

Table 2. Bond lengths (Å) and angles (°)

Re(1)–P(1)	2.481 (4)	O(1)–Re(1)–C(3)	171.9 (5)
Re(1)–O(1)	2.174 (9)	O(1)–Re(1)–C(4)	87.4 (6)
Re(1)–C(2)	1.951 (15)	O(1)–Re(1)–C(51)	74.4 (4)
Re(1)–C(3)	1.952 (15)	C(2)–Re(1)–C(3)	94.1 (7)
Re(1)–C(4)	1.938 (18)	C(2)–Re(1)–C(4)	89.8 (7)
Re(1)–C(51)	2.199 (10)	C(2)–Re(1)–C(51)	167.9 (5)
P(1)–C(11)	1.843 (11)	C(3)–Re(1)–C(4)	90.2 (7)
P(1)–C(21)	1.829 (12)	C(3)–Re(1)–C(51)	97.8 (5)
P(1)–C(31)	1.838 (9)	C(4)–Re(1)–C(51)	87.4 (6)
C(1)–O(1)	1.240 (17)	Re(1)–O(1)–C(1)	117.7 (9)
C(1)–C(41)	1.497 (17)	Re(1)–C(2)–O(2)	176.6 (14)
C(1)–C(52)	1.427 (17)	Re(1)–C(3)–O(3)	174.2 (15)
C(2)–O(2)	1.134 (20)	Re(1)–C(4)–O(4)	173.1 (18)
C(3)–O(3)	1.130 (21)	Re(1)–C(51)–C(52)	112.6 (7)
C(4)–O(4)	1.134 (25)	Re(1)–C(51)–C(56)	127.3 (8)
		O(1)–C(1)–C(52)	119.1 (12)
Re(1)–P(1)–C(11)	117.7 (4)	O(1)–C(1)–C(41)	116.7 (11)
Re(1)–P(1)–C(21)	116.7 (4)	C(41)–C(1)–C(52)	124.1 (11)
Re(1)–P(1)–C(31)	110.0 (3)	C(1)–C(52)–C(51)	115.7 (10)
C(11)–P(1)–C(21)	101.1 (5)	C(1)–C(52)–C(53)	124.2 (10)
C(11)–P(1)–C(31)	107.6 (5)	P(1)–C(11)–C(12)	120.0 (9)
C(21)–P(1)–C(31)	102.2 (5)	P(1)–C(11)–C(16)	119.9 (9)
P(1)–Re(1)–O(1)	89.8 (3)	P(1)–C(21)–C(22)	119.4 (8)
P(1)–Re(1)–C(2)	91.9 (5)	P(1)–C(21)–C(26)	120.1 (8)
P(1)–Re(1)–C(3)	92.4 (5)	P(1)–C(31)–C(32)	116.5 (7)
P(1)–Re(1)–C(4)	176.8 (6)	P(1)–C(31)–C(36)	123.5 (7)
P(1)–Re(1)–C(51)	90.4 (3)	C(1)–C(41)–C(42)	118.9 (10)
O(1)–Re(1)–C(2)	93.6 (5)	C(1)–C(41)–C(46)	120.8 (10)

atomic coordinates, bond distances and angles are given in Tables 1 and 2.

Of special interest in the molecule is the heterocyclic five-membered ring containing Re(1), O(1), C(1), C(52) and C(51), the geometry of which, apart from the angle at the metal atom, agrees with the corresponding ring in $[\text{Mn}(\text{CH}_3\text{COC}_6\text{H}_4)(\text{CO})_4]$ (Knobler, Crawford & Kaesz, 1975): C–Mn–O 79.4 (1), C(51)–Re(1)–O(1) 74.4 (4)°. The maximum distance of the atoms of the five-membered ring from the least-squares plane of the phenyl ring, atoms C(51) to C(56), is 0.125 (1) Å.

The coordination around the Re atom is a distorted octahedron. Each of the three CO ligands at the Re atom is *trans* to a different atom.

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Dichlorooxobis(triphenylphosphine oxide)vanadium(IV)

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Abstract. $\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{O}_3\text{P}_2\text{V}$, $[\text{V}(\text{C}_{18}\text{H}_{15}\text{OP})_2\text{Cl}_2\text{O}]$, monoclinic, $P2_1/c$, $a = 17.19$ (1), $b = 18.34$ (1), $c = 11.15$ (1) Å, $\beta = 98.67$ (5)°, $V = 3473.3$ Å³, $M_r = 694.4$, $Z = 4$, $D_c = 1.328$, $D_m = 1.33$ Mg m⁻³ (by flotation); $\mu(\text{Mo } K\alpha) = 0.51$ mm⁻¹. The V atom is pentacoordinate with the triphenylphosphine oxide ligands in a *trans* arrangement; the O atoms from these ligands and two Cl atoms comprise the base of a square pyramid which is completed by an apical double-bonded O atom.

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Introduction. Complexes of oxovanadium(IV) have been studied extensively (Kepert, 1972) and, in particular, complexes of the type $\text{VOCl}_2 \cdot 2L$ (du Preez & Gibson, 1970). However, despite the large number of compounds studied, not much reliable spectroscopic information has become available which is of use for making stereochemical predictions by comparison with compounds of known structure. Usually only infrared measurements are reported, and assignments on the basis of these alone are only tentative. In an investigation of the vibrational spectra of some oxovanadium(IV) complexes (Gellatly & Cairn, 1979), a strong band at 384 cm⁻¹ in the infrared spectrum of

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$\text{VOCl}_2 \cdot (\text{tppo})_2$ (tppo = triphenylphosphine oxide) was assigned to a V-Cl stretch. Other workers (Cave, Dixon & Seddon, 1978) have assigned this stretching frequency to an asymmetric mode on the assumption of a *trans* square-pyramidal arrangement around the V atom. On the other hand, the Raman spectrum (Gellatly & Cairns, 1979) shows no strong shift that can confidently be assigned to the corresponding symmetric mode; the stereochemistry of the complex has thus remained uncertain. The X-ray analysis shows that a *trans* square-pyramidal arrangement is adopted.

Green-blue crystals of the title compound were prepared as described by du Preez & Gibson (1970) and single crystals obtained from methyl cyanide. The space group $P2_1/c$ was deduced from systematic absences ($h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$) on Weissenberg and precession photographs taken with $\text{Cu } K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$.

With a crystal $0.24 \times 0.28 \times 0.32 \text{ mm}$, cell dimensions were obtained by least squares from angular data on 25 high-order reflections measured on a Philips PW 1100 four-circle diffractometer (graphite-monochromated $\text{Mo } K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$). In the range $3 < \theta < 20^\circ$, 3341 reflection intensities were measured by the $\omega-2\theta$ technique (scan width $1.2^\circ \theta$, speed $0.04^\circ \theta \text{ s}^{-1}$); background counts on each side of the peak were recorded for half the peak scan time. The maximum deviation from the averages of the intensities of three reference reflections measured periodically during data collection was 3%. Refinement was based on 2207 observed data corrected for Lorentz and polarization effects; 138 of the data collected were systematically absent while a further 996 reflections with $I < 1.65\sigma(I)$ were eliminated. The large fraction of unobserved data is discussed below. Absorption corrections were not applied. The initial data set above referred to the following cell: $a = 19.03(1)$, $b = 18.34(1)$, $c = 11.15(1) \text{ \AA}$, $\beta = 116.72(5)^\circ$, this setting in $P2_1/c$ having been chosen on the basis of crystal morphology. An oscillation photograph taken about a showed relatively weak odd layer lines, implying approximate repetition of the structure along this direction with a period half that of a . This was confirmed by the presence of a vector peak at $\frac{1}{2}, 0, 0$ in the Patterson map, of height 0.6 times that of the origin. The Patterson map yielded several possible solutions for the V atom position, but trial electron-density syntheses based on some of these were unsuccessful. In retrospect, the ambiguities in the Patterson map were due to certain special structural features discussed below. Since the contribution of the V atom to the total scattering is fairly small, the use of direct methods was considered appropriate. The intensity bias in the remaining 2207 data was not treated by scaling, and the direct-methods procedure of *SHELX* (Sheldrick, 1977) was used in the automatic mode. Origin definition involved two reflections (413 and 241,

with $E = 2.664$ and 3.108 respectively), those (weak) reflections from parity groups with h odd not appearing in the list of reflections used in the sign-expansion process. All the non-hydrogen atoms were revealed in the first E map phased with 386 reflections. Refinement of the model proceeded satisfactorily. However, parameter interdependence was indicated by the presence of a large number of correlation-coefficient matrix elements exceeding 0.5, involving the x and z coordinates of individual atoms. The reflection data and the atomic coordinates were transformed to the setting of the reported cell (with $\beta = 98.67^\circ$) and the subsequently refined parameters were entirely free of correlation effects, confirming that the latter had been due to the larger β value. Limitations in

Table 1. Fractional coordinates ($\times 10^4$) with e.s.d.'s in parentheses for non-hydrogen atoms

	x	y	z
V	2420 (1)	5038 (1)	2007 (1)
Cl(1)	3607 (1)	4438 (1)	2508 (3)
Cl(2)	1410 (1)	5648 (1)	2716 (2)
O(1)	1958 (3)	4104 (3)	2503 (5)
O(2)	3018 (3)	5966 (3)	2277 (4)
O(3)	2192 (4)	5009 (3)	576 (4)
P(1)	1449 (1)	3600 (1)	3087 (2)
P(2)	3545 (1)	6501 (1)	1775 (2)
C(11)	1949 (5)	2759 (4)	3446 (8)
C(12)	2577 (5)	2576 (5)	2875 (8)
C(13)	2973 (6)	1928 (6)	3149 (10)
C(14)	2766 (7)	1465 (6)	4010 (10)
C(15)	2132 (8)	1643 (6)	4581 (9)
C(16)	1727 (7)	2289 (6)	4310 (8)
C(21)	1216 (6)	3946 (5)	4484 (8)
C(22)	1836 (8)	4173 (6)	5308 (11)
C(23)	1699 (11)	4435 (8)	6473 (14)
C(24)	956 (14)	4448 (9)	6711 (15)
C(25)	345 (11)	4232 (9)	5910 (17)
C(26)	458 (7)	3973 (6)	4750 (11)
C(31)	552 (5)	3429 (6)	2076 (8)
C(32)	225 (7)	4014 (6)	1392 (9)
C(33)	-451 (8)	3919 (9)	594 (12)
C(34)	-820 (7)	3244 (10)	463 (12)
C(35)	-497 (8)	2669 (8)	1117 (13)
C(36)	189 (6)	2757 (6)	1954 (10)
C(41)	3015 (5)	7334 (4)	1392 (7)
C(42)	2375 (6)	7489 (5)	1972 (8)
C(43)	1930 (6)	8114 (6)	1674 (9)
C(44)	2133 (7)	8576 (5)	793 (10)
C(45)	2760 (7)	8426 (6)	216 (9)
C(46)	3200 (6)	7809 (5)	511 (8)
C(51)	3885 (6)	6195 (4)	417 (7)
C(52)	3346 (6)	6073 (5)	-600 (9)
C(53)	3612 (7)	5798 (6)	-1655 (9)
C(54)	4394 (8)	5681 (5)	-1655 (10)
C(55)	4915 (7)	5808 (6)	-617 (12)
C(56)	4677 (7)	6073 (5)	408 (9)
C(61)	4389 (5)	6683 (5)	2890 (8)
C(62)	4638 (6)	6145 (6)	3708 (9)
C(63)	5310 (8)	6253 (8)	4572 (11)
C(64)	5708 (8)	6884 (10)	4585 (13)
C(65)	5470 (8)	7410 (7)	3780 (13)
C(66)	4799 (6)	7336 (6)	2910 (9)

computer memory allowed a maximum of 151 parameters to be refined simultaneously by the full-matrix procedure so that in the final cycles a blocked-matrix technique was used. The refinement strategy paralleled that recently employed for a related W complex (de Wet, Cairns & Gellatly, 1978). The final model included individual anisotropic thermal parameters for all non-hydrogen atoms and common isotropic parameters for the H atoms of each phenyl group, with the H atoms geometrically located and refining in a riding model (C—H 1.08 Å). Most of the H atoms had been located in difference syntheses. The function minimized was $\sum w\Delta^2$ ($\Delta = |F_o| - |kF_c|$) with $w \propto 1/[gF_o^2 + \sigma^2(F_o)]$. Refinement converged* with $R = 0.068$, $R_w = 0.066$ and $g = 5.95 \times 10^{-4}$. No trends due to systematic errors were revealed by one-way analyses of $\langle w\Delta^2 \rangle$ with $\sin \theta/\lambda$ and $|F_o/F_c(\max.)|^{1/2}$. The final average shift/e.s.d. values were 0.18 and 0.04 for the non-carbon and C atoms respectively. Final common U_{iso} values for the H atoms of phenyl rings (1) to (6) were 0.10, 0.17, 0.13, 0.08, 0.09 and 0.12 Å². The largest peak (1.7 e Å⁻³) in a final difference synthesis was 1.2 Å from the V atom. Scattering factors and anomalous-dispersion corrections were those from *International Tables for X-ray Crystallography* (1974). Fractional coordinates for the non-hydrogen atoms are listed in Table 1.

Discussion. Selected bond lengths and angles are given in Tables 2 and 3 respectively. The molecular conformation and atomic nomenclature are shown in Fig. 1; only two identifying labels are given in each phenyl group, the remaining atom numbers following cyclically round each ring. The coordination geometry is based on a square pyramid with the O atoms of the tppo ligands and two Cl atoms forming the square and the doubly bonded O atom the apex. This geometry and the *trans* arrangement of the oxygen-donor ligands are also observed in dichlorooxobis(tetramethylurea)vanadium(IV) (Coetzer, 1970). Members of the pairs of independent V—O and V—Cl distances do not differ significantly. The distances V—O [mean 1.994 (7) Å] and V=O [1.584 (5) Å] agree with those observed in the tetramethylurea analogue [2.00 (2) and 1.61 (3) Å respectively]. However, the mean V—Cl distance in the title compound, 2.308 (4) Å, lies intermediate between the analogous length [2.250 (5) Å] in dichlorooxobis(trimethylamine)vanadium(IV) (Drake, Vekris & Wood, 1968), which displays trigonal-bipyramidal coordination, and that in dichlorooxobis(tetramethyl-

urea)vanadium(IV), 2.340 (5) Å, which exhibits square-pyramidal coordination. Although quite significant, these bond-length differences are not readily explained. The equation of the least-squares plane through the four atoms comprising the base of the pyramid is $0.2272X + 0.0301Y + 0.9734Z = 3.3263$ (based on a right-handed orthogonal system in Å with $Z \parallel c$, $X \parallel a^*$). O(1) and O(2) are the same distance (0.12 Å) above this plane as the Cl atoms are below, with V 0.55 Å from the plane on the side of the O atoms.

For a related complex, dichlorodioxobis(triphenylphosphine oxide)tungsten(VI) (de Wet *et al.*, 1978), in which the coordination number of the metal is six and the bulky tppo ligands are *cis* coordinated, the W—O=P angles are 159.0 (4) and 165.4 (5)°. While the V—O=P angles here differ by 13°, the relatively unstrained *trans* coordination of these ligands permits closure of one of them to 146.2 (3)°. In contrast to the tetramethylurea complex (Coetzer, 1970), which possesses twofold molecular symmetry, there is no crystallographic symmetry imposed on the title molecule. However, as is shown in Fig. 1, the tppo ligands are approximately centrosymmetrically disposed to one another. As in the W complex referred to above, there are several intramolecular H...Cl and

Table 2. Selected bond distances (Å) with e.s.d.'s in parentheses

V—Cl(1)	2.312 (3)	P(1)—C(11)	1.781 (8)
V—Cl(2)	2.304 (3)	P(1)—C(21)	1.781 (10)
V—O(1)	2.002 (5)	P(1)—C(31)	1.795 (8)
V—O(2)	1.986 (5)	P(2)—C(41)	1.797 (8)
V—O(3)	1.584 (5)	P(2)—C(51)	1.793 (9)
P(1)—O(1)	1.489 (6)	P(2)—C(61)	1.793 (8)
P(2)—O(2)	1.502 (6)		

Table 3. Selected bond angles (°) with e.s.d.'s in parentheses

Cl(1)—V—Cl(2)	146.3 (1)	Cl(1)—V—O(3)	107.7 (3)
O(1)—V—O(2)	155.4 (2)	Cl(2)—V—O(3)	106.0 (2)
Cl(1)—V—O(1)	84.2 (2)	O(1)—V—O(3)	101.6 (3)
O(1)—V—Cl(2)	88.3 (2)	O(2)—V—O(3)	103.0 (3)
Cl(2)—V—O(2)	86.1 (2)	V—O(1)—P(1)	159.4 (4)
O(2)—V—Cl(1)	87.3 (2)	V—O(2)—P(2)	146.2 (3)

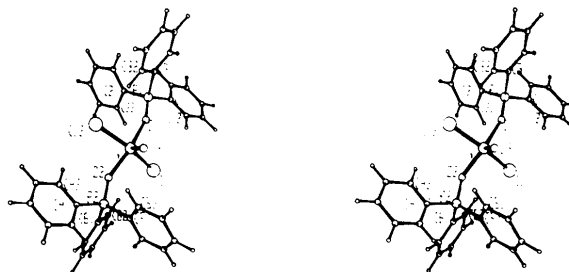


Fig. 1. Stereoscopic view of the molecule drawn by CRISTEP (de Wet, 1980).

* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35018 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

H...O contacts (involving H atoms in the *ortho* positions and generally occurring in pseudo-related pairs) which may contribute to the stability of this arrangement. These distances have not been listed as they are of borderline significance and, furthermore, involve calculated H positions. Deviations from a true centrosymmetric relationship between the tppo ligands are reflected in the angles between the normals to the planes of pseudo-related phenyl groups [rings (1) and (4), 2.8°; (2) and (5), 12.7°; (3) and (6), 10.0°]. Angles around the P atoms range from 109 to 114° for O-P-C (mean 111°) and from 106 to 110° for C-P-C (mean 108°). Bond distances in the ligands are in the expected ranges. The degree of coplanarity of the C atoms in each of the six phenyl rings is high, all deviations from the respective least-squares planes being <0.01 Å. The molecular packing is illustrated in Fig. 2. The combination of two factors, namely the positions of the centres of gravity of the molecules (V is near the point $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$) and the intramolecular pseudo-symmetry described above, results in a structure which is approximately B-centred (excluding V and its

immediate neighbours). Thus, pairs of molecules related by crystallographic inversion centres are also related by translations of approximately $\frac{1}{2}, 0, \frac{1}{2}$. This can be seen in Fig. 2. The molecules at the top left and lower right, for example, occupy the equipoints x, y, z and $1-x, 1-y, 1-z$. For these (and for the *c*-glide related pair) the pseudo-centring of the tppo ligands is evident in this projection.

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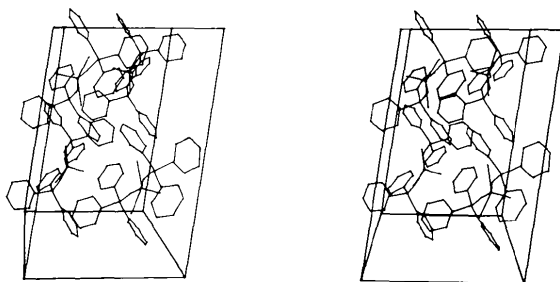


Fig. 2. Stereoscopic view down [010]. The origin is at the top left with *c* across and *a* down.

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Structure of the Potassium Thiocyanate Complex of 3,6,9,12,15-Pentaoxa-21-azabicyclo[15.3.1]hencosa-1(21),17,19-triene-2,16-dione

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Abstract. $C_{15}H_{19}NO_7 \cdot KSCN$, monoclinic, $P2_1/m$, $a = 7.8833$ (12), $b = 14.2868$ (20), $c = 8.6449$ (13) Å, $\beta = 91.383$ (10)°, $V = 972.44$ Å³, $Z = 2$, $D_c = 1.44$, $D_m = 1.44$ Mg m⁻³; colorless to pale-orange prismatic crystals, m.p. 470-471.5 K; model refined to $R = 0.066$ and $R_w = 0.036$. The potassium is positioned in

the cavity of the polyether ring and is coordinated to every hetero-atom in the ring.

Introduction. The ligand of the title compound is a cyclic polyether containing a pyridine ring and carbonyl oxygens as well as ether oxygens. It has been shown to form a very stable complex with potassium (Izatt, Lamb, Asay, Maas, Bradshaw & Christensen,

* Contribution No. 190.