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## Structure of the Linear Chain Tetraammineplatinum(II)diidotetraammineplatinum(IV) Hydrogensulfate Dihydrate

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**Abstract.**  $[\text{Pt}(\text{NH}_3)_4][\text{PtI}_2(\text{NH}_3)_4](\text{HSO}_4)_4 \cdot 2\text{H}_2\text{O}$ ,  $M_r = 1204.53$ , monoclinic,  $C2/m$ ,  $a = 18.609(2)$ ,  $b = 7.563(1)$ ,  $c = 11.862(1)$  Å,  $\beta = 126.22(1)^\circ$ ,  $V = 1346.8(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.97$  Mg m<sup>-3</sup>,  $D_m$  not measured,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu(\text{Mo K}\alpha) = 13.61$  mm<sup>-1</sup>,  $F(000) = 1116$ , room temperature,  $R = 0.041$ ,  $wR = 0.053$  for 1815 observed reflections [ $|F_o| > 3\sigma(|F_o|)$ ]. This compound comprises linear chains  $\dots\text{I}-\text{Pt}^{\text{IV}}-\text{I}\dots\text{Pt}^{\text{II}}\dots$  which consist of the alternately arranged octahedral  $\text{trans}[\text{PtI}_2(\text{NH}_3)_4]^{2+}$  and square-planar  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  units along the  $c$  axis.  $\text{Pt}^{\text{IV}}-\text{I}$  and  $\text{Pt}^{\text{II}}\dots\text{I}$  distances are 2.699(1) and 3.237(1) Å respectively. There is three-dimensional ordering among chains, different from other I-bridged Wolfram's red salt analogues. The difference between the  $\text{Pt}^{\text{IV}}-\text{X}$  and  $\text{Pt}^{\text{II}}\dots\text{X}$  distances is found to decrease linearly with an increase in the ratio of  $\text{Pt}^{\text{IV}}-\text{X}$  to  $\text{Pt}^{\text{II}}\dots\text{X}$  distances in Wolfram's red salt analogues, irrespective of the kind of bridging halogen atom  $X$ . The data presented in this paper are consistent with this relationship.

**Introduction.** Since Wolfram's red salt  $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_4][\text{PtCl}_2(\text{C}_2\text{H}_5\text{NH}_2)_4]\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  was synthesized, many analogues have been synthesized and studied, through substitution of the ligand amines,

bridging halide ions, and counter ions (Endres, Keller, Martin & Traeger, 1979; Matsumoto, Yamashita, Kida & Ueda, 1979; Endres, Keller, Martin, Traeger & Novotny, 1980). They comprise linear chains of halide-bridged platinum ions in the two different oxidation states  $\text{Pt}^{\text{II}}$  and  $\text{Pt}^{\text{IV}}$  and counter anions. These analogues exhibit considerable interactions between platinum ions in each chain through bridging halide ions. The XPS spectral measurement suggests that the oxidation state of Pt is not strictly divalent or tetravalent (Yamashita, Matsumoto & Kida, 1978). A theoretical treatment related to the Peierls state in one-dimensional solids has been carried out by Nasu (1984).

The compounds also show interesting physical properties: a conductivity of  $10^{-8}$ – $10^{-12}$  Ω<sup>-1</sup> cm<sup>-1</sup> at room temperature with semiconductive temperature dependence, a strong absorption in the visible region (Yamada & Tsuchida, 1956; Day, 1975; Matsumoto, Yamashita & Kida, 1978; Papavassiliou & Zdetris, 1980), photoluminescence (Tanino & Kobayashi, 1983). The conductivity increases by a factor of  $10^3$  or more under a pressure of about  $10^9$  Pa (Thomas & Underhill, 1971; Hamaue, Aoki, Yamashita & Kida, 1981; Aoki, Hamaue, Kida, Yamashita, Takemura, Furuta & Kawamori, 1982).

Concerning the ordering of the chains comprising Pt and halogen atoms, Woffram's red salt and its analogues are classified into three groups: class (i), those which have a three-dimensional long-range order (Matsumoto, Yamashita & Kida, 1978; Endres, Keller, Martin, Traeger & Novotny, 1980); class (ii), those which have a one-dimensional order in each chain but have no correlation or a short-range order among chains (Craven & Hall, 1961; Brown & Hall, 1976; Breer, Endres, Keller & Martin, 1978; Fanwick & Huckaby, 1982); and class (iii), those which have a short-range order in each chain and have no correlation or a short-range order among chains (Endres, Keller, Martin, Traeger & Novotny, 1980).

Recently the compounds containing the simplest amine, NH<sub>3</sub>, as in-plane ligands of Pt atoms have been synthesized and their crystal structures have been determined (Fanwick & Huckaby, 1982; Clark, Kurmoo, Galas & Hursthouse, 1982; Tanaka, Tsujikawa, Toriumi & Ito, 1982). The analogues with Cl and Br as bridging halide ions, which are isomorphous, have one-dimensionally ordered chains. They have no correlation or a short-range order between the positions of Pt<sup>II</sup> or Pt<sup>IV</sup> in neighbouring chains – that is, they belong to class (ii).

Clark *et al.* also reported the synthesis and structure of an I-bridged analogue, [Pt(NH<sub>3</sub>)<sub>4</sub>][PtI<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>](HSO<sub>4</sub>)<sub>3</sub>(OH)·H<sub>2</sub>O. We were able to prepare a similar I-bridged analogue, [Pt(NH<sub>3</sub>)<sub>4</sub>][PtI<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>](HSO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O, which has different counter anion composition and contains water of crystallization. The synthesis and crystal structure are reported in this paper.

**Experimental.** The title complex was prepared by the reaction of [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and [PtI<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> in sulfuric acid, and evaporation to 62% concentration of sulfuric acid. Lustrous golden needles crystallized on cooling in a day. Analysis, calculated for [Pt(NH<sub>3</sub>)<sub>4</sub>][PtI<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>](HSO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O: Pt 32.39, I 20.93, S 10.65, O 23.91, N 9.30, H 2.68%; found: Pt 31.54, I 20.38, S 11.30, O 24.77, N 9.02, H 2.98%.

The needle crystals elongated along the *c* axis are dark brown and light yellow for light polarized parallel and perpendicular to the needle axis, respectively. Crystal 0.10 × 0.12 × 0.30 mm coated with a thin layer of paraffin. Rigaku AFC-5 four-circle diffractometer, graphite-monochromatized Mo *K*α radiation. Unit-cell dimensions determined by least-squares fit of 48 2θ values (25° < 2θ < 30°). 8731 intensities in the range 2θ ≤ 60° measured with θ–2θ scan technique. *h* 0→21, *k* –10→10, *l* –16→16. Three reference reflections monitored periodically showed no significant intensity deterioration. *R*<sub>int</sub> = 0.031 for 1731 equivalent reflections. 1815 unique reflections measured [*|F<sub>o</sub>*| > 3σ(*|F<sub>o</sub>*)]. Intensity data corrected for Lorentz–polarization factors and for absorption. The systematic absences showed possible

space groups *C2/m*, *Cm* and *C2*. The positions of the Pt and I atoms were determined from the Patterson maps. From successive Fourier syntheses, positions of non-hydrogen atoms was determined. Block-diagonal least-squares calculations based on *|F|* were carried out with anisotropic thermal parameters, and proved to be successful in the centrosymmetric space group *C2/m*. H atoms bonded to N atoms or O atoms of the hydrogensulfate ion and water of crystallization were not observed in the difference maps and were not included in the refinement. The scattering factors and anomalous-scattering corrections were taken from *International Tables for X-ray Crystallography* (1974). Weighting scheme  $w = [\sigma_{\text{count}}^2 + (0.015|F_o|)^2]^{-1}$  employed. *R* = 0.041, *wR* = 0.053. Δ/σ < 0.2, –3.7 < Δρ < 3.8 e Å<sup>–3</sup>. No correction for secondary extinction. Calculations carried out on the HITAC M-200H computer at the Computer Center of the Institute for Molecular Science with the *Universal Crystallographic Computation Program System UNICSIII* (Sakurai & Kobayashi, 1979).

**Discussion.** The atomic parameters are listed in Table 1.\* A stereoscopic view of the crystal structure is shown in Fig. 1. Bond lengths and angles are listed in Table 2. The Pt atoms occupy 2/*m* sites. The I, S, O(1), O(5) and O(7) atoms sit on a mirror plane. The oxidation states of the Pt atoms are structurally identified and the position of the I atom is unequivocally determined. The tetravalent Pt(1) is coordinated in a plane by four N atoms of the ligand amines with Pt(1)–N distance of 2.070 (6) Å and axially by I atoms with Pt(1)–I distance of 2.699 (1) Å. The divalent Pt(2) is coordinated in a plane by four N atoms of the ligands with Pt(2)–N distances of 2.052 (11) and 2.076 (10) Å. The square planes comprising Pt and N atoms are staggered by 39° with respect to each other when viewed down the chain axis. The complex units stack in the *c* direction, along which the Pt and I atoms alternate. The chain is, however, not strictly linear but a little distorted. The deviation from linearity, that is, the angle between the Pt(1)–I bond and the *c* axis is 1.2 (2)°. Unlike other I-bridged Woffram's red salt analogues, there exists three-dimensional ordering in the chains composed of Pt and I, *i.e.* this compound belongs to class (i).

There are two kinds of hydrogensulfate ions, those including S(1) and S(2), which are located in the channel among the chains. That including S(1) is disordered in such a way that the positions of the O atoms are related by the rotation around the S(1)–O(1)

\* Lists of anisotropic thermal parameters for non-hydrogen atoms and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42893 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

bond, while that including S(2) has no disorder. In both sets of hydrogensulfate ions, the hydrogen atoms were not observed, but their presence is clearly indicated by the variation in the S—O bond lengths. The hydrogen atoms are strongly bound to O(2) and O(7) as the S—O(2 or 7) bond is significantly longer than any other S—O bonds.

Table 1. Fractional coordinates ( $\times 10^4$ , for Pt and I  $\times 10^5$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for  $[\text{Pt}(\text{NH}_3)_4][\text{PtI}_2(\text{NH}_3)_4](\text{HSO}_4)_4 \cdot 2\text{H}_2\text{O}$

$$B_{\text{eq}} = \frac{4}{3} \sum_i \beta_i a_i^2$$

|       | x         | y         | z         | $B_{\text{eq}}$ |
|-------|-----------|-----------|-----------|-----------------|
| Pt(1) | 0         | 0         | 0         | 1.5             |
| Pt(2) | 0         | 0         | 50000     | 1.6             |
| I     | 857 (5)   | 0         | 23524 (7) | 2.3             |
| N(1)  | 971 (4)   | 1941 (9)  | 878 (6)   | 2.3             |
| N(2)  | 0         | 2713 (14) | 5000      | 5.8             |
| N(3)  | 1373 (7)  | 0         | 6482 (11) | 5.4             |
| S(1)  | 3231 (2)  | 0         | 1185 (3)  | 2.8             |
| S(2)  | 2961 (2)  | 0         | 4565 (3)  | 2.9             |
| O(1)  | 3480 (6)  | 0         | 234 (9)   | 3.8             |
| O(2)* | 3053 (11) | 1919 (18) | 1446 (14) | 4.5             |
| O(3)* | 3836 (10) | 725 (22)  | 2472 (13) | 5.7             |
| O(4)* | 2333 (9)  | 784 (26)  | 424 (15)  | 7.0             |
| O(5)  | 3906 (6)  | 0         | 5527 (9)  | 5.4             |
| O(6)  | 2607 (5)  | 1573 (11) | 3708 (8)  | 5.6             |
| O(7)  | 2596 (7)  | 0         | 5450 (10) | 6.5             |
| Ow    | 5355 (5)  | 0         | 1605 (8)  | 3.0             |

\* Occupancy factor = 0.5

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with their estimated standard deviations (in parentheses)

|            |            |                  |            |
|------------|------------|------------------|------------|
| Pt(1)—I    | 2.699 (1)  | I—Pt(1)—N(1)     | 88.8 (2)   |
| Pt(1)—N(1) | 2.070 (6)  | N(1)—Pt(1)—N(1)* | 90.4 (3)   |
| Pt(2)—N(2) | 2.052 (11) | N(2)—Pt(2)—N(3)  | 90.0       |
| Pt(2)—N(3) | 2.076 (10) | O(1)—S(1)—O(2)   | 111.0 (8)  |
| S(1)—O(1)  | 1.450 (14) | O(1)—S(1)—O(3)   | 116.0 (10) |
| S(1)—O(2)  | 1.561 (15) | O(1)—S(1)—O(4)   | 106.9 (8)  |
| S(1)—O(3)  | 1.366 (13) | O(2)—S(1)—O(3)*  | 106.4 (9)  |
| S(1)—O(4)  | 1.475 (16) | O(2)—S(1)—O(4)*  | 101.4 (10) |
| S(2)—O(5)  | 1.423 (9)  | O(3)—S(1)—O(4)   | 114.2 (11) |
| S(2)—O(6)  | 1.446 (8)  | O(5)—S(2)—O(6)   | 113.4 (4)  |
| S(2)—O(7)  | 1.550 (16) | O(5)—S(2)—O(7)   | 106.6 (6)  |
|            |            | O(6)—S(2)—O(7)   | 106.1 (5)  |
|            |            | O(6)—S(2)—O(6)*  | 110.7 (5)  |

\* Key to symmetry operation:  $x, -y, z$ .

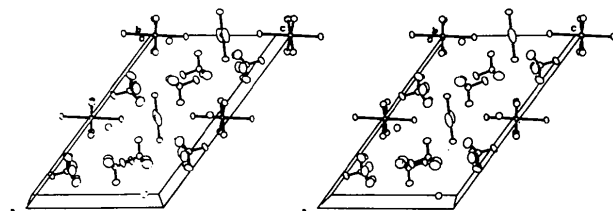


Fig. 1. Stereoscopic drawing of the crystal along the  $b$  axis.

Hydrogen-bond distances are listed in Table 3. Hydrogen-bond schemes are shown in Fig. 2. There is no hydrogen bond between the counter ions, contrary to the case of the Br-bridged analogue (Tanaka, Tsujikawa, Toriumi & Ito, 1982). Water of crystallization, which does not exist in the case of the Cl- and Br-bridged analogues, is hydrogen-bonded with N(1) and the O atoms of the hydrogensulfate ion. Bridging I atoms are not involved in any hydrogen bonding.

The  $\text{Pt}^{\text{IV}}-\text{N}$  and  $\text{Pt}^{\text{II}}-\text{N}$  bond lengths are almost equal within the limits of experimental error. These distances are comparable with the distances of 2.06  $\text{\AA}$  for Magnus green salt  $[\text{Pt}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{IV}}\text{Cl}_4]$  (Atoji, Richardson & Rundle, 1957) and 2.03  $\text{\AA}$  for  $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$  (Bakii & Porai-Koshits, 1949).

Table 3. Hydrogen-bond distances ( $\text{\AA}$ ) with their estimated standard deviations

|     |                           | Key to symmetry operations |  |
|-----|---------------------------|----------------------------|--|
| (a) | N(1)...O(1) <sup>v</sup>  | 3.119 (12)                 | (i) $x, y, z$                                  |
| (b) | N(1)...O(4) <sup>i</sup>  | 3.015 (22)                 | (ii) $x, -y, z$                                |
| (c) | N(1)...O(6) <sup>j</sup>  | 2.922 (8)                  | (iii) $1-x, -y, 1-z$                           |
| (d) | N(1)...Ow <sup>iv</sup>   | 2.929 (11)                 | (iv) $-\frac{1}{2} + x, \frac{1}{2} + y, z$    |
| (e) | N(2)...O(3) <sup>vi</sup> | 2.721 (13)                 | (v) $\frac{1}{2} - x, \frac{1}{2} - y, -z$     |
| (f) | N(2)...O(5) <sup>vi</sup> | 3.004 (13)                 | (vi) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ |
| (g) | N(3)...O(2) <sup>vi</sup> | 3.083 (16)                 |  |
| (h) | N(3)...O(7) <sup>j</sup>  | 3.159 (22)                 |  |
| (i) | Ow...O(1) <sup>ii</sup>   | 2.849 (13)                 |  |
| (j) | Ow...O(5) <sup>iii</sup>  | 2.818 (14)                 |  |

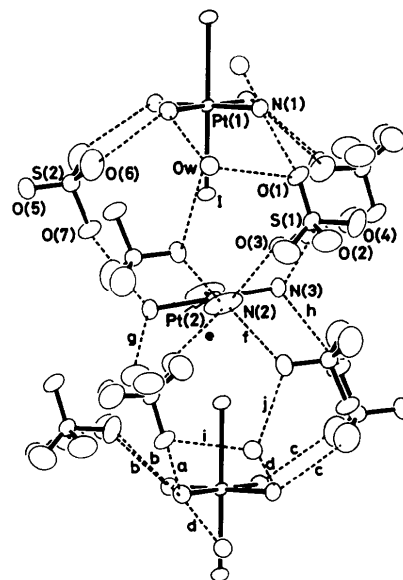


Fig. 2. A perspective drawing of the I— $\text{Pt}^{\text{IV}}$ —I... $\text{Pt}^{\text{II}}$ ... chain. Hydrogen bonds are indicated by the dashed lines. Lower-case letters indicate the hydrogen bonds designated in Table 3. The thermal ellipsoids are drawn at the 50% probability level.

In Wolfram's red salt analogues, the distances between Pt and bridging halogen atoms are very interesting quantities which determine various physical properties. The oxidation state of the Pt atoms is only identified by the position of the bridging halogen atom  $X$ , *i.e.*  $X$  is located closer to the tetravalent Pt atom. In Fig. 3, relevant interatomic distances are plotted against the ratio of the Pt<sup>IV</sup>- $X$  and Pt<sup>II</sup>... $X$  distances for a series of analogous complexes involving different amine ligands and counter ions. In this figure,  $d(\text{Pt}^{\text{II}}\dots X)$ , for example, stands for the Pt<sup>II</sup>... $X$  distance. Both  $d(\text{Pt}^{\text{II}}\dots X)$  and  $d(\text{Pt}^{\text{IV}}\dots\text{Pt}^{\text{II}})$  containing the same  $X$  decrease roughly linearly with increase in  $d(\text{Pt}^{\text{IV}}-X)/d(\text{Pt}^{\text{II}}\dots X)$ , while  $d(\text{Pt}^{\text{IV}}-X)$  increases with the ratio. It is to be noted here that  $d(\text{Pt}^{\text{II}}\dots X)-d(\text{Pt}^{\text{IV}}-X)$  changes almost linearly with increase in the ratio  $d(\text{Pt}^{\text{IV}}-X)/d(\text{Pt}^{\text{II}}\dots X)$  irrespective of the kind of  $X$ . Such a linear relationship is considered to reflect the valency state of the Pt atoms. As seen from Fig. 3, the trend towards the trivalent Pt increases in the sequence: Cl < Br < I. The effect of the coordinating amine ligand is not explained definitely.

In the present compound, the ratio  $d(\text{Pt}^{\text{IV}}-I)/d(\text{Pt}^{\text{II}}\dots I)$  is smaller than that for any other I-bridged analogues: the oxidation state of the Pt atoms is closer to the state of the divalent and tetravalent limit. This is also the case with the Br-bridged analogue with NH<sub>3</sub> as the amine ligand, and results from the introduction of the simplest amine (NH<sub>3</sub>) as ligand. It may be owing to the weak ligand field of NH<sub>3</sub> which allows the bridging halide ion to come into closer contact with Pt<sup>IV</sup>, and to the difference in forming hydrogen bonding with the counter ions.

Concerning the ordering among one-dimensional chains, other I-bridged analogues have no correlation or a short-range order among chains. On the other hand our complex has three-dimensional ordering.

There are several hydrogen bonds among N atoms of the amine ligand and O atoms of the counter ion and water of crystallization. Each hydrogensulfate ion is bound to N atoms of ammine ligands of both Pt(1) and Pt(2), not only within a chain but also in neighbouring chains. Each ammine ligand is bound to O atoms of two different hydrogensulfate ions. Water of crystallization is bound to N(1) and O atoms of two different hydrogensulfate ions. Thus a three-dimensional network of hydrogen bonding is formed. The hydrogen bonding plays a very important role not only in connecting the units of Pt<sup>II</sup> and Pt<sup>IV</sup> in each chain but also in constructing three-dimensional ordering. Furthermore, N(2) has strong hydrogen bonding, N(2)-O(3) 2.72 Å. Large librational motions of N(2) and N(3) around the chain axis are strongly correlated to the disorder in the hydrogensulfate ion through this strong hydrogen bonding.

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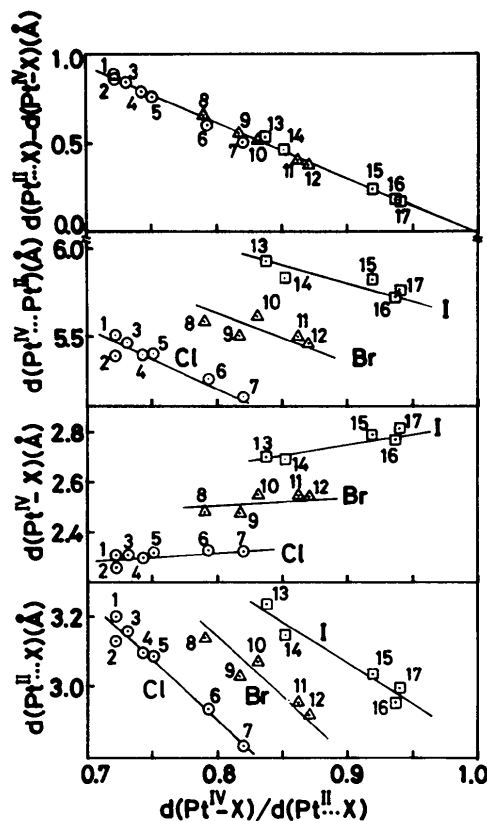


Fig. 3. Plots of the distances between Pt and halogen atoms [ $d(\text{Pt}^{\text{II}}\dots X)$  and  $d(\text{Pt}^{\text{IV}}-X)$ ], and between the Pt<sup>II</sup> and Pt<sup>IV</sup> atoms [ $d(\text{Pt}^{\text{IV}}\dots\text{Pt}^{\text{II}})$ ], and the difference between  $d(\text{Pt}^{\text{II}}\dots X)$  and  $d(\text{Pt}^{\text{IV}}-X)$  as a function of the ratio  $d(\text{Pt}^{\text{IV}}-X)/d(\text{Pt}^{\text{II}}\dots X)$ . Circles, triangles and squares correspond to the values for Cl-, Br- and I-bridged analogues, respectively. Lines are guides to the eye. The numbers identify the complexes, as below. The complex  $[\text{Pt}_2\text{A}_2][\text{PtX}_2\text{A}_2]Y_4$  is abbreviated as  $[A, X, Y]$ , where  $Y$  includes water of crystallization, if any. 1,  $[(\text{C}_2\text{H}_5\text{NH}_2)_2, \text{Cl}, \text{Cl}\cdot\text{H}_2\text{O}]$  (Craven & Hall, 1961); 2,  $[\text{pn}, \text{Cl}, \text{ClO}_4]$  (Matsumoto, Yamashita, Ueda & Kida, 1978); 3,  $[(\text{NH}_3)_2, \text{Cl}, \text{HSO}_4]$  (Fanwick & Huckaby, 1982); 4,  $[\text{tn}, \text{Cl}, \text{BF}_4]$  (Matsumoto, Yamashita & Kida, 1978); 5,  $[\text{en}, \text{Cl}, \text{ClO}_4]$  (Matsumoto, Yamashita, Ueda & Kida, 1978); 6,  $[\text{en}, \text{Cl}, \frac{1}{2}(\text{CuCl}_4)]$  (Endres, Keller, Martin & Traeger, 1979); 7,  $[\text{chn}, \text{Cl}, \text{Cl}]$  (Larsen & Toftlund, 1977); 8,  $[(\text{C}_2\text{H}_5\text{NH}_2)_2, \text{Br}, \text{Br}\cdot\text{H}_2\text{O}]$  (Brown & Hall, 1976); 9,  $[(\text{NH}_3)_2, \text{Br}, \text{HSO}_4]$  (Tanaka, Tsujikawa, Toriumi & Ito, 1982); 10,  $[\text{pn}, \text{Br}, \frac{1}{2}(\text{Cu}_3\text{Br}_3)]$  (Keller, Martin & Traeger, 1978); 11,  $[\text{tn}, \text{Br}, \text{ClO}_4]$  (Matsumoto, Yamashita & Kida, 1978); 12,  $[\text{tn}, \text{Br}, \text{BF}_4]$  (Matsumoto, Yamashita & Kida, 1978); 13, this work; 14,  $[(\text{NH}_3)_2, \text{I}, \frac{1}{2}(\text{HSO}_4)\frac{1}{2}(\text{OH})\frac{1}{2}(\text{H}_2\text{O})]$  (Clark, Kurmoo, Galas & Hursthouse, 1982); 15,  $[\text{en}, \text{I}, \text{ClO}_4]$  (Endres, Keller, Martin, Gung & Traeger, 1979); 16,  $[\text{pn}, \text{I}, \text{ClO}_4]$  (Breer, Endres, Keller & Martin, 1978); 17,  $[\text{pn}, \text{I}, \text{I}]$  (Endres, Keller, Martin, Traeger & Novotny, 1980).

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### Structure de l'Oxysulfure d'Uranium et d'Erbium (UO)<sub>2</sub>ErS<sub>3</sub>

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**Abstract.** Erbium diuranium dioxide trisulfide, (UO)<sub>2</sub>ErS<sub>3</sub>,  $M_r = 771.5$ , tetragonal,  $I4/mmm$ ,  $a = 3.785$  (2),  $c = 20.83$  (1) Å,  $V = 298.4$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_m$ (293 K) = 8.4 (1),  $D_x = 8.585$  Mg m<sup>-3</sup>,  $\lambda$ (Mo K $\alpha$ ) = 0.71069 Å,  $\mu = 83.26$  mm<sup>-1</sup>,  $F(000) = 632$ ,  $T = 293$  K,  $R = 0.037$  for 247 unique non-zero reflections. The U atoms are in (UO) sheets, and the Er atoms in (ErS<sub>3</sub>) sheets, alternately. The apparent oxidation state of U is 3.5, and there is only one series of positions for this element. However, it is presently impossible to choose between mixed valencies or intermediate valency to represent the electronic state of U.

**Introduction.** Au cours de l'étude des combinaisons oxysulfurées formées par les lanthanoïdes et un second métal, qui a conduit à l'isolement de nombreuses combinaisons quaternaires, nous avons préparé une série de phases nouvelles formées par combinaison de l'oxysulfure d'uranium UOS et d'un monosulfure de lanthanoïde RS ( $R = \text{Er à Lu}$ ). La combinaison est réalisée sous atmosphère d'argon, à température voisine

de 1770 K, et achevée par une rapide fusion vers 2070 K, suivie d'une trempe. Des monocristaux ont été isolés dans tous les composés préparés qui s'avèrent posséder la même structure cristalline. L'étude de la structure a été réalisée sur le dérivé de l'erbium et a établi la composition (UO)<sub>2</sub>ErS<sub>3</sub>.

**Partie expérimentale.** Cristal utilisé: parallélépipède noir, dimensions 51 × 34 × 10 μm. Masse volumique mesurée par pycnométrie. Quinze réflexions indépendantes utilisées pour affiner les paramètres de la maille (6,12 <  $\theta$  < 12,46°). 247 réflexions indépendantes non nulles enregistrées à 293 K à l'aide d'un diffractomètre automatique à quatre cercles Syntex P2<sub>1</sub>;  $\sin\theta/\lambda < 0,806$  Å<sup>-1</sup>.  $5 \geq h \geq 0$ ,  $4 \geq k \geq 0$ ,  $32 \geq l \geq 0$ ; balayage  $\omega - 2\theta$ ,  $2\theta$  variant de  $2\theta_1 - 0,7$  à  $2\theta_2 + 0,7^\circ$ ,  $\theta_1$  et  $\theta_2$  angles de diffraction correspondant aux longueurs d'onde  $K\alpha_1$  et  $K\alpha_2$  du molybdène. Réflexions de contrôle: 110 et  $1\bar{1}0$  vérifiées toutes les cinquante mesures, valeur de l'écart-type relatif sur l'instabilité  $\sigma_i = 0,03$ . Corrections d'absorption réalisées par le programme de J. A. Ibers,