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*Acta Cryst.* (1991). **C47**, 547–550

## Structure of Imidazolium Hexachlorotantalate(V)

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(Received 7 June 1990; accepted 21 August 1990)

**Abstract.**  $C_3H_5N_2^+[TaCl_6]^-$ ,  $M_r = 462.75$ , orthorhombic,  $Pnma$ ,  $a = 14.796$  (8),  $b = 6.985$  (3),  $c = 11.011$  (6) Å,  $V = 1138.0$  Å<sup>3</sup>,  $D_x = 2.701$  Mg m<sup>-3</sup>,  $Z = 4$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 10.92$  mm<sup>-1</sup>,  $F(000) = 848$ ,  $T = 185$  K,  $R = 0.042$  for 847 observed reflections. The structure consists of roughly octahedral  $[TaCl_6]^-$  anions [Ta—Cl = 2.317 (3)–2.362 (3) Å] and imidazolium cations interacting via N—H...Cl hydrogen bonds. There is also cohesion between the layers due to normal van der Waals contacts.

**Introduction.** The reactions of Nb and Ta halides with various nitrogen-containing aromatic ligands are currently being investigated in this laboratory. When imidazole ligands are reacted with TaCl<sub>5</sub> in 1:1 ratio in benzene or toluene, the main product is the sparingly soluble TaCl<sub>5</sub>(imidazole) monoadduct (Levasseur & Beauchamp, 1990). The filtrate from one such preparation was kept under argon in a Schlenk tube at room temperature. Three months later, a few red crystals had appeared. Under similar conditions, NbCl<sub>5</sub> and 7-azaindole had produced a condensed [(7-azaindoly)-7-azaindoly]<sup>+</sup> cation (Poitras & Beauchamp, 1990). The few crystals available of the red imidazole material were used to identify the compound by X-ray diffraction. Our results show that the imidazole unit remains monomeric in the present case.

**Experimental.** Red crystals very sensitive to moisture. Specimen transferred under dry argon and sealed in a Lindemann capillary. Bounded by the following pairs of faces (separation in mm): (010)/(0 $\bar{1}$ 0), 0.10; (001)/(00 $\bar{1}$ ), 0.20; ( $\bar{1}$ 01)/(10 $\bar{1}$ ), 0.17; (100)/( $\bar{1}$ 00), 0.24.

Nonius CAD-4 diffractometer, equipped with an N<sub>2</sub> cooling system, graphite-monochromatized Mo  $K\alpha$  radiation. Unit-cell dimensions from 25 centered reflections in the range  $20 \leq 2\theta \leq 25^\circ$ . Laue symmetry and cell dimensions checked with long-exposure axial photographs along the three axes.  $\omega$ - $2\theta$  scan,  $\omega = (1.00 + 0.35 \tan \theta)^\circ$ ,  $2\theta_{\max} = 50.0^\circ$ . Orientation monitored every 200 measurements, intensity checked every hour by using seven standard reflections, intensity fluctuation within  $\pm 2.5\%$ . 3393  $hkl$ ,  $\bar{h}\bar{k}l$ ,  $\bar{h}kl$  reflections measured ( $h$ : 0–17,  $k$ : 0–8,  $l$ : 0–12). Absorption correction based on crystal geometry applied (Gaussian integration, grid  $10 \times 10 \times 10$ , transmission range 0.05–0.14). 1093 independent  $hkl$  reflections after octant averaging ( $R_{av} = 0.042$ ), 847 with  $I \geq 3.0\sigma(I)$  retained for structure determination and refinement. Data corrected for Lp.

Orthorhombic Laue symmetry and systematic absences ( $0kl$   $k + l \neq 2n$ ,  $hk0$   $h \neq 2n$ ) consistent with space groups  $Pnma$  and  $Pn2_1a$  (alternate setting for  $Pna2_1$ ). Structure solved in the centrosymmetric space group  $Pnma$  by the heavy-atom method. Ta found to lie on mirror plane [equipoint 4(c)] from a Patterson map. Four Cl [two in general position, two on 4(c)] and the five non-H atoms [all on 4(c)] of the imidazolium cation located from difference Fourier ( $\Delta F$ ) maps.

Special care was taken to identify the N and C atoms in the imidazole unit. The five ring atoms were first defined as carbons C\* $\ddagger$  and refined isotropically, whereas the Ta and Cl atoms were refined anisotropically. All H atoms were visible on the  $\Delta F$  synthesis. They were fixed at idealized positions [C(N)—H = 0.95 Å,  $U = 0.10$  Å<sup>2</sup>] and repositioned after each

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$\ddagger$  Asterisked symbols represent the ring atoms defined as carbon at this early stage.

cycle. In light-atom structures, the small deviations from perfect pentagonal geometry (see Table 3) could be used to recognize the N atoms, but our e.s.d.'s (0.03 Å and 2°) were of the same magnitude as the differences expected among the ring distances and angles. C\*(1), C\*(3) and C\*(4) were first retained as reasonable candidates for N because the attached H atoms were within 2.8 Å from a Cl atom and could participate in H bonding. At this stage, the temperature factors ( $U$ , Å<sup>2</sup>) were: C\*(1), 0.068; C\*(2), 0.081; C\*(3), 0.077; C\*(4), 0.092; C\*(5), 0.073. The higher value for C\*(4) was considered as evidence that it could not be nitrogen, since refining an N atom as carbon should have led to a low temperature factor. Hence, C\*(1) and C\*(3) were relabeled N(1) and N(3), respectively, and a few more refinement cycles were run. Atomic positions did not change appreciably and the temperature factors converged to normal values: N(1), 0.088 (6); C(2), 0.080 (6); N(3), 0.101 (7); C(4), 0.090 (7); C(5), 0.070 (6) Å<sup>2</sup>. All non-H atoms were finally refined anisotropically.

Full-matrix least-squares refinement based on  $|F|$ , function minimized:  $\sum w(|F_o| - |F_c|)^2$ . Final  $R = 0.042$ ,  $wR = 0.049$ , weights based on counting statistics [ $w = 1/\sigma^2(F) + 0.001F^2$ ],  $S = 1.22$  for 67 parameters refined. Maximum ( $\Delta/\sigma$ ) = 0.08, average ( $\Delta/\sigma$ ) = 0.01, residual electron density fluctuation on final  $\Delta F$  synthesis: between +2.14 and -1.43 e Å<sup>-3</sup> near Ta or Cl, below  $\pm 0.86$  e Å<sup>-3</sup> elsewhere. Absence of artificial disorder or abnormal thermal ellipsoids indicates that the structure does not deviate perceptibly from  $Pnma$  and rules out space group  $Pn2_1a$ .

Scattering curves from Cromer & Waber (1965) for the non-H atoms and from Stewart, Davidson & Simpson (1965) for H. Anomalous-dispersion factors from Cromer (1965). Refined coordinates are given in Table 1.†

**Discussion.** The red compound is identified as the imidazolium salt of the  $[\text{TaCl}_6]^-$  anion. Its precipitation in the filtrate from which the  $\text{TaCl}_5$ :imidazole monoadduct had been isolated undoubtedly results from hydrolysis due to traces of moisture slowly diffusing into the Schlenk tube over a period of several months. The  $[\text{TaCl}_6]^-$  and  $[\text{C}_3\text{H}_5\text{N}_2]^+$  ions are shown in Fig. 1.

The  $[\text{TaCl}_6]^-$  ion shows the expected octahedral geometry with distortions  $< 2^\circ$  (Table 2, planes). The bond lengths [2.317 (3)–2.362 (3) Å, mean 2.338 Å]

† Lists of structure factors, anisotropic thermal parameters, least-squares planes, literature data on the structure of the imidazolium ion and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53504 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final coordinates ( $\times 10^4$ ; Ta  $\times 10^5$ ) and equivalent isotropic temperature factors (Å<sup>2</sup>  $\times 10^3$ )

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

	x	y	z	$U_{\text{eq}}$
Ta	15843 (4)	25000	15603 (5)	40
Cl(1)	3092 (2)	2500	948 (4)	49
Cl(2)	85 (2)	2500	2250 (3)	50
Cl(3)	1240 (2)	116 (5)	172 (3)	55
Cl(4)	1933 (2)	144 (5)	3026 (3)	56
N(1)	1216 (13)	2500	7240 (16)	93
N(3)	-46 (13)	2500	6389 (21)	109
C(2)	345 (15)	2500	7443 (21)	78
C(4)	613 (24)	2500	5534 (17)	99
C(5)	1369 (15)	2500	6008 (22)	71

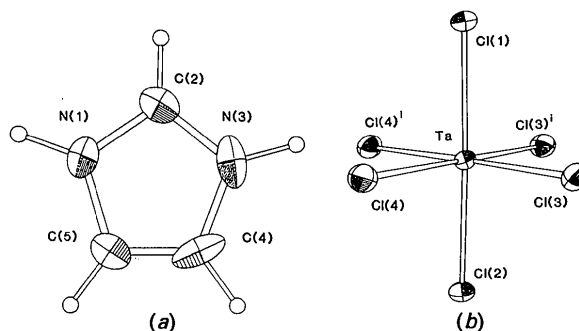


Fig. 1. ORTEP drawings of (a) the imidazolium cation and (b) the  $[\text{TaCl}_6]^-$  anion with atomic numbering. The ellipsoids correspond to 50% probability, except for H atoms which are shown as spheres of arbitrary size. (i) =  $x, \frac{1}{2} - y, z$ .

compare well with those observed in other salts [2.30–2.36 Å, mean 2.33 Å] (Bradley, Hursthouse, Newton & Walker, 1984; Brownstein, Gabe, Irish, Lee, Louie & Piotrowski, 1987; Ershova, Glushkova, Chumaevsii, Porai-Koshits, Buslaev, Butman, Minaeva & Sadikov, 1981; Preiss, 1971).

Standard values for the distances and angles in the imidazolium cation are given in Table 3. Our results show no significant differences from these values, but the e.s.d.'s are large in the present structure, where most of the electron density is located in the  $\text{TaCl}_6$  unit. Since the expected differences on distances or angles in the ring are of the same order as the e.s.d.'s, they could not be used to identify which of these atoms are N atoms. The absence of Cl atoms to act as H-bond acceptors within 2.8 Å from the idealized H positions for C(2) and C(5) is consistent with these atoms being labeled as carbon. On the basis of the H...Cl distance (Table 2), the protons on N(1), N(3) and C(4) remain potential donors. Considering that the N atoms cannot occupy consecutive positions in the ring, N(1) must be an N atom. The temperature factors are more consistent with the N(3) position being assigned to nitrogen (see *Experimental*).

Fig. 2 shows a layer of thickness  $c/2$ , parallel to the unit cell  $ab$  face. It consists of rows of  $[\text{TaCl}_6]^-$

Table 2. Distances (Å) and angles (°) in the  $[\text{TaCl}_6]^-$  ion and the H bonds (idealized H positions used)

Ta—Cl(1)	2.331 (4)	Ta—Cl(3)	2.317 (3)
Ta—Cl(2)	2.344 (4)	Ta—Cl(4)	2.362 (3)
Cl(1)—Ta—Cl(2)	177.9 (1)	Cl(3)—Ta—Cl(4)	89.9 (1)
Cl(1)—Ta—Cl(3)	91.1 (1)	Cl(3)—Ta—Cl(3) <sup>i</sup>	91.9 (1)
Cl(1)—Ta—Cl(4)	89.4 (1)	Cl(3)—Ta—Cl(4) <sup>j</sup>	178.2 (1)
Cl(2)—Ta—Cl(3)	90.3 (1)	Cl(4)—Ta—Cl(4) <sup>k</sup>	88.3 (1)
Cl(2)—Ta—Cl(4)	89.2 (1)		
A—H...Cl	A...Cl	H...Cl	A—H...Cl
N(1)—H(1)...Cl(4) <sup>ii,vi</sup>	3.42 (2)	2.78	125.1
N(1)—H(1)...Cl(3) <sup>ii,iv</sup>	3.63 (2)	3.12	115.8
N(3)—H(3)...Cl(4) <sup>v,vi</sup>	3.41 (2)	2.74	128.5
N(3)—H(3)...Cl(1)		3.03	136.2
C(4)—H(4)...Cl(2)		2.75	176.0

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

ions on the mirror plane at  $y = 0.75$ , separated by rows of imidazolium ions lying in the mirror plane at  $y = 0.25$ . The rows are connected by N—H...Cl hydrogen bonds. N(1)—H and N(3)—H each form a pair of symmetry-equivalent H bonds, in which Cl(4) atoms (two per anion) are the acceptors. These bifurcated H bonds are not individually very strong [ $\text{H}(1)\cdots\text{Cl}(4) = 2.78 \text{ \AA}$ ,  $\text{H}(3)\cdots\text{Cl}(4) = 2.74 \text{ \AA}$ ]. In the only other structure containing an imidazolium...Cl H bond (Keppler, Wehe, Endres & Rupp, 1987), the calculated H...Cl distance is shorter (2.29 Å) but the H bond is not bifurcated. Typical H...Cl distances found for bifurcated, but dissymmetric, N—H...Cl bonds in pyridinium salts are: 2.48/2.75 Å (James, Millikan & Mackay, 1983),\* 2.62/2.80 and 2.45/2.85 Å (Subbotin & Aslanov, 1985),\* 2.31/2.87 Å (Smart & Webster, 1976). In these pyridinium salts, the  $\alpha$  H atoms make C—H...Cl contacts of 2.61–2.70 Å, and contacts as short as 2.48–2.52 Å have been found when non-bifurcated H bonds are formed (Hensen, Pullmann & Bats, 1988;\* Begley, Hall, Nunn & Sowerby, 1986). Hence, the H(4)...Cl(2) contact of 2.75 Å observed here is not unusual. Beside this interaction, cohesion between the layers involves normal van der Waals contacts.

Considering that the H(4)...Cl(2) contact is similar to the H...Cl distances in the N—H...Cl bonds, mild disorder whereby the N(3)/C(2) and C(4)/C(5) pairs would be interchanged remains a possibility. However, no such disorder could be detected from our data.

We wish to thank M. Simard and F. Bélanger-Gariépy for collecting the X-ray data and the Natural Sciences and Engineering Research Council of Canada for financial support.

\* Hydrogen coordinates not provided, idealized H positions calculated, C(N)—H = 0.95 Å.

Table 3. Comparison of the distances (Å) and angles (°) in the imidazolium cation with literature values

	This work	Literature*
N(1)—C(2)	1.31 (3)	1.319 (16)
C(2)—N(3)	1.30 (3)	1.319 (16)
N(3)—C(4)	1.36 (4)	1.370 (16)
C(4)—C(5)	1.23 (4)	1.344 (11)
C(5)—N(1)	1.38 (3)	1.370 (16)
C(2)—N(1)—C(5)	109 (2)	108.5 (13)
N(1)—C(2)—N(3)	107 (2)	108.9 (12)
C(2)—N(3)—C(4)	107 (2)	108.5 (13)
N(3)—C(4)—C(5)	111 (2)	107.1 (10)
N(1)—C(4)—C(5)	106 (2)	107.1 (10)

\* Mean values from 12 structures extracted from the Cambridge Structure Database (Allen, Kennard & Taylor, 1983), CISTI, National Research Council of Canada, Ottawa (details in supplementary material).

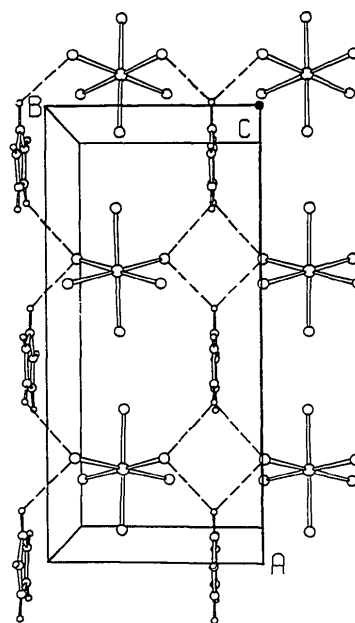


Fig. 2. View of the unit cell down the  $c$  axis. The origin is represented by a black dot. Atoms are shown as spheres of arbitrary sizes:  $\text{Ta} > \text{Cl} > \text{C} = \text{N} > \text{H}$ . Dashed lines correspond to H bonds.

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*Acta Cryst.* (1991). **C47**, 550–553

## Structures of the Tetrafluoroborate Salts of Triphenylcarbenium Ions with One and with Two 4-Methoxy Substituents: Stable Carbocations

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(Received 23 April 1990; accepted 1 June 1990)

**Abstract.** *p*-Methoxyphenyldiphenylcarbenium tetrafluoroborate (1):  $[C_{20}H_{17}O][BF_4]$ ,  $M_r = 360.2$ , monoclinic,  $P2_1/n$ ,  $a = 7.962$  (1),  $b = 15.463$  (2),  $c = 14.567$  (1) Å,  $\beta = 95.54$  (1)°,  $V = 1785.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.340$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 1.0$  cm<sup>-1</sup>,  $F(000) = 744$ ,  $T = 295$  K,  $R = 0.063$  for 2356 unique observed reflections. Di(*p*-methoxyphenyl)phenylcarbenium tetrafluoroborate (2):  $[C_{21}H_{19}O_2][BF_4]$ ,  $M_r = 390.2$ , monoclinic,  $P2_1/n$ ,  $a = 7.942$  (2),  $b = 16.773$  (4),  $c = 14.447$  (2) Å,  $\beta = 90.54$  (2)°,  $V = 1924.4$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.347$  g cm<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.54184$  Å,  $\mu = 9.2$  cm<sup>-1</sup>,  $F(000) = 808$ ,  $T = 295$  K,  $R = 0.114$  for 1259 unique observed reflections. Both cations have a propeller structure, with the aryl rings twisted out of the plane of the carbenium-ion centre. The angle of twist is smaller for the 4-methoxyphenyl groups [26.6 (2), 27.8 (5) and 29.6 (5)°] than for the phenyl groups [31.3 (2), 38.6 (2) and 37.3 (5)°] as a consequence of greater conjugation.

**Introduction.** Previous crystal structure analyses of triarylcarbenium ions  $[Ar_3C]^+$  have been almost entirely restricted to substances in which the aryl groups are identical, the one exception being the 4,4'-biphenylbis(diphenylmethyl) ion (McKechnie & Paul, 1971), in which two triphenylcarbenium ions are joined together through a *para*-biphenyl link between a phenyl group of each one. All the cations adopt a propeller shape, the tendency of at least one aryl group to be coplanar

with the carbenium centre being opposed by steric interactions between neighbouring *ortho* H atoms. The aryl rings are twisted about 30° out of the central carbenium plane in each case, for unsubstituted triphenylcarbenium ions with a variety of counterions (Gomes de Mesquita, MacGillavry & Eriks, 1965; Krebs & Paulat, 1979; Fenske, Kujanek & Dehnicke, 1983; Cook, Dahl & Dickerhoof, 1972) and for tris(4-aminophenyl)carbenium perchlorate (Koh & Eriks, 1971). A similar angle of twist has been estimated for the tris(4-methoxyphenyl)carbenium ion in a structure subject to considerable disorder (Andersen & Klewe, 1965).

We report here the crystal structures of 4-(methoxyphenyl)diphenylcarbenium tetrafluoroborate [4-methoxytritylium tetrafluoroborate, (1)] and bis(4-methoxyphenyl)phenylcarbenium tetrafluoroborate [4,4'-dimethoxytritylium tetrafluoroborate, (2)]. We have recently shown that these salts are very useful reagents for the protection of alcohols including nucleosides and sugars (Bleasdale, Ellwood & Golding, 1990). It was of interest to determine the precise structures of the salts and, in particular, the relative degrees of interaction of the 4-methoxyphenyl and phenyl groups with the carbenium centre, for comparison with the triphenyl and tris(4-methoxyphenyl) end members of the series. This will assist the correlation of structure with reactivity, and the design of new 'fine-tuned' protecting groups for amino, hydroxy and thiol functions.

**Experimental.** The red-orange, air-stable salt (2) was prepared as previously described by Bleasdale, Ell-

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