

## Cp,Cp\*-Dimethyltantalum Triflate

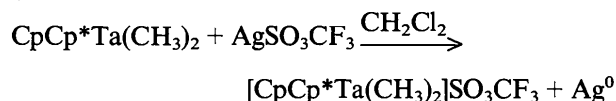
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**Abstract.** ( $\eta^5$ -Cyclopentadienyl)(dimethyl)( $\eta^5$ -pentamethylcyclopentadienyl)tantalum trifluoromethylsulfonate,  $[\text{Ta}(\text{C}_5\text{H}_5)(\text{C}_{10}\text{H}_{15})(\text{CH}_3)_2]\text{CF}_3\text{SO}_3$ ,  $M_r = 560.41$ , orthorhombic,  $Pbca$ ,  $a = 14.230(4)$ ,  $b = 19.283(4)$ ,  $c = 14.628(4)$  Å,  $V = 4014(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.855$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 55.3$  cm<sup>-1</sup>,  $F(000) = 2192$ , room temperature,  $R(F) = 0.038$  for 1882 reflections with  $F_o^2 > 3\sigma(F_o^2)$ . The Ta—C(methyl) distances are virtually equal at 2.171(12) Å, with a C—Ta—C angle of 95.8(5)°. The coordination of the two  $\eta^5$  ligands is normal; the Cp(centroid)—Ta—Cp\*(centroid) angle is 136.2°. Intermolecular contacts are all approximately at van der Waals distances, with indications of CH...O hydrogen bonding between methyl groups and the triflate anion.

**Introduction.** Interest in cationic Group 4 (Jordan, Bajgur, Willett & Scott, 1986) and actinide (Yang, Stern & Marks, 1991) bent metallocene complexes reflects to their potential in modeling Ziegler-Natta polymerization. Our recent interest in reactive cationic Ta complexes has led to studies of  $[\text{Cp}_2^+\text{Ta}(\text{CH}_3)_2]^+$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) and  $\text{CpCp}^+\text{Ta}(\text{CH}_3)_2^+$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ). A major factor which will influence the reactivity of these cations is the coordinating ability of the counter anion  $[\text{BF}_4^-, \text{SO}_3\text{CF}_3^-$  and  $\text{B}(\text{C}_6\text{F}_5)_4^-]$ . For this reason,  $[\text{CpCp}^+\text{Ta}(\text{CH}_3)_2]\text{SO}_3\text{CF}_3$  was prepared by the oxidation of  $\text{CpCp}^+\text{Ta}(\text{CH}_3)_2$  with silver trifluoromethanesulfonate:



The crystal structure of this complex is described herein.

**Experimental.** A flat plate crystal,  $0.52 \times 0.54 \times 0.10$  mm, was used for data collection on a CAD-4 diffractometer. 25 reflections with  $34 < 2\theta < 36^\circ$  were used to determine cell dimensions. An empirical absorption correction based on  $\varphi$  scans, with relative transmission from 0.336 to 1.260, was applied to the

Table 1. Final refined positional parameters ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^4$ ) for Cp,Cp\*-dimethyltantalum triflate

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$			
	x	y	z	$U_{\text{eq}}$
Ta	2389 (2)	4223 (2)	4047 (3)	351 (1)
C1	969 (8)	3873 (7)	4326 (8)	651 (37)
C2	2069 (9)	4692 (7)	2732 (8)	694 (39)
Cp1	1804 (11)	5239 (13)	4798 (17)	1167 (72)
Cp2	2501 (16)	5447 (9)	4283 (12)	1030 (59)
Cp3	3286 (11)	5177 (10)	4564 (11)	804 (48)
Cp4	3127 (10)	4769 (8)	5331 (10)	699 (43)
Cp5	2156 (13)	4813 (10)	5488 (11)	897 (53)
Cp6	3450 (7)	3560 (5)	3053 (7)	410 (35)
Cp7	2635 (8)	3162 (5)	3130 (6)	416 (27)
Cp8	2562 (7)	2965 (5)	4048 (7)	454 (24)
Cp9	3301 (9)	3235 (7)	4538 (8)	584 (35)
Cp10	3877 (7)	3638 (6)	3907 (9)	511 (32)
Cp11	3877 (9)	3864 (8)	2176 (9)	758 (39)
Cp12	2021 (9)	2944 (7)	2367 (8)	723 (39)
Cp13	1897 (9)	2413 (7)	4404 (9)	743 (41)
Cp14	3551 (12)	3056 (9)	5519 (9)	964 (53)
Cp15	4833 (8)	3927 (8)	4101 (11)	883 (47)
S	334 (2)	985 (2)	2323 (2)	524 (8)
O1	1276 (5)	1223 (5)	2281 (7)	897 (33)
O2	89 (6)	510 (5)	1613 (6)	740 (28)
O3	6 (6)	798 (6)	3212 (6)	913 (30)
C3	-354 (9)	1742 (8)	2050 (9)	638 (38)
F1	-232 (5)	2249 (4)	2638 (6)	940 (27)
F2	-1265 (5)	1612 (5)	2073 (7)	1033 (30)
F3	-140 (8)	1991 (5)	1254 (6)	1402 (40)

data. Data were collected to  $(\sin\theta/\lambda)_{\text{max}} = 0.54$  Å<sup>-1</sup>;  $h$  from -13 to 15,  $k$  from -18 to 20,  $l$  from -15 to 15. Three standard reflections ( $20\bar{4}$ ,  $04\bar{3}$  and 420) showed a linear decay of 2% in  $F$  in 41.8 h of data collection; data were corrected for this decay. 5808 reflections were measured, of which 2614 were independent. Goodness of fit for merging was 2.65 ( $R_{\text{merge}}$  for 2081 reflections with exactly two observations, 0.042). All reflections were used in solution and refinement of the structure. The Ta position was found from a Patterson map; the remaining atoms were located by successive structure factor-Fourier cycles.  $F^2$  magnitudes were used in full-matrix least-squares refinement, which minimized  $\sum w(F_o^2 - F_c^2)^2$ . H atoms were placed at idealized positions (C—H = 0.95 Å) based on difference maps calculated in their expected planes, with isotropic displacement parameters about 20% greater than the equivalent isotropic displacement parameter of the bonded C atom. H-atom parameters were not refined, but the atoms were repositioned once near the end of the refine-

† Contribution No. 8516.

Table 2. Distances (Å) and angles (°) not involving H atoms for Cp,Cp\*-dimethyltantalum triflate

Ta—C1	2.168 (12)	Cp7—Cp12	1.478 (16)
Ta—C2	2.174 (12)	Cp8—Cp9	1.375 (16)
Ta—Cp	2.095	Cp8—Cp13	1.516 (16)
Ta—Cp*	2.124	Cp9—Cp10	1.459 (17)
Cp1—Cp2	1.31 (3)	Cp9—Cp14	1.52 (2)
Cp1—Cp5	1.39 (3)	Cp10—Cp15	1.497 (18)
Cp2—Cp3	1.30 (3)	S—O1	1.418 (10)
Cp3—Cp4	1.39 (2)	S—O2	1.429 (9)
Cp4—Cp5	1.40 (2)	S—O3	1.428 (10)
Cp6—Cp7	1.395 (15)	S—C3	1.801 (14)
Cp6—Cp10	1.399 (15)	C3—F1	1.315 (16)
Cp6—Cp11	1.536 (17)	C3—F2	1.322 (16)
Cp7—Cp8	1.399 (14)	C3—F3	1.294 (17)
C1—Ta—C2	95.8 (5)	Cp13—Cp8—Cp9	124.3 (10)
Cp—Ta—Cp*	136.2	Cp10—Cp9—Cp8	107.6 (10)
C1—Ta—Cp	104.7	Cp14—Cp9—Cp8	125.9 (11)
C1—Ta—Cp*	105.5	Cp14—Cp9—Cp10	125.9 (11)
C2—Ta—Cp	102.5	Cp9—Cp10—Cp6	105.3 (10)
C2—Ta—Cp*	105.2	Cp15—Cp10—Cp6	127.2 (11)
Cp5—Cp1—Cp2	108.9 (19)	Cp15—Cp10—Cp9	126.2 (11)
Cp3—Cp2—Cp1	110.3 (18)	O2—S—O1	114.0 (5)
Cp4—Cp3—Cp2	110.1 (16)	O3—S—O1	115.5 (6)
Cp5—Cp4—Cp3	105.0 (14)	O3—S—O2	114.8 (6)
Cp4—Cp5—Cp1	105.7 (16)	C3—S—O1	104.0 (6)
Cp10—Cp6—Cp7	110.4 (9)	C3—S—O2	103.1 (6)
Cp11—Cp6—Cp7	127.3 (10)	C3—S—O3	103.3 (6)
Cp11—Cp6—Cp10	122.2 (10)	S—C3—F1	112.7 (9)
Cp8—Cp7—Cp6	106.8 (9)	S—C3—F2	111.9 (9)
Cp12—Cp7—Cp6	125.9 (10)	S—C3—F3	111.9 (10)
Cp12—Cp7—Cp8	127.1 (10)	F2—C3—F1	104.7 (11)
Cp9—Cp8—Cp7	109.9 (9)	F3—C3—F1	106.4 (11)
Cp13—Cp8—Cp7	124.5 (9)	F3—C3—F2	108.9 (11)

ment. Coordinates and anisotropic displacement parameters of all non-H atoms plus a scale factor (236 parameters) were refined. For 2400 reflections with  $F_o^2 > 0$ ,  $R$  (on  $F$ ) = 0.053, for 1882 reflections with  $F_o^2 > 3\sigma(F_o^2)$ ,  $R$  (on  $F$ ) = 0.038,  $wR$  (on  $F^2$ ) = 0.008;  $S = 2.27$ . Weights were taken as  $1/\sigma^2(F_o^2)$ ; variances [ $\sigma^2(F_o^2)$ ] were derived from counting statistics plus an additional term,  $(0.014I)^2$ ; variances of the merged data by propagation of e.s.d. plus another additional term,  $(0.014I)^2$ . In the final least-squares cycle, maximum  $\Delta/\sigma < 0.01$ ;  $-1.50 \leq \Delta\rho \leq 1.54 \text{ e } \text{Å}^{-3}$  in the final difference Fourier map; all peaks greater than  $|0.8| \text{ e } \text{Å}^{-3}$  within  $1.8 \text{ Å}$  of Ta. Atomic scattering factors and values for  $f'$  were taken from Cromer & Waber (1974) and Cromer (1974). Programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEPII* (Johnson, 1976). Final refined parameters of the atoms are listed in Table 1 with selected distances and angles in Table 2.\* The extremely air-sensitive crystal was in a capillary and obscured by grease, so exact measurement of it was not possible and we could not attempt an analytical absorption correction. Our empirical correction

\* Lists of assigned H-atom parameters, anisotropic displacement parameters, complete distances and angles, and observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55137 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0590]

improved the goodness of fit for merging from 5.96 to 2.35, but there were still 22 individual reflections with goodness of fit values greater than 10.0. Our inability to correct for absorption is the major difficulty with this structure. Because  $x(\text{Ta})$  is approximately  $\frac{1}{4}$ , reflections with  $k$  odd are systematically weak (on average, only 37% as large as those with  $k$  even, based on  $F$ ), but there is no trend in  $R$  with index, parity,  $(\sin^2\theta/\lambda^2)$  or  $|F_o^2|$  discernible.

**Discussion.** A view of the Ta cation is given in Fig. 1. Bond distances are all in normal ranges. The Ta—CH<sub>3</sub> bonds are virtually identical, at 2.171 (12) Å; this compares to 2.217 (35) Å for seven examples located by Orpen, Brammer, Allen, Kennard, Watson & Taylor (1989). (Further comparison lengths are from this same compilation.) The

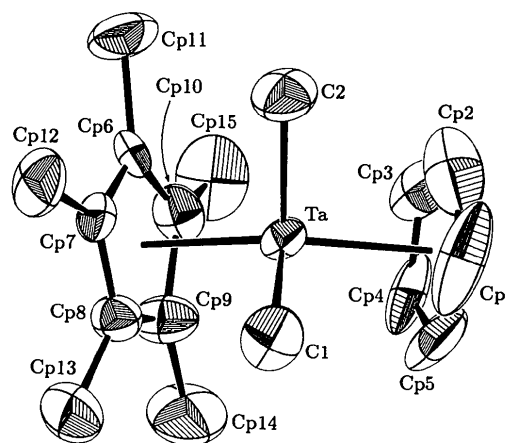


Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the cation with 50% probability ellipsoids showing the numbering system. H atoms are not shown.

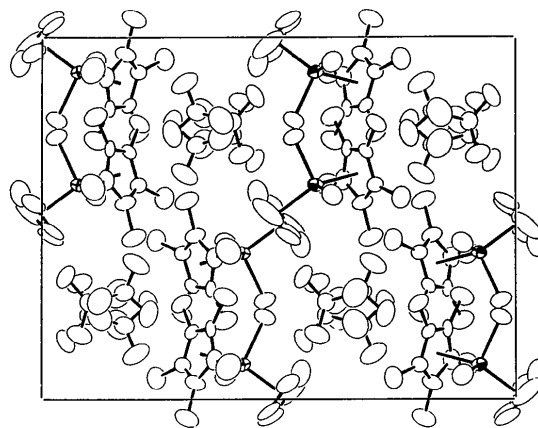


Fig. 2. An *ORTEPII* (Johnson, 1976) packing drawing projected down  $a$  showing the contents of a unit cell, with the unit cell outlined. The  $c$  axis is horizontal. Atoms are shown as 50% probability ellipsoids, with Ta atoms shaded; H atoms are not shown.

Ta—Cp(centroid) distance is slightly long – 2.095 compared to 2.072 (31) Å – but the Ta—Cp\* (centroid) distance is nearly identical to the others cited: 2.124 vs 2.122 (29) Å. In the Cp ring, the C—C distances are somewhat short, averaging 1.359 (50) Å; the compilation of Orpen *et al.* (1989) gives 1.397 (28) Å for this distance (804 examples). The Cp\* ring is more nearly normal, with C—C(ring) distances averaging 1.405 (32) Å [1.417 (24) Å, 164 examples] and C—CH<sub>3</sub> distances 1.509 (22) Å [1.512 (25) Å]. In both rings, the average deviation of the interior angles from 108° is 2°.

The triflate anion is also essentially normal, with O atoms showing slightly smaller anisotropic displacement parameters than F atoms; all six terminal atoms are well behaved for this group, however. In the crystal, the triflate anions pack in columns along *a* (see Fig. 2), with one oxygen—methyl group contact less than 3.4 Å and two less than 3.5 Å, indicating some weak interactions. There are similar C—F distances as well: one 3.31 Å, five less than 3.5 Å. No H—O or H—F contact is less than 2.43 Å.

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#### References

- CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 149–151. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99–101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- DUCHAMP, D. J. (1964). *CRYM* crystallographic computing system. Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Paper B14, p. 29.
- JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-3794, third revision. Oak Ridge National Laboratory, Tennessee, USA.
- JORDAN, R. F., BAJGUR, C. S., WILLETT, R. & SCOTT, B. (1986). *J. Am. Chem. Soc.* **108**, 7410–7411.
- ORPEN, A. G., BRAMMER, L., ALLEN, F. H., KENNARD, O., WATSON, D. G. & TAYLOR, R. (1989). *J. Chem. Soc. Dalton Trans.* S1–S83.
- YANG, X., STERN, C. & MARKS, T. J. (1991). *Organometallics*, **10**, 840–842.

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## Structure of $\mu$ -Chloro-bis{bis[2-(2-pyridyl)ethylamine-*N,N'*]copper(II)} Trishexafluorophosphate

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**Abstract.**  $\{[\text{Cu}(\text{C}_7\text{H}_{10}\text{N}_2)_2]_2\text{Cl}\}(\text{PF}_6)_3$ , (3),  $M_r = 1086.12$ , monoclinic,  $C2/m$ ,  $a = 16.428$  (4),  $b = 12.721$  (3),  $c = 12.526$  (6) Å,  $\beta = 114.53$  (3)°,  $V = 2381.7$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.51$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 23.04$  cm<sup>-1</sup>,  $F(000) = 1092$ ,  $T = 293$  K,  $R = 0.065$  and  $wR = 0.095$  for 1425 unique diffractometer data with  $I > 3\sigma(I)$ . The structure reveals a dimer molecule with a  $\mu$ -Cl atom linking two Cu<sup>II</sup> atoms with a linear bridge. The coordination geometry around the Cu atoms is square-based pyramidal.

**Introduction.** Tyrosinase is a Cu-containing enzyme (type III or binuclear coupled) which catalyzes *ortho*-hydroxylation of phenols into catechols and oxidation of catechols into *ortho*-quinones (Robb, 1984; Latour, 1988; Tyeklar & Karlin, 1989). According to many structural studies, the formation of a  $\mu$ -peroxo

copper(II) and a catecholate-dicopper(II) species have been postulated during the catalytic process (Wilcox, Porras, Hwang, Lerch, Winkler & Solomon, 1985).

Recently, we have reported (Reglier, Jorand & Waegell, 1990) the synthesis of a binuclear Cu complex (1) which exhibits in the presence of phenols and catechols the same activity as the tyrosinase. With this model, we have shown the occurrence of the catecholate-dicopper(II) species (2), ( $R_1 = \text{Bu}$  and  $R_2 = \text{H}$ ). Unfortunately, we have not been able to isolate these complexes which are very sensitive to dioxygen. In order to obtain these species, we treated the Cu complex (2) with 1 equivalent of tetrachloro-*ortho*-benzoquinone which is known to give stable catecholate-copper species (Karlin, Gultneh, Nicholson & Zubieta, 1985). Under argon, a stable catecholate-dicopper species is obtained, but when