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## On the Peroxydes of Zinc and Cadmium

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An original method for the preparation of zinc- and cadmium-peroxide is described. The products were identified by X-ray powder analysis as well as quantitative chemical analysis. They were also studied by thermogravimetric analysis. The experimental diffraction data were used for the confirmation and refinement of the already described crystal structures of these compounds made by different methods.

### INTRODUCTION

In the course of the investigation of metal peroxides in this laboratory, with special interest in new methods of their preparation, mercuric peroxides have been synthesized and the crystal structure of  $\alpha$ - $\text{HgO}_2$  solved.<sup>1</sup> It was noted that in the same manner, with variations in the reaction conditions, other peroxides of the IIB group could be obtained, as well as of other metals belonging to the group IIB elements. Thus, the investigation of cadmium and zinc peroxides was undertaken.

Preparations of zinc peroxide have generally yielded hydrous compounds.<sup>2,3</sup> Vannerberg<sup>3</sup> used two methods, either precipitation of  $\text{ZnO}_2$  from a solution of zinc nitrate in hydrogen peroxide with sodium oxide, or by treating zinc oxide with hydrogen peroxide. The best preparations with the highest peroxide content were obtained by the second method. Such samples were used for structure determination. They were found to crystallize in a pyrites type structure (space group  $Pa\bar{3}$ ) with  $a = (4.871 \pm 0.006)$  Å. Zinc atoms are in the 4 (a) positions and oxygen atoms in 8 (c) ( $x = 0.412$ ).

Cadmium peroxide of doubtful purity had been prepared before by different methods. Vannerberg<sup>4</sup> dissolved cadmium nitrate in hydrogen peroxide solutions of different strength and various temperatures. He used a compound of the composition  $7\text{CdO}_2 \cdot \text{Cd}(\text{OH})_2$  for the X-ray powder diffraction study and found that it crystallizes in a pyrites type structure with a cell edge of  $(5.273 \pm 0.003)$  Å. Hoffman *et al.*<sup>5</sup> used a cadmium salt such as acetate, nitrate or sulfate to obtain fairly pure  $\text{CdO}_2$  (water content 2—3%). By powder X-ray structure analysis they also arrived at the pyrites type structure with  $a = (5.313 \pm 0.003)$  Å; cadmium atoms being in special 4 (a) positions and oxygen atoms in 8 (c) with  $x = 0.4192$ . These parameters gave the final value of the R-factor 0.057.

In a more recent work, Kjekshus and Rakke<sup>6</sup> undertook an investigation of a number of  $\text{MX}_2$  compounds, among which the peroxides of zinc and cadmium. They employed the already described methods of preparation and confirmed the established cell dimensions, while the quality of the samples did not justify structure determination. The chemical analysis and DTA results were in agreement with previous investigations but a more thorough insight into the exact composition was not given.

In the present investigation new methods have been developed for the synthesis of these peroxides using elementary metal as the starting material. Samples were identified by X-ray powder diffraction and the data used for refinement of these structures. The composition was studied by chemical quantitative analysis and thermogravimetric analysis.

#### EXPERIMENTAL

##### Materials

Hydrogen peroxide was p.a. grade from »Zorka«, Šabac. Zinc granules were from »Kemika«, Zagreb and cadmium granules from »Laphoma«, Skopje.

##### Preparation of $\text{ZnO}_2$ and $\text{CdO}_2$

About 1 g of zinc (cadmium) in the form of fine powder or grains was placed in an Erlenmeyer flask and an excess of  $\text{H}_2\text{O}_2$  (30%) was added. The mixture was kept at  $-20^\circ\text{C}$  until no traces of the metal could be noticed. Fresh hydrogen peroxide was added several times. The time needed for the reaction can be shortened by allowing the temperature to be higher, but a much larger amount of hydrogen peroxide is needed in that case.

##### Electrolytic Preparation

A rod of zinc (cadmium) was used as the anode with iron as the cathode. Electrolysis was carried out for an hour with a current of 10 mA for zinc and 70 mA for cadmium. During the experiment, voltage had to be adjusted to ensure a constant current. Much higher values were needed at the beginning than towards the end of the reaction. With higher currents heat evolution causes decomposition. Although the reaction mixture was cooled with ice, an increase in temperature of  $5^\circ\text{C}$  could not be avoided with the available apparatus. Longer reaction times caused a larger temperature increase. The products were identified as peroxides of zinc and cadmium.

##### Chemical Analysis

For the determination of zinc and cadmium, the samples were dissolved in  $\text{HCl}$  (1:1) with the addition of two drops of concentrated  $\text{HNO}_3$  and then heated to remove nitrogen oxides. The solutions were then titrated with EDTA. Several different samples of zinc and cadmium peroxides were analyzed and for each one five to ten titrations were performed. The given values are the mean values of the samples.

Zn; calcd. for  $\text{ZnO}_2$  : 67.14%  
calcd. for  $\text{ZnO}_2 \cdot 1/2 \text{H}_2\text{O}$  : 61.45%

found: 63.25%

Cd; calcd. for  $\text{CdO}_2$  : 77.83%  
calcd. for  $\text{CdO}_2 \cdot 1/2 \text{H}_2\text{O}$  : 73.27%

found: 70.67%

Active oxygen was determined by titration with potassium permanganate after dissolution in dilute sulfuric acid.

O<sub>2</sub>; calcd. for ZnO<sub>2</sub> : 32.87%  
 calcd. for ZnO<sub>2</sub> · 1/2 H<sub>2</sub>O : 30.08%

found: 27.8%

O<sub>2</sub>; calcd. for CdO<sub>2</sub> : 22.16%  
 calcd. for CdO<sub>2</sub> · 1/2 H<sub>2</sub>O : 20.86%

found: 18.4%

These results will be discussed below.

### X-ray Diffraction Procedure

X-ray diffraction patterns were taken on samples produced under various experimental conditions. The instrument used was a General Electric XRD-6 Horizontal Powder Diffraction Goniometer using CuK $\alpha$  (Ni-filtered) radiation.

## RESULTS AND DISCUSSION

### Properties

The properties of the obtained products resemble those described earlier. e. g. they have to be stored at low temperatures. Both zinc and cadmium peroxide are a white or yellowish-white powder. They decompose slowly at room temperature. Their solubility in water is very slight. If dissolved in dilute acids, they yield a zinc (cadmium) salt and a hydrogen peroxide solution.

### The crystal structure refinement procedure

The positions of the oxygen atoms in both crystal structures were refined using a computer program which treats overlapping powder data.<sup>7</sup> Cell parameters were taken as found by Vannerberg<sup>2</sup> and Hoffman *et al.*<sup>5</sup>

In the case of ZnO<sub>2</sub>, a temperature factor for zinc and oxygen was applied and the refinement performed with the positional parameters found by Vannerberg.<sup>3</sup> Next, positional parameters were varied and the temperature factor refined again. The final results gave the R-factor of 0.029 with  $x(\text{oxygen}) = 0.413$ ,  $B_{\text{O}} = 1.6 \text{ \AA}^2$ ,  $B_{\text{Zn}} = 1.0 \text{ \AA}^2$  (Table I).

TABLE I

Diffraction Data for ZnO<sub>2</sub>,  $a = 4.871 \text{ \AA}$ ,  $x(\text{oxygen}) = 0.413$ ,  $B_{\text{O}} = 1.61 \text{ \AA}^2$ ,  
 $B_{\text{Zn}} = 1.02 \text{ \AA}^2$ ; R = 0.029

h	k	l	$d_0$	$d_c$	$d^2$	$I_0$	$I_c$	$I^2$
1	1	1	2.814	2.812	2.802	67.3	68.4	58.7
2	0	0	2.445	2.436	2.426	100	100	100
2	1	0	2.171	2.178	2.174	2.8	3.8	3.9
2	1	1	1.993	1.989	1.983	3.6	3.8	4.0
2	2	0	1.728	1.722	1.72	48.7	51.2	50.4
2	2	1	—	1.624	1.622	—	0.4	—
3	1	1	1.470	1.469	1.467	50.5	49.2	53.7
2	2	2	1.408	1.406	1.403	13.5	14.2	15.7
2	3	0	1.351	1.351	1.349	—	1.3	2.1
2	3	1	1.300	1.302	1.301	1.6	1.7	2.1
4	0	0	1.225	1.218	1.217	2.6	3.8	2.8
4	1	0	—	1.181	—	—	0.3	—
3	2	2	—	—	—	—	—	—
4	1	1	—	1.148	—	—	—	—
3	3	1	1.118	1.118	1.117	29.7	28.7	21.5
4	2	0	1.091	1.089	1.088	—	—	16.5
4	2	1	—	1.063	—	—	—	—

The refinement of cadmium peroxide was done in the same manner but the result was different. No acceptable value for the temperature factor could be fitted with a satisfactory R-value. The best results were obtained when no temperature factor was applied ( $R = 0.050$ ) (Table II). The best fit using a temperature factor was obtained with the values of B for oxygen  $1 \text{ \AA}^2$  and for cadmium  $0.66 \text{ \AA}^2$ . Although such low values were also found for mercury<sup>8</sup> and barium<sup>9,10</sup>, we do not feel that in this case they are very probable since they do not lead to an improvement of the R-factor. This situation might be caused by the quality of diffraction data.

TABLE II

*Diffraction Data for CdO<sub>2</sub>. a = 5.313 \AA, x(oxygen) = 0.419 \AA, R = 0.050*

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>0</sub>	<i>d</i> <sub>c</sub>	<i>d</i> <sup>5</sup>	<i>I</i> <sub>0</sub>	<i>I</i> <sub>c</sub>	<i>I</i> <sup>5</sup>
1	1	1	3.062	3.067	3.067	92.8	91.4	95.8
2	0	0	2.655	2.656	2.657	100	100	100
2	1	0	2.368	2.376	2.379	1.45	1.6	1.5
2	1	1	2.161	2.169	2.167	1.1	1.7	1.1
2	2	0	1.877	1.878	1.879	66.5	61.4	56.5
2	2	1	—	1.771	1.77	—	0.3	< 0.7
3	1	1	1.600	1.602	1.602	66.2	62.7	49.7
2	2	2	1.534	1.534	1.534	19.6	19.8	14.4
2	3	0	—	1.414	1.47	—	0.9	< 0.7
2	3	1	—	1.420	1.418	—	1.3	1.0
4	0	0	1.327	1.328	1.328	7.6	7.0	3.5
4	1	0	—	1.289	—	—	0.4	—
3	2	2	—	—	—	—	—	—
4	1	1	—	1.252	—	—	0.2	—
3	3	1	1.218	1.219	1.219	27.8	26.7	17.7
4	2	0	1.191	1.188	1.188	23.7	22.4	14.0
2	4	1	—	1.159	—	—	0.1	—
3	3	2	—	1.133	—	—	0.1	—
4	2	2	1.085	1.085	1.085	13.9	18.7	10.1
4	3	0	—	1.063	—	—	0.3	—
4	3	1	—	1.042	—	—	0.4	—
5	1	1	1.023	1.023	1.023	23.0	28.0	16.7
3	3	3	—	—	—	—	—	—

### *Structure and Composition*

The lengths of the O—O peroxide bond show a constancy throughout a number of metal peroxides.<sup>5,11</sup> The distance found for zinc (1.465 \AA) and cadmium (1.49 \AA) peroxide after refinement is in the region 1.47—1.50 \AA accepted for this bond.

The low value of active oxygen, found for both zinc and cadmium peroxide, can be caused by partial decomposition during dissolution. The evolution of gas was observed in the process, which was not surprising since the medium was acidic.

This explanation is supported by the results of the thermogravimetric analysis. A series of such experiments show a slow, continuous decrease of weight from room temperature to about 130 °C for ZnO<sub>2</sub> and 150 °C for CdO<sub>2</sub>. Above these temperatures a sharp weight loss occurs (up to 240° and 290 °C, respectively) corresponding to the decomposition to the oxides (Table III).

TABLE III

Results of Thermogravimetric Analyses for $ZnO_2$ and $CdO_2$			
Weight loss calculated for the reaction $ZnO_2 \rightarrow ZnO + 1/2O_2$ : 16.4%			
	sample 1	sample 2	sample 3
found (130°—240°C)	15.6%	15.4%	16.4%
water content	10%	9%	8%
Weight loss calculated for the reaction $CdO_2 \rightarrow CdO + 1/2O_2$ : 11.1%			
	sample 1	sample 2	
found (170°—290°C)	11.6%	12.8%	
water content	4%	5%	

These values showed a constancy through a number of samples, while the weight loss up to these temperatures, due to a loss of water, varied slightly more from sample to sample. It was in the range 8—10% for zinc peroxide which corresponds to the formula  $ZnO_2 \cdot 1/2H_2O$  cited by Vannerberg.<sup>2</sup> The water content for cadmium peroxide is 4—6% which is a little more than found by Hoffman *et al.*<sup>5</sup>

The amount of zinc found by chemical analysis is slightly higher than the calculated value for the formula with half a molecule of water. This can be accounted for by the presence of small amounts of elementary zinc that cannot be detected by the available X-ray methods and could not be removed by being in contact with hydrogen peroxide for a reasonably long period.

The water content for cadmium peroxide, calculated from the difference between the theoretical and experimental values found for cadmium by chemical analysis, is higher than shown by TGA. Since we feel that thermogravimetric analysis gives a better insight into the amount of water present, the observed discrepancy between the theoretical and measured amounts might be explained by other causes besides the presence of water. Microscopical examination of the samples showed small amounts of morphologically different particles, so the difference in the chemical analyses would be caused by the presence of water, as well as some impurities.

The nature of the preparation procedures is such that the contaminations in both cases are very difficult to avoid.

To determine whether the water was included in the structure or only physically adsorbed, a variation of the thermogravimetric experiments was performed. Different samples of zinc peroxide were kept overnight at 100° and 120 °C, while cadmium peroxide was kept at 100° and 140 °C. The X-ray powder patterns were taken before and after heating. If water molecules were part of the structure, their loss would cause a change in structure that would show as a change in the X-ray pattern while a loss of physically adsorbed water would cause no such changes.

The results for zinc peroxide show no significant changes in the pattern at either temperature. At 140 °C cadmium peroxide was to a great extent transformed into the oxide while at the lower temperature no such transition was observed. Since the point of transition from the release of water to the release of oxygen cannot be exactly determined on the thermogravimetric curve, it was concluded that the latter process could already begin at 140 °C and the results at this temperature cannot be unambiguously interpreted.

The possibility of a solid solution of oxide and peroxide has also been assumed, but in such a case better diffraction data are needed.

Finally, these results lead to the conclusion that water is only physically included in these compounds. Since all the investigations performed so far have not completely explained the nature of the water present, for a more decisive insight into this problem, NMR and neutron diffraction experiments are planned.

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#### SAŽETAK

##### **Prilog poznavanju peroksida cinka i kadmija**

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Opisana je originalna metoda za dobivanje cink- i kadmij-peroksida. Identifikacija produkata izvršena je rendgenografskim snimanjem polikristalnih uzoraka kao i kvantitativnom kemijskom analizom. Načinjena je i termogravimetrijska analiza. Na temelju dobivenih eksperimentalnih difrakcijskih podataka potvrđene su prethodno opisane kristalne strukture tih spojeva dobivenih drugim metodama i izvršeno utočnjavanje.