J. inorg. nucl. Chem., 1967, Vol. 29, pp. 2899 to 2901. Pergamon Press Ltd. Printed in Northern Ireland

SODIUM HYPONITRITE HEXAHYDRATE

C. N. POLYDOROPOULOS and S. D. VOLIOTIS
Laboratory of Physical Chemistry, University of Athens,
Navarinou 13A, Athens 144, Greece

(*First received* 19 *July* 1966; *in revised form* 10 *March* 1967)

Abstract—The preparation, the habit and the crystallographic parameters of monoclinic $Na_2N_2O_2 \cdot 6H_2O$ are reported.

SODIUM hyponitrite tetra- and hexahydrate have been reported once before.[1] Since the hexahydrate is more easily recrystallizable, it was prepared again to be used as a standard of definite composition in the spectrophotometric method of determination of hyponitrite described elsewhere.[2] Apart from an observation[3] that the powder patterns of anhydrous *cis* and *trans*-$Na_2N_2O_2$ are different, there is no more crystallographic information on hyponitrites. The morphology and some X-ray data are reported in this paper for identification purposes.

(a) PREPARATION

An alkaline solution of sodium hyponitrite was obtained by the electrolytic method.[4] Anhydrous $Na_2N_2O_2$ was precipitated from this, by ethyl alcohol. Some 50 g of the anhydrous salt were dissolved in 1 M NaOH to obtain an almost saturated solution. This was filtered through sintered glass, and left to concentrate over solid NaOH. By suitable recrystallizations large crystals (0·1–0·5 g) were obtained.

(b) PROPERTIES

In the ordinary atmosphere the crystals of $Na_2N_2O_2 \cdot 6H_2O$ effloresce rapidly. If tightly closed in a test tube they can be kept for several months. They can be dehydrated over $CaCl_2$.

They cannot be rinsed with absolute ethanol or diethylether, because they dehydrate in these solvents. To remove their alkaline mother solution, 90–95% ethanol can be used. Finally they can be rinsed with a mixture of equal volumes of diethylether and 95% ethanol. They are insoluble in benzene.

Analysis

The water content was determined by dehydration first over $CaCl_2$ and finally at 50°C. Sodium was determined in the residue by transformation with $(NH_4)_2SO_4$ into

[1] C. N. POLYDOROPOULOS, *Chim. Chron.* **24A**, 147 (1959).
[2] C. N. POLYDOROPOULOS and S. D. VOLIOTIS, The spectrophotometric determination of hyponitrites. *Anal. Chim. Acta*, In print.
[3] E. ZINTL and A. HARDER, *Ber. dt. chem. Ges.* **66**, 760 (1933).
[4] C. N. POLYDOROPOULOS, *Chemy. Ind.* 1686 (1963).

Na_2SO_4. The $N_2O_2^{2-}$ content was determined by precipitation with $AgNO_3$.[5] The analysis was performed in triplicate with the following results:

	H_2O	Na^+	$N_2O_2^{2-}$
Found	50·38	21·15	27·68%
Calculated	50·49	21·48	28·03%

Density

The density was measured in duplicate, by flotation in benzene–iodobenzene mixtures and accurate pyknometer weighings, and found to be 1·657 ± 0·002 at 20°C.

(c) MORPHOLOGY

Under a magnifying glass the crystals seemed to be perfect. Miller indices have definitely been assigned to all ninety-seven faces studied on fourteen single crystals, and ninety-eight interfacial angles among them have been measured. The measurements were made with an accurate double cross reflection goniometer.

The values of the angles observed are shown in the fourth column in Table 1. The number of measurements, *n*, and the individual probable error (±) are shown in the last two columns.

TABLE 1.—NATURAL FACES AND ANGLES OF $Na_2N_2O_2 \cdot 6H_2O$

	Angle	Calculated	Found	±	*n*
1	(001)(201)	134°44′	134°48′	20′	8
2	(00$\bar{1}$)(201)	45 16	45 12	20	5
3	(001)($\bar{2}$01)	131 55	132 10	—	1
4	(001)(011)	134 30	134 29	7	12
5	(011)(01$\bar{1}$)	91 1	90 58	—	1
6	(001)(110)	91 14	91 12	6	2
7	(001)($\bar{1}$10)	88 46	88 48	6	12
8	(011)(110)	130 22	130 20	6	8
9	(011)($\bar{1}$10)	128 9	128 15	8	13
10	(201)(110)	110 3	109 56	13	17
11	(110)($\bar{1}$10)	124 58	125 8	11	4
12	(110)(210)	161 21	161 18	20	2
13	(110)(100)	117 31	117 12	—	1
14	(201)(011)	119 33	119 30	10	4
15	($\bar{1}$11)(001)	130 22	130 49	—	1
16	($\bar{1}$11)($\bar{1}$10)	138 24	138 18	20	2
17	($\bar{1}$11)(011)	159 24	159 26	—	1
18	($\bar{2}$10)($\bar{2}$01)	120 55	120 22	—	1
19	(210)(201)	122 23	125 38	—	1
20	($\bar{2}$10)(001)	88 5	87 7	—	1
21	(210)(2$\bar{1}$0)	92 20	91 27	—	1

If the axes are given the values $a:b:c = 1{\cdot}922:1:1{\cdot}019$ and $\beta = 92°\ 40'$, the angles are calculated as shown in the third column. This combination of values for the crystallographic parameters is the best fit to the observations by least squares. By a variation in the region $a:b = 1{\cdot}920$–$1{\cdot}924$, $c:b = 1{\cdot}018$–$1{\cdot}020$ and $\beta = 92°\ 30$–$50'$, one still obtains values of the angles lying within the regions of the individual errors.

[5] C. N. POLYDOROPOULOS and M. PIPINIS, *Chim. Chron.* **28A**, 107 (1963).

In these calculations the observed value of the last four angles (N° 18–21) was not considered because they were encountered (once only), around a ($\bar{2}10$) face of a crystal which showed pronounced discontinuity 2 mm away from the region of measurements.

The relative area of the faces observed, visually estimated, is shown in Table 2, as a fraction of the total free surface of the crystal. No other face has been detected.

TABLE 2.—DISTRIBUTION OF THE FREE SURFACE OF THE CRYSTAL

(001)	(201)	(110)	(1$\bar{1}$0)	(011)	(0$\bar{1}$1)	($\bar{2}$10)	(100)	($\bar{1}\bar{1}$1)	($\bar{2}$01)
25	25	19	15	7·7	5·3	2·0	0·5	0·3	0·2%

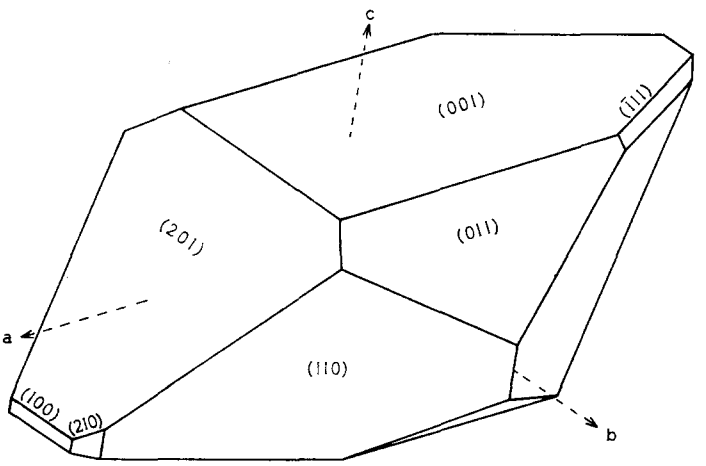

FIG. 1.—Habit of $Na_2N_2O_2 \cdot 6H_2O$.

(d) X-RAY EXAMINATION

The unit cell axes were found to be as follows: $a = 11{\cdot}75$, $b = 6{\cdot}071$, $c = 6{\cdot}128$, $\beta = 92°\ 30'$, and the space group $P2_1/a$.

The Debye–Scherrer pattern is rich in reflections the most intense of which (for Cu K_α $\lambda = 1{\cdot}54$ Å) are as follows:

ϑ	10°22′	11°12′	14°55′	15°22′	16°51′	17°10′	17°27′
I	0·17	0·40	0·36	0·26	0·41	1·00	0·35

The consistency of the goniometric measurements with the X-ray data suggests that the crystals used as a spectrophotometric standard[2] can safely be assigned the composition $Na_2N_2O_2 \cdot 6H_2O$.

A complete crystal structure analysis is hoped to appear shortly.

Acknowledgements—The authors gratefully acknowledge the support of this work by the Royal Hellenic Research Foundation. They are also indebted to Dr. H. J. MILLEDGE (Crystallography Department of University College, London) and Dr. A. G. PANAGOS (Mineralogy Laboratory of the University of Athens) for the X-ray examination.