Studies on Synthesis Methods of Bis(eugenolato)-Zinc(II) and Its Basic Properties(I)*

by

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1. Introduction

Zinc oxide-eugenol cement is widely used as it has sedative effect on the dental pulp. This medicinal effect has been considered due to eugenol and bis(eugenolato)-zinc(II).

But very few have ever reported with regard to the formation and structure of bis(eugenolato)-zinc(II). Copeland, et al[1]. report that the crystal of bis(eugenolato)-zinc(II) can be obtainable by extracting zinc oxide-eugenol mixture with chloroform, and that this crystal is a chelate compound of 2 mol eugenol and 1 mol Zn. But there remain many points unexplained in these report regarding the synthesis method of bis(eugenolato)-zinc(II) and the structure of the product.

The authors, as a result of hitherto-performed examinations purposing to synthesize bis(eugenolato)-zinc(II) of high purity, find that bis(eugenolato)-zinc(II) can be obtained with high yields by making eugenol and zinc methylate react in methanol solvent or by making zinc chloride react with sodium eugenolate.

The authors also examine the structure of the compound and its basic properties.

2. Experimental Methods

2.1 Materials

- 1) Methanol: 1000 ml of methanol with 50.0 g of sodium sulfate added is used after being filtrated and distilled.
- 2) Zinc chloride: The product in the market is used after being recrystallized and melted.
- 3) Eugenol: Eugenol is used after being distilled under the ordinary pressure at 255°C.
- 4) Synthesis of zinc methylate: 2 mol of sodium methylate and 1 mol of methanol solution of zinc chloride are made to react. Then this mixed solution is left for 24 hours and is filtrated to prepare methanol solution of zinc methylate. With this solution thus prepared methanol solution of eugenol is made to react to form white

* *Studies on the Dental Cement 23.*

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precipitate, which is filtrated and washed with a large amount of water and ethyl ether to be white crystal of bis(eugenolato)-zinc(II).

5) Synthesis of sodium eugenolate: 2 mol of sodium methylate solution and 2 mol of methanol solution of eugenol are made to react. Then the mixed solution is left for 24 hours to prepare methanol solution of sodium eugenolate. With this solution thus prepared methanol solution of zinc chloride is made to react to form white precipitate, which is filtrated and washed with a large amount of water and ethyl ether to be white crystal of bis(eugenolate)-zinc(II).

2.2 Measurement

1) Elemental analysis: C and H are analyzed by Mitamura Riken's micro carbon and hydrogen analysis method.

2) Observation of crystal: Crystal of bis(eugenolato)-zinc(II) is observed by the electron microscope.

3) Infrared spectrum: IR is measured using Hitachi Type 295, by the potassium bromide tablet method.

3. Experimental Results and Discussion

3.1 Yields by zinc methylate method

As shown in Table 1, yields vary to a great degree according to the amount of eugenol in case methanol solution containing 4.12, 5.15 and 8.24 g of eugenol are respectively made to react with 225.0 ml of methanol solution of zinc methylate containing 1.70 g of zinc chloride. A preferable yield can be obtained when zinc methylate (methanol 22.5 ml) containing 1.70 g of zinc chloride and 5.15 g of eugenol (methanol 75.0 ml) are made to react. In this case, the yield shows 62.0% (3.0 g of product).

3.2 Yields by sodium eugenolate method

As shown in Table 2, yields vary according to the amount of eugenol in case methanol solutions of sodium eugenolate containing 4.12, 5.15 and 6.18 g of eugenol are respectively made to react with 225.0 ml of methanol solution containing 1.70 g of zinc chloride. The optimum yield can be obtained when 1.70 g of zinc chloride

Table 1. Zinc methylate method

	Zinc chloride (g)	MeOH (ml)	Eugenol (g)	MeOH (ml)	mol	Yield (%)
1	1.70	225.0	4.12	50.0	2	45
2	1.70	225.0	5.15	75.0	2.5	62
3	1.70	225.0	8.24	100.0	4	55

Table 2. Sodium eugenolate method

	Zinc chloride (g)	MeOH (ml)	Eugenol (g)	MeOH (ml)	mol	Yield (%)
1	1.70	225.0	4.12	50.0	2	78
2	1.70	225.0	5.15	75.0	2.5	82
3	1.70	225.0	6.18	80.0	3	80

(methanol 225.0 ml) and sodium eugenolate (methanol 75.0 ml) containing 5.15 g of eugenol are made to react. In this case, the yield becomes high as 82.0% (4.0 g of product).

As shown above, the sodium eugenolate method is very effective to synthesize bis(eugenolato)-zinc(II), giving high yields.

3.3 Elemental analysis

The result of the elemental analysis of the synthesized crystal is as follows:

Elemental analysis found: C: 59.78, H: 5.54, Ash: 17.65%

Elemental analysis calculated as $C_{20}H_{22}O_4Zn$: C: 61.32, H: 5.62, Ash: 16.71%

The analysis found are slightly small both in C and H, while in Ash it is slightly large contrarily.

3.4 Electron-microscopic observation

Fig. 1 shows the electron-microscopic photo of bis(eugenolato)-zinc(II) synthesized.

The crystal is 10~40 μ in size and of column- and needle-like shapes.

3.5 IR spectrum

Fig. 2 shows the IR spectrum of bis(eugenolato)-zinc(II) synthesized and that of bis(eugenolato)-zinc(II) shown in the literature.

As shown here, the IR spectrum of bis(eugenolato)-zinc(II) synthesized coincides with the spectrum shown in the literature. That is, the characteristic absorption of

Fig. 1. Electron micrograph of bis(eugenolato)-zinc(II) crystals.

Fig. 2. Infrared absorption spectra.
Solid line: synthesized bis(eugenolato)-zinc(II)
Broken line: bis(eugenolato)-zinc(II) of literature¹⁾

bis(eugenolato)-zinc(II) appears at 1570, 1403, 1340, 1320 and 1292 cm^{-1} . The absorption appearing at 1570 cm^{-1} is especially sharp, whose assignment is not identified.

As to the synthesis methods of bis(eugenolato)-zinc(II), it is obvious that in both cases of zinc methylate method [2] and sodium eugenolate method [3], [1] can be formed.

This can be proved by the facts that in either case of the synthesis methods, the elemental analysis found coincide with the analysis calculated, and that [2] in [1] is not isomerized, as proved from the fact that [2] can be obtained by hydrolyzing [1], treated with 1 N hydrochloric acid. That is, bis(eugenolato)-zinc(II) is considered to be a Zn-centering five-membered ring chelate compound of [1] structure.

Table 1 and Table 2 show that sodium eugenolate method gives higher yields of [1] than zinc methylate method. Zinc methylate method gives low yields, presumably because zinc methylate becoming insoluble in the reaction solvent, precipitates as time goes on.

On the other hand, it is proved that the yield decreases to a great degree in case the reaction solvent, methanol, is replaced with ethanol.

Again, as it is insoluble in various kinds of solvents it can be presumed that Copeland, et al.'s [1] method to obtain it by mixing zinc oxide powder which is not

of high purity, as it is difficult to separate or exclude unreacted zinc oxide.

After all, it can be said that sodium eugenolate method is preferable to synthesize it.

The authors' coming examinations would be on the X-ray diffraction, differential thermal analysis of the product and its stability to acid and alkali.

4. Conclusions

The experimental results can be itemized as follows:

1) The optimum synthesis condition of bis(eugenolato)-zinc(II) is to make sodium eugenolate and zinc chloride react in methanol solvent under the room temperature. High yields of bis(eugenolato)-zinc(II) can be obtained.

2) Bis(eugenolato)-zinc(II) synthesized is a chelate compound of 1 mol Zn and 2 mol eugenol, presumably of five-membered ring structure with Zn in the center, between OH groups of eugenol and ortho-positioned OCH_3 groups.

3) The characteristic absorption of bis(eugenolato)-zinc(II) appears at 1570 cm^{-1} .

4) The crystal of this compound is of column- and needle-like shapes, $10 \sim 40 \mu$ in size, and insoluble in water and many other kinds of solvents.

Reference

- [1] Copeland, H.I., G.M., Sweeney, W.T. & Forziati, A.F.: Setting reaction of zinc oxide and eugenol; J. Res. National Bureau of Standard, **55**, 134~138 (1955).