

the methyl group. In two related structures,  $(\mu_3\text{-CH})\text{Co}_2\text{Mo}(\text{CO})_6\text{Cp}(\mu\text{-dppm})$  (Duffy, Kassis & Rae, unpublished) and  $(\mu_3\text{-CH})\text{Co}_2\text{Mn}(\text{CO})_8(\mu\text{-dppm})$  (Duffy, Kassis & Rae, 1990), the upper two phenyl groups are even further inclined toward the apical substituent atom. This indicates a reasonable degree of flexibility in the dppm ligand with the final orientation being controlled by both inter and intramolecular interactions.

The phenyl rings disposed below the metal triangle also display a reasonable degree of flexibility as indicated in (1) by the appearance of disorder in them. The flexibility of the dppm unit and its ability to accommodate steric strain by adopting various configurations is manifest in the position that the methylene C atom adopts in these types of structures. In (1) and the methyl analogue the methylene C atom is in the 'up position'; the unit defined by the carbyne C atom, the two bridged metals and the P—C—P dppm backbone is in a boat configuration. In the two heterometal clusters,  $(\mu_3\text{-CH})\text{Co}_2\text{Mo}(\text{CO})_7\text{Cp}(\mu\text{-dppm})$  (Duffy *et al.*, unpublished) and  $(\mu_3\text{-CH})\text{Co}_2\text{Mn}(\text{CO})_8(\mu\text{-dppm})$  (Duffy *et al.*, 1990), the methylene C atom is in the 'down position', *i.e.* the chair configuration is adopted by the carbyne C atom, the two bridged metals and the P—C—P dppm backbone.

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## Structures of Chlorohydroxobis(pentamethylcyclopentadienyl)tantalum(V) Trifluoromethanesulfonate (Triflate) and Dihydroxobis(pentamethylcyclopentadienyl)tantalum(V) Triflate

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**Abstract.**  $[\text{Ta}(\text{C}_{10}\text{H}_{15})_2(\text{Cl})(\text{OH})][\text{CF}_3\text{SO}_3]$  (I),  $M_r = 652.94$ , monoclinic,  $P2_1/n$ ,  $a = 9.965$  (7),  $b = 18.796$  (5),  $c = 13.269$  (3) Å,  $\beta = 94.02$  (3)°,  $V = 2479.2$  (19) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.75$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 46$  cm<sup>-1</sup>,  $F(000) = 1288$ , room temperature,  $R = 0.107$  for 3702 reflections with  $F_o^2 > 0$  [ $R = 0.053$  for 2094 reflections with  $F_o^2 > 3\sigma(F_o^2)$ ].  $[\text{Ta}(\text{C}_{10}\text{H}_{15})_2(\text{OH})_2][\text{CF}_3\text{SO}_3]$  (II),  $M_r = 634.49$ , triclinic,  $P\bar{1}$ ,  $a = 10.052$  (2),  $b = 10.111$  (2),  $c = 12.739$  (2) Å,  $\alpha = 71.38$  (2),  $\beta = 78.21$  (1),  $\gamma =$

$77.40$  (2)°,  $V = 1184.7$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.78$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 47$  cm<sup>-1</sup>,  $F(000) = 628$ , room temperature,  $R = 0.032$  for 4046 reflections with  $F_o^2 > 0$  [ $R = 0.026$  for 3664 reflections with  $F_o^2 > 3\sigma(F_o^2)$ ]. Severe disorder of the triflate anion in (I) led to a less satisfactory structure, but cations in both compounds are well defined, with normal Ta—Cp\* geometry. Ta—Cl 2.343 (4), Ta—O 1.853 (8) Å and Cl—Ta—O 96.4 (3)° in (I); Ta—O 1.907 (6) Å and O—Ta—O 100.4 (2)° in (II). Tantalum-bound OH groups are hydrogen bonded to triflate O atoms.

† Contribution No. 8234.

**Introduction.** Transition-metal complexes with reactive oxo or imido ligands (Nugent & Mayer, 1988) are of increasing interest due to their possible role in activation of hydrocarbons. Early transition-metal bent-sandwich complexes of the type  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}=\text{NR}]$  (Walsh, Hollander & Bergman, 1988),  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}=\text{O}]$  (Carney, Walsh, Hollander & Bergman, 1989),  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{W}=\text{O}]$  (Parkin & Bergaw, 1988, 1989) and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}=\text{O}]$  (Jernakoff, Geoffroy, Rheingold & Geib, 1987; Plato, Housmekerides, Jernakoff, Rubin, Geoffroy & Rheingold, 1990) have been shown to undergo 2 + 2 reactions with unsaturated substrates such as acetylenes and isocyanates or 1,2-addition of Si—Cl, Si—H, H—H and in the case of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}=\text{NR}]$ , even the C—H bonds of benzene.

We have been investigating possible synthetic routes to  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ta}=\text{O}]^+$ , an early transition-metal oxo cation which we anticipate will be even more reactive than the neutral, isoelectronic complex  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}=\text{O}]$ . Initial attempts to prepare this cation were by reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ta}(=\text{O})\text{Cl}]$  with silver trifluoromethanesulfonate. Crystals of two different triflate salts, neither of which was the desired product, were isolated from these reaction mixtures:  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ta}(\text{OH})\text{Cl}]^+ \cdot [\text{SO}_3\text{CF}_3]^-$  (I) and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ta}(\text{OH})_2]^+ \cdot [\text{SO}_3\text{CF}_3]^-$  (II). Herein, we describe the crystal structures for these two compounds.

**Experimental.** (I) thin yellow needle, trapezoidal cross section, 0.11 × 0.10 × 1.15 mm; (II) irregular pale-yellow chunk, 0.15 × 0.44 × 0.34 mm; CAD-4 diffractometer. For (I) 25 reflections with  $12 < 2\theta < 15^\circ$  and for (II) 25 reflections with  $16 < 2\theta < 18^\circ$ , used for cell dimensions;  $\omega$ - $2\theta$  scans. Data corrected for absorption as a function of  $\theta$  based on  $\psi$  scans at  $\chi > 84^\circ$ ; correction factors varied for (I) from 0.76 to 1.18 and for (II) from 0.69 to 1.23.  $(\sin\theta/\lambda)_{\text{max}} = 0.59 \text{ \AA}^{-1}$ ; data collected for (I):  $h = -11$  to  $11$ ,  $k = -18$  to  $22$ ,  $l = 0$  to  $15$  and for (II):  $h = -11$  to  $11$ ,  $k = -12$  to  $12$ ,  $l = -15$  to  $15$ . Standard reflections were (I) 060,  $13\bar{4}$ ,  $1\bar{2}4$  and (II) 420, 141 and  $2\bar{3}1$ ; variation for (I) -6% and for (II) -3%. Total reflections measured were (I) 7108 and (II) 8366; unique reflections were (I) 4308 and (II) 4141; goodness of fit for merging was (I) 1.27 and (II) 1.46;  $R_{\text{int}}$  for merging was (I) 0.036 and (II) 0.021. All reflections used in solution and refinement of the structures; Ta-atom coordinates found from Patterson map, remaining atoms located by successive structure factor-Fourier calculations; refinement on  $F^2$ . H atoms on Cp\* rings located on difference Fourier maps calculated in the expected planes and placed at idealized positions in those planes. H atoms not refined but repositioned once toward the end of refinement. For (I), coordinates and anisotropic dis-

Table 1. Final heavy-atom positional parameters ( $\times 10^4$ ) and  $U_{\text{eq}}$  ( $\text{\AA}^2 \times 10^4$ ) or  $B$  ( $\text{\AA}^2$ ) values for (I)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}/B$
Ta	1823 (4)	1830 (2)	3336 (3)	585 (1)
Cl	1617 (4)	2704 (2)	2076 (3)	1499 (15)
O1	430 (7)	1259 (4)	2810 (6)	1148 (27)
C1	1055 (12)	2903 (6)	4227 (9)	748 (39)
C2	22 (11)	2404 (6)	4178 (8)	622 (31)
C3	487 (11)	1831 (6)	4800 (8)	688 (30)
C4	1841 (10)	1969 (7)	5135 (9)	748 (37)
C5	2171 (11)	2627 (7)	4808 (10)	791 (39)
C6	934 (13)	3643 (7)	3820 (11)	1277 (53)
C7	-1362 (11)	2488 (7)	3662 (9)	985 (42)
C8	-358 (14)	1210 (6)	5077 (10)	1164 (44)
C9	2490 (13)	1596 (7)	6037 (9)	1234 (48)
C10	3422 (12)	3070 (7)	5117 (12)	1554 (57)
C11	3396 (16)	1416 (12)	2123 (11)	1132 (63)
C12	4169 (11)	1786 (8)	2873 (14)	1007 (50)
C13	4150 (10)	1407 (7)	3777 (8)	659 (34)
C14	3299 (12)	809 (6)	3590 (11)	760 (40)
C15	2900 (13)	811 (8)	2538 (14)	927 (49)
C16	3298 (17)	1597 (12)	1011 (11)	2295 (98)
C17	5020 (13)	2436 (9)	2701 (16)	2130 (95)
C18	5167 (11)	1504 (7)	4639 (11)	1280 (51)
C19	3105 (14)	230 (7)	4272 (12)	1387 (55)
C20	2139 (16)	252 (9)	1996 (15)	2241 (84)
Sa	6987 (7)	386 (4)	2304 (6)	4.1 (2)*
O4a	7717 (18)	1027 (10)	2550 (13)	6.8 (4)*
F3a	9063 (22)	-439 (11)	2456 (16)	14.4 (6)*
O2	6130 (11)	-29 (5)	2872 (7)	11.4 (3)*
O3a	6089 (23)	-437 (13)	1262 (18)	11.7 (6)*
O3b	6663 (19)	1011 (10)	1972 (14)	12.0 (5)*
F1	8641 (8)	130 (4)	982 (6)	12.0 (2)*
F2	7706 (9)	-783 (5)	1491 (7)	14.8 (3)*
Sb	7327 (14)	349 (7)	2659 (9)	13.3 (4)*
O4b	8407 (21)	271 (10)	3162 (14)	12.4 (6)*
F3b	6689 (16)	-116 (8)	734 (11)	12.2 (5)*
C21a	8179	-204	1798	10.8*
C21b	7600	-103	1476	10.8*

\* Isotropic displacement parameters  $B$ .

Table 2. Selected distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (I)

Ta—Cl	2.343 (4)	F2—C21a	1.24 (5)
Ta—O1	1.853 (8)	F3a—C21a	1.28 (5)
Ta—Cp*1	2.339 (11)	O2—Sb	1.433 (16)
Ta—Cp*2	2.346 (15)	O3b—Sb	1.65 (2)
Sa—O2	1.412 (12)	O4b—Sb	1.23 (2)
Sa—O3a	1.60 (2)	Sb—C21b	1.82 (5)
Sa—O4a	1.433 (19)	F1—C21b	1.34 (5)
Sa—Sb	0.564 (15)	F2—C21b	1.28 (5)
Sa—C21a	1.79 (5)	F3b—C21b	1.29 (5)
F1—C21a	1.36 (5)	C21a—C21b	0.72 (7)
Cl—Ta—O1	96.4 (3)	C21b—Sb—O2	96.7 (18)
Cp*1—Ta—Cp*2	138.2 (5)	O4b—Sb—O3b	133.4 (15)
O2—Sa—O4a	131.2 (10)	C21b—Sb—O3b	87.4 (18)
O3a—Sa—O4a	113.0 (12)	C21b—Sb—O4b	103.5 (20)
C21a—Sa—O4a	105.5 (18)	F2—C21b—F1	105.5 (36)
O3a—Sa—O2	99.9 (10)	Sb—C21b—F1	115.9 (32)
C21a—Sa—O2	107.5 (17)	F3b—C21b—F1	99.2 (34)
C21a—Sa—O3a	93.3 (18)	Sb—C21b—F2	118.0 (34)
O3b—Sb—O2	100.1 (11)	F3b—C21b—F2	92.6 (34)
O4b—Sb—O2	122.7 (14)	F3b—C21b—Sb	121.8 (35)

placement parameters of heavy atoms in the cation were refined. The triflate anion is disordered. One O atom and two F atoms occupy single positions while two O atoms, one F atom and the S and C atoms occupy two positions. The positional and isotropic thermal parameters of these atoms, except those of the C atom, were refined. Population parameters for the two orientations refined to 0.56 (2) and 1 - 0.56. The carbon positional parameters were taken from difference maps and an isotropic thermal parameter,

Table 3. Final refined positional parameters ( $\times 10^4$ ) and  $U_{eq}$  ( $\text{\AA}^2 \times 10^4$ ) or  $B$  ( $\text{\AA}^2$ ) values for (II)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}/B$
Ta	2898 (2)	1373 (2)	1858 (2)	353 (5)
O1	4105 (5)	-404 (5)	2177 (5)	718 (14)
O2	2509 (5)	1484 (5)	429 (4)	686 (12)
C1	1451 (5)	-444 (5)	3040 (4)	494 (12)
C2	708 (5)	423 (6)	2197 (4)	524 (13)
C3	397 (5)	1801 (6)	2320 (5)	548 (14)
C4	899 (5)	1766 (6)	3266 (5)	549 (13)
C5	1605 (5)	402 (6)	3695 (4)	493 (13)
C6	1961 (7)	-1994 (7)	3238 (5)	749 (18)
C7	253 (7)	1 (8)	1328 (6)	822 (18)
C8	-509 (7)	3019 (8)	1604 (7)	945 (23)
C9	404 (7)	2861 (8)	3906 (6)	902 (20)
C10	2248 (7)	-159 (8)	4756 (5)	831 (20)
C11	4996 (5)	2331 (6)	1008 (5)	526 (13)
C12	4899 (6)	2130 (6)	2152 (5)	618 (15)
C13	3783 (7)	3020 (7)	2493 (5)	643 (15)
C14	3152 (5)	3822 (6)	1559 (6)	588 (15)
C15	3923 (6)	3436 (6)	631 (4)	546 (14)
C16	6105 (8)	1609 (8)	272 (7)	1076 (24)
C17	5937 (9)	1148 (9)	2895 (8)	1243 (29)
C18	3558 (10)	3334 (11)	3602 (6)	1382 (30)
C19	2043 (8)	5129 (8)	1476 (9)	1293 (34)
C20	3734 (10)	4128 (8)	-558 (6)	1119 (26)
S	7677 (2)	-2818 (2)	2727 (1)	596 (4)
O3	6772 (4)	-1963 (4)	1922 (3)	707 (11)
O4	7918 (6)	-2115 (5)	3451 (4)	982 (15)
O5	8825 (5)	-3624 (5)	2255 (5)	1086 (17)
C21	6666 (7)	-4116 (7)	3638 (5)	739 (19)
F1	5498 (5)	-3520 (6)	4089 (4)	1225 (16)
F2	6420 (7)	-4932 (6)	3116 (4)	1522 (20)
F3	7284 (5)	-4958 (4)	4490 (3)	1092 (15)
H1	4715 (52)	-607 (62)	2067 (49)	3.4 (16)*
H2	2853 (83)	1729 (87)	-12 (62)	8.9 (27)*

\* Isotropic displacement parameters  $B$ .

 Table 4. Selected distances ( $\text{\AA}$ ) and ( $^\circ$ ) angles for (II)

Ta—O1	1.911 (5)	S—O5	1.406 (6)
Ta—O2	1.903 (5)	S—C21	1.798 (7)
Ta—Cp*1	2.315 (5)	C21—F1	1.307 (9)
Ta—Cp*2	2.320 (6)	C21—F2	1.300 (9)
O1—H1	0.60 (6)	C21—F3	1.321 (8)
O2—H2	0.60 (8)		
S—O3	1.449 (4)		
S—O4	1.413 (6)		
O2—Ta—O1	100.4 (2)	C21—S—O5	103.8 (3)
Cp*1—Ta—Cp*2	138.4 (2)	F1—C21—S	111.4 (5)
O4—S—O3	114.5 (3)	F2—C21—S	111.8 (5)
O5—S—O3	112.8 (3)	F3—C21—S	112.5 (5)
C21—S—O3	102.9 (3)	F2—C21—F1	109.2 (6)
O5—S—O4	117.2 (3)	F3—C21—F1	105.2 (6)
C21—S—O4	103.5 (3)	F3—C21—F2	106.4 (6)

20% less than the average of the F-atom thermal parameters, was assigned to each partial atom. For (II), positional and anisotropic displacement parameters of all heavy atoms were refined, plus positional and isotropic thermal parameters of the H atoms of the tantalum-bound hydroxo groups. Final values of  $R$ ,  $wR$  and  $S$ : (I) 0.107, 0.009 and 1.61; (II) 0.032, 0.003 and 1.87 ( $R$  on  $F$ ,  $wR$  on  $F^2$ ). Weights taken as  $1/\sigma^2(F_o^2)$ ; variances of the individual reflections assigned based on counting statistics plus an additional term  $(0.014 I)^2$ . Variances of the merged reflections determined by standard propagation of error plus another additional term  $(0.014 I)^2$ . In the final least-squares cycles, the max.  $\Delta/\sigma$  ratio was 0.15 for (I) and (II). In the final difference maps the max.

excursions were for (I) +2.1 and -1.8  $e \text{\AA}^{-3}$  (near Ta) and for (II) +1.5 and -1.1  $e \text{\AA}^{-3}$  (again near Ta). No corrections for extinction were made because the final refinement showed no extinction problems. Scattering factors and corrections for anomalous scattering were taken from Cromer & Waber (1974) and Cromer (1974). Computer programs used were those of *CRYM* (Duchamp, 1964) and *ORTEP* (Johnson, 1976).

The final heavy-atom parameters are listed in Tables 1\* and 3, with selected distances and angles given in Tables 2 and 4; Figs. 1, 2, 3 and 4 show the cations and the overall packing.

\* Lists of structure factors, anisotropic displacement parameters, complete distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54087 (51 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

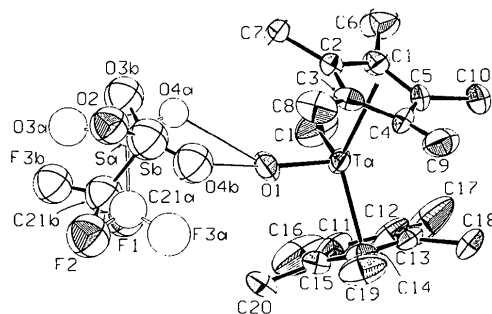


Fig. 1. An *ORTEP* (Johnson, 1976) drawing of (I) showing the numbering system and the two orientations of the disordered triflate and the hydrogen bonding (thin lines). The three atoms common to the two triflate anions are shown with octant shading; atoms of one anion have open bonds, of the other filled-in bonds. Thermal ellipsoids are shown at the 30% probability level; H atoms are not shown.

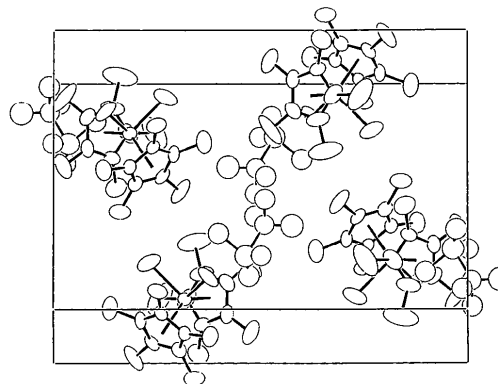


Fig. 2. An *ORTEP* (Johnson, 1976) drawing showing the packing in (I) projected down  $a$ . Only one orientation of the triflate anion is shown. Thermal ellipsoids are shown at the 30% probability level; H atoms are not shown.

**Discussion.** These two similar compounds crystallize in different space groups but the geometry of the cations is quite similar, and it is similar to that of other bis(Cp\*)Ta compounds (van Asselt, Trimmer, Henling & Bercaw, 1988). The Ta—Cp\* geometry is unexceptional. Ta—O distances [(I) 1.853 (8) Å, (II) 1.907 (6) Å] are significantly shorter than the Ta—O (peroxide) distances reported in van Asselt *et al.* (1988) [1.955 (6) and 1.996 (6) Å] and shorter than Ta—O ( $\mu$ -O or  $\mu$ -OH) distances (Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). The bonding about Ta is approximately tetrahedral in both compounds, considering the centroids of the Cp\* rings and the two other ligands, with the Cp\*—Ta—Cp\* angles somewhat greater than 110° and the Cl(or O)—Ta—O angles somewhat smaller.

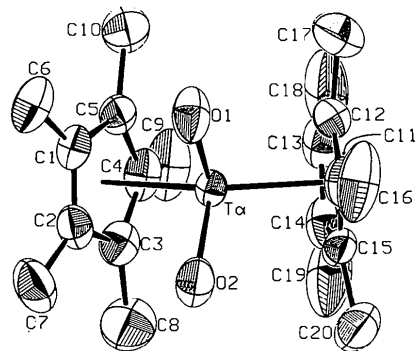


Fig. 3. An ORTEP (Johnson, 1976) drawing of the cation of (II) showing the numbering system. Thermal ellipsoids are shown at the 50% probability level; H atoms are not shown.

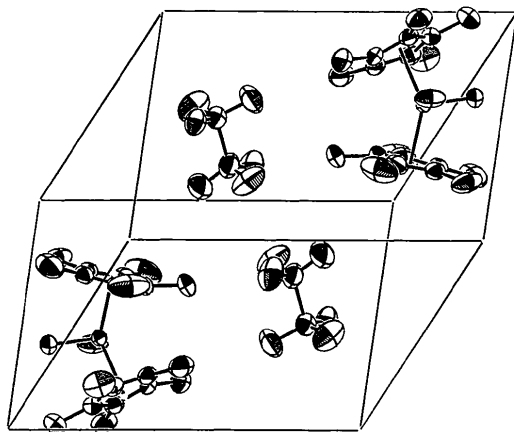


Fig. 4. An ORTEP (Johnson, 1976) drawing showing the packing in (II). The view is perpendicular to the least-squares plane of all the atoms. Thermal ellipsoids are shown at the 50% probability level; H atoms are not shown.

In both compounds, there are hydrogen bonds between the Ta-coordinated hydroxyl groups and triflate O atoms. In (I), the O atom of the Ta-bound hydroxyl group is 2.75 (2) Å from an O atom of the triflate in one of its disordered positions and 2.80 (2) Å from a triflate oxygen in the alternate position. The Ta—O...O angles are 147.8 (6) and 148.0 (6)° for the two possibilities, while the S—O...O angles are 130.0 (12) and 116.0 (14)°. The triflate was modeled as two ions with two F atoms and one O atom in common; the other atoms are independent. One ion had population 0.44, the other 0.56 (taken from an early least squares; the fractions do not differ significantly from  $\frac{1}{2}$ ). The hydrogen bond does not fix one triflate O atom in place, but its two locations have nearly identical geometries. In (II) where the triflate ion is ordered we observed the H atoms in a difference map and included their parameters in the refinement. The O(H)...O distances are 2.812 (6) and 2.841 (7) Å, O—H...O angles are 163 (7) and 144 (10)°, Ta—O...O angles are 149.1 (3) and 152.2 (3)°, and S—O...O angles are 132.0 (3) and 123.9 (2)°. All of these are normal values for O—H...O hydrogen bonds; our observation of the hydroxyl H atoms in the difference map and these distances and angles in the two compounds are our best evidence for identifying the oxygen ligands as hydroxyl groups and fixing the oxidation number of Ta as +5.

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