

FT-IR and XRD Analyses of Commercial Methionine-Mineral Chelates

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Compositions of methionine-metal chelates have been investigated by FT-IR and XRD studies to elucidate their molecular structures. It was concluded that Copamin and Zincamin contain a high percentage of crystalline products, presumably 2:1 Methionine-Cu or Zn complexes. On the contrary, FT-IR and XRD spectra of Ferramin didn't show any characteristics of the chelate and it was concluded to contain major components of starting FeSO₄ and methionine without chelation.

Key words: *mineral chelate, methionine, FT-IR, XRD, antibiotic substitute*

While growing strict regulations on the antibiotic usage for livestock enforce development of new antibiotic alternatives,¹⁾ supplementation of Cu, Zn, Fe, and Mn inorganic salts has been reported to improve live stock production when they are used at high concentrations without antibiotics. But high level of metal ions in excretions has caused their accumulation in soils and resulted in environmental problems. It was recently reported supplementary mineral-amino acid chelates, instead of inorganic mineral salts, increased egg production, weight gain and feed efficiency in hens at lower concentrations.²⁾ Supplementary uses of mineral-methionine chelates for chicken and poultry have also shown promising results as a possible antibiotic substitute.³⁾ It has been suggested mineral chelates are absorbed better than the inorganic salts due to the enhanced bioavailability.⁴⁾ Although these methionine-metal complexes are practically useful, their chemical compositions and chemical properties are still not clear.⁵⁾ To discover antibiotics alternatives for livestock based on scientific rationale, study on the chemical characteristics of the methionine-metal complexes is required.

We have chosen three commercial methionine-metal complexes available from Korean animal supplementary markets⁶⁾ to find out if they really are methionine-mineral chelates. Chelation of metal ion to organic ligands is achieved by electron donating atoms, such as N, O, and S. From the ligand side, coordination of these atoms to the metal center restricts some rotational and vibrational movements of the molecule, which can be detected by vibrational spectroscopy, such as infrared or Raman. Metal complexes usually form crystalline products and its crystallinity can be measured by XRD (X-ray diffraction) study. XRD measurement can also

provide quantitative information of the crystalline product. Hence, FT-IR and XRD analyses are adopted for the chemical characterization of commercial methionine-metal chelates. Here we report chemical composition, structure and physical property of Copamin, Ferramin, and Zincamin.

Materials and Methods

Copamin (methionine-copper(II) complex), Ferramin (methionine-iron(II) complex), and Zincamin (methionine-zinc(II) complex) have kindly been supplied by INNOBIO at Ansan, Korea. Each contains about 40% of methionine-metal chelates in total weight of the product. L-Methionine was purchased from Aldrich. Chiral Complex of L-methionine-copper complex was synthesized by reported methods.⁷⁾ FT-IR spectra were measured on Shimadzu FT-IR 8400S with a resolution of 4 cm⁻¹ and XRD spectra of methionine-mineral chelates were obtained by Rigaku dmax 2000 X-ray diffractometer with a wavelength of 1.5418Å. For Copamin and Zincamin, the scan range was 2° < 2θ < 70° at 30mA and 40kV. Ferramin was measured with a scan range of 5° < 2θ < 70° at the same current and voltage.

Results and Discussion

Infrared Spectra. The infrared spectra of Copamin and Zincamin were very similar and showed characteristic C=O stretchings at 1,616 cm⁻¹ and 1,604 cm⁻¹, respectively (Fig. 1). Free methionine showed several corresponding peaks at around 1,600 cm⁻¹. Therefore, the C=O stretching of the complexes was characteristic signature of metal complexation. Generally, metal complexes show simpler C=O stretching in spectrum than their corresponding ligand does because the freedom of C=O stretching vibrations are limited when it is coordinated to metal center.⁸⁾ The IR spectra of Copamin and

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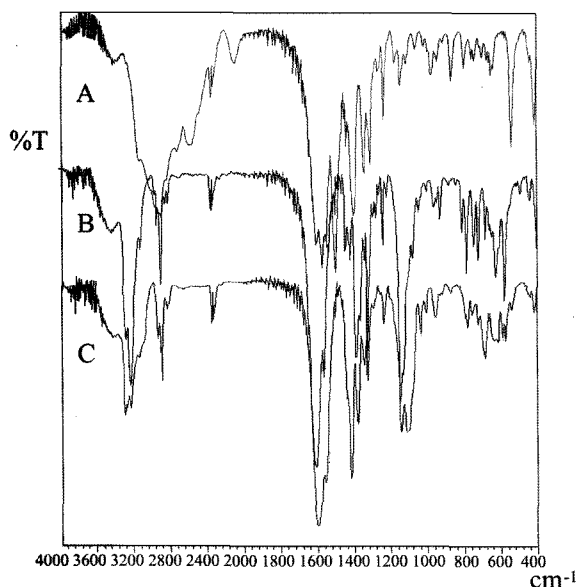


Fig. 1. Infrared spectra of *L*-methionine (A), Copamin (B) and Zincamin (C). Several strong peaks at $1,508\text{ cm}^{-1}$, $1,558\text{ cm}^{-1}$, $1,583\text{ cm}^{-1}$, and $1,610\text{ cm}^{-1}$ are due to CO stretchings of methionine in A. The strong peaks at $1,616\text{ cm}^{-1}$ (B) and $1,604\text{ cm}^{-1}$ (C) are due to the CO stretchings of the coordinated methionine to Cu(II) and Zn(II), respectively.

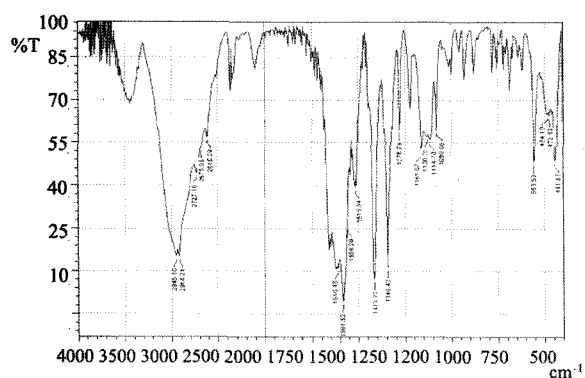


Fig. 2. Infrared spectrum of Ferramin. Several strong peaks including the ones at $1,558\text{ cm}^{-1}$, $1,581\text{ cm}^{-1}$, $1,610\text{ cm}^{-1}$ are from unbound CO's stretchings.

Zincamin were overall much simpler than the one of free methionine. The IR spectrum of Ferramin showed multiple C=O stretchings compared to others and the spectrum is relatively complicated. (Fig. 2) Several C=O stretching peaks at between $1,500\text{ cm}^{-1}$ and $1,700\text{ cm}^{-1}$ implied that methionine-iron complex, unlike Copamin and Zincamin, was not a major component of the Ferramin. Ferramin could be a mixture of several compounds. The strong peaks at around $1,150\text{ cm}^{-1}$ shown at B and C in Fig. 1 are due to the non-coordinating sulfate ion. When we compared Copamin with synthesized *L*-methionine-copper complex, C=O stretching of the latter was found at $1,618\text{ cm}^{-1}$. This is probably due to the facts that commercial Copamin contains *D,L*-methionine.

XRD measurements. Based on the infrared spectroscopic study, Copamin and Zincamin appear to contain significant

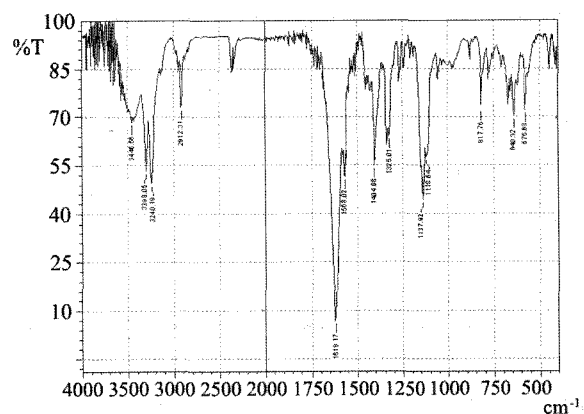


Fig. 3. Infrared spectrum of $\text{Cu}(\text{L-Met})_2$. The strong CO stretching peak is found at $1,618\text{ cm}^{-1}$ and the SO stretching peaks are found at $1,137\text{ cm}^{-1}$ and $1,118\text{ cm}^{-1}$.

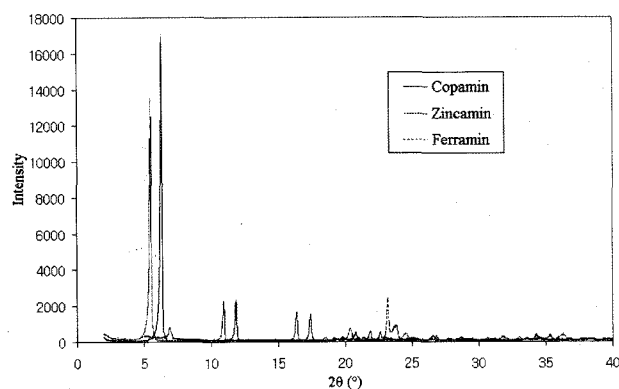


Fig. 4. XRD spectra of Copamin, Zincamin and Ferramin.

amount of methionine-metal complexes. XRD measurements of Copamin, Ferramin, and Zincamin, as well as copper sulfate, iron sulfate, and zinc sulfate were carried out. Copamin and Zincamin showed a high crystallinity with strong intensity on the spectra, but Ferramin shows only about 15% intensity of Copamin. (Fig. 4) Ferramin seems to contain only about 15% of crystalline product compared to Copamin, based on the X-ray diffraction intensity. To identify the 15% of crystalline material, XRD spectrum of Ferramin were compared to those of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, *D,L*-methionine and *D,L*-methionium sulfate. The X-ray diffraction pattern of Ferramin was very similar to the mixture of *D,L*-methionine and *D,L*-methionium sulfate (data not shown). Thus, it appears there is no methionine-iron complex in Ferramin.

Composition of methionine-metal Complexes. In solid state, the major composition of Copamin and Zincamin is methionine-metal crystalline products. Based on IR measurements, both complexes seem to be homogeneous and contain a single product. The structure of the $\text{Cu}(\text{L-Met})_2$ complex has been reported⁷ and its spectral properties of IR and XRD have been compared with Copamin. C=O stretching is found at $1,616\text{ cm}^{-1}$ and 1618 cm^{-1} for Copamin and $\text{Cu}(\text{L-Met})_2$, respectively. The XRD spectra of Copamin and $\text{Cu}(\text{L-Met})_2$ complex are similar but Copamin shows higher angle diffractions, which

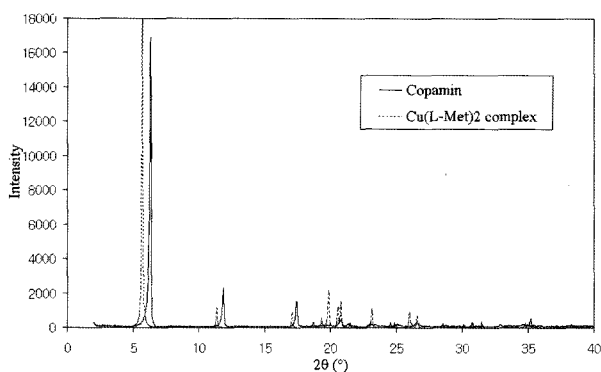


Fig. 5. Comparison of XRD spectra of Copamin and $\text{Cu}_{(\text{L-Met})_2}$ complex.

implies smaller unit cell than the known $\text{Cu}_{(\text{L-Met})_2}$ complex.⁹ (Fig.5) Different trend is observed for Zincamin when it compared to $\text{Zn}_{(\text{L-Met})_2}$ complex. The XRD spectrum of Zincamin shows lower angle diffractions and which shows larger unit cell of Zincamin than that of $\text{Zn}_{(\text{L-Met})_2}$ complex. One of possible explanations of the differences is Copamin and Zincamin have D,L -methionine, and which changed the unit cell parameters of $\text{Cu}_{(\text{D,L-Met})_2}$ and $\text{Zn}_{(\text{D,L-Met})_2}$ complexes from $\text{Cu}_{(\text{L-Met})_2}$ and $\text{Zn}_{(\text{L-Met})_2}$, respectively. The IR spectrum of Zincamin is similar to Copamin, which implies analogous coordination mode of Zincamin. But, X-ray crystallographic structure of $\text{Zn}_{(\text{L-Met})_2}$ shows different coordination geometry of $\text{Zn}(\text{II})$.¹⁰ While $\text{Cu}(\text{II})$ in $\text{Cu}_{(\text{L-Met})_2}$ complex shows a distorted octahedral coordination geometry, $\text{Zn}(\text{II})$ in $\text{Zn}_{(\text{L-Met})_2}$ shows a distorted square pyramidal coordination geometry.

On the contrary, Ferramin shows poor crystallinity and the IR spectrum shows no detectible coordination of ferrous ion to methionine. The XRD data suggests Ferramin contains some crystalline products, which contain a mixture of D,L -methionine and D,L -methionium sulfate in an unknown ratio.

In conclusion, chemical compositions of Copamin, Ferramin, and Zincamin were investigated by IR and XRD measurements. The results were compared with the known compounds of synthetic $\text{Cu}_{(\text{L-Met})_2}$ and reported $\text{Zn}_{(\text{L-Met})_2}$. Copamin and Zincamin appear to be 2 to 1 methionine-metal complexes, while analysis on Ferramin does not show any evidences of methionine-metal complex.

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