

the Institute of Physics, Chinese Academy of Sciences, Beijing, was used for the structure refinements.

**Discussion.** As mentioned before, the phase transition from  $P6_3$  to  $P31c$  is associated with the cooperative reorientation of the  $\text{SO}_4$  tetrahedra (Bansal *et al.*, 1980). The rotation of one of the two tetrahedra in one cell in  $P6_3$  causes two types of domain in  $P31c$ , in equal proportions. No matter whether the crystal is merohedrally twinned or not at room temperature, the twin fraction in  $P31c$  should be the same. In this experiment the twin fraction  $f$  is 0.464 (4); the small difference of  $f$  from  $\frac{1}{2}$  may be caused by the inhomogeneous distribution of the defects in the crystal.

The splitting of both O(1) and O(2) into three sites means that the rigid  $\text{SO}_4$  tetrahedra are disordered in three positions with equal probability, which is rather similar to the results at room temperature reported by Schulz *et al.* (1985).

With the method reported by Tomaszewski & Lukaszewicz (1983), pure  $P31c$  phase was obtained in our experiment. Using a similar method, Bhakay-Tamhane *et al.* (1985) did not obtain a pure phase in a single crystal grown by themselves. During the transformation from  $F1$  to  $F2$ , one of the two tetrahedra turns about  $57^\circ$ . This rotation may be sensitive to the concentration of defects in the crystal, which depends on the growth conditions.

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## Structure of Yttrium Nitrate Trihydrate

BY BÉLA RIBÁR AND PAVLE RADIVOJEVIĆ

*Institute of Physics, Faculty of Sciences, Ilije Djuričića 4, 21000 Novi Sad, Yugoslavia*

AND GYULA ARGAY AND ALAJOS KÁLMÁN

*Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest, PO Box 17, H-1525 Hungary*

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**Abstract.**  $\text{Y}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ ,  $M_r = 328.97$ , triclinic,  $P\bar{1}$ ,  $a = 6.946$  (2),  $b = 7.323$  (1),  $c = 10.948$  (1) Å,  $\alpha = 71.47$  (1),  $\beta = 78.38$  (1),  $\gamma = 67.64$  (1)°,  $V = 486.2$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.246$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu = 93.7$  cm<sup>-1</sup>,  $F(000) = 324$ ,  $T = 296$  (1) K,  $R = 0.028$  for 1878 unique observed reflections. The compound was prepared by thermal decomposition of crystals of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Merck, Art. 12516) at 382 K. Three bidentate nitrate groups and three water molecules produce a nine-coordinated Y atom. The coordination polyhedra are linked by hydrogen bonds into a three-dimensional network.

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**Introduction.** Differential thermal analysis of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  shows two strong endothermic peaks at 361 and 378 K. At the first peak a complex of  $[\text{Y}(\text{H}_2\text{O})_5(\text{NO}_3)_2][\text{Y}(\text{H}_2\text{O})_2(\text{NO}_3)_4]$  (Radivojević, Milinski, Ribár & Lazar, 1984) arises and at the second one the title compound is formed which has been grown from the melt of hexahydrate at 382 K. The crystals were sealed into Lindemann capillary tubes.

**Experimental.** A crystal  $ca$   $0.20 \times 0.25 \times 0.40$  mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator. Scan range  $3.0 < 2\theta < 150^\circ$ ,

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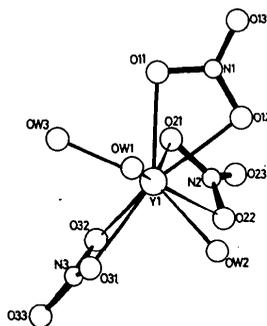
Table 1. Final fractional coordinates with e.s.d.'s in parentheses

$B_{eq} = \frac{1}{3}$  trace (B.G) where G is the direct metric tensor.

	x	y	z	$B_{eq}(\text{\AA}^2)$
Y1	0.73060 (4)	0.61572 (4)	0.74814 (2)	1.64 (2)
N1	0.7477 (4)	0.8085 (4)	0.9329 (3)	2.2 (2)
O11	0.7666 (4)	0.6223 (3)	0.9629 (2)	2.6 (2)
O12	0.7230 (4)	0.9056 (4)	0.8165 (2)	2.7 (2)
O13	0.7550 (5)	0.8877 (4)	1.0129 (2)	3.3 (2)
N2	0.3052 (4)	0.8787 (4)	0.7551 (2)	2.1 (2)
O21	0.3856 (4)	0.7336 (3)	0.8525 (2)	2.4 (2)
O22	0.4277 (4)	0.8963 (4)	0.6531 (2)	2.5 (2)
O23	0.1261 (4)	0.9874 (5)	0.7605 (3)	4.3 (3)
N3	0.6524 (5)	0.3689 (4)	0.6173 (3)	2.5 (2)
O31	0.8308 (4)	0.3908 (4)	0.6069 (2)	3.0 (2)
O32	0.5137 (4)	0.4666 (4)	0.6881 (2)	2.5 (2)
O33	0.6231 (5)	0.2645 (4)	0.5627 (2)	3.5 (2)
OW1	1.0915 (4)	0.4852 (5)	0.7586 (3)	4.0 (3)
OW2	0.8453 (4)	0.8043 (4)	0.5529 (2)	3.8 (2)
OW3	0.7798 (4)	0.2960 (3)	0.8947 (2)	2.8 (2)

Table 2. Interatomic distances ( $\text{\AA}$ ) and selected angles ( $^\circ$ ) with e.s.d.'s in parentheses

Y1-O11	2.431 (3)	N1-O11	1.257 (5)
Y1-O12	2.445 (4)	N1-O12	1.256 (4)
Y1-O21	2.396 (4)	N1-O13	1.212 (6)
Y1-O22	2.442 (4)	N2-O21	1.283 (5)
Y1-O31	2.429 (4)	N2-O22	1.263 (5)
Y1-O32	2.450 (4)	N2-O23	1.196 (7)
Y1-OW1	2.331 (5)	N3-O31	1.287 (8)
Y1-OW2	2.321 (4)	N3-O32	1.253 (6)
Y1-OW3	2.323 (3)	N3-O33	1.201 (6)
O11-Y1-O12	52.0 (2)	O31-Y1-OW1	80.2 (2)
O11-Y1-O21	72.5 (2)	O31-Y1-OW2	76.2 (2)
O11-Y1-OW1	76.9 (2)	O31-Y1-OW3	77.6 (2)
O11-Y1-OW3	68.8 (2)	O32-Y1-OW2	104.6 (2)
O12-Y1-O21	75.5 (2)	O32-Y1-OW3	73.8 (2)
O12-Y1-O22	76.1 (2)	OW1-Y1-OW2	78.3 (3)
O12-Y1-OW1	88.0 (2)	OW1-Y1-OW3	77.6 (3)
O12-Y1-OW2	80.5 (2)	O11-N1-O12	116.5 (7)
O21-Y1-O22	52.8 (2)	O11-N1-O13	121.1 (8)
O21-Y1-O32	72.0 (2)	O12-N1-O13	122.5 (8)
O21-Y1-OW3	88.6 (2)	O21-N2-O22	115.2 (7)
O22-Y1-O31	103.0 (2)	O21-N2-O23	122.1 (7)
O22-Y1-O32	72.2 (2)	O22-N2-O23	122.7 (8)
O22-Y1-OW2	71.6 (2)	O31-N3-O32	114.2 (7)
O31-Y1-O32	51.8 (2)	O31-N3-O33	122.4 (8)
		O32-N3-O33	123.5 (8)

Fig. 1. A perspective view of  $\text{Y}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  showing atomic numbering.

$\omega$ - $2\theta$  scan,  $h$ -8 to 0,  $k$ -9 to 9,  $l$ -13 to 13, no systematic absences. Cell parameters by least-squares fit for 25 centred reflections with  $\theta$  range from 35 to 40°. Of 2111 measured reflections 1878 were taken as observed with  $I > 3\sigma(I)$ . Three standard reflections ( $\bar{5}11$ ,  $03\bar{5}$ ,  $\bar{3}31$ ) were measured every 60 min, no intensity variation was observed. Extinction coefficient  $4.7 \times 10^{-6}$ . Structure was solved by Patterson and Fourier methods. No H positions could be located. Full-matrix refinement,  $\sum w(\Delta F)^2$  minimized, 146 parameters refined. At the end of isotropic refinement an empirical absorption correction was performed with the program *DIFABS* (Walker & Stuart, 1983), min. and max. absorption corrections 0.788 and 1.802. Anomalous dispersion for all non-H atoms. Final  $R=0.028$ ,  $wR=0.033$ ,  $R_{\text{tot}}=0.029$ ,  $w=4F_o^2/\sigma^2(F_o)^2$ . Residual electron density in final difference map  $0.71(10) \text{ e \AA}^{-3}$ . Max.  $\Delta/\sigma=0.263$ . Scattering factors were taken from Enraf-Nonius (1983) *SDP-Plus*. Programs applied: Enraf-Nonius *SDP-Plus* with local modification adapted to PDP 11/34 minicomputer.

Table 3. O-O distances ( $\text{\AA}$ ) between neighbouring coordination polyhedra

OW1-O13	$[2-x, 1-y, 2-z]$	3.061 (4)
OW1-O32	$[1+x, y, z]$	2.840 (4)
OW2-O22	$[1-x, 2-y, 1-z]$	2.984 (4)
OW2-O31	$[2-x, 1-y, 1-z]$	2.779 (4)
OW3-O13	$[x, y-1, z]$	2.913 (4)
OW3-O21	$[1-x, 1-y, 2-z]$	2.749 (4)

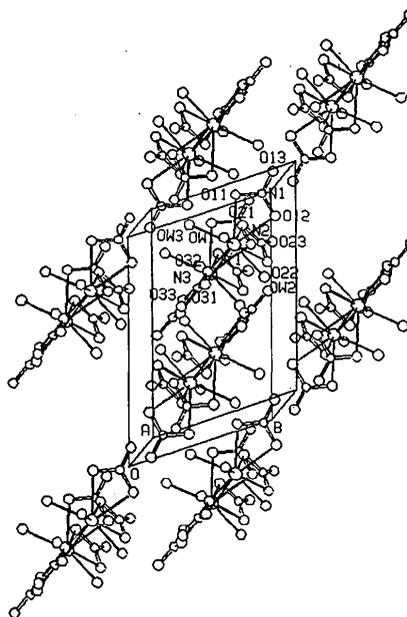


Fig. 2. Packing of coordination polyhedra.

**Discussion.** Atomic coordinates of non-H atoms are in Table 1.\* The atomic arrangement around Y is shown in Fig. 1. The atomic distances and angles are listed in Table 2.

The Y atom has nine oxygen neighbours, six from three bidentate nitrate groups and three from water molecules. The coordination polyhedron around Y can be described as a distorted pentagonal pyramid with three additional atoms from the other side of the base of the pyramid. The basal plane of the pyramid is defined by O11, O12, OW2, O31 and OW3. The distances of the atoms from the least-squares basal plane are 0.158 (3), 0.195 (3), 0.163 (4), 0.076 (3) and 0.034 (3) Å respectively. The apex of the pyramid is occupied by OW1 at a distance of 1.922 (4) Å from the basal plane. Y is displaced out of the basal plane by 0.404 (1) Å. Three additional atoms from the other side of the base are O21, O22 and O32 at distances of 2.461 (3), 2.393 (3) and 2.006 (3) Å from the basal

plane. All Y—O(water) distances [ave. 2.325 (4) Å] are shorter than Y—O(nitrate) distances [ave. 2.432 (4) Å]. In each nitrate group the non-coordinated O atom is closer to N than the other two, and the metal-bound O—N—O angles are significantly smaller than the other O—N—O angles, which is a common property of all bidentate nitrate groups. The Y atom lies in the plane of each nitrate group [max. dev. 0.028 (1) Å]. Dihedral angles formed by (NO<sub>3</sub>)1 and (NO<sub>3</sub>)2, (NO<sub>3</sub>)1 and (NO<sub>3</sub>)3, (NO<sub>3</sub>)2 and (NO<sub>3</sub>)3 are 73.4 (2), 82.4 (2) and 81.7 (2)° respectively. Water oxygen distances from the O atoms of neighbouring coordination polyhedra listed in Table 3 indicate possible hydrogen bonds which hold the coordination polyhedra in a three-dimensional network (Fig. 2.).

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\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44588 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Structure of a Copper(III) Periodate Complex

BY VOLRATH ADELSKÖLD, LARS ERIKSSON, PEI-LING WANG\* AND PER-ERIK WERNER

*Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden*

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**Abstract.** Tetrasodium potassium bis(periodato)cuprate dodecahydrate,  $\text{KNa}_4[\text{Cu}(\text{HIO}_6)_2] \cdot 12\text{H}_2\text{O}$ ,  $M_r = 858.60$ , monoclinic,  $P2_1/c$ ,  $a = 6.119$  (3),  $b = 25.118$  (8),  $c = 14.741$  (5) Å,  $\beta = 97.87$  (4)°,  $V = 2244.15$  Å<sup>3</sup>,  $D_x = 2.560$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 38.37$  cm<sup>-1</sup>,  $F(000) = 1664$ ,  $Z = 4$ , room temperature,  $R = 0.068$  for 2991 independent reflections. The complex anion consists of two IO<sub>5</sub>(OH) octahedra, each sharing an edge with a square-planar coordination around a Cu atom so as to form a planar O<sub>2</sub>—I—O<sub>2</sub>—Cu—O<sub>2</sub>—I—O<sub>2</sub> network. The octahedra around the I atoms are distorted, and hydrogen bonds between anions are formed by the hydroxy groups located perpendicular to the network. Water

molecules are situated axial to the square-planar-coordinated copper at 2.708 (10) and 3.576 (10) Å.

**Introduction.** Copper(III) ( $d^8$ ) complexes of general formula  $M_x\text{H}_{7-x}[\text{Cu}(\text{IO}_6)_2] \cdot n\text{H}_2\text{O}$  ( $M = \text{K}, \text{Na}$ ) were first reported by Malaprade (1937). Malatesta (1941*a,b*) prepared a number of crystallizable compounds of this type by complexing copper with periodic acid, and it was evident that these compounds were much more stable than the trivalent copper compounds obtained previously. From chemical analysis, IR spectra and conductimetric measurements Balikungeri, Pelletier & Monnier (1977) showed that the anion of bis(periodato)cuprate(III) is  $[\text{Cu}(\text{HIO}_6)_2]^{5-}$ . The trivalent state of Cu was confirmed from magnetic measurements by Malatesta (1941*a*), and the diamagnetic character has also been confirmed by the present

\* On leave from Shanghai Institute of Ceramics, Academia Sinica, 865 Chang-Ning Road, Shanghai, China.