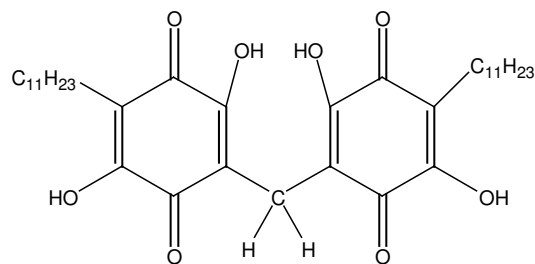
Molecule (**1**) is expected to be bidentate, with carbonyl and the hydroxyl oxygen atoms as coordination sites. The C=O and the O-H bands in embelin appear at 1610 cm^{-1} and 3300 cm^{-1} , respectively. The IR spectrum of the complex (**2**) showed a shift of the carbonyl peak to 1520 cm^{-1} . This indicates a decrease in the stretching frequency $\nu_{C=O}$ as a consequence of coordination through the carbonyl oxygen atom [7]. The absorption attributed to the hydroxyl group appeared as a broad peak in the region 3600 to 3050 cm^{-1} with a maximum at 3550 cm^{-1} . Similar changes have been associated with hydrogen bonding in enols and chelates [8]. The strong signal in the region 1400 - 1300 cm^{-1} with a maximum at 1365 cm^{-1} in complex (**2**) is assigned to co-ordinated nitrate, suggesting that the nitrate groups contribute to the coordination sphere. Other IR bands in complex **2** are the same as those in **1**.

In the IR spectrum of complex **(3)**, there is a considerable shift of the carbonyl absorption from 1610 cm^{-1} to 1460 cm^{-1} and of the sharp hydroxyl peak at 3300 cm^{-1} to a broad absorption in the region $3600\text{--}3100\text{ cm}^{-1}$ with a maximum at 3400 cm^{-1} . This broad peak may also indicate the presence of coordinated water. The rest of the 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. A summary of the IR bands of embelin and the two complexes are listed in Table 1.

Table 1. Selected infrared signals of the embelin molecule and its' complexes.

Compound	Infrared bands (cm^{-1})			
	$\nu(\text{O-H})$	$\nu(\text{C-H str.})$	$\nu(\text{C=O str.})$	$\nu(\text{C-H out of plane})$
Embelin, $\text{C}_{17}\text{H}_{26}\text{O}_4$	3300	2900, 2850	1610	860, 825, 770
$\text{ZnC}_{34}\text{H}_{50}\text{N}_2\text{O}_{14}$	3350	2900, 2850	1520	860, 825, 770
$\text{CuC}_{34}\text{H}_{54}\text{O}_{10}$	3400	2900, 2850	1460	860, 825, 770





(4)

Embelin (**1**), also called embelic acid, contains acidic protons [9, 10]. The reactions between the metal ions and the ligand **1** are acid-base reactions. Both complex **2** (purple) and complex **3** (green) decompose upon acidification to yield orange solutions indicating that embelin is regenerated. A similar reaction was exhibited by vilangin (**4**); which contains two embelin moieties. The latter molecule has been isolated from *Embelia ribes* [11].

The octahedral structure postulated for copper(II) complex (**3**) is consistent with the elemental analysis and infrared evidence, but the water molecules may well be only weakly bound. The proposed structure of copper(II) complex is consistent with elemental analyses, and it is not surprising that the two water molecules are coordinated at axial positions. The water-Cu bonds are slightly longer than the oxygen-Cu bonds giving a distorted octahedral structure due to Jahn-Teller effect. Polymeric structures based on **3** are also possible in the solid state. The six-coordinate structure is proposed for the zinc(II) complex (**2**) in order to accommodate nitrate in the coordination sphere. The isomer drawn is the most probable, but other isomers are possible. Six-fold coordination is rare for zinc(II), since the d^{10} metal usually utilizes its empty sp^3 hybridized orbitals to give structures with tetrahedral coordination [12, 13]. However, octahedral co-ordination has been reported in formyl amino acid, glutamic acid and formyl dipeptide complexes [14] and in several other complexes involving bidentate ligands [15].

CONCLUSION

Zinc(II) and copper(II) ions react with embelin in a 1:2 ratio to yield six-coordinate complexes. The embelin molecule, upon loss of protons, is a bidentate ligand giving five-membered chelate rings. Acidification leads to regeneration of embelin molecule.

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