Synthesis and Study of Heteronuclear Citrates

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Abstract: Terms of synthesis were determined for creation of new generation premixes and for their testing in experiments. Heteronuclear chelate citrates of general formula: $M_1^I M_2^{II} L_2 \cdot nH_2O$ (where, $M_1^I = \text{Zn, Co, Fe, Mn, Cu}$; $M_2^{II} = \text{Mn, Zn, Co, Cu}$; $n = O/4$) were synthesized. Identity and composition of synthesized compounds were defined by microelemental analysis, determination of melting temperature and X-ray diffraction analysis. X-ray diffraction method was used also to define crystallinity of the compounds and their citric acid ($H_4L$) component. X-ray amorphous and iso-structural orders were also revealed.

Key words: Bio-metals, chelate compounds, microelemental analysis, X-ray diffraction analysis.

1. Introduction

Even the most primitive forms of live organisms are unable to provide vital processes without participation of bio-metals. In optimal doses they are able to affect actively growth and development, propagation, productivity, resistance of organisms to diseases. Investigations of researchers prove that bio-metals play active role in the physiological and biological processes going on in poultry and animals. Up to 75 chemical elements are found in their organisms and namely this conditioned the interest shown to the so-called “vital metals” by wide specter of researchers. We considered five microelements (Zn, Co, Fe, Mn, Cu), because these microelements belong to a number of very critical and essential for life elements that animal organisms have. They play an important role in a water and organic compounds metabolism, absorption and utilization of nutrients. They generate optimal conditions for the normal function of many organs including cardiac muscle and nervous system [1-4]. Their role and significance are exemplified by the fact that one of the main factors which defines low quantity and quality indices of foodstuff is the deficiency of bio-metals in plants, soil, as well as in agricultural animals and poultry. Decisive role in the resolution of this problem is attributed to the provision of live organisms with optimal quantity and ratio of microelements. Since bio-metals in live organisms fulfill their functions in the form of chelates, at filling up of deficit in bio-metals in the form of chelates, we observe sharp increase in their biological activity [5-8].

2. Materials and Methods

For synthesis, we used the following original compounds: $\text{ZnO, MnCO}_3$, $\text{CoCO}_3\text{Co(OH)}_2$, $\text{CuCO}_3\text{Cu(OH)}_2$, $\text{Fe(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}$, and important for vital processes oxyacid-citric acid ($H_4L$). Composition of compounds and their identity were defined by well-known methods: microelemental analysis (CHN Analyser, Labertherm GmbH). Purity was determined by melting temperature measuring (Dynalon SMP10) and X-ray diffraction method on DPOH-3Mtype diffractometer, at copper anode emission. The same method was used to define their crystallinity, and X-ray amorphous and iso-structural orders were also revealed.

3. Results

Investigations are continued at the Laboratory of
Problems Agrarian Chemistry for creation of new generation premixes and for their testing in experiments [9-17]. With this in view heteronuclear chelate citrates of the following general formula:

\[ \text{MI}_2\text{MII}_2\text{L}_2\text{nH}_2\text{O} \] (where, MI = Zn, Co, Fe, Mn, Cu; MII = Mn, Zn, Co, Cu; n = 0/4) were created. To obtain these citrates, we take a mix: (1) ZnO:MnbCO_3, (2) CoCO_3Co(OH)_2:ZnO, (3) CuCO_3Cu(OH)_2, (4) CoCO_3Co(OH)_2:MnCO_3, (5) CoCO_3Co(OH)_2:CuCO_3Cu(OH)_2, (6) Fe(CH_3COO)_2·4H_2O:MnCO_3, (7) Fe(CH_3COO)_2·4H_2O:ZnO, (8) Fe(CH_3COO)_2·4H_2O:CoCO_3Co(OH)_2 and (9) MnCO_3:CuCO_3Cu(OH)_2 at 2:1 molar ration on porcelain cup, crush intensely till it is reduced to fine dispersion condition, then we add citric acid dissolved in minimal volume of hot water. We observe intense isolation of CO_2 and changes of color. The obtained solutions are left at room temperature till the next day, are filtered and the residue after its washing by ether is dried on air.

Identity and composition of synthesized chelate composites: Zn\textsubscript{2}Mn\textsubscript{L}_2·2H\textsubscript{2}O, Co\textsubscript{2}Zn\textsubscript{L}_2, Cu\textsubscript{2}:Co\textsubscript{L}_2·H\textsubscript{2}O, Fe\textsubscript{2}:Mn\textsubscript{L}_2·2H\textsubscript{2}O, Co\textsubscript{2}:Mn\textsubscript{L}_2·4H\textsubscript{2}O, Co\textsubscript{2}Cu\textsubscript{L}_2·4H\textsubscript{2}O, Mn\textsubscript{2}Cu\textsubscript{L}_2·4H\textsubscript{2}O, Fe\textsubscript{2}Zn\textsubscript{L}_2·2H\textsubscript{2}O and Fe\textsubscript{2}Co\textsubscript{L}_2·4H\textsubscript{2}O were defined by microelemental analysis (Table 1), by melting temperature detection (Table 2), by X-ray diffraction method (Table 3).

We also defined their crystallinity and revealed X-ray amorphous and iso-structural orders by X-ray diffraction analysis.

Table 3 represents the results of relative intensities \((I/I_0)\), reflection angle \((2\theta)\), inter-plane distances \((d)\) obtained by deciphering of X-ray diffraction patterns of the composites.

### 4. Discussions

X-ray diffraction studies did not reveal presence of starting compounds in the samples in the form of separate phase. Therefore, we can conclude that

#### Table 1  Results of microelemental analysis of chelates.

| # | Formula                  | Practical (%) | Theoretical (%) |
|---|--------------------------|---------------|-----------------|
|   |                          | M\textsuperscript{I} | M\textsuperscript{II} | C   | H   | M\textsuperscript{I} | M\textsuperscript{II} | C   | H   |
| 1 | Zn\textsubscript{2}Mn\textsubscript{L}_2·4H\textsubscript{2}O | 20.94         | 9.05            | 24.03 | 2.15 | 21.69         | 9.17            | 24.00 | 2.34 |
| 2 | Co\textsubscript{2}Zn\textsubscript{L}_2   | 20.87         | 10.72           | 25.09 | 2.17 | 21.01         | 11.58           | 25.66 | 2.49 |
| 3 | Cu\textsubscript{2}:Co\textsubscript{L}_2·H\textsubscript{2}O | 22.11         | 9.96            | 24.45 | 1.91 | 21.81         | 10.12           | 24.73 | 2.06 |
| 4 | Co\textsubscript{2}:Mn\textsubscript{L}_2·4H\textsubscript{2}O | 19.03         | 8.73            | 20.96 | 2.72 | 19.81         | 8.83            | 21.11 | 2.89 |
| 5 | Co\textsubscript{2}:Cu\textsubscript{L}_2·4H\textsubscript{2}O | 18.21         | 9.79            | 22.75 | 2.63 | 18.66         | 10.05           | 22.79 | 2.85 |
| 6 | Fe\textsubscript{2}:Mn\textsubscript{L}_2·2H\textsubscript{2}O | 19.33         | 9.14            | 24.62 | 2.15 | 19.27         | 9.46            | 24.77 | 2.41 |
| 7 | Fe\textsubscript{2}:Zn\textsubscript{L}_2·2H\textsubscript{2}O | 19.15         | 11.13           | 24.79 | 2.23 | 18.94         | 10.99           | 24.35 | 2.37 |
| 8 | Fe\textsubscript{2}:Co\textsubscript{L}_2·4H\textsubscript{2}O | 17.78         | 8.93            | 22.98 | 2.65 | 18.03         | 9.49            | 23.18 | 2.89 |
| 9 | Mn\textsubscript{2}:Cu\textsubscript{L}_2·4H\textsubscript{2}O | 17.17         | 10.09           | 22.97 | 2.77 | 17.63         | 10.18           | 23.08 | 2.89 |

#### Table 2  Results of measurements of composites melting temperatures.

| # | Formula | Melting, T (°C) | Color        |
|---|---------|-----------------|--------------|
| 1 | Zn\textsubscript{2}:Mn\textsubscript{L}_2·4H\textsubscript{2}O | > 286 | White        |
| 2 | Co\textsubscript{2}:Zn\textsubscript{L}_2 | > 286 | Lilac        |
| 3 | Cu\textsubscript{2}:Co\textsubscript{L}_2·H\textsubscript{2}O | > 286 | Dark light-blue |
| 4 | Co\textsubscript{2}:Mn\textsubscript{L}_2·4H\textsubscript{2}O | > 286 | Grey-lilac   |
| 5 | Co\textsubscript{2}:Cu\textsubscript{L}_2·4H\textsubscript{2}O | > 286 | Dark lilac   |
| 6 | Fe\textsubscript{2}:Mn\textsubscript{L}_2·2H\textsubscript{2}O | > 286 | Mustard yellow |
| 7 | Fe\textsubscript{2}:Zn\textsubscript{L}_2·2H\textsubscript{2}O | > 286 | Light brown  |
| 8 | Fe\textsubscript{2}:Co\textsubscript{L}_2·4H\textsubscript{2}O | > 286 | Grey-brown   |
| 9 | Mn\textsubscript{2}:Cu\textsubscript{L}_2·4H\textsubscript{2}O | > 286 | Light green  |
### Table 3  Results of X-ray diffraction analysis of chelate composites and citric acid.

| Zn₂Mn·L₂·4H₂O  | Co₂·Mn·L₂       | Cu₂·Co·L₂·H₂O  |
|-----------------|-----------------|-----------------|
| 2θ d J/J₀ d J/J₀ | 2θ d J/J₀       | 2θ d J/J₀       |
| 11.5 0.3 2.5    | 10.66 8.301 0.0608 | 8.500 8.152 1.1696 | 10.89 8.120 0.2350 |
| 15.2 4.5 37.5   | 11.49 7.699 0.0043 | 11.37 7.782 0.0395 | 12.31 7.187 0.1800 |
| 17.0 1.6 13.3   | 11.93 7.419 0.0530 | 12.27 7.214 0.2606 | 13.30 6.656 0.1033 |
| 18.3 6.5 54.2   | 12.09 7.323 0.2286 | 13.32 6.645 0.1818 | 14.53 6.096 0.0100 |
| 19.0 0.4 3.3    | 13.06 6.778 0.0156 | 15.72 5.636 0.0909 | 15.81 5.605 1.0000 |
| 22.3 4.5 37.5   | 15.52 5.711 0.0486 | 15.83 5.599 0.2545 | 17.20 5.157 0.0866 |
| 23.1 12.0 100.0 | 15.50 5.717 0.0660 | 16.66 5.322 0.0303 | 18.41 4.820 0.0533 |
| 23.8 0.5 4.2    | 16.20 5.473 0.0173 | 17.23 5.147 0.0787 | 19.39 4.577 0.0683 |
| 24.5 1.0 8.3    | 16.93 5.238 0.0269 | 18.47 4.803 0.0484 | 19.86 4.470 0.2166 |
| 27.1 0.5 4.2    | 18.23 4.865 0.0026 | 20.03 4.434 1.0000 | 21.77 4.083 0.1316 |
| 28.8 0.4 3.3    | 19.38 4.579 0.0382 | 20.34 4.367 0.3454 | 22.82 3.896 0.0350 |
| 29.4 2.5 20.8   | 19.8 4.484 1.0000 | 20.67 4.298 0.0636 | 23.17 3.839 0.1533 |
| 30.8 1.5 12.5   | 20.13 4.411 0.0376 | 21.70 4.095 0.0757 | 23.72 3.751 0.0933 |
| 32.7 1.5 12.5   | 20.57 4.318 0.0339 | 21.75 4.085 0.1151 | 24.66 3.611 0.0816 |
| 33.5 0.8 6.7    | 21.39 4.155 0.0921 | 22.36 3.976 0.0515 | 25.44 3.502 0.1183 |
| 37.0 1.0 8.3    | 22.78 3.904 0.0269 | 22.90 3.881 0.1181 | 26.82 3.373 0.2483 |
| 41.9 0.5 4.2    | 23.51 3.784 0.0113 | 23.81 3.737 0.0818 | 28.15 3.170 0.0433 |
| 45.8 0.5 4.2    | 24.09 3.695 0.1052 | 24.31 3.661 0.0575 | 28.97 3.082 0.1216 |
| 56.8 0.5 4.2    | 24.4 3.648 0.0113 | 24.69 3.606 0.0303 | 30.44 2.937 0.0600 |
| 24.62 3.615 0.0147 | 26.54 3.358 0.2696 | 26.07 3.418 0.0400 | 28.79 3.101 0.1242 |
| 28.58 3.123 0.0800 | 29.41 3.035 0.0151 | 29.24 3.056 0.0756 | 29.99 2.979 0.0878 |
| 29.76 3.002 0.0939 | 31.07 2.879 0.2424 | 30.32 2.948 0.0182 | 31.89 2.806 0.1515 |
| 31.36 2.852 0.0313 | 32.43 2.761 0.0575 | 32.25 2.775 0.0521 | 34.37 2.609 0.0424 |
| 34.88 2.572 0.0252 | 35.87 2.503 0.0454 | 35.64 2.512 0.0800 | 38.56 2.335 0.0181 |
| 37.34 2.408 0.0443 | 40.26 2.240 0.0545 | 38.77 2.323 0.0243 | 40.58 2.223 0.0424 |
| 40.23 2.242 0.0104 | 42.22 2.190 0.0606 | 40.39 2.233 0.0260 |
| 41.05 2.199 0.0330 |
| 42.91 2.107 0.0252 |
| 43.56 2.078 0.0269 |
| 43.70 2.072 0.0339 |
| 44.64 2.030 0.0313 |
| 45.49 1.994 0.0034 |
| 46.10 1.969 0.0243 |
| 46.19 1.965 0.0078 |
| 47.41 1.918 0.0365 |
| 48.15 1.890 0.0313 |
| 48.07 1.893 0.0495 |
| 49.2 1.852 0.0269 |
Table 3 continued

|     | 4. Co₂·Mn·L₂·4H₂O | 5. Co₂·Cu·L₂·4H₂O | 6. Fe₂·Zn·L₂·2H₂O | 7. Mn₂·Cu·L₂·4H₂O |
|-----|------------------|--------------------|-------------------|-------------------|
| 2θ  | d                | J/J₀               | 2θ                | d                | J/J₀               |
| 10.70 | 8.267           | 0.0636             | 9.800             | 9.024            | 0.0645             |
| 11.75 | 7.532           | 0.0454             | 10.84             | 8.160            | 0.1612             |
| 13.17 | 6.725           | 0.0606             | 12.28             | 7.206            | 0.1612             |
| 14.27 | 6.208           | 1.0000             | 15.49             | 5.719            | 0.0645             |
| 14.84 | 5.968           | 0.0666             | 15.77             | 5.619            | 1.0000             |
| 15.61 | 5.677           | 0.0909             | 17.07             | 5.193            | 0.0645             |
| 17.02 | 5.210           | 0.0303             | 18.30             | 4.847            | 0.0967             |
| 17.83 | 4.974           | 0.0393             | 19.77             | 4.488            | 0.1612             |
| 18.39 | 4.824           | 0.4121             | 21.32             | 3.845            | 0.2580             |
| 18.70 | 4.744           | 0.2303             | 23.28             | 3.820            | 0.1459             |
| 20.42 | 4.348           | 0.3333             | 24.62             | 3.616            | 0.0967             |
| 21.50 | 4.133           | 0.1333             | 25.36             | 3.511            | 0.1541             |
| 21.61 | 4.110           | 0.3272             | 26.25             | 3.394            | 0.0645             |
| 23.20 | 3.833           | 0.2303             | 27.48             | 3.245            | 0.0032             |
| 23.59 | 3.772           | 0.1939             | 28.31             | 3.151            | 0.0516             |
| 23.90 | 3.723           | 0.1393             | 29.30             | 3.047            | 0.0288             |
| 24.65 | 3.612           | 0.0575             | 31.00             | 2.884            | 0.1290             |
| 25.90 | 3.440           | 0.1606             | 31.49             | 2.840            | 0.0870             |
| 26.96 | 3.307           | 0.2303             | 34.5              | 2.599            | 0.0645             |
| 27.74 | 3.216           | 0.0606             | 37.41             | 2.404            | 0.0645             |
| 28.70 | 3.111           | 0.1666             | 42.00             | 2.120            | 0.0419             |
| 29.98 | 2.980           | 0.1515             |                   | 48.95            | 1.861              |
| 31.74 | 2.819           | 0.100              |                   | 55.10            | 1.666              |
| 32.64 | 2.795           | 0.1763             |                   | 33.10            | 2.706              |
| 33.91 | 2.662           | 0.1536             |                   | 33.56            | 2.671              |
| 35.86 | 2.504           | 0.1667             |                   | 34.84            | 2.575              |
| 35.87 | 2.503           | 1.393              |                   | 35.78            | 2.510              |
| 36.55 | 2.458           | 0.0787             |                   | 36.87            | 2.438              |
| 38.12 | 2.361           | 0.0515             |                   | 37.32            | 2.409              |
| 42.46 | 2.129           | 0.0939             |                   | 39.85            | 2.262              |
| 43.21 | 2.094           | 0.1333             |                   | 41.36            | 2.183              |
| 44.18 | 2.050           | 0.1288             |                   | 43.67            | 2.073              |
| 47.45 | 1.916           | 0.1060             |                   | 46.43            | 1.956              |
| 48.27 | 1.885           | 0.0303             |                   | 47.94            | 1.898              |
| 49.08 | 1.856           | 0.0606             |                   |                   |                    |

absolutely new individual compounds are obtained which are in full conformity with the results of the above given micro elemental analysis and melting point measurements (Tables 1 and 2).

X-ray diffraction patterns of the composites Fe₂·Mn·L₂·H₂O and Fe₂·Co·L₂·4H₂O are characterized by weakly expressed diffuse peaks, therefore they represent X-ray-amorphous compounds. Other compounds are characterized by clearly expressed crystalline structures, various relative intensities (I/I₀), reflection angles (2θ), and definite intra-spatial distance (d) values. It should be stated that X-ray diffraction patterns of the composites Cu₂·Co·L₂·H₂O and Co₂·Cu·L₂·4H₂O are identical, which speaks of their iso-structure that is conditioned by analoguousness of their chemical composition and geometrical characteristics of crystalline structure, which can not be said about the composites: Zn₂·Mn·L₂·2H₂O, Co₂·Zn·L₂, Co₂·Mn·L₂·4H₂O, Mn₂·Cu·L₂·4H₂O, Fe₂·Zn·L₂·2H₂O (Table 3).
5. Conclusions

For the first time, we synthesized Heteronuclear chelate citrates of general formula: $M^{II}_1M^{III}_2L_2nH_2O$ by using modified and simplified methods. We studied identity and composition of synthesized compounds, determined their crystallinity, and revealed X-ray amorphous and iso-structural orders.

We have conducted preliminary studies on these synthesized compounds as new poultry premixes. Based on good preliminary data, we concluded to conduct large-scale studies in this direction.

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