Synthesis and Study of Glutamine Acid Containing Citrates

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Abstract: Terms of synthesis were defined for the creation of new generation chelate fertilizers and for their experimental testing. Glutamine acid and citric acid containing chelate citrates of the general formulae $M \cdot gl \cdot HL \cdot nHO$ were synthesized, where, $M = Mn, Zn, Fe, Co, Cu$; $n = 0; 1; 1.5$; gl -glutamine acid; HL -citric acid anion. Identity and composition of synthesized compounds were determined by microelemental analysis, melting temperature and X-ray diffraction analysis. X-ray diffraction analysis of the compounds and glutamine acid and citric acid (H_4L) was used to determine their crystalline structure and roentgen-amorphous and iso-structural orders. Their solubility was studied in various solvents.

Key words: Fertilizer, chelate compounds, melting, microelemental analysis, X-ray diffraction study.

1. Introduction

Humanity entered the new millennium with serious problems of hunger and insufficient nutrition. Therefore one of the most urgent problems today is creation of ecologically safe, farm produce of high quantity and quality indices, which in its turn is the necessary term for stability of human health. One of the main causes that conditions low quantitative and qualitative indices of agricultural products is a deficit of microelements in plants and soil. This is why the decisive role in a matter of solution of this problem is attributed to the provision of a plant as well as soil by optimal quantity and ratio of microelements in chelate form, since it is known that bio-metals fulfill their function in a live body when they are presented in chelate form and when deficiency is compensated by bio-metals in chelate form, biological activity of a live organisms sharply increases [1-7]. Proceeding from

the above stated, significance of fertilizers, which contain organic substances (vitamins, amino acids, oxy-acids) and microelements, for the growth and development of agricultural crops and quantitative and qualitative indices of the product obtained therein is theoretically and practically proved today [8-12].

Irrespective of the above stated, determination of methods of synthesis of chelate compounds which will contain oxy-acids (citric acid), amino acids (glutamine acid) and microelements (Zn, Co, Fe, Mn, Cu), investigation of physical and chemical properties of the synthesized compounds and determination of efficiency of their application as fertilizers is still actual.

2. Computational Methods

To obtain chelate compounds we have used the methods developed, refined and simplified by us. Composition of compounds and their identity was proved by microelement analysis (CHN Analyser, Labertherm GmbH). Purity—by defining the melting point (Dynalon SMP10) and by X-ray diffraction

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method, by DPOH-3M type diffractometer, by copper anode emission. The same method was used to determine their crystalline structure, roentgen-amorphous and iso-structural orders were revealed. Qualitative solubility of the synthesized compounds have been studied in various solvents.

3. Results and Discussion

Investigations are in progress in the sphere of creation of the new generation fertilizers and their experimental testing at the Laboratory of Problems of Agrarian Chemistry [13-20]. Thus, we synthesized glutamine acid-containing chelate citrates which had the following general formula: $M \cdot gl \cdot HL \cdot nH_2O$, where, $M = Mn$ (1), Zn (2), Fe (3), Co (4), Cu (5); $n = 0; 1; 1.5$; gl = glutamine acid; HL -citric acid anion. We take $MCO_3M(OH)_2 \cdot HL$ mix in molar ratio 1:2 on a porcelain cup to receive (1), (4) and (5) compounds and take $ZnO:HL$ and $Fe(CH_3COO)_2 \cdot 4H_2O:HL$ by 1:1 molar ratio to receive (2) and (3), correspondingly, and triturate them separately and mix intensely till homogeneous mass is obtained, then add small quantity of hot water at the terms of intense mixing. In case of (1), (4) and (5), we observe release of CO_2 , while in case of (3) we observe acute release of acetic acid. After treatment by water several times we add

glutamine acid to (1), (4) and (5) at 1:2 molar ratio, then heat each of them, mix and stand on water vapor bath till complete drying of the compound (treat it several times by hot water), wash by ether and dry at room temperature.

Identity and composition of the synthesized chelate compounds $Mn \cdot gl \cdot HL$, $Zn \cdot gl \cdot HL$, $Fe \cdot gl \cdot HL \cdot 1.5H_2O$, $Co \cdot gl \cdot HL \cdot 1.5H_2O$, $Cu \cdot gl \cdot HL \cdot H_2O$ were determined by microelement analysis (Table 1), by measuring of melting point (Table 2) and X-ray diffraction analysis (Table 3). By X-ray diffraction study of the compounds and its constituents, bioorganic ligands, glutamine acid (gl) and citric acid (H_4L), their crystalline structure and roentgen-amorphous and iso-structural orders were determined.

Table 3 offers the results of relative intensities (I/I_0), reflection angle (2θ), inter-planar spacing (d) obtained by deciphering of diffraction patterns of compounds Continuation.

Table 4 offers the results of measuring qualitative solubility of chelate compounds in various solvents.

4. Discussions

Microelemental analysis and melting temperature determination proved composition and identity of synthesized compounds.

Table 1 Results of microelemental analysis of chelate compounds.

#	Formula	Practical (%)				Theoretical (%)			
		M	C	H	N	M	C	H	N
1	$Mn \cdot gl \cdot HL$	14.01	33.25	4.00	3.07	13.95	33.48	3.8	3.55
2	$Zn \cdot gl \cdot HL$	16.06	32.14	3.15	3.88	16.08	32.65	3.71	3.46
3	$Fe \cdot gl \cdot HL \cdot 1.5H_2O$	14.99	33.75	4.09	3.26	14.17	33.39	4.55	3.54
4	$Co \cdot gl \cdot HL \cdot 1.5H_2O$	13.57	30.77	3.95	3.57	13.85	31.04	4.23	3.29
5	$Cu \cdot gl \cdot HL \cdot H_2O$	14.76	30.02	3.86	3.07	15.16	31.52	4.06	3.34

Table 2 Results of measuring of melting temperatures of chelate compounds.

#	Formula	Melting T ($^{\circ}C$)	Colour
1	$Mn \cdot gl \cdot HL$	200	Light cream
2	$Zn \cdot gl \cdot HL$	203	White
3	$Fe \cdot gl \cdot HL \cdot 1.5H_2O$	210	Light brown
4	$Co \cdot gl \cdot HL \cdot 1.5H_2O$	199	Pink
5	$Cu \cdot gl \cdot HL \cdot H_2O$	> 286	Dark blue

Mn-gl·HL			Zn-gl·HL			Cu-gl·HL·H ₂ O			Co-gl·HL·1.5H ₂ O		
2θ	D	I/I_0	2θ	D	J/J_0	2θ	d	J/J_0	2θ	d	J/J_0
5.13	17.218	1.0892	5.19	17.027	0.7767	10.85	8.154	0.2144	10.80	8.192	0.3615
10.79	8.201	0.7321	7.74	11.422	0.9328	12.31	7.190	0.1566	11.01	8.036	0.8384
13.16	6.729	0.3714	9.03	9.793	0.3357	13.33	6.642	0.0955	13.22	6.697	0.4076
15.68	5.651	1	10.34	8.555	0.3728	15.80	5.609	1	13.40	6.607	0.700
16.22	5.465	0.1357	12.26	7.219	0.5271	17.11	5.182	0.1366	15.90	5.574	0.9384
17.10	5.185	0.2883	15.53	5.706	0.1614	18.35	4.835	0.1000	17.25	5.140	0.3923
18.29	4.849	0.3714	17.29	5.129	0.1557	19.35	4.587	0.0577	18.56	4.780	0.3923
19.82	4.480	0.1214	18.09	4.904	0.3642	19.82	4.479	0.1800	20.19	4.398	0.2846
20.21	4.393	0.0428	20.07	4.424	1	21.80	4.077	0.1211	20.77	4.277	0.5538
20.68	4.295	0.1642	20.34	4.366	0.3900	23.15	3.842	0.1422	21.83	4.071	0.6076
21.58	4.118	0.8428	20.74	4.283	0.6671	23.84	3.732	0.0377	22.02	4.036	0.3769
22.24	3.998	0.1750	21.60	4.114	0.3328	24.62	3.616	0.0566	23.05	3.858	0.1615
22.67	3.922	0.1000	22.00	4.040	0.0928	25.46	3.498	0.0977	23.92	3.720	0.400
23.60	3.769	0.3178	22.22	4.001	0.2114	26.41	3.375	0.1944	26.51	3.362	1
24.02	3.705	0.0571	23.34	3.811	0.0800	29.03	3.076	0.0722	29.15	3.063	0.2769
26.04	3.421	0.1321	24.43	3.643	0.3200	30.52	2.929	0.0600	30.23	2.956	0.2846
26.23	3.397	0.8464	25.86	3.445	0.1357	31.05	2.880	0.0933	31.11	2.875	0.9461
29.07	3.072	0.1142	26.38	3.378	0.0857	31.85	2.810	0.0788	32.02	2.795	0.1307
30.54	2.927	0.5714	26.84	3.322	0.0714	34.04	2.634	0.0854	33.92	2.643	0.2384
31.25	2.862	0.1964	27.59	3.233	0.0500	37.35	2.408	0.0755	34.42	2.605	0.1230
31.63	2.829	0.1607	28.47	3.135	0.0242	37.82	2.379	0.0688	35.37	2.538	0.1538
32.67	2.741	0.0750	28.84	3.096	0.2014	40.47	2.229	0.0711	35.82	2.507	0.4230
33.29	2.712	0.1464	29.88	2.990	0.0842	44.29	2.045	0.0488	37.74	2.384	0.3000
33.84	2.649	0.3571	30.05	2.974	0.1442	45.80	1.981	0.0233	37.88	2.375	0.3538
35.09	2.557	0.2357	30.17	2.962	0.0714	46.96	1.935	0.0488	40.33	2.228	0.3307
35.90	2.501	0.2250	30.55	2.926	0.0371	48.72	1.869	0.0944	40.71	2.216	0.3692
37.08	2.425	0.2034	31.40	2.849	0.2785	50.20	1.817	0.0366	44.26	2.046	0.4538
37.47	2.400	0.4301	32.48	2.757	0.3857				44.57	2.033	0.3538
38.25	2.353	0.3464	33.88	2.646	0.2585				47.02	1.932	0.2153
40.10	2.248	0.3254	34.91	2.570	0.0728				46.99	1.934	0.2230
40.15	2.246	0.1324	35.91	2.501	0.2385				48.71	1.869	0.2076
42.39											

H ₄ L			gl		
2θ	d	J/J_0	2θ	d	J/J_0
11.5	0.3	2.5	10.2	8.672	12.0
15.2	4.5	37.5	18.2	4.874	82.7
17	1.6	13.3	20.4	4.353	30.7
18.3	6.5	54.2	21.5	4.133	10.7
19	0.4	3.3	22	4.040	24.0
22.3	4.5	37.5	23.8	3.738	53.3
23.1	12	100.0	26.7	3.339	100.0
23.8	0.5	4.2	28.6	3.121	18.7
24.5	1	8.3	30	2.978	4.0
27.1	0.5	4.2	31	2.885	8.0
28.8	0.4	3.3	32.5	2.755	6.7
29.4	2.5	20.8	33.2	2.698	33.3
30.8	1.5	12.5	33.8	2.652	25.3
32.7	1.5	12.5	35.6	2.522	8.0
33.5	0.8	6.7	37.1	2.423	26.7
37	1	8.3	38.8	2.321	10.7
41.9	0.5	4.2	40.6	2.222	34.7
45.8	0.5	4.2	45	2.014	5.3
56.8	0.5	4.2	48.6	1.873	

Table 4 Qualitative solubility of chelate compounds.

#	Compound	Solubility			
		Water	Alcohol	Acetone	Dimethyl formamide
1	Mn·gl·HL	+ t	—	Weakly soluble	—
2	Zn·gl·HL	+ t	—	—	Weakly soluble
3	Fe·gl·HL·1.5H ₂ O	—	—	—	—
4	Co·gl·HL·1.5H ₂ O	+ t	Weakly soluble	Weakly soluble	Weakly soluble
5	Cu·gl·HL·H ₂ O	+ t	Weakly soluble	Weakly soluble	Weakly soluble

X-ray diffraction investigations showed that presence of starting compounds in the samples is not expressed in the form of separate phase, which enables us to conclude that absolutely new individual compounds are obtained, which is in full conformity with the results of the above stated microelemental analysis and melting temperature measurements (Tables 1 and 2). Roentgenogram of the chelate compound Fe·gl·HL·1.5HO is characterized by weakly expressed diffuse peaks, that the main phase is roentgen-amorphous, on the base of which we can conclude that the above referred compound is roentgen amorphous compound. Other compounds are characterized by clearly expressed crystalline structure, various relative intensities (I/I_0), definite reflection angle (2θ), and inter-planar spacing (d). It

should be stated that roentgenograms of the compounds Mn·gl·HL, Cu·gl·HL·H₂O are identical, which refers to their iso-structuring and is conditioned by analogousness of their chemical composition and geometrical characteristics of their crystalline structures, which can't be said about the compounds Zn·gl·HL, Co·gl·HL·1.5HO (Table 3).

Measurements of qualitative solubility of chelate compounds in various solvents (Table 4) proved that the compounds are dissolved at heating in water, while in organic solvents (alcohol, acetone, dimethyl formamide) are insoluble or are characterized by weak solubility.

5. Conclusions

Glutamine acid containing chelate citrates of

general formula: $M \cdot gl \cdot HL \cdot nHO$, where, $M = Mn$ (1), Zn (2), Fe (3), Co (4), Cu (5); $n = 0-1.5$; gl -glutamine acid; HL -citric acid anion were synthesized by the methods developed and simplified by us, in order to create on their base the new generation chelate fertilizers for agricultural crops and to test experimentally. Identity and composition of synthesized compounds were determined. Their crystalline structure was studied, roentgen amorphous iso-structural orders were revealed. Qualitative solubility of the synthesized compounds was determined in various solvents. Fertilizers made on the base of synthesized compounds were tested for maize crop in field conditions. On the base of the obtained results, the conclusion was made about purposefulness to carry out more wide-scale experiments in this direction.

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