

**Structure and Twinning in**  
 **$(\text{Na}_{0.12}, \text{H}_3\text{O}^+_{0.38}, \text{H}_2\text{O}_{0.50})_6(\text{Na}_{0.12}, \text{H}_3\text{O}^+_{0.88})[\text{K}_2(\text{K}_{0.333}, \text{H}_2\text{O}_{0.667})_6\text{Na}_2\text{Fe}_6^3+\text{O}_2(\text{SO}_4)_{12} \cdot 6\text{H}_2\text{O}]$**

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**Abstract.**  $\text{Na}_{2.84}\text{K}_4(\text{H}_3\text{O}^+)_{3.16}\text{Fe}_6\text{S}_{12}\text{O}_{50} \cdot 13\text{H}_2\text{O}$ ,  $M_r = 2035.83$ ,  $P\bar{3}1c$ ,  $a = b = 9.620$  (6),  $c = 35.971$  (8) Å,  $V = 2882.92$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 2.35$  (by flotation),  $D_x = 2.34$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 2.66$  mm<sup>-1</sup>,  $F(000) = 1020$ ,  $T = 290$  K, final  $R = 0.12$  for 462 observed reflections. Suitable crystals for this study were prepared from an aqueous solution containing sodium, potassium and iron sulphates at about 350 K. The structure solution confirmed the hypothesis that the crystal investigated was really a merohedric twin. The percentages found for the two individuals are 48 and 52% respectively. The most important structural units are sandwich sheets of composition  $[\text{Na}_2\text{K}_2\text{Fe}_6^3+\text{O}_2(\text{SO}_4)_{12}(\text{H}_2\text{O})_6]^{6-}$  (simplified formula), which have previously been found in other similar compounds.

**Introduction.** This paper is part of a series of investigations of some sulphates containing the same  $\text{Fe}^{3+}$  trinuclear complex (Giacovazzo, Scordari & Menchetti, 1975; Giacovazzo, Scordari, Todisco & Menchetti, 1976; Scordari, 1980a, 1981). The analysis of the title compound presented some difficulties. Crystals from the same batch showed changeable Na/K ratio (Scordari, 1977). Moreover, all the crystals examined by Weissenberg photographs indicated a symmetry higher than expected. Finally, X-ray powder patterns proved that the  $(\text{K}, \text{H}_3\text{O}^+)$ -rich crystals were more stable than the Na-rich ones. The reasons for undertaking this structural analysis are: (a) to determine the sites involved in the Na, K and  $\text{H}_3\text{O}^+$  replacement; (b) to understand the reasons which make the Na-enriched compounds unstable; (c) to examine the relationships between the title compound and other closely related salts (Scordari, 1980a, 1981); (d) to verify the correct stacking sequence of  $[\text{Na}_2\text{K}_2\text{Fe}_6^3+\text{O}_2(\text{SO}_4)_{12}(\text{H}_2\text{O})_6]^{6-}$  double sheets (Scordari, 1980b); and (e) to prove that the unusual symmetry exhibited by the compound was due to a twinning effect.

**Experimental.** Title compound grows at about 350 K by evaporation of an aqueous solution containing  $\text{K}_2\text{SO}_4$  (0.6 g),  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (3.4 g) and

$\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$  (4.3 g). The crystals obtained usually effloresce slowly; however, the crystal analysed was stable and hexagonal with approximate dimensions  $0.014 \times 0.014 \times 0.016$  cm.  $D_m$  was determined by flotation with the same crystal used for the X-ray analysis. Philips PW 1100, graphite-monochromated Mo  $K\alpha$ ,  $\omega$ - $2\theta$  scan mode, three standard reflections (11,1,0, 0,0,18 and  $\bar{1}\bar{2},1,0$ ) measured every 100 reflections showed no significant changes. 10 reflections in the range  $7^\circ < \theta < 13^\circ$  were used for measuring lattice parameters; no absorption correction ( $\mu R_{\text{max}} = 0.43$ ). Scattering curves from Cromer & Waber (1965). Within a range of  $(\sin\theta)/\lambda < 0.50$  Å<sup>-1</sup>, 864 reflections with  $|F_o| > 3\sigma(F_o)$  were selected from a total of 1491 measured;  $h_{\text{max}} = k_{\text{max}} = 8$  and  $l_{\text{max}} = 36$ .

A piezoelectric test did not confirm the lack of a centre of symmetry.

Problems concerning a symmetry higher ( $P6/mmm$ ) than the structure allowed were overcome by assuming that the crystal was a  $[11\bar{2}0]$  twin.  $P\bar{3}1c$  proved to be more reliable than  $P\bar{6}2c$  for the structure solution. Were the crystal a merohedric twin, the pairs of reflections  $hkl$  and  $kh\bar{l}$  would be exactly superimposed. So, if the two individuals have equal volumes, about one half of the reflections (462) are needed to prove the correctness of the structural model here proposed. Close analogies (concerning chemistry, symmetry and parameters) with two other salts (Scordari, 1980a, 1981) convinced us that in the title compound there were  $[\text{Na}_2\text{K}_2\text{Fe}_6^3+\text{O}_2(\text{SO}_4)_{12}(\text{H}_2\text{O})_6]^{6-}$  sandwich sheets (simplified formula). This assumption and the sequences put forward by Scordari (1980b) were taken into account when the Patterson map was analysed.

The atomic parameters used to calculate  $F_c$  are those of salt  $X$  (Scordari, 1980a) and of its topotactic product (Scordari, 1981) duly adapted to the  $c$  length. The first were employed for the atoms belonging to the sandwich sheets, the latter to characterize the intersandwich-sheet atomic content. So the structure factors for the twin  $||F_{c,T(hkl)}||$  could be calculated according to  $|F_{c,T(hkl)}| = [Y|F_{c(hkl)}|^2 + (1-Y)|F_{c(kh\bar{l})}|^2]^{1/2}$  where  $Y$  is the volume fraction of one individual and  $1-Y$  is that of the other.  $R = \sum ||F_{o,T(hkl)}| - |F_{c,T(hkl)}|| /$



As far as the sandwich-sheet relationships between the title compound and salt *X* are concerned, we notice that two Fe<sup>3+</sup> clusters belonging to two adjacent sandwich sheets are differently related. In fact, in our compound they are opposite and rotated with respect to each other by about 30°; in salt *X* the same clusters are shifted with respect to each other by  $\pm (\frac{1}{3} \mathbf{a} - \frac{1}{3} \mathbf{b})$  and are rotated by about 60°.

The last question concerns the decrease of stability with the lowering of the Na/K ratio. Briefly, this effect is connected with the shortening of the distance between opposite Fe<sup>3+</sup> clusters caused by the replacement

Na → (H<sub>3</sub>O<sup>+</sup>, K), which in turn causes an increase in the potential energy.

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## Diphosphure de Trirhodium, Rh<sub>3</sub>P<sub>2</sub>: Premier Exemple d'une Structure Lacunaire Ordonnée de Type *anti*-PbFCl

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**Abstract.**  $M_r = 370.7$ , tetragonal,  $P\bar{4}m2$ ,  $a = 3.327$  (1),  $c = 6.151$  (3) Å,  $V = 68.1$  (1) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 9.04$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 18.6$  mm<sup>-1</sup>,  $F(000) = 165$ ,  $T = 291$  K,  $R = 0.044$  for 181 reflections. The structure shows for the first time ordered vacancies in an *anti*-PbFCl-type structure; indeed, Rh(1) atoms occupy all the square-pyramidal phosphorus sites and Rh(2) atoms only half of the regular tetrahedral phosphorus sites. The structural relationship with Cr<sub>2</sub>As (*anti*-PbFCl type) is also discussed.

**Introduction.** Nos travaux sur les phosphures ternaires de rhodium et d'éléments de transition 3d nous ont conduits, en étude préliminaire, à reprendre le système binaire rhodium–phosphore dans lequel seuls trois composés ont fait antérieurement l'objet d'études structurales satisfaisantes: Rh<sub>2</sub>P (Zumbusch, 1940), Rh<sub>4</sub>P<sub>3</sub> (Rundqvist & Hede, 1960), RhP<sub>3</sub> (Rundqvist & Ersson, 1968).

Nous avons pour notre part redéterminé sur monocristal la structure du binaire RhP<sub>2</sub> qui n'avait été qu'amorcée précédemment (Kjekshus, 1971) et isolé deux nouveaux phosphures, l'un RhP de structure type MnP (El Ghadraoui, 1982), l'autre Rh<sub>3</sub>P<sub>2</sub> dont la structure fait l'objet du présent travail.

**Partie expérimentale.** Monocristaux de Rh<sub>3</sub>P<sub>2</sub> obtenus par technique de flux à l'étain dans un rapport atomique Rh:P:Sn de 3:2:20. Ampoule de silice scellée sous vide, portée à 1423 K une semaine et refroidie lentement (5 K h<sup>-1</sup>) jusqu'à l'ambiante. Excès d'étain dissous dans HCl dilué qui n'affecte pas les monocristaux formés. Forme parallélépipédique, monocristal étudié: 0.05 × 0.03 × 0.01 mm, paramètres cristallins affinés sur Nonius CAD-4 à l'aide de 25 réflexions indépendantes, monochromateur de graphite; réflexions de référence: 003 et 111; 248 réflexions avec  $\theta < 40^\circ$ ,  $0 \leq h \leq 5$ ,  $0 \leq k \leq 5$ ,  $0 \leq l \leq 11$ , 181 réflexions indépendantes avec  $I > 3\sigma(I)$ , correction de Lp, absorption ignorée, méthode de Patterson pour Rh(1) et P, synthèse-différence pour Rh(2), affinement basé sur  $F$ , facteurs de température anisotropes, extinction secondaire ( $2 \times 10^{-6}$ ),  $R:0.044$ ,  $R_w:0.046$ ,  $w = 1/\sigma^2(F)$ . Les facteurs de diffusion sont ceux de *International Tables for X-ray Crystallography* (1974). Les programmes *SDP* (Frenz, 1978)\* ont été utilisés.

\* Les listes des facteurs de structure et des paramètres thermiques anisotropes ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 38730: 4 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.