

- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- GRDENIĆ, D. & SIKIRICA, M. (1973). *Inorg. Chem.* **12**, 544–546.
- MATKOVIĆ, B., RIBAR, B., PRELESNIK, B. & HERAK, R. (1974). *Inorg. Chem.* **13**, 3006–3008.
- POLISHCHUK, S. A., KHMELEVA, M. G., ZADNEPROVSKII, G. M., KAIDALOVA, T. A. & KUPTSOVA, N. V. (1970). *J. Less-Common Met.* **21**, 63–69.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WEISS, A., LYNG, S. & WEISS, A. (1960). *Z. Naturforsch. Teil B*, **15**, 678.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

*Acta Cryst.* (1979). **B35**, 951–954

## Structure of Tetraphenylarsonium *trans*-Dichlorobis(2,4-pentanedionato)rhenate(III), [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>][Re(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]

BY C. J. L. LOCK AND C. N. MURPHY

*Institute for Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada*

(Received 8 August 1978; accepted 7 November 1978)

**Abstract.** [C<sub>24</sub>H<sub>20</sub>As]<sup>+</sup>. [C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>4</sub>Re]<sup>-</sup>, *M<sub>r</sub>* = 838.69, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.874 (2), *b* = 26.953 (9), *c* = 15.511 (4) Å, β = 102.37 (2)°, *Z* = 4, *V* = 3215.4 Å<sup>3</sup>, *D<sub>c</sub>* = 1.73, *D<sub>o</sub>* = 1.70 Mg m<sup>-3</sup>. Refinement by full-matrix least squares based on 4226 reflections gave *R* = 0.068 and *R<sub>w</sub>* = 0.053. The Re atom has pseudo-octahedral coordination to four O atoms of the acetylacetonate groups [range Re–O, 1.996 (9) to 2.016 (12) Å] and two *trans* Cl atoms [Re–Cl, 2.385 (5), 2.425 (5) Å].

**Introduction.** Courier (1971) first showed that the reaction of reducing agents with *trans*-dichlorobis(2,4-pentanedionato-*O,O*)rhenium(IV) (*A*) produced a blue-green species in solution. Later it was possible to isolate this species as a potassium salt and show that it was the one-electron reduction product of *A*, and, further, that the same salt could be produced by the reduction of the *cis* form of *A* (Lock, Murphy & Turner, 1979). Subsequent experiments suggested that the potassium salt contained the *trans* form of the reduction product, but it was of interest to confirm this by X-ray crystallography. Also, a fairly accurate X-ray study of *A* had been made (Brown, Lock & Wan, 1973), so that it may be possible to determine how the extra electron modified the molecular structure. Attempts to produce crystals of the potassium salt suitable for X-ray studies were unsuccessful, but the corresponding tetraphenylarsonium salt did give suitable crystals.

The title compound was prepared by the reaction of aqueous solutions of K[Re(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] (Lock, Murphy & Turner, 1979) with [As(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>]Cl. The product precipitated immediately, and was purified by dissolving it in dichloromethane followed by precipitation with diethyl ether. Crystals suitable for X-ray

diffraction studies were prepared by the vapour-diffusion technique, allowing diethyl ether vapour to diffuse into a dichloromethane solution of the title compound over several days:

A roughly spherical blue-green crystal of 0.2 mm diameter was used for the X-ray diffraction studies. Precession photographs revealed the systematic absences *h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1. Accurate lattice parameters were obtained from a Syntex *P1* diffractometer by a least-squares fit to 15 well centered reflections with 19 < 2θ < 26° [Mo *K*<sub>α</sub> radiation, λ(*K*<sub>α</sub>) = 0.71069 Å]. Crystal density was measured by flotation in an aqueous ZnBr<sub>2</sub> solution. The intensities of 4700 reflections with 2θ ≤ 45° were measured on the same diffractometer; of these, 2420 had *I* > 3σ<sub>*I*</sub>. The stability of the system was monitored by measuring three standard reflections after every 47 reflections. The standard errors of the 113, 151, and 202 reflections were 1.9, 2.2 and 1.6% respectively. All reflections were corrected for Lorentz, polarization and absorption (spherical correction, μ = 1.32 mm<sup>-1</sup>; absorption correction factor, *A*<sup>\*</sup>, range 2.08 to 2.05). Equivalent reflections were averaged and those systematically absent were removed to give 4226 independent intensities of which 2219 had *I* > 3σ<sub>*I*</sub>.

A Patterson map gave the position of the Re atom and subsequent difference syntheses revealed all the other non-hydrogen atoms. The structure was refined using the full-matrix least-squares program *CUDLS* which minimized ∑ w(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>, where w = [σ<sub>*F*</sub><sup>2</sup> + (*kF*)<sup>2</sup>]<sup>-1</sup> except for reflections for which *F*<sub>c</sub> < *F*<sub>o</sub> and *I* < 3σ<sub>*I*</sub>, for which w = 0 (σ<sub>*I*</sub> and σ<sub>*F*</sub> are the standard errors in *I* and *F*, respectively, based on counting statistics). The value of *k* = 0.01 in the weighting scheme was chosen to make ⟨w(|*F*<sub>o</sub>| - |*F*<sub>c</sub>|)<sup>2</sup>⟩

Table 1. Atomic positional parameters ( $\times 10^3$ )

	x	y	z
Re	240.36 (9)	85.51 (3)	227.69 (5)
Cl(1)	143.6 (6)	154.7 (2)	304.9 (3)
Cl(2)	332.6 (6)	17.3 (2)	150.9 (3)
O(1)	10 (1)	84.7 (5)	141.9 (7)
C(1)	-117 (2)	57.7 (7)	148 (1)
C(2)	-127 (2)	23.2 (7)	218 (1)
C(3)	4 (2)	17.7 (7)	293 (1)
O(2)	152 (1)	38.3 (4)	308.9 (7)
C(4)	-270 (2)	58.7 (7)	67 (1)
C(5)	-24 (2)	-17.2 (7)	368 (1)
O(3)	469 (1)	87.7 (5)	313.1 (7)
C(6)	610 (2)	111.1 (6)	304 (1)
C(7)	619 (2)	140.4 (6)	230 (1)
C(8)	490 (2)	150.5 (6)	159 (1)
O(4)	332 (1)	132.9 (4)	148.4 (7)
C(9)	763 (2)	107.4 (7)	382 (1)
C(10)	526 (2)	184.1 (7)	86 (1)
C(11)	69 (2)	801.5 (6)	356 (1)
C(12)	48 (2)	750.7 (7)	341 (1)
C(13)	-43 (2)	724.6 (7)	395 (1)
C(14)	-105 (2)	750.3 (7)	460 (1)
C(15)	-84 (2)	797.6 (7)	473 (1)
C(16)	6 (2)	825.9 (7)	420 (1)
C(21)	346 (2)	882.0 (6)	352 (1)
C(22)	441 (2)	862.6 (6)	431 (1)
C(23)	563 (2)	891.8 (6)	486 (1)
C(24)	588 (2)	940.5 (7)	458 (1)
C(25)	493 (2)	960.7 (7)	380 (1)
C(26)	370 (2)	929.1 (7)	323 (1)
C(31)	9 (2)	871.5 (6)	199 (1)
C(32)	-159 (2)	869.4 (7)	209 (1)
C(33)	-296 (2)	893.3 (7)	143 (1)
C(34)	-252 (2)	914.8 (8)	72 (1)
C(35)	-87 (2)	915.6 (9)	61 (1)
C(36)	51 (2)	894.0 (7)	125 (1)
C(41)	309 (2)	798.2 (6)	218 (1)
C(42)	231 (2)	777.5 (7)	138 (1)
C(43)	324 (2)	750.0 (8)	90 (1)
C(44)	497 (2)	737.9 (7)	129 (1)
C(45)	576 (2)	756.2 (7)	208 (1)
C(46)	483 (2)	786.8 (6)	255 (1)
As	183.4 (2)	840.42 (7)	280.4 (1)

independent of  $F$ . The scattering factors were taken from Cromer & Waber (1974), the Re, Cl, and As factors being corrected for anomalous dispersion (Cromer, 1974).

H atoms were not found and not included in the refinement. Refinement was terminated at  $R = 0.068$ ,  $R_w = 0.053$ , and in the final cycle of refinement no parameter shifted by more than 0.04 of its standard deviation. A final difference map was essentially featureless, the maximum being  $0.52 \text{ e } \text{Å}^{-3}$  at 0.26, 0.93, 0.60 near C(9) and the minimum being  $-0.63 \text{ e } \text{Å}^{-3}$  at 0.26, 0.09, 0.23 near the Re atom.\*

**Discussion.** The final atomic coordinates are given in Table 1 and the numbering is shown in Fig. 1. Selected interatomic distances and angles are given in Table 2. The anion has the expected geometry. A detailed comparison of the bond lengths and angles found for the anion with those found for *A* (Brown, Lock & Wan, 1973) shows no significant differences except for the Re—Cl distances. Within the anion the Re—Cl distances [Re—Cl(1) 2.425 (5), Re—Cl(2) 2.385 (5) Å] are significantly different ( $5.7\sigma$ ) and both distances are substantially longer than the value of 2.326 (8) Å found for *A* [a difference of  $8.4\sigma$  from the anion average of 2.405 (5) Å].† The detectable effect of the

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34047 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Because the temperature factors varied slightly for the Cl atoms, riding corrections were applied to the Re—Cl bond lengths. The corrected values are Re—Cl(1) 2.424 (5) Å, Re—Cl(2) 2.387 (5) Å and Re—Cl (*A*) 2.356 (8) Å. Thus, the difference in Re—Cl(1) and Re—Cl(2) is still  $5.23\sigma$ , and Re—Cl(2) is still  $3.28\sigma$  longer than Re—Cl in *A*.

Table 2. Selected interatomic distances (Å) and angles ( $^\circ$ )

Re—Cl(1)	2.425 (5)	Re—Cl(2)	2.385 (5)	Re—O(1)	2.008 (9)
Re—O(2)	2.016 (12)	Re—O(3)	1.996 (9)	Re—O(4)	2.011 (12)
O(1)—C(1)	1.26 (2)	C(1)—C(2)	1.44 (3)	C(1)—C(4)	1.54 (2)
C(2)—C(3)	1.39 (2)	C(3)—C(5)	1.55 (3)	C(3)—O(2)	1.27 (2)
O(3)—C(6)	1.31 (2)	C(6)—C(7)	1.40 (3)	C(6)—C(9)	1.52 (2)
C(7)—C(8)	1.36 (2)	C(8)—C(10)	1.52 (3)	C(8)—O(4)	1.31 (2)
Cl(1)—Re—Cl(2)	179.4 (2)	Cl(1)—Re—O(1)	90.1 (4)	Cl(1)—Re—O(2)	89.4 (4)
Cl(1)—Re—O(3)	89.1 (4)	Cl(1)—Re—O(4)	90.3 (4)	Cl(2)—Re—O(1)	89.4 (4)
Cl(2)—Re—O(2)	90.5 (4)	Cl(2)—Re—O(3)	91.5 (5)	Cl(2)—Re—O(4)	89.8 (4)
O(1)—Re—O(2)	91.4 (4)	O(1)—Re—O(3)	178.9 (5)	O(1)—Re—O(4)	89.6 (4)
O(2)—Re—O(3)	89.3 (4)	O(2)—Re—O(4)	179.0 (4)	O(3)—Re—O(4)	89.8 (4)
Re—O(1)—C(1)	125 (1)	Re—O(2)—C(3)	126 (1)	Re—O(3)—C(6)	127 (1)
Re—O(4)—C(8)	127 (1)	O(1)—C(1)—C(4)	115 (2)	O(1)—C(1)—C(2)	127 (1)
C(4)—C(1)—C(2)	118 (2)	C(1)—C(2)—C(3)	124 (2)	C(2)—C(3)—C(5)	120 (2)
C(2)—C(3)—O(2)	127 (2)	C(5)—C(3)—O(2)	113 (1)	O(3)—C(6)—C(9)	115 (1)
O(3)—C(6)—C(7)	124 (1)	C(9)—C(6)—C(7)	121 (1)	C(6)—C(7)—C(8)	128 (2)
C(7)—C(8)—C(10)	120 (2)	C(7)—C(8)—O(4)	124 (2)	C(10)—C(8)—O(4)	116 (1)
C(11)—As—C(21)	108.1 (7)	C(11)—As—C(31)	106.6 (7)	C(11)—As—C(41)	110.1 (7)
C(21)—As—C(31)	116.5 (7)	C(21)—As—C(41)	107.4 (7)	C(31)—As—C(41)	108.1 (7)

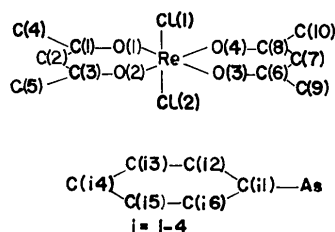


Fig. 1. The numbering of the atoms in the cation and anion.

addition of the electron to *trans*-Re(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> is a lengthening of the Re—Cl bonds. Thus the electron must be added to an orbital which is antibonding for the Cl—Re—Cl system.

Results from best least-squares-planes calculations for the acetylacetonate rings are shown in Table 3. The rings are planar although Re and C(4) are significantly out of the plane in the opposite direction to C(5) in one ring and Re and C(9) are out of the plane in opposite directions in the other. The tetraphenylarsonium ion is normal. The phenyl rings are planar and the As atom lies outside the plane of the rings in two cases. The As—C(*i*1) distances [1.36 (2)—1.93 (2) Å] and C—C distances within the rings [1.37 (3)—1.45 (2) Å], As—C(*i*1)—C(*i*2) and As—C(*i*1)—C(*i*6) angles [118 (1)—121 (1)°], and C—C—C angles [117 (2)—124 (1)°] are consistent with values observed previously (Kennard, Allen & Watson, 1977).

A problem remains as to why the two Re—Cl bonds, which should be chemically identical, differ significantly in length. The only apparent reason lies in the packing of the ions in the unit cell. This is shown in Fig. 2. The structure comprises rippled layers of anions at 0 and  $\frac{1}{2}$  along **b** separated by rippled layers of cations at  $\frac{1}{4}$  and  $\frac{3}{4}$  along **b**. Cl(2) is arranged so that it points into the anion layer lying close to C(6) (3.82 Å), C(7) (4.05 Å) and C(8) (3.79 Å) of the centrosymmetrically related anion, although Cl(2) is also close to one atom of an interleaved phenyl [C(35), 3.31 Å]. Cl(1) is arranged so that it interacts with the C(*i*1) and C(*i*4) (*i* = 1–6) rings of a tetraphenylarsonium cation [C(15), 3.80; C(16), 4.42; C(14), 4.52; C(44), 3.58; C(45), 3.55; C(46), 4.58 Å].

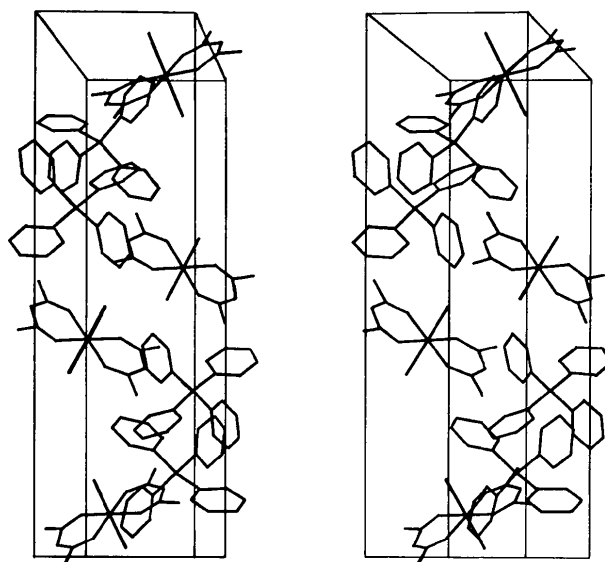


Fig. 2. Stereogram (stereoscopic pair of perspective projections) of the contents of the unit cell. **a** and **b** are parallel to the top and side of the page, respectively, and the view is down **c**\*.

The attractive interaction between a Cl atom, which, as is shown above, is likely to have at least some excess negative charge, and a cation will be much greater than that between a Cl atom and an anion. The bond-valence concept of Brown & Shannon (1973) predicts that the stronger Cl(1)—cation interaction will result in a weaker (and thus longer) Re—Cl(1) bond and the weaker Cl(2)—anion interaction will result in a stronger (and shorter) Re—Cl(1) bond, as is observed.

There are no significant features in the remainder of the packing. No two rings are arranged in parallel contact in order to maximize  $\pi$ -cloud interactions, as we have observed before (Lock & Turner, 1978). The closest approach of this type is between the O(3)—O(4) acetylacetonate ring and the C(3*i*) phenyl ring, but even here the dihedral angle is 24.5° and the closest approach is C(8)—C(34), 3.94 Å.

We thank the National Research Council of Canada for financial support.

### References

- BROWN, I. D., LOCK, C. J. L. & WAN, C. (1973). *Can. J. Chem.* **51**, 2073–2076.  
 BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* **A29**, 266–282.  
 COURRIER, W. D. (1971). PhD Thesis, McMaster Univ., Hamilton, Canada.  
 CROMER, D. T. (1974). *International Tables for X-ray Crystallography*. Vol. IV, Table 2.3.1, pp. 149–150. Birmingham: Kynoch Press.  
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*. Vol. IV, Table 2.2A, pp. 72 ff. Birmingham: Kynoch Press.

Table 3. *Least-squares planes through selected atoms and distances (Å) of atoms from these planes*

Plane 1: Re\* O(1)O(2)C(1)C(2)C(3)C(4)\*C(5)\*  
 Re, 0.13; O(1), 0.00; O(2), 0.01; C(1), -0.01; C(2), 0.02; C(3), -0.02; C(4), 0.08; C(5), -0.10

Plane 2: Re\* O(3)O(4)C(6)C(7)C(8)C(9)\*C(10)\*  
 Re, 0.09; O(3), 0.01; O(4), 0.00; C(6), -0.01; C(7), 0.00; C(8), 0.00; C(9), -0.12; C(10), -0.01

\* These atoms were given no weight in calculating the planes. All other atoms were given unit weight,  $\sigma = 0.02$  Å.

KENNARD, O., ALLEN, F. H. & WATSON, D. G. (1977). Editors. *Molecular Structures and Dimensions. Guide to the Literature 1935–76. Organic and Organometallic Crystal Structures*, p. OC 25. Utrecht: Bohn, Scheltema & Holkema.

LOCK, C. J. L., MURPHY, C. N. & TURNER, M. L. (1979). *Can. J. Chem.* To be submitted.

LOCK, C. J. L. & TURNER, G. (1978). *Can. J. Chem.* **56**, 179–188.

*Acta Cryst.* (1979). **B35**, 954–957

## $\eta$ -Cyclopentadienylcarbonylbis(diphenylphosphino)methaneiron Tetraphenylborate

BY ROBIN B. ENGLISH AND MARGOT M. DE V. STEYN

*Department of Chemistry, University of South Africa, PO Box 392, Pretoria, South Africa*

(Received 27 November 1978; accepted 19 December 1978)

**Abstract.** [Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO){[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Pl<sub>2</sub>CH<sub>2</sub>]}]B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, C<sub>31</sub>H<sub>27</sub>FeOP<sub>2</sub>·C<sub>24</sub>H<sub>20</sub>B<sup>-</sup>, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 20.503 (5), *b* = 15.937 (5), *c* = 13.724 (5) Å, *D*<sub>c</sub> = 1.26 Mg m<sup>-3</sup> for *Z* = 4. An approximate mirror plane bisects the cation. A correlation was shown to exist between Fe–C length and C–O stretching frequency of a number of {Fe(cp)(CO)XY} complexes, including the title compound.

**Introduction.** Attempts to prepare the binuclear Fe complex [Fe(cp)(CO)<sub>2</sub>(SC<sub>2</sub>H<sub>5</sub>)(dppm)]B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> [dppm = bis(diphenylphosphino)methane; cp =  $\eta$ -C<sub>5</sub>H<sub>5</sub>] by refluxing [Fe<sub>2</sub>(cp)<sub>2</sub>(CO)<sub>3</sub>(SC<sub>2</sub>H<sub>5</sub>)]B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> (English, Haines & Nolte, 1975; English, Nassimbeni & Philpott, 1978) with dppm in acetone led to the formation of glossy yellow needles of the title complex. A crystal, 0.07 × 0.07 × 0.15 mm, was used for data collection. Intensities were measured on a four-circle Philips PW1100 diffractometer with graphite-monochromated Mo *K*α radiation ( $\lambda$  = 0.7107 Å) and the  $\omega$ -2 $\theta$  scan mode. 2387 independent reflections were collected of which 1294 unique observed [*I* ±  $\sigma$ (*I*)] reflections were employed in the analysis. No crystal decomposition was observed. Lorentz–polarization but no absorption corrections were applied.

The position of the Fe atom was found from a Patterson map. Peaks corresponding to the two P atoms were present in a difference synthesis based on the Fe atom. Subsequent isotropic refinement followed by difference syntheses revealed the positions of the remaining non-hydrogen atoms; phenyl and cyclopentadienyl rings were treated as rigid perfect polygons with C–C = 1.395 and 1.42 Å respectively (Sheldrick, 1978). Refinement continued with blocked-matrix (two blocks, for the cation and anion, refining in alternate

cycles) least-squares calculations with Fe, P, O and B anisotropic, to an *R* of 0.18.

In the final blocked-matrix refinement, H atom positions were calculated with C–H = 1.080 Å, and geometric constraints were removed from the ring C atoms. Phenyl C atoms were refined isotropically, as were C(1), R5C(2) and R5C(3): attempts to refine these latter three atoms anisotropically resulted in non-positive-definite temperature-factor-matrix determinants. *R* fell to its final value of 0.079 and *R*<sub>w</sub> was 0.059 with a weighting scheme  $w = 1.6397/\sigma^2 F$ .

The final *R* values did not distinguish between the two possible enantiomorphs: *R*<sub>G</sub> (Sheldrick, 1978) for the coordinates given = 0.0528; *R*<sub>G</sub> for the enantiomorph = 0.0542.

The isotropic temperature factors of the H atoms of the phenyl groups bound to the P and B atoms, the cyclopentadienyl group and methylene group were refined as three single variables and converged to *U* = 0.15 (2), 0.03 (2) and 0.07 (5) Å<sup>2</sup> respectively. No peak >0.4 e Å<sup>-3</sup> appeared in a difference map based on all atoms and the average shift/error in the last two cycles was in no case >0.1. Scattering factors and anomalous-dispersion corrections were from *International Tables for X-ray Crystallography* (1974). Final positional parameters for the non-hydrogen atoms are given in Table 1.\* Fig. 1 shows the structure of the cation and the atomic labelling, and Fig. 2 is a stereo pair depicting the somewhat complex packing in this structure, projected on to (001). Tables 2 and 3 list some bond lengths and angles.

\* Lists of structure factors, anisotropic and isotropic thermal parameters and H atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34160 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.