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Structure of Bis(tetraethylammonium) Hexanitratouranium(IV)

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Abstract. $[U(NO_3)_6][N(C_2H_5)_4]_2$, $M_r = 870{\cdot}57$, monoclinic, $C2/c$, $a = 18{\cdot}329\,(5)$, $b = 11{\cdot}603\,(3)$, $c = 15{\cdot}629\,(5)$ Å, $\beta = 108{\cdot}13\,(3)°$, $V = 3158{\cdot}9\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}830$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu = 4{\cdot}9526$ mm^{-1}, $F(000) = 1712$, $T = 295\,(1)$ K, $R = 0{\cdot}046$ for 1697 observed reflections. The U atom is twelve-coordinated by O atoms which belong to six nitrate ions. All the nitrate groups are disordered with two positions for each of the bonding oxygens. The coordination polyhedron around the U is an irregular icosahedron. The U—O coordination distances range from 2·43 (2) to 2·56 (1) Å. The connection between the $[U(NO_3)_6]^{2-}$ anions and the $[N(CH_2CH_3)_4]^+$ cations is realized through hydrogen bonds.

Introduction. Nitrato complexes of actinide elements are known to play an important role in the separation chemistry of these elements. They usually exhibit high coordination numbers. While several crystallographic investigations of nitratothorium(IV) complexes are reported in the literature (Scavnicar & Prodic, 1965; Taylor, Mueller & Hitterman, 1966; Veki, Zalkin & Templeton, 1966; Alcock, Esperas, Bagnall & Hsian-Yun, 1978; English, Du Preez, Nassimbeni & Van Vuuren, 1979; Khan, Kumar & Tuck, 1984), no structural information is available on any nitratouranium(IV) complex.

Experimental. The title complex was prepared by reaction of well dried tetraethylammonium chloride with uranium tetrachloride and silver nitrate in dried acetone under argon atmosphere:

$$UCl_4 + 2(C_2H_5)_4NCl + 6AgNO_3 \rightarrow [(C_2H_5)_4N]_2U(NO_3)_6 + 6AgCl\downarrow.$$

After filtration of the AgCl precipitate, the solution was concentrated by distillation of the acetone and cooled by liquid nitrogen. The green crystalline residue was re-extracted several times from dried acetone. Single crystals suitable for X-ray investigation were grown by slow cooling of a saturated acetone solution. The purity of the crystals was checked by infrared and electron absorption spectroscopy techniques. Since the crystals are sensitive towards oxygen and moisture, they were sealed in thin-walled glass capillaries under nitrogen.

The specimen selected for measurements was 0·25 × 0·25 × 0·20 mm. Intensity data recorded on an Enraf–Nonius CAD-4 X-ray diffractometer, graphite-monochromated Mo $K\bar{\alpha}$ radiation. Cell parameters refined by least squares from angle data of 25 reflections ($11 < \theta < 18°$). Systematic absences consistent with space groups Cc and $C2/c$. 2453 unique reflections [$I > 1\sigma(I)$] measured (θ–2θ scan mode) in range $3 \le 2\theta \le 45°$. Intensities of three standard reflections measured at 30 min intervals, anisotropic decay correction applied (total decay 11·4%). Intensities corrected for Lorentz–polarization effects; empirical absorption corrections (relative transmission factors 76·15 to 99·25%). Structure solved by direct methods and Fourier techniques that established unequivocally space group $C2/c$. Full-matrix least-squares refinement minimizing $\sum(\Delta F)^2$. Last cycles of refinement with $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = \sigma(F_o)^2/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (PI)^2]^{1/2}/\mathrm{Lp}$, P (ignorance factor used to downweight intense reflections) = 0·07, on 1697 independent reflections with $F^2 \ge 3\sigma(F^2)$, index range $h\,0/+21$, $k\,0/+13$, $l\,-18/+16$. Anisotropic thermal parameters. H atoms not included. A secondary-extinction coefficient refined to $g = 2{\cdot}94 \times 10^{-7}\{F_c = F_c/[1 + g(F_c)^2\mathrm{Lp}]\}$. $R = 0{\cdot}046$,

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Table 1. *Atomic positional and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

	x	y	z	B_{eq}
U	0·250	0·250	0·500	3·83 (1)
N(1)	0·3101 (5)	0·0376 (7)	0·5979 (6)	5·6 (2)
O(11)	0·3362 (5)	−0·0543 (7)	0·6375 (6)	8·2 (3)
O(12)	0·2505 (7)	0·036 (1)	0·5335 (9)	4·0 (3)
O(13)	0·3417 (5)	0·1347 (9)	0·6223 (7)	3·2 (2)
O(14)	0·259 (1)	0·108 (1)	0·617 (1)	8·3 (5)
O(15)	0·3364 (8)	0·078 (1)	0·531 (1)	7·3 (5)
N(2)	0·3740 (4)	0·3805 (7)	0·6244 (6)	5·3 (2)
O(21)	0·4227 (4)	0·4386 (8)	0·6789 (6)	8·0 (3)
O(22)	0·3782 (6)	0·341 (1)	0·5553 (7)	3·6 (3)
O(23)	0·3122 (5)	0·3654 (9)	0·6399 (7)	3·3 (2)
O(24)	0·3238 (8)	0·430 (1)	0·557 (1)	7·2 (5)
O(25)	0·369 (1)	0·264 (1)	0·631 (2)	9·6 (7)
N(3)	0·3487 (5)	0·2128 (8)	0·3846 (7)	5·1 (2)
O(31)	0·3855 (5)	0·1999 (9)	0·3337 (6)	7·2 (2)
O(32)	0·3519 (6)	0·1423 (9)	0·4498 (8)	3·6 (3)
O(33)	0·3022 (6)	0·301 (1)	0·3733 (8)	3·5 (2)
O(34)	0·370 (1)	0·269 (1)	0·457 (1)	6·5 (5)
O(35)	0·2804 (9)	0·167 (1)	0·371 (1)	8·7 (5)
N(4)	0·3885 (5)	−0·2362 (5)	0·4167 (7)	4·5 (2)
C(1)	0·362 (1)	−0·260 (1)	0·501 (1)	9·9 (6)
C(2)	0·4266 (8)	−0·297 (1)	0·588 (1)	8·3 (4)
C(3)	0·4334 (7)	−0·132 (1)	0·430 (1)	10·0 (5)
C(4)	0·4573 (8)	−0·089 (1)	0·3558 (9)	8·7 (4)
C(5)	0·315 (1)	−0·234 (1)	0·336 (1)	10·6 (6)
C(6)	0·2631 (7)	−0·124 (1)	0·3405 (9)	8·0 (4)
C(7)	0·4338 (9)	−0·346 (1)	0·398 (1)	9·8 (5)
C(8)	0·3968 (7)	−0·4588 (9)	0·3871 (9)	7·6 (3)

$wR = 0{\cdot}063$, $S = 1{\cdot}75$. Final $(\Delta/\sigma)_{max} < 0{\cdot}01$. Maximum and minimum heights in final difference Fourier map +0·7 and −0·8 e Å^{-3}. Atomic scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1983) *SDP* programs.

Attempts to refine an ordered model failed in both space groups *C*2/*c* and *Cc*. In each case high residual positive peaks appeared between neighbouring oxygens and anisotropic refinement of oxygen atoms in ordered positions led to non-positive-definite values of thermal parameters. The *R* agreement factor remained higher than 18%.

Discussion. Table 1* contains final atomic positional parameters for the non-H atoms. Selected intramolecular distances and angles are listed in Table 2. The structure is illustrated in Figs. 1, 2 and 3. In the $[U(NO_3)_6]^{2-}$ anion, the U atom is surrounded by 12 O atoms which belong to six bidentate nitrate ligands. Because of the centrosymmetrical position [(*d*)] of the uranium, there are three pairs of centrosymmetrically related nitrate ions. These appear disordered with

Table 2. *Intramolecular distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Symmetry code (i) $-x+0{\cdot}5$, $-y-0{\cdot}5$, $-z+1$.

(*a*) The $[U(NO_3)_6]^{2-}$ anion with polyhedron orientation *A* (*cf.* Fig. 2)

U—O(12)	2·54 (1)	U—O(23)	2·51 (1)
U—O(13)	2·50 (1)	U—O(32)	2·56 (1)
U—O(22)	2·47 (1)	U—O(33)	2·52 (1)
O(11)···O(12)	2·15 (1)	O(13)···O(33^{i})	2·74 (2)
O(11)···O(13)	2·21 (1)	O(13)···O(22)	2·77 (2)
O(21)···O(22)	2·17 (1)	O(13)···O(23)	2·76 (2)
O(21)···O(23)	2·10 (1)	O(13)···O(33^{i})	2·76 (2)
O(31)···O(32)	2·20 (1)	O(22)···O(23)	2·07 (2)
O(31)···O(33)	2·17 (1)	O(22)···O(32)	2·79 (2)
O(12)···O(13)	2·14 (2)	O(22)···O(33)	2·79 (1)
O(12)···O(22^{i})	2·74 (2)	O(23)···O(32^{i})	2·90 (2)
O(12)···O(23^{i})	2·83 (2)	O(23)···O(33^{i})	2·81 (2)
O(12)···O(32)	2·86 (2)	O(32)···O(33)	2·23 (2)
N(1)—O(11)	1·25 (1)	N(2)—O(23)	1·24 (1)
N(1)—O(12)	1·23 (2)	N(3)—O(31)	1·20 (1)
N(1)—O(13)	1·27 (1)	N(3)—O(32)	1·29 (1)
N(2)—O(21)	1·23 (1)	N(3)—O(33)	1·31 (2)
N(2)—O(22)	1·20 (1)		

O(12)—U—O(13)	50·3 (4)	O(13)—U—O(32^{i})	114·0 (4)
O(12)—U—O(13^{i})	129·7 (4)	O(13)—U—O(33)	113·4 (4)
O(12)—U—O(22)	113·8 (4)	O(13)—U—O(33^{i})	66·7 (4)
O(12)—U—O(22^{i})	66·2 (4)	O(22)—U—O(23)	49·1 (4)
O(12)—U—O(23)	111·7 (4)	O(22)—U—O(23^{i})	131·0 (4)
O(12)—U—O(23^{i})	68·3 (4)	O(22)—U—O(32)	67·1 (4)
O(12)—U—O(32)	68·3 (4)	O(22)—U—O(32^{i})	112·8 (4)
O(12)—U—O(32^{i})	111·7 (4)	O(22)—U—O(33)	67·8 (4)
O(12)—U—O(33)	114·6 (4)	O(22)—U—O(33^{i})	112·1 (4)
O(12)—U—O(33^{i})	65·6 (4)	O(23)—U—O(32)	110·4 (4)
O(13)—U—O(22)	67·7 (4)	O(23)—U—O(32^{i})	69·6 (4)
O(13)—U—O(22^{i})	112·2 (4)	O(23)—U—O(33)	112·1 (4)
O(13)—U—O(23)	66·8 (4)	O(23)—U—O(33^{i})	67·8 (4)
O(13)—U—O(23^{i})	113·2 (4)	O(32)—U—O(33)	52·1 (4)
O(13)—U—O(32)	66·0 (4)	O(32)—U—O(33^{i})	128·0 (4)

(*b*) The $[U(NO_3)_6]^{2-}$ anion with polyhedron orientation *B* (*cf.* Fig. 2)

U—O(14)	2·43 (2)	U—O(25)	2·49 (2)
U—O(15)	2·50 (1)	U—O(34)	2·51 (2)
U—O(24)	2·49 (2)	U—O(35)	2·45 (2)
O(11)···O(14)	2·32 (2)	O(15)···O(24^{i})	2·83 (2)
O(11)···O(15)	2·27 (2)	O(15)···O(25)	2·62 (2)
O(21)···O(24)	2·18 (2)	O(15)···O(34)	2·66 (2)
O(21)···O(25)	2·28 (2)	O(15)···O(35)	2·60 (3)
O(31)···O(34)	2·18 (2)	O(24)···O(25)	2·27 (3)
O(31)···O(35)	2·21 (2)	O(24)···O(34)	2·74 (2)
O(14)···O(15)	2·27 (3)	O(24)···O(35^{i})	2·74 (2)
O(14)···O(24^{i})	2·71 (3)	O(25)···O(34)	2·74 (3)
O(14)···O(25)	2·66 (3)	O(25)···O(35^{i})	2·84 (3)
O(14)···O(34^{i})	2·70 (3)	O(34)···O(35)	2·13 (2)
O(14)···O(35^{i})	2·73 (3)		
N(1)—O(14)	1·35 (2)	N(2)—O(25)	1·36 (3)
N(1)—O(15)	1·36 (3)	N(3)—O(34)	1·25 (2)
N(2)—O(24)	1·29 (2)	N(3)—O(35)	1·32 (2)

O(14)—U—O(15)	54·8 (7)	O(15)—U—O(34^{i})	115·8 (5)
O(14)—U—O(15^{i})	125·3 (7)	O(15)—U—O(35)	63·4 (6)
O(14)—U—O(24)	113·1 (6)	O(15)—U—O(35^{i})	116·6 (6)
O(14)—U—O(24^{i})	69·7 (6)	O(24)—U—O(25)	54·1 (7)
O(14)—U—O(25)	65·4 (7)	O(24)—U—O(25^{i})	130·1 (7)
O(14)—U—O(25^{i})	114·3 (7)	O(24)—U—O(34)	66·4 (5)
O(14)—U—O(34)	113·8 (6)	O(24)—U—O(34^{i})	115·8 (5)
O(14)—U—O(34^{i})	66·3 (6)	O(24)—U—O(35)	112·8 (6)
O(14)—U—O(35)	112·1 (5)	O(24)—U—O(35^{i})	68·0 (6)
O(14)—U—O(35^{i})	68·1 (5)	O(25)—U—O(34)	66·5 (7)
O(15)—U—O(24)	111·0 (6)	O(25)—U—O(34^{i})	113·8 (7)
O(15)—U—O(24^{i})	73·3 (6)	O(25)—U—O(35)	109·9 (6)
O(15)—U—O(25)	63·5 (6)	O(25)—U—O(35^{i})	70·3 (6)
O(15)—U—O(25^{i})	116·6 (6)	O(34)—U—O(35)	50·8 (5)
O(15)—U—O(34)	64·2 (5)	O(34)—U—O(35$_{i}$)	129·1 (5)

(*c*) The $[N(C_2H_5)_4]^+$ cation

N(4)—C(1)	1·55 (2)	C(1)—C(2)	1·56 (2)
N(4)—C(3)	1·44 (1)	C(3)—C(4)	1·45 (2)
N(4)—C(5)	1·53 (2)	C(5)—C(6)	1·61 (2)
N(4)—C(7)	1·59 (2)	C(7)—C(8)	1·46 (2)

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* Lists of structure amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51221 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (*cont.*)

(*d*) O···O forbidden contacts

O(12)···O(14)	1·52 (2)	O(22)···O(34)	1·72 (2)
O(12)···O(15)	1·66 (2)	O(23)···O(24)	1·56 (3)
O(13)···O(14)	1·52 (2)	O(23)···O(25)	1·60 (2)
O(13)···O(15)	1·55 (2)	O(32)···O(34)	1·50 (2)
O(13)···O(25)	1·57 (3)	O(32)···O(35)	1·52 (2)
O(15)···O(32)	1·57 (3)	O(33)···O(34)	1·54 (2)
O(22)···O(24)	1·44 (2)	O(33)···O(35)	1·61 (2)
O(22)···O(25)	1·54 (3)		

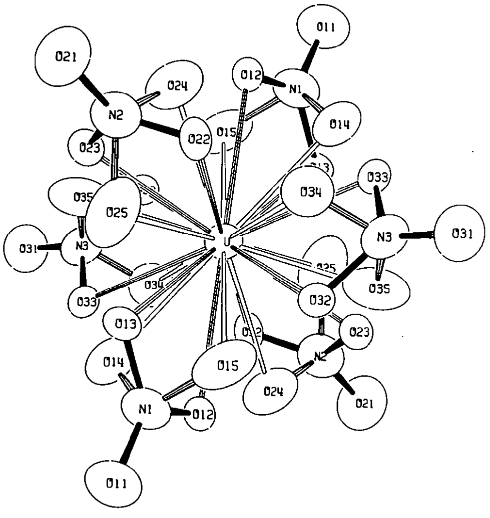
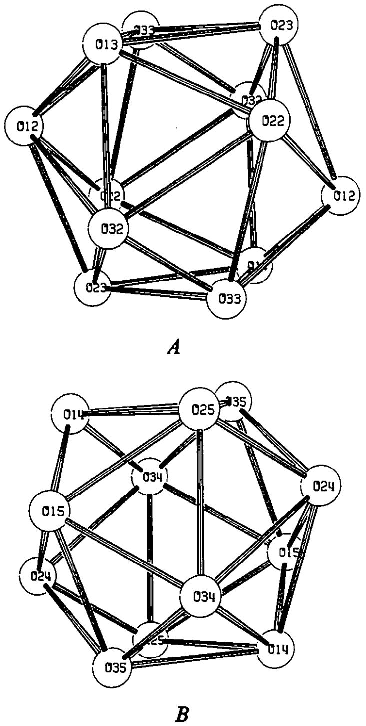


Fig. 1. Structure of the $[U(NO_3)_6]^{2-}$ anion.



A

B

Fig. 2. The 12-coordinate polyhedron about the U in its two possible orientations *A* and *B*.

two positions for each of the bonding oxygens [the bonding oxygens are numbered O(*i*2) to O(*i*5) for each nitrate ion, the non-bonding oxygens O(*i*1)] which correspond to two possible orientations for each nitrate ion [O(*i*2) and O(*i*3) or O(*i*4) and O(*i*5)]. Thus there would be theoretically eight possibilities for combining the nitrate ions in their different orientations on the coordination sphere of the U. However, examination of intramolecular O···O distances (Table 2) shows that some combinations are forbidden, leaving only two possibilities (*A* and *B* in Fig. 2); that corresponding, for all nitrate ions simultaneously, to the bonding oxygens O(*i*2) and O(*i*3) on the one hand, and that corresponding to the bonding oxygens O(*i*4) and O(*i*5) on the other hand. In each case the O atoms are at the corners of an irregular icosahedron, as illustrated in Fig. 2. A distorted icosahedral geometry is typical of most $M(L-L)_6$ type molecules. It has been previously observed and described for the following nitrato-complexes: $MgTh(NO_3)_6.8H_2O$ (Scavinar & Prodic, 1965), $[Th(NO_3)_3(PMe_3O)_4]_2[Th(NO_3)_6]$ (Alcock *et al.*, 1978), $[(C_{10}H_8N_2H)_3NO_3][Th(NO_3)_6]$ (Khan *et al.*, 1984), $(NH_4)_2Ce(NO_3)_6$ (Beineke & Delgaudio, 1968). The icosahedron can be considered as a bicapped pentagonal antiprism, the two capping atoms subtending an angle of 180° at the metal (Drew, 1977). The O···O edge lengths are reported in Table 2. They vary between 2·07 (2) and 2·90 (2) Å. Likewise there are significant differences in the U—O bond distances, the average value being 2·49 (1) Å (Table 2). The distortions within the UO_{12} icosahedron are also reflected by the O—U—O angles which vary from 49·1 (4) to 131·0 (4)° (Table 2). In a regular icosahedron, the O—U—O angles involving a particular

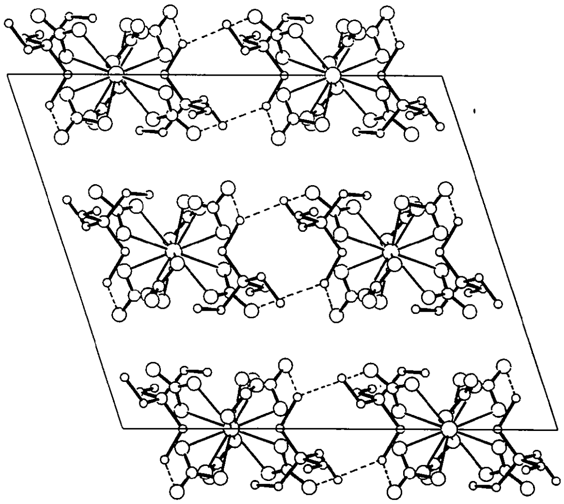


Fig. 3. Crystal packing of $[U(NO_3)_6][N(C_2H_5)_4]_2$. For clarity the coordination polyhedra are represented only in their orientation *B* (*cf.* Fig. 2). Projection is along **b**. **a** is horizontal from left to right.

Table 3. *Non-bonded interionic distances* (Å) *corresponding to probable hydrogen bonds and corresponding angles* (°)

O(12)···C(8^{i})	3·42 (2)	O(31)···C(2^{iii})	3·47 (2)
O(21)···C(2^{ii})	3·39 (2)		
N(1)–O(12)···C(8^{i})	108 (1)	O(12)···C(8^{i})–C(7^{i})	126 (1)
N(2)–O(21)···C(2^{ii})	108 (1)	O(21)···C(2^{ii})–C(1^{ii})	120 (1)
N(3)–O(31)···C(2^{iii})	115 (1)		

Symmetry code (i) $-x+0{\cdot}5,-y-0{\cdot}5,-z+1$; (ii) $x,y+1,z$; (iii) $-x+1,-y,-z+1$.

oxygen would be 63·5 (five such angles), 116·5 (five such) and 180° (one such). In the nitrate groups (planar within the limits of e.s.d.'s) a number of oxygens exhibit large anisotropic thermal motions. This would explain the differences observed among N—O bond lengths and O—N—O angles.

The tetraethylammonium cation has the expected tetrahedral geometry. The large thermal vibrations of the C atoms are probably responsible for the differences between some interatomic distances and angles (Table 2). The crystal packing is illustrated in Fig. 3. Interionic distances and angles (Table 3) show that the connection between the $[U(NO_3)_6]^{2-}$ anions and the $[N(CH_2CH_3)_4]^{+}$ cations is realized through hydrogen bonds between nitrate oxygens and methyl carbons.

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Octacarbonyl-bis(μ-diphenylphosphido)-dirhenium and Heptacarbonyl-μ-diphenylantimonido-μ-diphenylphosphido-triphenylstibinedirhenium

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Abstract. $[Re_2(CO)_8\{P(C_6H_5)_2\}_2]$, $M_r = 966{\cdot}8$, monoclinic, $P2_1/n$, $a = 12{\cdot}183$ (5), $b = 16{\cdot}803$ (6), $c = 15{\cdot}707$ (5) Å, $\beta = 99{\cdot}99$ (4)°, $V = 3167$ (2) Å^3, $Z = 4$, $D_x = 2{\cdot}026$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 74{\cdot}5$ cm^{-1}, $F(000) = 1824$, $T = 298$ (1) K, final $R = 0{\cdot}0407$ for 2895 unique observed reflections. $[Re_2(CO)_7\{P(C_6H_5)_2\}\{Sb(C_6H_5)_2\}\{Sb(C_6H_5)_3\}]$, $M_r = 1382{\cdot}7$, triclinic, $P\bar{1}$, $a = 11{\cdot}093$ (4), $b = 13{\cdot}352$ (5), $c = 17{\cdot}466$ (6) Å, $\alpha = 86{\cdot}50$ (3), $\beta = 75{\cdot}55$ (3), $\gamma = 67{\cdot}36$ (3)°, $V = 2310$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}987$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 65{\cdot}1$ cm^{-1}, $F(000) = 1304$, $T = 298$ (1) K, $R = 0{\cdot}0626$ for 4979 unique observed reflections. Each compound contains an edge-shared coordination octahedra pair with a nearly planar four-membered ring. The isovalent exchange of one bridging ring member enlarges the subtended bond angle of the remaining μ-P atom by about 7·8 (1)°. The mean value of the Re—(μ-Sb) bond length is 2·740 (1) Å and the terminal Re—Sb bond 2·671 (1) Å.

Introduction. The structures of the diamagnetic title compounds can be related to those of the A_2X_{10} class of molecules (A = metal atom, X = ligand) (Wells, 1984). Each of these dirhenium substances contains an edge-shared coordination octahedra pair with a heteronuclear four-membered $A_2(\mu\text{-}X)_2$ ring without a metal—metal bond. The structural parameters determined for the $Re_2(\mu\text{-}PPh_2)_2$ and $Re_2(\mu\text{-}PPh_2)(\mu\text{-}SbPh_2)$ rings are relevant to the study of the ring-bond-angle dependency on the isovalent exchange of one ring member. Furthermore, the present structural determination has

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