Acta Cryst. (1985). C**41**, 304–306

Tripotassium *cis*-Dichloro(hydrogenbissulfito)palladate(II), $K_3[Pd\{(SO_3)_2H\}Cl_2]$

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(*Received* 25 *June* 1984; *accepted* 23 *October* 1984)

Abstract. $M_r = 455{\cdot}7$, orthorhombic, $Cmc2_1$, $a = 15{\cdot}083$ (3), $b = 10{\cdot}391$ (4), $c = 7{\cdot}002$ (4) Å, $V = 1097{\cdot}4$ (8) Å^3, $Z = 4$, $D_m = 2{\cdot}69$, $D_x = 2{\cdot}757$ Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}55830$ Å, $\mu = 1{\cdot}718$ mm^{-1}, $F(000) = 868$, $T = 298$ K, $R = 0{\cdot}024$, $R_w = 0{\cdot}026$ for 1341 unique reflections. The structure, solved by the heavy-atom method, is the same as for the analogous Pt compound. Again, short Pd—S [2·254 (1) Å] and long Pd—Cl bonds [2·384 (1) Å] in the complex anion are caused by the *trans* influence of the two sulfite ligands in *cis* position. A very short, symmetric and almost linear hydrogen bond O···H···O [2·396 (4) Å] closes a six-membered chelate ring. The two types of connecting K^+ ions exhibit trigonal-prismatic (four Cl and two O atoms) and irregular eight-coordination, respectively. The bromine compound $K_3[Pd\{(SO_3)_2H\}Br_2]$, $M_r = 544{\cdot}6$, is found to be isotypic, $a = 15{\cdot}29$ (3), $b = 10{\cdot}51$ (2), $c = 7{\cdot}13$ (2) Å, $V = 1146$ (4) Å^3, from 20 standardized powder reflections.

Introduction. Continuing structural investigations of sulfite complexes of platinum metals (Breitinger, Petrikowski & Bauer, 1982, and references therein; Petrikowski & Breitinger, 1985), our recent attention is focused onto appropriate palladium compounds. Vibrational spectra of $K_3[Pd\{(SO_3)_2H\}Cl_2]$ (1) (Raidel, 1985) suggested similar structural features as in the analogous platinum complex $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (2), *viz* a strong *trans* influence of the sulfite ligands and a very short intramolecular hydrogen bond (Kehr, Breitinger & Bauer, 1980). In order to corroborate these suggestions, the X-ray structure analysis of the title compound was performed.

Experimental. 300 mg (0·755 mmol) K_2PdCl_6 and 52 mg (0·38 mmol) K_2CO_3 were dissolved in 10 ml H_2O by passing through SO_2, cooling with ice. After lightening to pale yellow the solution was mixed with acetone (*ca* 50 ml) for precipitation of the compound (1) (analytical data deposited). Yellow needle-shaped single crystals were grown from an aqueous solution, carefully covered with a layer of acetone, at *ca* 278 K.

Under the same conditions reaction of 300 mg (1·17 mmol) $PdBr_2$ and 78 mg (0·56 mmol) K_2CO_3 in 10 ml H_2O with SO_2 yielded a yellow solution, from which yellow $K_3[Pd\{(SO_3)_2H\}Br_2]$ (3) was precipitated with 30 ml acetone (analytical data deposited).

D_m by flotation in benzene–bromoform mixture. Guinier photographs indicate isomorphism of (1) and (2). Crystal of (1) 0·12 × 0·15 × 0·27 mm; Philips PW 1100 four-circle diffractometer, graphite-monochromated Ag $K\alpha$ radiation; lattice parameters by least-squares refinement of 25 reflections ($2\theta \approx 25°$); intensity data ($-19 \le h \le 19$, $-13 \le k \le 13$, $-7 \le l \le 7$) recorded in ω-scan mode for $3° \le \theta \le 18°$ [$(\sin\theta/\lambda)_{max} = 0{\cdot}55$ Å^{-1}]; three standard reflections (602, 60$\bar{2}$, $\bar{6}0\bar{2}$) measured every 60 min with no significant variations; Lp corrections; 4274 intensity data with $I \ge \sigma(I)$ measured and used for merging to 1341 independent reflections with $R_{int} = 0{\cdot}03$ as defined in *SHELX*76 (Sheldrick, 1976); ψ scans with minor variations of intensities, therefore no correction for absorption; scattering factors from *International Tables for X-ray Crystallography* (1974).

After checking the positions of the heavy atoms in a three-dimensional Patterson map, starting positional parameters for non-hydrogen atoms were taken from the isostructural Pt compound (2). Anisotropic full-matrix least-squares refinement on F; H atoms from difference Fourier synthesis; final refinement of 73 parameters (H atom isotropic) gave $R = 0{\cdot}024$, $R_w = 0{\cdot}026$; weighting scheme $w = 2{\cdot}3165/[\sigma^2(F_o) + 0{\cdot}000193 F_o^2]$; max. $\Delta/\sigma = 0{\cdot}664$ for U_{22} of O(1); no maxima higher than for H in final difference map.

Table 1. *Fractional coordinates* (×10^4) *and equivalent values* U_{eq} (Å^2 × 10^4) *of the anisotropic temperature factors* U_{ij}, *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Pd	0	2492·4 (3)	2500	165 (2)
Cl	1112 (1)	1205 (1)	3984 (2)	257 (4)
S	1089 (1)	3527 (1)	917 (2)	188 (4)
O(1)	1897 (2)	3725 (2)	2038 (4)	246 (10)
O(2)	1276 (2)	2739 (3)	−772 (5)	337 (10)
O(3)	794 (2)	4859 (3)	264 (4)	341 (10)
H	0	4836 (13)	239 (13)	498 (14)*
K(1)	2228 (1)	3595 (1)	5955 (2)	288 (4)
K(2)	0	1214 (1)	7732 (2)	285 (5)

* Isotropic.

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0108-2701/85/030304-03$01.50

Calculations performed with the *SHELX76* system (Sheldrick, 1976).

Lattice parameters of (3) by least-squares refinement from 20 reflections of a Guinier photograph [$\lambda(Cu\,K\alpha) = 1{\cdot}5418$ Å] with $Pb(NO_3)_2$ as external standard.

Discussion. Positional parameters and U_{eq} values are given in Table 1.* A view of the structure down the *c* axis is shown in Fig. 1, an isolated $[Pd\{(SO_3)_2H\}Cl_2]^{3-}$ anion in Fig. 2.

The overall arrangement of the lattice constituents is basically the same in the Pd (1) and Pt (2) compounds (*cf.* Kehr *et al.,* 1980), with minor differences in interatomic distances and angles. The same is true for the internal structures of the complex anions. Thus, the Pd atom in (1) deviates slightly [0·114 (2) Å] from the plane through the coordinated S and Cl atoms (equation of the plane deposited). The Pd—S bonds (Fig. 2), not significantly different from the Pt—S bonds in (2) [2·247 (2) Å], range near the lower limit of known Pd—S bonds in sulfite complexes (Messer, Breitinger & Haegler, 1979, 1981; Kehr *et al.,* 1980; and references in these papers). In contrast, the Pd—Cl bond lengths [the Pt—Cl length of 2·388 (2) Å in (2) is the same within experimental error, as expected, *cf.* Mais, Owston & Wood (1972)] tend to the upper limit of the range of a large body of Pd—Cl bonds (for recent examples see Ferguson, McCrindle & Parvez, 1983; Kitano, Kinoshita, Nakamura & Ashida, 1983; Steel, 1983; Keijsper, van der Poel, Polm, van Koten, Vrieze, Seignette, Varenhorst & Stam, 1983; and references in these papers). Once more, the strong *trans* influence of the sulfite ligands is evident.

The geometries of the sulfito ligands are quite similar to those in (2), and also to the averaged geometries of the different SO_3 groups in $K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (4) (Breitinger *et al.,* 1982). Thus, the averaged terminal S—O bond lengths [1·464 (4) in (1), 1·465 (6) in (2), and 1·464 (6) Å in (4)] are the same within experimental error. Also the long S—O(3) bonds, tending to S—O single bonds, are comparable in these three compounds; the lengthening of these S—O(3) bonds is again due to the involvement of the O(3) atoms in the strong hydrogen bond. This symmetry-restricted almost linear hydrogen bond [distance $O(3)\cdots H\cdots O(3^i)$ 2·396 (4) Å] adds a further example to the group of very short O···H···O bridge systems. A recent survey of such systems studied by neutron diffraction is given by Joswig, Fuess & Ferraris (1982). The present hydrogen bridge seems to be longer than in the above compounds (2) and (4) [2·382 (6) and 2·380 (8) Å, respectively]; however, on the basis of the given standard deviations the differences cannot be considered as significant. In the structural model under discussion here the proton is placed on a special position on a mirror plane, implying a symmetric single-minimum potential for the hydrogen bridge. However, on the basis of X-ray data alone, a statistical distribution of the proton in two symmetry-related positions (double-minimum potential) cannot be ruled out.

The potassium ions K(2) are surrounded by two symmetry-related pairs of Cl atoms and one pair of O atoms O(2) to form a distorted trigonal prism, whereas the ions K(1) are irregularly coordinated by six O and two Cl atoms (Table 2). The function of the K^+ ions in the structure has already been discussed for (2) by Kehr *et al.* (1980), as well as the overall structural arrangement.

* Lists of structure factors, anisotropic thermal parameters, distances and angles in the environments of the K^+ ions, the equation of the plane through the ligands of the anion, and analytical data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39856 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

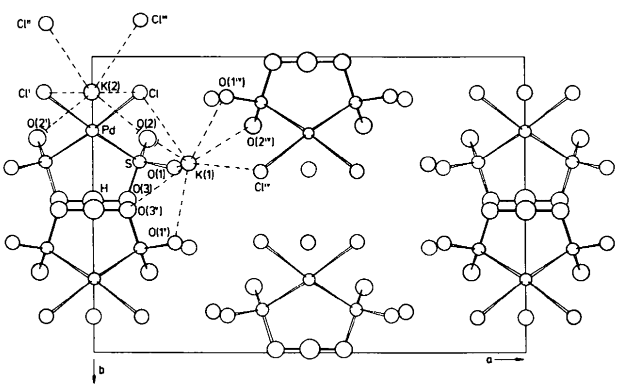

Fig. 1. Projection of the structure of $K_3[Pd\{(SO_3)_2H\}Cl_2]$ onto the (001) plane; K^+ cations and anions drawn in heavy lines and those in light lines differ in height by *c*/2. Balls correspond to the U_{eq} values at the 50% probability level.

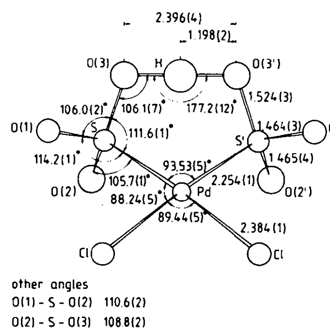

Fig. 2. The $[Pd\{(SO_3)_2H\}Cl_2]^{3-}$ anion. (Distances in Å, angles in degrees.)

Table 2. *Interatomic distances (Å) in the environments of the potassium ions* K(1) *and* K(2), *with e.s.d.'s in parentheses (a complete table of distances and angles has been deposited)*

K(1)—O(3^{v})	2·737 (3)	K(1)—O(2^{iv})	2·912 (3)
K(1)—O(1)	2·791 (3)	K(1)—O(1^{v})	2·929 (2)
K(1)—O(2^{vi})	2·847 (4)	K(1)—Cl^{iv}	3·288 (2)
K(1)—O(1^{iv})	2·852 (3)	K(1)—Cl	3·301 (2)
K(2)—O(2^{vi})	2·704 (3)	K(2)—Cl	3·114 (2)
		K(2)—Cl^{iii}	3·147 (2)

Symmetry code: (i) $-x, y, z$; (ii) $-x, -y, \frac{1}{2}+z$; (iii) $x, -y, \frac{1}{2}+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x, 1-y, z+\frac{1}{2}$; (vi) $x, y, 1+z$.

The structural differences of the bromine compounds $K_3[Pd\{(SO_3)_2H\}Br_2]$ (3) and $K_3[Pt\{(SO_3)_2H\}Br_2].H_2O$ (4) may be due to the different conditions of preparation. This point will be studied further, since corresponding Pd and Pt compounds are usually found to be isotypic, with few exceptions.

The authors thank Professor Klaus Brodersen for laboratory facilities, the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie – Fonds der Chemischen Industrie – for financial support.

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Acta Cryst. (1985). C**41**, 306–307

Structure of $Pb_{0.15}Nb_3S_4$

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(*Received* 10 *June* 1984; *accepted* 19 *November* 1984)

Abstract. $M_r = 439·80$, hexagonal, $P6_3$, $a = 9·626$ (4), $c = 3·390$ (2) Å, $V = 272·0$ (4) Å^3, $Z = 2$, $D_x = 5·37$ (3) Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 11·9$ mm^{-1}, $F(000) = 398·34$, room temperature, final $R = 0·043$ for 635 independent reflections. Pb partially occupies the large channel parallel to **c** in the Nb_3S_4 host lattice, with no long-range order of the Pb atoms. The S atoms form flat trigonal antiprisms around Pb with the Pb atom moved away from the centre, which gives three long and three short Pb—S distances. [Pb—S(1) is 3·156 (18) and 3·227 (18) Å.]

Introduction. In the course of our investigations of metal clusters we have become interested in substances that have two properties: (1) short metal bonds, which cause metallic behaviour, and (2) channels that are empty or filled. Examples of compounds with empty channels are Nb_3X_4 (X = S, Se, Te) with the Nb_3Te_4 structure (Selte & Kjekshus, 1964) where partial exchange of S by Se is possible, which leads to vanishing of the superconducting properties (Amberger, Polborn, Grimm, Dietrich & Obst, 1978). $Tl_xV_6S_8$ (Vlasse & Fournès, 1976) is an example with a filled channel. Exchange of V by Nb or Ti is possible in the case of $Tl_xV_6Se_8$ (Boller & Klepp, 1983). Nb_3S_4 needles, pressed to an electrode and electrolysed in a metal-ion (Li^+, Na^+, K^+ or Ca^{2+}) containing electrolyte show an uptake of metal, corresponding to the formula $M_xNb_3S_4$. The index x increases with decreasing Nb_3S_4 needle cross section ($Na_xNb_3S_4$: $1·56 \times 10^{-2}$ to $1·6 \times 10^{-4}$ mm^2 corresponds to $0·15 \le x \le 0·25$). So Schöllhorn & Schramm (1979) assumed a partial uptake of sodium into the channels. On the other hand, a single crystal of Nb_3S_4 as electrode does not take up

0108-2701/85/030306-02$01.50