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: $M^I_2M^{II}L_2 \cdot nH_2O$ (where, $M^I = Zn, Co, Fe, Mn, Cu$; $M^{II} = Mn, Zn, Co, Cu$; $n = 0/4$) 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: ZnO , $MnCO_3$, $CoCO_3$, $Co(OH)_2$, $CuCO_3$, $Cu(OH)_2$, $Fe(CH_3COO)_2 \cdot 4H_2O$, 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-3M type 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

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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:

$M^I_2 \cdot M^{II} \cdot L_2 \cdot nH_2O$ (where, $M^I = Zn, Co, Fe, Mn, Cu$; $M^{II} = Mn, Zn, Co, Cu$; $n = 0/4$) were created. To obtain these citrates, we take a mix: (1) $ZnO:MnCO_3$, (2) $CoCO_3Co(OH)_2:ZnO$, (3) $CuCO_3Cu(OH)_2:CoCO_3Co(OH)_2$, (4) $CoCO_3Co(OH)_2:MnCO_3$, (5) $CoCO_3Co(OH)_2:CuCO_3Cu(OH)_2$, (6) $Fe(CH_3COO)_2 \cdot 4H_2O:MnCO_3$, (7) $Fe(CH_3COO)_2 \cdot 4H_2O:ZnO$, (8) $Fe(CH_3COO)_2 \cdot 4H_2O:CoCO_3Co(OH)_2$ 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: $Zn_2 \cdot Mn \cdot L_2 \cdot 2H_2O$, $Co_2 \cdot Zn \cdot L_2$, $Cu_2 \cdot Co \cdot L_2 \cdot H_2O$, $Fe_2 \cdot Mn \cdot L_2 \cdot 2H_2O$, $Co_2 \cdot Mn \cdot L_2 \cdot 4H_2O$, $Co_2CuL_2 \cdot 4H_2O$, $Mn_2CuL_2 \cdot 4H_2O$, $Fe_2ZnL_2 \cdot 2H_2O$ and $Fe_2CoL_2 \cdot 4H_2O$ 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 (2θ), 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^I	M^{II}	C	H	M^I	M^{II}	C	H
1	$Zn_2 \cdot Mn \cdot L_2 \cdot 4H_2O$	20.94	9.05	24.03	2.15	21.69	9.17	24.00	2.34
2	$Co_2 \cdot Zn \cdot L_2$	20.87	10.72	25.09	2.17	21.01	11.58	25.66	2.49
3	$Cu_2 \cdot Co \cdot L_2 \cdot H_2O$	22.11	9.96	24.45	1.91	21.81	10.12	24.73	2.06
4	$Co_2 \cdot Mn \cdot L_2 \cdot 4H_2O$	19.03	8.73	20.96	2.72	18.91	8.83	21.11	2.89
5	$Co_2 \cdot Cu \cdot L_2 \cdot 4H_2O$	18.21	9.79	22.75	2.63	18.66	10.05	22.79	2.85
6	$Fe_2 \cdot Mn \cdot L_2 \cdot 2H_2O$	19.33	9.14	24.62	2.15	19.27	9.46	24.77	2.41
7	$Fe_2 \cdot Zn \cdot L_2 \cdot 2H_2O$	19.15	11.13	24.79	2.23	18.94	10.99	24.35	2.37
8	$Fe_2 \cdot Co \cdot L_2 \cdot 4H_2O$	17.78	8.93	22.98	2.65	18.03	9.49	23.18	2.89
9	$Mn_2 \cdot Cu \cdot L_2 \cdot 4H_2O$	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	$Zn_2 \cdot Mn \cdot L_2 \cdot 4H_2O$	> 286	White
2	$Co_2 \cdot Zn \cdot L_2$	> 286	Lilac
3	$Cu_2 \cdot Co \cdot L_2 \cdot H_2O$	> 286	Dark light-blue
4	$Co_2 \cdot Mn \cdot L_2 \cdot 4H_2O$	> 286	Grey-lilac
5	$Co_2 \cdot Cu \cdot L_2 \cdot 4H_2O$	> 286	Dark lilac
6	$Fe_2 \cdot Mn \cdot L_2 \cdot 2H_2O$	> 286	Mustard yellow
7	$Fe_2 \cdot Zn \cdot L_2 \cdot 2H_2O$	> 286	Light brown
8	$Fe_2 \cdot Co \cdot L_2 \cdot 4H_2O$	> 286	Grey-brown
9	$Mn_2 \cdot Cu \cdot L_2 \cdot 4H_2O$	> 286	Light green

Table 3 Results of X-ray diffraction analysis of chelate composites and citric acid.

H ₄ L			1. Zn ₂ ·Mn·L ₂ ·4H ₂ O			2. Co ₂ ·Zn·L ₂			3. Cu ₂ ·Co·L ₂ ·H ₂ O		
2 θ	<i>d</i>	<i>J/J</i> ₀	2 θ	<i>d</i>	<i>J/J</i> ₀	2 θ	<i>d</i>	<i>J/J</i> ₀	2 θ	<i>d</i>	<i>J/J</i> ₀
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	0.0393	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	30.90	2.893	0.1316
			26.07	3.418	0.0400	28.79	3.101	0.1242	31.81	2.813	0.0650
			28.58	3.123	0.0800	29.41	3.035	0.0151	33.93	2.642	0.1050
			29.24	3.056	0.0756	29.99	2.979	0.0878	35.49	2.529	0.0516
			29.76	3.002	0.0939	31.07	2.879	0.2424	37.31	2.410	0.0350
			30.32	2.948	0.0182	31.89	2.806	0.1515	40.36	2.235	0.0466
			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. $\text{Co}_2\cdot\text{Mn}\cdot\text{L}_2\cdot 4\text{H}_2\text{O}$			5. $\text{Co}_2\cdot\text{Cu}\cdot\text{L}_2\cdot 4\text{H}_2\text{O}$			6. $\text{Fe}_2\cdot\text{Zn}\cdot\text{L}_2\cdot 2\text{H}_2\text{O}$			7. $\text{Mn}_2\cdot\text{Cu}\cdot\text{L}_2\cdot 4\text{H}_2\text{O}$		
2θ	d	I/I_0	2θ	d	I/I_0	2θ	d	I/I_0	2θ	d	I/I_0
10.70	8.267	0.0636	9.800	9.024	0.0645	6.67	13.247	1.0000	9.02	9.804	0.3888
11.75	7.532	0.0454	10.84	8.160	0.1612	7.18	12.295	0.5714	10.77	8.213	0.5000
13.17	6.725	0.0606	12.28	7.206	0.1612	8.44	10.466	0.1428	12.30	7.196	0.1611
14.27	6.208	1.0000	15.49	5.719	0.0645	8.86	9.978	0.2857	13.10	6.760	0.2388
14.84	5.968	0.0666	15.77	5.619	1.0000	10.87	8.133	0.6642	13.70	6.461	0.1111
15.61	5.677	0.0909	17.07	5.193	0.0645	13.41	6.601	0.4285	13.74	6.445	0.0916
17.02	5.210	0.0303	18.30	4.847	0.0967	14.34	6.175	0.2000	14.57	6.079	0.2500
17.83	4.974	0.0939	19.77	4.488	0.1612	14.96	5.920	0.3214	15.58	5.688	0.7138
18.39	4.824	0.4121	23.12	3.845	0.2580	17.01	5.211	0.2000	16.79	5.279	0.0722
18.70	4.744	0.2303	23.28	3.820	0.1459	17.98	4.933	0.2857	16.93	5.236	0.2666
20.42	4.348	0.3333	24.62	3.616	0.0967	19.49	4.553	0.1785	18.15	4.888	0.2500
21.50	4.133	0.1333	25.36	3.511	0.1451	19.99	4.440	0.5000	18.22	4.870	0.1222
21.61	4.110	0.3272	26.25	3.394	0.0645	20.63	4.303	0.1428	19.64	4.520	0.1611
23.20	3.833	0.2303	27.48	3.245	0.0032	21.66	4.101	0.1785	20.21	4.393	0.1027
23.59	3.772	0.1939	28.31	3.151	0.0516	22.46	3.958	0.1785	21.43	4.147	0.3055
23.90	3.723	0.1393	29.30	3.047	0.0258	23.35	3.808	0.1428	21.83	4.072	0.2146
24.65	3.612	0.0575	31.00	2.884	0.1290	26.99	3.303	0.1428	22.47	3.957	0.0833
25.90	3.440	0.1606	31.49	2.840	0.0870	27.11	3.288	0.1785	23.44	3.795	0.1500
26.96	3.307	0.2303	34.5	2.599	0.0645	30.77	2.906	0.1214	26.01	3.426	0.5000
27.74	3.216	0.0606	37.41	2.404	0.0645	40.59	2.222	0.2142	28.77	3.103	0.1666
28.70	3.111	0.1666	42.00	2.120	0.0419	46.04	1.971	0.1214	30.24	2.955	0.4166
29.98	2.980	0.1515				48.95	1.861	0.1428	31.59	2.832	0.2547
31.74	2.819	0.1000				55.10	1.666	0.1571	31.70	2.823	0.0962
32.64	2.795	0.1763							33.10	2.706	0.1166
33.91	2.662	0.1536							33.56	2.671	0.1611
35.86	2.504	0.1667							34.84	2.575	0.1777
35.87	2.503	1.393							35.78	2.510	0.1666
36.55	2.458	0.0787							36.87	2.438	0.1444
38.12	2.361	0.0515							37.32	2.409	0.1166
42.46	2.129	0.0939							39.85	2.262	0.2222
43.21	2.094	0.1333							41.36	2.183	0.0527
44.18	2.050	0.1288							43.67	2.073	0.1666
47.45	1.916	0.1060							46.43	1.956	0.1611
48.27	1.885	0.0303							47.94	1.898	0.1388
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 $\text{Fe}_2\cdot\text{Mn}\cdot\text{L}_2\cdot\text{H}_2\text{O}$ and $\text{Fe}_2\cdot\text{Co}\cdot\text{L}_2\cdot 4\text{H}_2\text{O}$ 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/I_0),

reflection angles (2θ), and definite intra-spatial distance (d) values. It should be stated that X-ray diffraction patterns of the composites $\text{Cu}_2\cdot\text{Co}\cdot\text{L}_2\cdot\text{H}_2\text{O}$ and $\text{Co}_2\cdot\text{Cu}\cdot\text{L}_2\cdot 4\text{H}_2\text{O}$ are identical, which speaks of their iso-structure that is conditioned by analogousness of their chemical composition and geometrical characteristics of crystalline structure, which can not be said about the composites: $\text{Zn}_2\cdot\text{Mn}\cdot\text{L}_2\cdot 2\text{H}_2\text{O}$, $\text{Co}_2\cdot\text{Zn}\cdot\text{L}_2$, $\text{Co}_2\cdot\text{Mn}\cdot\text{L}_2\cdot 4\text{H}_2\text{O}$, $\text{Mn}_2\cdot\text{Cu}\cdot\text{L}_2\cdot 4\text{H}_2\text{O}$, $\text{Fe}_2\cdot\text{Zn}\cdot\text{L}_2\cdot 2\text{H}_2\text{O}$ (Table 3).

5. Conclusions

For the first time, we synthesized Heteronuclear chelate citrates of general formula: $M^I_2M^{II}L_2 \cdot nH_2O$ 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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