Diffraction patterns of ethylenebisdithiocarbamic acid and some its salts

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Pure ethylenebisdithiocarbamic acid and its salts containing the NH_4^+, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} cations were prepared. The diffraction patterns of these substances were investigated. Some conclusions about chemical character of mancozeb are also presented in this paper.

Была приготовлена этиленбисдитиокарбаматовая кислота и ее соли с катионами NH_4^+, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} в виде чистых веществ. Изучены их дифрактограммы. На основе экспериментальных данных сделаны выводы о химическом виде манкозеба.

At present the salts of ethylenebisdithiocarbamic acid (H_2EBDTC) are widely used for protection of plants against fungous diseases. The Zn(II) salt [1] and Mn(II) salt [2] which have obtained commercial names zineb and maneb and to a certain extent the Cu(II) salt [3] are applied in this manner. However, the maximum fungicidal effect is produced by the compound of H_2EBDTC acid containing both Mn(II) and Zn(II) (commercial name mancozeb, content of Zn(II) and Mn(II) at the minimum 2.5 % and 20 %, respectively — referred to the content of the efficacious substance in the whole product) [4—6].

Though a few patents (*e.g.* [6—9]) describe the method of preparation of mancozeb (frequently with the results of biological tests), the problem of character of the efficacious substance, which is important from the viewpoint of use, still remains open. As a matter of fact, it has not been proved whether mancozeb represents an isomorphous system, mechanical mixture or even chemical individual.

The analysis of the above-mentioned substances is usually based on their decomposition and determination of the produced CS_2. However, it is known that different products containing sulfur arise in the course of synthesis and storage of dithiocarbamates. These products may also decompose and give rise to CS_2 (*e.g.* ethylenethiourea).

The aim of this study is to elucidate the character of mancozeb by investigating the diffraction patterns of H_2EBDTC acid and some its salts.

As for these problems, there are only few data available in literature. Solely the diffraction pattern of the disodium salt of the H_2EBDTC acid [4] has been completely described. The information about diffraction of other salts is either deficient (data concerning maneb and zineb in papers [6—8]) or completely missing (other salts as well as H_2EBDTC acid itself).

One of the main causes of this state is considerable difficulty in preparing a certain chemical individual of convenient crystallinity (*e.g.* the disodium salt of H_2EBDTC acid of insufficient purity was used for studying the diffraction pattern as presented in paper [4]).

Experimental

Chemicals and solvents

The solution of the disodium salt of H_2EBDTC acid served as starting solution for preparing the investigated substances. H_2EBDTC acid was prepared by adding the stoichiometric amount of H_2SO_4 into solution of $EBDTC^{2-}$. The formed white crystalline substance of cotton-wool appearance was filtered and dried in a desiccator over P_4O_{10}. The elemental analysis with respect to the content of C, H, N was carried out after 24 h drying. The salts of H_2EBDTC acid were prepared by adding the stoichiometric amount of the corresponding cation in the form of aqueous solution (sulfate, chloride) into the solution of the $EBDTC^{2-}$ anion under constant stirring at 40—50 °C [3]. As for the Mn(II) salt, it is the dihydrate that arises first. But it is transformed into anhydrous salt in the course of drying over P_4O_{10}.

It has been stated in paper [8] that mancozeb is a chemical individual. This statement does not result from chemical composition which should correspond to a new compound, but it is based on the presence of a diffraction maximum at 7.36×10^{-10} m.

In order to verify the conclusions of paper [8], we prepared nine samples with the following contents of Zn (x/mole %): 5, 10, 15, 20, 30, 40, 50, 60, 80. The method of preparation consisted in adding the $(Mn^{2+} + Zn^{2+})$ solution into the calculated quantity of the aqueous solution of $EBDTC^{2-}$ at 40—45 °C. The diffraction patterns were obtained by using the samples dried in air at 20 °C as well as the samples dried for 5 h in a drier at 75 °C and cooled in a desiccator over P_4O_{10}.

The results of elemental analysis are as follows:

	w_i(found)/% (w_i(calc.)/%)		
	C	N	H
H_2EBDTC	22.50 (22.62)	13.17 (13.19)	3.86 (3.79)
$(NH_4)_2$EBDTC	19.72 (19.49)	21.90 (22.74)	5.58 (5.73)
MnEBDTC	18.04 (18.11)	10.35 (10.55)	2.28 (2.27)
MnEBDTC · $2H_2O$	15.91 (15.94)	9.09 (9.29)	3.29 (3.34)
ZnEBDTC	17.37 (17.42)	10.08 (10.11)	2.26 (2.19)

CoEBDTC	17.13 (17.83)	10.53 (10.40)	2.39 (2.24)
NiEBDTC	17.65 (17.85)	10.10 (10.41)	2.45 (2.24)
CuEBDTC	17.53 (17.53)	10.40 (10.22)	2.91 (2.21)

Instrumental equipment

All powder diffraction patterns were taken with an instrument Philips 1730, goniometer 1050/25 under the following conditions: radiation — Cu$K\alpha$1 (λ = = 1.5405 × 10^{-10} m), rate of taking the pattern — 1°/min, voltage — 40 kV, intensity of current — 20 mA, number of impulses — 400/s, angle of diffraction 2Θ — 10—40°.

Results and discussion

The values of d'_{hkl} calculated from eqn (*1*) for the maxima found with individual investigated substances are given in Table 1.

$$d'_{hkl} = \frac{d_{hkl}}{n} = \frac{\lambda}{2 \sin \Theta} \qquad (1)$$

The symbols λ, d'_{hkl}, n, and Θ stand for wavelength of the used radiation, interplanar distance, order of diffraction, and angle of diffraction, respectively.

The values of relative intensity are also given for each value of d'_{hkl} which has been possible because of almost ideal shape of the diffraction pattern (negligible noise, narrow and high peaks). For illustration, the table also contains the values obtained with Dithane M-45 (mancozeb).

The data in Table 1 may be summarized as follows. The compounds of the type M_2EBDTC (M = H, NH_4) or MEBDTC (M = Mn, Zn) are crystalline substances. A great number of diffraction maxima indicates a low degree of symmetry. The diffraction patterns of the samples containing 5—20 mole % of Zn, dried in air at laboratory temperature are identical with the diffraction pattern of the pure dihydrate of maneb. The diffraction patterns of the samples dried at 75 °C which contained equal amounts of Zn as in the preceding case are identical with the diffraction pattern of anhydrous maneb. The peaks of maneb appreciably decrease with increasing content of Zn and the diffraction pattern of the substance with 80 mole % of Zn is practically identical with the diffraction pattern of pure zineb. In neither case the maximum at 7.36 × 10^{10} m was observed.

It results from these facts that we did not succeed in preparing mancozeb as a chemical individual in the investigated concentration region. The compounds of the MEBDTC type (M = Ni, Co, Cu) prepared in aqueous medium do not

Table 1

Values of d'_{hkl} for some ethylenebisdithiocarbamates
(I_r — relative intensity)

H_2EBDTC		$(NH_4)_2$EBDTC		MnEBDTC · $2H_2O$		MnEBDTC		ZnEBDTC	
$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r
6.88	9	5.32	100	7.55	100	7.98	71	8.38	7
5.24	13	4.79	76	7.52	66	6.94	50	6.91	100
4.56	100	4.47	4	5.98	25	6.51	67	5.73	7
4.27	86	4.32	9	4.41	16	4.46	77	5.09	16
4.19	58	4.23	33	4.01	46	4.13	23	4.82	53
3.76	45	4.17	39	3.02	92	4.01	21	4.49	29
3.48	45	4.01	8	2.66	16	3.20	21	4.12	7
3.45	35	3.85	13	2.48	10	3.02	100	3.67	14
3.40	33	3.75	17	2.37	12	2.59	15	3.63	14
3.32	36	3.59	11	2.28	16	2.55	12	3.46	58
3.23	38	3.41	12			2.47	11	3.02	32
3.19	71	3.30	14			2.38	15	2.87	12
3.14	17	3.20	32			2.33	25	2.80	12
2.92	76	3.17	31			2.28	22	2.69	6

Table 1 (Continued)

H_2EBDTC		$(NH_4)_2EBDTC$		$MnEBDTC \cdot 2H_2O$		MnEBDTC		ZnEBDTC	
$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r	$d'_{hkl}/(10^{-10}\,m)$	I_r
2.77	37	3.15	57					2.59	5
2.69	36	3.11	31					2.53	9
2.63	23	3.03	34			Dithane M-45		2.47	5
2.56	5	2.96	33						
2.52	35	2.85	29			$d'_{hkl}/(10^{-10}\,m)$	I_r		
2.44	4	2.78	19						
2.39	3	2.72	9			7.93	556		
2.36	3	2.66	9			6.90	611		
2.29	5	2.64	33			6.48	722		
2.24	21	2.61	14			4.48	913		
		2.51	9			4.13	183		
		2.40	9			4.02	222		
		2.34	5			3.19	190		
		2.29	19			3.02	1000		

exhibit any diffraction maximum (even if the Fe$K\alpha$1 radiation is applied). Therefore they may be regarded as amorphous substances. The difference between the diffraction patterns of dihydrate and anhydrous Mn(II) salt of H_2EBDTC acid unambiguously implies a change in crystal structure in the course of dehydration, which is irreversible according to paper [5]. The obtained results are in good agreement with short information published in paper [6] for maneb and zineb.

The obtained chemical and diffraction data about pure ethylenebisdithiocarbamates (especially the Mn(II) and Zn(II) salt) have become a basis for studying the possibility of preparing mancozeb as chemical individual. According to some references [7—9] mancozeb is a compound different from maneb and zineb.

In regard to the presented results, we must accept the view of *Luginbuhl* [10] according to which the fungicidal properties of mancozeb improve owing to surface interaction between the Zn^{2+} ions and maneb.

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