Rhenium(V) Oxide Complexes. Crystal and Molecular Structures of the Compounds trans-ReI₂O(OR)(PPh₃)₂ (R = Et, Me) and of their Hydrolysis Derivative ReIO₂(PPh₃)₂

GIANI FRANCO CIANI*, GIUSEPPE D'ALFONSO, PIERFRANCESCO ROMITI*, ANGELO SIRONI and MARIA FRENI

Istituto di Chimica Generale ed Inorganica e Centro del C.N.R., Via G. Venezian 21, 20133 Milan, Italy

Received November 11, 1982

The structure of the complex $ReI_2O(OEt)(PPh_3)_2$. $3/2C_6H_6$ (I) has been investigated: the dark-yellow crystals are monoclinic, space group P2₁/n, with a = 17.410(8), b = 17.322(6), c = 15.039(5) Å, β = 103.49(3)°, Z = 4. Least-squares refinements based on 3636 significant counter data led to a final R value of 0.059. The compound exhibits a slightly distorted octahedral coordination, with the two PPh_3 groups trans between themselves (mean Re-P2.523 Å), as well as the two iodide ligands (mean Re-I 2.789 Å). The ethoxo group (Re-O 1.880(9) A) and the oxide ligand (Re-O 1.715(9) A) occupy the other two coordination sites. Compound I in methanol transforms into ReI₂O(OMe)(PPh₃)₂ (II), which has been characterized by X-ray analysis in crystals containing CHCl₃ molecules of solvation. The crystals are triclinic, space group P1, a = 12.835(3), b = 13.067(4), c = 13.485(4) Å, $\alpha = 89.71(2)^{\circ}$, $\beta =$ $71.61(2)^{\circ}$, $\gamma = 70.19(2)^{\circ}$, Z = 2. The refinements gave a final R value of 0.036, on the basis of 4524 significant counter intensities. The stereochemistry and the bond parameters are similar to those found in compound I. In particular the Re-O (methoxo) and Re-O (oxide) bond lengths are 1.859(5) and 1.698(5) A respectively.

Hydrolysis reactions of both compounds I and II give the violet derivative $ReIO_2(PPh_3)_2$ (III). The crystal data are: orthorhombic, space group Aba2, a=19.834(5), b=16.144(3), c=10.560(2) Å, Z=4.1435 significant counter reflections were used in the refinements, the final R value being 0.039. The compound is an unusual example of a five coordinate Re(V) complex. It possesses a rigorous C_2 crystallographic symmetry and exhibits a distorted trigonal bipyramidal stereochemistry, with the two PPh₃ groups in an axial direction (Re-P 2.488(3) Å) and the two oxide and the iodide ligands in equa-

torial positions. The Re-I and Re-O interactions have values of 2.664(2) and 1.742(11) Å respectively.

Introduction

The syntheses of a variety of Re(V) oxide complexes are known [1] but few structural characterizations of these species have, as yet, been reported. As a part of a study on rhenium complexes with oxygen donor ligands and on the nature of the Re-O interactions we decided to carry out an X-ray investigation of the well known complex ReI₂O(OEt)(PPh₃)₂ (I) [2, 3], whose structure has never been reported. It was so far suggested [3, 4] that in this type of Re(V) complexes the Re-O (oxide) interaction has a triple-bond character, on the basis of dipole moments and of a rough value of 1.60 Å for the Re-O bond length in ReCl₃O(PEt₂Ph)₂ [5]. Few other structural analyses on Re(V) oxide species were successively reported, showing more reliable values for the Re-O interactions, but affected in some cases by rather high uncertainties [6, 7]. We have, therefore, performed this study in order to achieve better bonding parameters and to clarify the nature of the rhenium—oxide bond in these species.

Compound I treated with methanol in acetone solution gives a species whose analytical and spectroscopic data suggest that the ethoxo ligand can be replaced by a methoxo group to form ReI₂O(OMe)-(PPh₃)₂ (II). This formulation has been confirmed by a structural analysis of the compound. The hydrolysis reaction of ReI₂O(OEt)(PPh₃)₂, which was previously studied [8], has been re-investigated. The violet derivative has been fully characterized as the diamagnetic five coordinate Re(V) species ReIO₂-(PPh₃)₂ (III). The complete results of the X-ray analyses and spectroscopic data of compounds I, II and III are here reported and discussed.

^{*}Authors to whom correspondence should be addressed.

TABLE I. Crystallographic Parameters.

Compound	$ReI_2O(OEt)(PPh_3)_2 \cdot 3/2C_6H_6$ (I)	Rel ₂ O(OMe)(PPh ₃) ₂ ·CHCl ₃ (II)	$ReIO_2(PPh_3)_2$ (III)
Form. wt.	1142.8	1131.0	869.7
System	Monoclinic	Triclinic	Orthorhombic
Space group	P2 ₁ /n (No 14)	P1 (No 2)	Aba2 (No 41)
a, A	17.410(8)	12.835(3)	19.834(5)
b, A	17.322(6)	13.067(4)	16.144(3)
c, Å	15.039(5)	13.485(4)	10.560(2)
α, deg.	90.0	89.71(2)	90.0
β , deg.	103.49(3)	71.61(2)	90.0
γ , deg.	90.0	70.19(2)	90.0
U , \mathbb{A}^3	4410.3	2005.9	3381.3
$D_{\rm e}$, g cm ⁻³	1.72	1.87	1.71
Z	4	2	4
F(000)	2212	1080	1680
$\mu(\text{Mo-K}\alpha), \text{cm}^{-1}$	42.80	49.04	46.72
Crystal size, mm	$0.06 \times 0.11 \times 0.36$	$0.15 \times 0.18 \times 0.30$	$0.24\times0.30\times0.34$
θ range, deg.	3.5-25	3-23	3.5 - 28
No. collected data	8406	6247	2349
No. significant reflections	3636 (I > $2.5\sigma(I)$)	4524 (I > $3\sigma(I)$)	1435 (I > $2.5\sigma(I)$)
R	0.059	0.036	0.039
Rw	0.061	0.046	0.054

Experimental

Preparation of the Complexes

Diiodooxoethoxobis(triphenylphosphine)rhenium-(V)(I)

The preparation was performed along the lines of previous reports [2, 3]. A mixture of perrhenic acid (1 g), 56% hydriodic acid (5 ml), triphenylphosphine (5 g) and ethanol (30 ml) was boiled for about 15 min. The green crystals were filtered off, washed successively with ethanol, and dried *in vacuo* over anhydrous CaCl₂. *Anal.*: Found C 44.7%, H 3.9%, I 25.1%, (OC₂H₅) 4.26%; calculated for C₃₈H₃₅· I₂O₂P₂Re C 44.5%, H 3.4%, I 24.7%, (OC₂H₅) 4.4%.

Crystals suitable for X-ray analysis were obtained by recrystallization of the product in benzene—ethanol, and contain benzene molecules of solvation.

Diiodooxomethoxobis(triphenylphosphine)rhenium(V)(II)

A suspension of compound I (1 g) in acetone (20 ml) and methanol (1 ml) was stirred at room temperature for 4 h. The yellow-grey plates were filtered off, washed successively with acetone, and dried *in vacuo* over anhydrous CaCl₂. *Anal.* data: Found C 43.2%, H 3.28%, I 25.68%; calculated for C₃₇H₃₃I₂O₂P₂Re C 43.9%, H 3.3%, I 25.12%.

Crystals suitable for X-ray analysis were obtained by recrystallization of the product in chloroform— hexane and contain CHCl₃ molecules of solvation.

Iododioxobis(triphenylphosphine)rhenium(V) (III) Compound I or II (1 g), in acetone (50 ml) and

compound I or II (I g), in acetone (50 mI) and water (2 ml) suspension, was stirred at room temperature for 1 h. The resultant suspension deposited a violet microcrystalline compound which, recrystallized from benzene-hexane, gave violet crystals of compound III. (Yield 88%). Anal. data: Found C 49.7%, H 3.46%, I 14.4%, O 3.50%; calculated for C₃₆H₃₀IO₂P₂Re C 49.7%, H 3.48%, I 14.6%, O 3.69%.

The complex is diamagnetic in the solid state at room temperature.

X-Ray Analyses

The principal crystallographic data are reported in Table I.

The intensities for compounds I and III were collected on the BASIC diffractometer [9], while those for compound II were measured on an ENRAF-NONIUS CAD-4 diffractometer. The collections were performed by the ω -scan method, using graphite monochromated Mo-K $_{\alpha}$ radiation. The treatment of the intensities was carried out, in the case of compound II, with the NONIUS structure determination

TABLE II.^a Positional and Thermal Parameters within Compound Rel₂O(OEt)(PPh₃)₂·3/2C₆H₆ (I).

Atom	×	y	Z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Re 11	0.11158(4)	0.12633(4)	0.22338(5)	0.00251(2)	0.00194(2)	0.00290(2)	-0.00018(5)	0.00094(3)	-0.00009(6)
12	0.02337(7)	0.12376(8)	0.04432(7)	0.00341(4)	0.00398(4)	0.00353(5)	0.00013(9)	0.00037(8)	0.0008(1)
P1	-0.0135(2)	0.1329(2)	0.2809(2)	0.0027(1)	0.0028(1)	0.0033(1)	-0.0002(3)	0.0009(2)	-0.0002(3)
12	0.2340(2)	0.1241(2)	0.1613(2)	0.0029(1)	0.0021(1)	0.0036(1)	-0.0001(3)	0.0018(2)	-0.0002(3)
01	0.1214(7)	0.2247(5)	0.2320(9)	0.0050(4)	0.0011(3)	0.0078(6)	-0.0018(7)	0.0061(8)	-0.0005(9)
05	0.1062(7)	0.0180(5)	0.2170(9)	0.0036(4)	0.0012(3)	0.0076(6)	-0.0022(7)	0.0056(7)	-0.0008(9)
3 5	0.1074(13)	-0.0634(8)	0.2114(15)	0.0084(9)	0.0009(4)	0.0094(11)	-0.0024(13)	0.0103(15)	-0.0008(14)
3	0.1320(10)	-0.0904(11)	0.5102(15)	0.0124(13)	0.0021(6)	0.0032(10)	0.0029(16)	0.0038(19)	0.0050(13)
Atom	×	y	z	B, A ²	Atom	×	у	z	B, A ²
C1111	-0.0067(8)	0.1864(7)	0.3882(7)	3.5(3)	C211	0.3263(5)	0.1640(7)	0.2334(7)	3.6(3)
C112	0.0519(6)	0.2422(7)	0.4120(8)	4.6(4)	C212	0.3997(7)	0.1441(5)	0.2183(6)	5.0(4)
C113	0.0546(7)	0.2893(6)	0.4877(9)	5.4(4)	C213	0.4682(5)	0.1763(7)	0.2720(8)	4.5(4)
C114	-0.0012(8)	0.2805(7)	0.5397(7)	5.8(5)	C214	0.4633(5)	0.2284(7)	0.3409(7)	4.5(4)
C115	-0.0600(6)	0.2247(7)	0.5159(8)	5.4(4)	C215	0.3900(7)	0.2483(5)	0.3561(6)	4.4(4)
C116	-0.0627(7)	0.1776(6)	0.4401(9)	4.6(4)	C216	0.3215(5)	0.2161(7)	0.3024(8)	3.2(3)
C121	-0.0516(10)	0.0354(6)	0.2917(6)	3.5(3)	C221	0.2559(8)	0.0261(4)	0.1317(6)	3.0(3)
C122	-0.0539(8)	0.0004(6)	0.3744(6)	4.8(4)	C222	0.2118(6)	-0.0066(5)	0.0515(6)	3.5(3)
C123	-0.0811(8)	-0.0749(6)	0.3755(6)	6.1(5)	C223	0.2213(7)	-0.0843(5)	0.0331(5)	3.7(3)
C124	-0.1061(10)	-0.1154(6)	0.2939(6)	6.7(5)	C224	0.2751(8)	-0.1292(4)	0.0949(6)	4.2(3)
C125	-0.1038(8)	-0.0805(6)	0.2112(6)	5.4(4)	C225	0.3192(6)	-0.0964(5)	0.1751(6)	5.1(4)
C126	-0.0766(8)	-0.0050(6)	0.2101(6)	4.4(4)	C226	0.3096(7)	-0.0187(5)	0.1935(5)	4.5(4)
C131	(9)0660'0-	0.1839(7)	0.2104(8)	4.0(3)	C231	0.2284(9)	0.1830(6)	0.0572(7)	3.5(3)
C132	-0.1753(8)	0.1606(6)	0.2113(8)	4.9(4)	C232	0.1915(7)	0.2547(7)	0.0519(7)	4.5(4)
C133	-0.2398(6)	0.2033(8)	0.1641(9)	5.4(4)	C233	0.1882(8)	0.3018(5)	-0.0238(8)	5.7(5)
C134	-0.2279(6)	0.2691(7)	0.1159(8)	5.2(4)	C234	0.2218(9)	0.2771(6)	-0.0943(7)	5.6(4)
C135	-0.1515(8)	0.2923(6)	0.1150(8)	6.0(5)	C235	0.2586(7)	0.2054(7)	-0.0890(7)	5.2(4)
C136	-0.0871(6)	0.2497(8)	0.1622(9)	4.7(4)	C236	0.2619(8)	0.1583(5)	-0.0132(8)	4.1(3)
Solvent Molecules	Iolecules								,
Atom	x	у	Z	B, A ²	Atom	×	У	z	B, A ²
CB11	-0.3052(20)	-0.0021(20)	0.2716(24)	10.4(9)	CB16	-0.3238(21)	-0.0055(20)	0.1757(24)	10.4(9)
CB12	-0.3652(24)	-0.0007(24)	0.3177(27)	12.4(12)	CB21	0.4374(16)	0.0493(15)	0.4630(19)	7.8(6)
CB13	-0.4439(22)	-0.0185(21)	0.2577(26)	11.3(10)	CB22	0.5074(19)	0.0818(18)	0.5134(22)	9.1(7)
CB14	-0.4635(27)	-0.0234(25)	0.1640(31)	13.8(13)	CB23	0.5707(17)	0.0264(16)	0.5521(20)	8.1(7)
CDIO	-0.3997(49)	-0.0113(20)	0.1107(32)	14.7(14)					

^aThe form of the anisotropic thermal parameter is: $\exp(-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl))$.

TABLE III.⁸ Positional and Thermal Parameters within Compound Rel₂O(OMe)(PPh₃)₂•CHCl₃ (II).

Re 0.08906(3) 0.2949(3) 0.21384(3) 0.00445(2) 0.00429(4) 0.00284(3) 0.00245(5) 0.00245(5) 0.00245(5) 0.00245(5) 0.00245(6) 0.1384(3) 0.00245(3) 0.00345(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00424(4) 0.00441(8) 0.00441(8) 0.00441(1) 0.00418(4) 0.00441(1) 0.00418(4) 0.00441(1) 0.00418(4) 0.00441(1) 0.00418(4) 0.00418(4) 0.00441(1) 0.00418(4) 0.00441(1) 0.00418(4) 0.00441(1)	Atom	×	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
0.00284(5) 0.50716(5) 0.16529(5) 0.00472(4) 0.00429(4) 0.00448(6) 0.00448(6) 0.000428(7) 0.15939(5) 0.00744(5) 0.21678(5) 0.00817(4) 0.0087(3) 0.00448(6) 0.00644(7) 0.2308(3) 0.158(4) 0.5818(3) 0.0121(2) 0.0147(3) 0.0047(3) 0.0067(3) 0.0358(3) 0.158(4) 0.5818(3) 0.0134(3) 0.0147(3) 0.0147(3) 0.0067(3) 0.0358(3) 0.120(2) 0.0121(2) 0.0147(3) 0.0148(4) 0.0147(3) 0.0178(4) 0.0087(1) 0.0358(4) 0.120(1) 0.0247(1) 0.0045(1) 0.0045(1) 0.0044(2) 0.0044(2) 0.0044(1) 0.0045(1) 0.0044(2) 0.0037(4) 0.0017(2) 0.0037(4) 0.0044(2) 0.0044(2) 0.0044(2) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4) 0.0037(4)	Re	0.08006(3)	0.29479(3)	0.21384(3)	0.00445(2)	0.00371(2)	0.00399(2)	-0.00335(3)	-0.00265(3)	0.00156(3)
0.12933(S) 0.06744(S) 0.12767(S) 0.004214(S) 0.06718(S) 0.00438(A) 0.00418(G) 0.00444(T) 0.2298(3) 0.0524(3) 0.0581(3) 0.0121(12) 0.01182(4) 0.0047(3) 0.0067(5) 0.0134(4) 0.0238(3) 0.2624(3) 0.5621(2) 0.0118(3) 0.0087(2) 0.0134(3) 0.0087(3) 0.00184(4) 0.0288(4) 0.2091(2) 0.0132(4) 0.0136(3) 0.0047(1) 0.0047(1) 0.0047(2) 0.0017(5) 0.0288(4) 0.23034(2) 0.0169(1) 0.0044(1) 0.0044(2) 0.0017(5) 0.0017(5) 0.0288(4) 0.23034(2) 0.0169(1) 0.0044(1) 0.0044(2) 0.0041(2) 0.0017(5) 0.0083(4) 0.23034(2) 0.0144(9) 0.0044(1) 0.0042(2) 0.0033(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.0032(6) 0.00	==	0.00284(5)	0.50716(5)	0.16529(5)	0.00772(4)	0.00429(4)	0.00699(4)	-0.00418(6)	-0.00525(6)	0.00354(6)
0.2388(3) 0.1881(4) 0.6818(3) 0.0132(1) 0.0183(3) 0.01881(4) 0.681(3) 0.01881(4) 0.0181(4) 0.01881(4) 0.01881(3) 0.0138(3) -0.01087(5) -0.0138(4) -0.0138(4) -0.0138(4) -0.0138(4) -0.0088(1) -0.0087(1) -0.0087(1) -0.0087(1) -0.0087(1) -0.0087(1) -0.0088(1) -0.0088(1) -0.0088(1) -0.0088(1) -0.0088(1) -0.0088(1) -0.0088(1) -0.0084(1) -0.0084(1) -0.0084(1) -0.0088(1) -0.0031(2) -0.0017(2)	12	0.15939(5)	0.06744(5)	0.21678(5)	0.00817(4)	0.00422(4)	0.00875(4)	-0.00418(6)	-0.00644(7)	0.00317(7)
0.0366(3) 0.2654(3) 0.5627(2) 0.0032(4) 0.00136(3) 0.0118(4) −0.0089(3) 0.0366(4) 0.0366(4) 0.0202(4) 0.0202(4) 0.0032(4) 0.0154(3) 0.01184(4) −0.0089(3) 0.0286(4) 0.1100(3) 0.1100(3) 0.0203(4) 0.0056(4) 0.0045(1) 0.0045(1) −0.0041(2) −0.0031(3) 0.0284(2) 0.0304(2) 0.0056(4) 0.0045(1) 0.0045(1) −0.0041(2) −0.0035(2) 0.0384(3) 0.0322(4) 0.0326(4) 0.0056(4) 0.0056(4) 0.0058(4) 0.0058(4) 0.0045(1) −0.0041(2) −0.0031(3) 0.0383(5) 0.0257(3) 0.0249(1) 0.0056(4) 0.0058(4) 0.005	CI1	0.2308(3)	0.1861(4)	0.6818(3)	0.0121(2)	0.0182(4)	0.0143(3)	-0.0067(5)	-0.0154(4)	0.0020(6)
0.0366(3) 0.1100(3) 0.7120(3) 0.0232(4) 0.0156(3) 0.0133(3) -0.0177(5) 0.0386(3) 0.1100(4) 0.046(2) 0.0036(1) 0.0045(1) 0.0045(1) -0.0041(2) -0.0037(1) -0.1293(2) 0.2044(2) 0.0049(1) 0.0045(1) 0.0045(1) -0.0041(2) -0.0031(2) 0.0633(4) 0.2322(4) 0.2745(2) 0.0049(1) 0.0045(3) -0.0047(2) -0.0035(6) 0.0633(4) 0.2322(4) 0.0346(4) 0.0054(4) 0.0045(4) -0.0035(6) -0.0033(6) 0.0835(3) 0.2579(5) 0.0744(9) 0.0306(16) 0.0042(3) -0.0033(6) -0.0033(6) 0.0875(9) 0.2212(9) 0.6823(8) 0.0103(6) 0.0048(7) -0.008(1) -0.0034(1) 0.0875(9) 0.2252(7) 0.0183(7) 0.0144(9) 0.0306(16) 0.0043(7) 0.1031(6) 0.4420(8) 0.1524(9) 0.0183(9) 0.0183(9) 0.0123(9) 0.1034(1) 0.0004(1) 0.0004(1) 0.4420(8) 0.1524(8) 0.0183(8) 4.	Cl2	0.0758(3)	0.2624(3)	0.5627(2)	0.0123(2)	0.0171(3)	0.0087(2)	-0.0128(4)	-0.0089(3)	0.0051(4)
0.2884(2) 0.2915(2) 0.1609(2) 0.0050(1) 0.0045(1) -0.0041(2) -0.0021(2) 0.0584(4) 0.0534(4) 0.2362(4) 0.2372(4) 0.0494(1) 0.0045(1) -0.0044(2) -0.0035(2) 0.0534(4) 0.2362(4) 0.3407(4) 0.0064(4) 0.0042(1) -0.0032(6) -0.0035(2) 0.0534(5) 0.2379(5) 0.0749(4) 0.0061(4) 0.0044(6) -0.0043(6) -0.0035(6) 0.1203(10) 0.2202(13) 0.0374(4) 0.0064(4) 0.0044(6) -0.003(7) -0.0033(6) 1 x y z B, A² Atom x y z 0.4420(8) 0.1254(9) 0.2352(7) 0.0183(7) 3.32 C211 -0.1679(7) 0.1204(1) -0.003(1) 0.4420(8) 0.1254(9) 0.1372(9) 4.6(2) C212 -0.1579(7) 0.1020(8) 0.4450(8) 0.1254(9) 0.1372(8) 4.6(2) C212 -0.1579(7) 0.1020(8) 0.4450(8) 0.1273(9) 0.1374(8) 4.6(2)	CI3	0.0360(3)	0.1100(3)	0.7120(3)	0.0232(4)	0.0136(3)	0.0153(3)	-0.0198(5)	-0.0177(5)	0.0067(5)
−0.1293(2) 0.3034(2) 0.2744(2) 0.0049(1) 0.0045(1) 0.0045(1) −0.0045(1) −0.0045(2) −0.0032(6) −0.0032(6) 0.0053(4) 0.2362(4) 0.2362(4) 0.0364(4) 0.0054(4) −0.0043(6) −0.0033(6) 0.0083(5) 0.2203(13) −0.0316(8) 0.0144(9) 0.0036(16) 0.0044(6) −0.003(1) −0.003(1) 0.1203(10) 0.2212(9) 0.0218(8) 0.01144(9) 0.0036(16) 0.0044(6) −0.003(1) −0.003(1) 0.1203(10) 0.2212(9) 0.0103(8) 0.0103(8) 0.0044(8) 0.0044(8) −0.005(1) −0.009(1) 0.252(7) 0.0183(7) 0.0103(8) 0.0103(8) 4.6(2) C212 −0.202(8) 0.3571(8) 0.1020(8) 0.4420(8) 0.1254(9) −0.0260(8) 4.6(2) C212 −0.202(8) 0.3571(8) 0.1020(8) 0.4420(8) 0.1254(9) −0.0260(8) 4.6(2) C212 −0.204(9) 0.0100(8) 0.4420(8) 0.1254(9) −0.01354(8) 4.6(2) C214	P1	0.2884(2)	0.2915(2)	0.1609(2)	0.0050(1)	0.0047(1)	0.0045(1)	-0.0041(2)	-0.0021(2)	0.0016(2)
0.0653(4) 0.3262(4) 0.3407(4) 0.0056(4) 0.0058(4) 0.0042(3) -0.0022(6) -0.0033(6) 0.0983(5) 0.2579(5) 0.0749(4) 0.0066(14) 0.0052(4) -0.0042(6) -0.0033(6) 0.0873(5) 0.0279(4) 0.0066(14) 0.0057(4) 0.0052(4) -0.0034(6) -0.0034(6) 0.0875(9) 0.2212(9) 0.6823(8) 0.0149(9) 0.0104(8) 0.0004(1) -0.0058(1) -0.009(1) 1 x y z Atom x y z 0.5608(7) 0.2552(7) 0.0183(7) 3.3(2) C211 -0.1679(7) 0.0401(1) 0.0009(1) 0.4420(8) 0.1524(9) -0.1326(8) 4.6(2) C212 -0.2026(8) 0.1020(8) 0.4420(8) 0.1524(9) -0.1326(8) 4.9(2) C214 -0.2111(10) 0.1037(9) 0.4421(8) 0.2079(9) -0.1986(8) 4.9(2) C214 -0.1450(1) 0.0137(9) 0.3222(8) 0.1324(8) 4.9(2) C214 -0.1566(1)	P2	-0.1293(2)	0.3034(2)	0.2745(2)	0.0049(1)	0.0049(1)	0.0045(1)	-0.0040(2)	-0.0035(2)	0.0025(2)
0.0983(5) 0.02579(5) 0.0048(4) 0.0061(4) 0.0057(4) 0.0043(6) 0.0043(6) 0.00033(6) 0.1203(10) 0.2050(13) 0.0212(9) 0.6823(8) 0.0104(8) 0.0306(16) 0.00044(6) 0.0052(2) 0.0009(1) 0.0875(9) 0.2212(9) 0.6823(8) 0.0104(8) 0.00084(7) 0.005(1) 0.0009(1) 0.3608(7) 0.2252(7) 0.0183(7) 3.3(2) C211 -0.1679(7) 0.153(6) 0.0008(1) 0.4420(8) 0.1524(9) -0.0266(8) 4.6(2) C212 -0.2247(9) 0.3571(8) 0.1020(8) 0.4420(8) 0.1524(9) -0.1586(8) 4.6(2) C212 -0.2247(9) 0.3571(8) 0.1020(8) 0.4420(8) 0.1234(9) -0.1586(8) 4.6(2) C212 -0.2247(9) 0.0100(8) 0.4589(9) 0.1398(8) -0.1354(8) 4.6(2) C212 -0.1534(9) 0.0100(8) 0.3322(8) 0.2312(8) 0.2136(8) 0.1466(8) 4.4(2) C212 -0.2147(9) 0.334(8)	01	0.0653(4)	0.3262(4)	0.3407(4)	0.0056(4)	0.0058(4)	0.0042(3)	-0.0052(6)	-0.0033(6)	0.0030(6)
0.1203(10) 0.2050(13) -0.0316(8) 0.0144(9) 0.0306(16) 0.0044(6) -0.028(2) -0.009(1) 1 X y z B, A² Atom x y z 0.3608(7) 0.2552(7) 0.0183(7) 3.3(2) C211 -0.1679(7) 0.1531(8) -0.1030(8) 0.4420(8) 0.1524(9) -0.0260(8) 4.6(2) C212 -0.2025(8) 0.3571(8) 0.1030(8) 0.4420(8) 0.1524(9) -0.1372(9) 5.3(3) C213 -0.2247(9) 0.1631(6) 0.4420(8) 0.1293(9) -0.1372(9) 5.3(3) C212 -0.2025(8) 0.3571(8) 0.1030(8) 0.4420(8) 0.1293(9) -0.1372(9) 5.3(3) C214 -0.1247(9) 0.3357(9) 0.0100(8) 0.3453(9) 0.2131(9) -0.1554(8) 4.9(2) C215 -0.1247(9) 0.1340(6) 0.3522(8) 0.4938(8) 4.6(2) C221 -0.1685(7) 0.1340(6) 0.345(8) 0.3078(7) 0.4387(8) 4.6(2)	02	0.0983(5)	0.2579(5)	0.0749(4)	0.0061(4)	0.0057(4)	0.0052(4)	-0.0043(6)	-0.0035(6)	0.0010(7)
0.0875(9) 0.2212(9) 0.6823(8) 0.0103(8) 0.0086(9) 0.0083(7) -0.005(1) -0.008(1) 0.0008(1) 1 x y z B, A² Atom x y z 1 0.3608(7) 0.2552(7) 0.0183(7) 3.3(2) C211 -0.1679(7) 0.2730(7) 0.1631(6) 0.4420(8) 0.1534(9) -0.026(8) 4.6(2) C213 -0.2247(9) 0.3571(8) 0.1020(8) 0.4420(8) 0.1534(9) -0.137(9) 5.3(3) C213 -0.2247(9) 0.3571(9) 0.0103(8) 0.4599(9) 0.2079(9) -0.1354(8) 4.9(2) C214 -0.1460(10) 0.0193(9) 0.0103(9) 0.3222(8) 0.2376(8) 4.9(2) C215 -0.1551(8) 0.137(7) 0.137(7) 0.137(7) 0.137(8) 0.3078(7) 0.188(7) 0.188(7) 0.188(7) 0.137(7) 0.137(7) 0.137(7) 0.137(7) 0.137(7) 0.137(7) 0.137(8) 0.137(1) 0.137(1) 0.137(1) 0.137(1)	CI	0.1203(10)	0.2050(13)	-0.0316(8)	0.0144(9)	0.0306(16)	0.0044(6)	-0.028(2)	-0.009(1)	0.011(2)
n x y z B, A² Atom x y z 0.3608(7) 0.2552(7) 0.0183(7) 3.3(2) C211 -0.1679(7) 0.1531(6) 0.1020(8) 0.4420(8) 0.1524(9) -0.0260(8) 4.6(2) C212 -0.2026(8) 0.3571(8) 0.1020(8) 0.4454(9) 0.1234(9) -0.1372(9) 5.3(3) C213 -0.2247(9) 0.3357(8) 0.0100(8) 0.4544(9) 0.2079(9) -0.1554(8) 4.9(2) C214 -0.2447(9) 0.3357(8) 0.0100(8) 0.3522(8) 0.2079(9) -0.1554(8) 4.9(2) C214 -0.2447(9) 0.01937(9) 0.0100(8) 0.3522(8) 0.2079(9) -0.1554(8) 4.9(2) C215 -0.156(10) 0.01937(9) 0.0100(8) 0.3022(8) 0.4387(8) 4.4(2) C216 -0.156(10) 0.01937(9) 0.01321(8) 0.1321(9) 0.1321(9) 0.1321(9) 0.1321(9) 0.1321(9) 0.1321(9) 0.1321(10) 0.1321(10) 0.1321(10) 0.1321(10)	: C	0.0875(9)	0.2212(9)	0.6823(8)	0.0103(8)	0.0086(9)	0.0083(7)	-0.005(1)	-0.008(1)	0.002(1)
0.3608(7) 0.2552(7) 0.0183(7) 3.3(2) C211 -0.1679(7) 0.2730(7) 0.1631(6) 0.4420(8) 0.1524(9) -0.0260(8) 4.6(2) C212 -0.2025(8) 0.3571(8) 0.1020(8) 0.4905(9) 0.1534(9) -0.1372(9) 5.3(3) C213 -0.2247(9) 0.3571(8) 0.0100(8) 0.4943(9) 0.1293(9) -0.1372(8) 4.9(2) C214 -0.2111(10) 0.2302(10) -0.1034(9) 0.3222(8) 0.2073(1) 0.1354(8) 4.9(2) C215 -0.2111(10) 0.1360(10) 0.01034(9) 0.3222(8) 0.3355(8) -0.0438(8) 4.4(2) C216 -0.1561(8) 0.1314(8) 0.0311(9) 0.3078(7) 0.4188(7) 0.1895(7) 3.2(2) C221 -0.1668(7) 0.1324(8) 0.460(10) 0.1341(8) 0.4096(8) 0.4387(8) 0.1285(8) 4.6(2) C222 -0.1456(8) 0.1346(8) 0.3414(8) 0.4298(9) 0.5414(9) 0.1348(8) 5.6(3) C224 -0.1456(8) 0.1466(Atom	×	y	z	B, A ²	Atom	×	y	Z	B, A ²
0.4420(8) 0.1524(9) -0.0260(8) 4.6(2) C212 -0.2025(8) 0.3571(8) 0.1020(8) 0.4420(8) 0.1234(9) -0.1372(9) 5.3(3) C213 -0.2247(9) 0.3357(9) 0.0100(8) 0.4543(9) 0.1293(9) -0.1372(9) 5.3(3) C214 -0.111(10) 0.2302(10) -0.0193(9) 0.3269(9) 0.2107(9) -0.1554(8) 4.9(2) C215 -0.1150(10) 0.1460(10) 0.0103(9) 0.3259(9) 0.3110(9) -0.1554(8) 4.9(2) C215 -0.156(10) 0.1460(10) 0.0103(1) 0.3049(9) 0.310(9) 0.1857(1) 3.2(2) C221 -0.1567(1) 0.1324(1) 0.3341(1) 0.4096(8) 0.1285(8) 4.6(2) C222 -0.2450(8) 0.1046(8) 0.5436(8) 0.2447(9) 0.5871(9) 0.1587(8) 5.6(3) C224 -0.2450(8) 0.1046(8) 0.5436(8) 0.2447(1) 0.1934(7) 0.3042(8) 5.0(2) C225 -0.1430(8) 0.1469(8) 0.4504(8)	C111	0.3608(7)	0.2552(7)	0.0183(7)	3.3(2)	C211	-0.1679(7)	0.2730(7)	0.1631(6)	3.0(2)
0.4905(9) 0.1293(9) -0.1372(9) 5.3(3) C213 -0.2247(9) 0.3357(9) 0.0100(8) 0.4543(9) 0.2079(9) -0.1386(8) 4.9(2) C214 -0.2111(10) 0.2302(10) -0.0193(9) 0.3453(8) 0.01554(8) 4.9(2) C215 -0.1156(10) 0.166(8) 0.0193(9) 0.3458(8) 0.01354(8) 4.9(2) C216 -0.1551(8) 0.166(8) 0.1321(8) 0.3438(1) 0.4188(7) 3.2(2) C221 -0.185(7) 0.1321(8) 0.1321(8) 0.4096(8) 0.4387(8) 0.1285(8) 4.6(2) C222 -0.185(7) 0.317(7) 0.317(7) 0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C222 -0.245(8) 0.1046(8) 0.5436(8) 0.2485(9) 0.6044(9) 0.1578(9) 5.4(3) C222 -0.1430(8) 0.1466(8) 0.5284(7) 0.2485(9) 0.6044(9) 0.2438(9) 5.5(3) C222 -0.1430(8) 0.1406(8) 0.5284(7) 0.2283(1) 0.2485(9) <	C112	0.4420(8)	0.1524(9)	-0.0260(8)	4.6(2)	C212	-0.2025(8)	0.3571(8)	0.1020(8)	4.2(2)
0.4543(9) 0.2079(9) -0.1986(8) 4.9(2) C214 -0.2111(10) 0.2302(10) -0.0193(9) 0.3699(9) 0.3110(9) -0.1554(8) 4.9(2) C215 -0.1750(10) 0.1460(10) 0.031(9) 0.3222(8) 0.3315(8) -0.0436(8) 4.4(2) C216 -0.1551(8) 0.1460(10) 0.0371(9) 0.3222(8) 0.3488(7) 0.1895(7) 3.2(2) C221 -0.1685(7) 0.137(7) 0.311(8) 0.4096(8) 0.4387(8) 0.1285(8) 4.4(2) C222 -0.2726(7) 0.136(8) 0.446(8) 0.345(8) 0.4298(9) 0.64387(8) 0.1288(8) 5.4(3) C222 -0.2450(8) 0.146(8) 0.5431(7) 0.245(9) 0.6044(9) 0.2438(9) 5.4(3) C224 -0.2450(8) 0.146(8) 0.5436(8) 0.2467(9) 0.4438(1) 0.3042(8) 5.6(3) C222 -0.1430(8) 0.1269(8) 0.5436(8) 0.2238(8) 0.4404(8) 0.3042(8) 5.6(3) 0.225 -0.1430(8) 0.4569(8)	C113	0.4905(9)	0.1293(9)	-0.1372(9)	5.3(3)	C213	-0.2247(9)	0.3357(9)	0.0100(8)	5.0(2)
0.3469(9) 0.3110(9) -0.1554(8) 4.9(2) C215 -0.1750(10) 0.1460(10) 0.0371(9) 0.3222(8) 0.3355(8) -0.0436(8) 4.4(2) C216 -0.1551(8) 0.1666(8) 0.1321(8) 0.3078(7) 0.4188(7) 0.1895(7) 3.2(2) C221 -0.1685(7) 0.1374(6) 0.33740(6) 0.4096(8) 0.4387(8) 0.1285(8) 4.6(2) C222 -0.2756(7) 0.1374(7) 0.3340(6) 0.4298(9) 0.6044(9) 0.1278(9) 5.4(3) C223 -0.2450(8) 0.1466(8) 0.4568(8) 0.2487(9) 0.5871(9) 0.3042(8) 5.0(2) C224 -0.2450(8) 0.1466(8) 0.5346(8) 0.2283(8) 0.404(9) 0.3042(8) 4.2(2) C225 -0.1430(8) 0.4536(8) 0.2283(8) 0.1045(8) 4.6(2) C234 -0.1430(8) 0.4699(8) 0.4036(1) 0.3284(7) 0.1045(8) 0.3235(7) 3.3(2) C232 -0.1430(8) 0.4699(8) 0.4010(8) 0.5281(9)	C114	0.4543(9)	0.2079(9)	-0.1986(8)	4.9(2)	C214	-0.2111(10)	0.2302(10)	-0.0193(9)	6.2(3)
0.3222(8) 0.3355(8) -0.0436(8) 4.4(2) C216 -0.1551(8) 0.1666(8) 0.1321(8) 0.3078(7) 0.4188(7) 0.1895(7) 3.2(2) C221 -0.1685(7) 0.2137(7) 0.3740(6) 0.4096(8) 0.4387(8) 0.1285(8) 4.6(2) C222 -0.2726(7) 0.1924(7) 0.3740(6) 0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C223 -0.2156(7) 0.1366(8) 0.4758(8) 0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C224 -0.2450(8) 0.1046(8) 0.5478(8) 0.2467(9) 0.5871(9) 0.3042(8) 5.0(2) C222 -0.1430(8) 0.5288(7) 0.2283(8) 0.4904(8) 0.3042(8) 5.0(2) C222 -0.1430(8) 0.5288(7) 0.2283(8) 0.4904(8) 0.2769(8) 4.2(2) C222 -0.1052(7) 0.1802(7) 0.4403(7) 0.3294(7) 0.1045(8) 0.3235(7) 3.7(2) C232 -0.389(7) 0.4699(8) 0.4070(8) 0.5201(9) <t< td=""><td>C115</td><td>0.3699(9)</td><td>0.3110(9)</td><td>-0.1554(8)</td><td>4.9(2)</td><td>C215</td><td>-0.1750(10)</td><td>0.1460(10)</td><td>0.0371(9)</td><td>6.0(3)</td></t<>	C115	0.3699(9)	0.3110(9)	-0.1554(8)	4.9(2)	C215	-0.1750(10)	0.1460(10)	0.0371(9)	6.0(3)
0.3078(7) 0.4188(7) 0.1895(7) 3.2(2) C221 -0.1685(7) 0.2137(7) 0.3740(6) 0.4096(8) 0.4387(8) 0.1285(8) 4.6(2) C222 -0.2726(7) 0.1924(7) 0.3917(7) 0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C223 -0.3105(8) 0.1366(8) 0.4765(8) 0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C224 -0.2450(8) 0.1046(8) 0.5436(8) 0.2467(9) 0.5871(9) 0.2438(9) 5.6(2) C225 -0.1430(8) 0.1269(8) 0.5458(7) 0.2283(8) 0.4904(8) 0.2769(8) 4.2(2) C226 -0.1430(8) 0.1269(8) 0.5288(7) 0.2283(8) 0.1993(7) 0.2250(7) 3.3(2) C23 -0.1389(7) 0.4493(7) 0.3454(7) 0.3294(7) 0.1045(8) 0.3779(8) 4.6(2) C232 -0.389(7) 0.4699(8) 0.4070(8) 0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.568(9) 0.4717(8) <	C116	0.3222(8)	0.3355(8)	-0.0436(8)	4.4(2)	C216	-0.1551(8)	0.1666(8)	0.1321(8)	4.6(2)
0.4096(8) 0.4387(8) 0.1285(8) 4.6(2) C2222 -0.2726(7) 0.1924(7) 0.3917(7) 0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C223 -0.3105(8) 0.1366(8) 0.4765(8) 0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C224 -0.2450(8) 0.1046(8) 0.5436(8) 0.2467(9) 0.5871(9) 0.2438(9) 5.0(2) C225 -0.1430(8) 0.1269(8) 0.5258(7) 0.2283(8) 0.4904(8) 0.2769(8) 4.2(2) C226 -0.1052(7) 0.1802(7) 0.4403(7) 0.2283(8) 0.4904(8) 0.2756(7) 3.3(2) C231 -0.2389(7) 0.4832(7) 0.3454(7) 0.3294(7) 0.1045(8) 0.3235(7) 3.7(2) C232 -0.4385(9) 0.4699(8) 0.4070(8) 0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.5688(9) 0.4717(9) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C235 -0.2948(9) 0.5865(9) 0.4114(8)	C121	0.3078(7)	0.4188(7)	0.1895(7)	3.2(2)	C221	-0.1685(7)	0.2137(7)	0.3740(6)	2.9(2)
0.4298(9) 0.5319(9) 0.1578(9) 5.4(3) C223 -0.3105(8) 0.1366(8) 0.4765(8) 0.3485(9) 0.6044(9) 0.2438(9) 5.5(3) C224 -0.2450(8) 0.1046(8) 0.5436(8) 0.2467(9) 0.5871(9) 0.2438(9) 5.6(2) C225 -0.1430(8) 0.1269(8) 0.5258(7) 0.2283(8) 0.4904(8) 0.2769(8) 4.2(2) C226 -0.1052(7) 0.1802(7) 0.4403(7) 0.3294(7) 0.1993(7) 0.2256(7) 3.3(2) C231 -0.2389(7) 0.4342(7) 0.3454(7) 0.3294(7) 0.1045(8) 0.3235(7) 3.7(2) C232 -0.3537(8) 0.4699(8) 0.4010(8) 0.5201(9) 0.0697(9) 0.3779(8) 4.6(2) C234 -0.4095(9) 0.568(9) 0.4711(9) 0.5047(8) 0.0588(10) 0.2407(9) 5.6(3) C235 -0.2948(9) 0.5865(9) 0.4114(8)	C122	0.4096(8)	0.4387(8)	0.1285(8)	4.6(2)	C222	-0.2726(7)	0.1924(7)	0.3917(7)	3.6(2)
0.3485(9) 0.6044(9) 0.2438(9) 5.5(3) C224 -0.2450(8) 0.1046(8) 0.5436(8) 0.2467(9) 0.5871(9) 0.3042(8) 5.0(2) C225 -0.1430(8) 0.1269(8) 0.5258(7) 0.2283(8) 0.4904(8) 0.2769(8) 4.2(2) C226 -0.1052(7) 0.1802(7) 0.4403(7) 0.2283(8) 0.4994(7) 0.2250(7) 3.3(2) C231 -0.2389(7) 0.4342(7) 0.3454(7) 0.3294(7) 0.1703(7) 0.3235(7) 3.7(2) C232 -0.3537(8) 0.4699(8) 0.3410(8) 0.3294(7) 0.1045(8) 0.3779(8) 4.6(2) C233 -0.4385(9) 0.5668(9) 0.4070(8) 0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.5865(9) 0.4717(9) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C236 -0.2079(8) 0.4910(8) 0.4114(8)	C123	0.4298(9)	0.5319(9)	0.1578(9)	5.4(3)	C223	-0.3105(8)	0.1366(8)	0.4765(8)	4.3(2)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C124	0.3485(9)	0.6044(9)	0.2438(9)	5.5(3)	C224	-0.2450(8)	0.1046(8)	0.5436(8)	4.2(2)
0.2283(8) 0.4904(8) 0.2769(8) 4.2(2) C226 -0.1052(7) 0.1802(7) 0.4403(7) 0.3819(7) 0.1993(7) 0.2250(7) 3.3(2) C231 -0.2389(7) 0.4342(7) 0.3454(7) 0.3294(7) 0.1703(7) 0.3235(7) 3.7(2) C232 -0.3537(8) 0.4699(8) 0.3410(8) 0.3294(7) 0.1045(8) 0.3779(8) 4.6(2) C233 -0.4385(9) 0.5668(9) 0.4070(8) 0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.6233(9) 0.4717(9) 0.5719(9) 0.0988(10) 0.2407(9) 5.6(3) C235 -0.2948(9) 0.5865(9) 0.4712(8) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C236 -0.2079(8) 0.4910(8) 0.4114(8)	C125	0.2467(9)	0.5871(9)	0.3042(8)	5.0(2)	C225	-0.1430(8)	0.1269(8)	0.5258(7)	4.0(2)
0.3819(7) 0.1993(7) 0.2250(7) 3.3(2) C231 -0.2389(7) 0.4342(7) 0.3454(7) 0.3294(7) 0.1703(7) 0.3235(7) 3.7(2) C232 -0.3537(8) 0.4699(8) 0.3410(8) 0.3294(7) 0.1045(8) 0.3779(8) 4.6(2) C233 -0.4385(9) 0.5668(9) 0.4070(8) 0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.6233(9) 0.4717(9) 0.5719(9) 0.0988(10) 0.2407(9) 5.6(3) C235 -0.2948(9) 0.5865(9) 0.4772(8) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C236 -0.2079(8) 0.4910(8) 0.4114(8)	C126	0.2283(8)	0.4904(8)	0.2769(8)	4.2(2)	C226	-0.1052(7)	0.1802(7)	0.4403(7)	3.7(2)
0.3294(7) 0.1703(7) 0.3235(7) 3.7(2) C232 -0.3537(8) 0.4699(8) 0.3410(8) 0.3989(8) 0.1045(8) 0.3779(8) 4.6(2) C233 -0.4385(9) 0.5668(9) 0.4070(8) 0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.6233(9) 0.4717(9) 0.5719(9) 0.0988(10) 0.2407(9) 5.6(3) C235 -0.2948(9) 0.5865(9) 0.4772(8) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C236 -0.2079(8) 0.4910(8) 0.4114(8)	C131	0.3819(7)	0.1993(7)	0.2250(7)	3.3(2)	C231	-0.2389(7)	0.4342(7)	0.3454(7)	3.1(2)
0.3989(8) 0.1045(8) 0.3779(8) 4.6(2) C233 -0.4385(9) 0.5668(9) 0.4070(8) 0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.6233(9) 0.4717(9) 0.5719(9) 0.0988(10) 0.2407(9) 5.6(3) C235 -0.2948(9) 0.5865(9) 0.4772(8) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C236 -0.2079(8) 0.4910(8) 0.4114(8)	C132	0.3294(7)	0.1703(7)	0.3235(7)	3.7(2)	C232	-0.3537(8)	0.4699(8)	0.3410(8)	4.2(2)
0.5201(9) 0.0697(9) 0.3348(9) 5.3(3) C234 -0.4095(9) 0.6233(9) 0.4717(9) 0.5719(9) 0.0988(10) 0.2407(9) 5.6(3) C235 -0.2948(9) 0.5865(9) 0.4772(8) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C236 -0.2079(8) 0.4910(8) 0.4114(8)	C133	0.3989(8)	0.1045(8)	0.3779(8)	4.6(2)	C233	-0.4385(9)	0.5668(9)	0.4070(8)	5.2(2)
0.5719(9) 0.0988(10) 0.2407(9) 5.6(3) C233 -0.2948(9) 0.5865(9) 0.4772(8) 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C236 -0.2079(8) 0.4910(8) 0.4114(8)	C134	0.5201(9)	0.0697(9)	0.3348(9)	5.3(3)	C234	-0.4095(9)	0.6233(9)	0.4717(9)	5.3(3)
5 0.5047(8) 0.1659(9) 0.1846(8) 4.7(2) C2360.2079(8) 0.4910(8) 0.4114(8) 4	C135	0.5719(9)	0.0988(10)	0.2407(9)	5.6(3)	C235	-0.2948(9)	0.5865(9)	0.4772(8)	4.9(2)
	C136	0.5047(8)	0.1659(9)	0.1846(8)	4.7(2)	C236	-0.2079(8)	0.4910(8)	0.4114(8)	4.2(2)

^aThe form of the anisotropic thermal parameter is: $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

TABLE IV.^a Positional and Thermal Parameters within Compound ReIO₂(PPh₃)₂ (III).

Atom	×	٨	2	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Re I P O	0 0 0.1068(1) -0.0392(4)	0 0 0.0789(2) 0.0886(6)	0 0.2523(1) -0.0263(3) -0.0580(11)	0.0021(1) 0.0037(1) 0.0021(1) 0.0024(2)	0.0031(1) 0.0086(1) 0.0033(1) 0.0049(4)	0.0063(1) 0.0066(1) 0.0070(2) 0.0166(13)	0.0002(1) -0.0031(1) 0.0006(1) 0.0011(6)	0 0 0.0011(2) 0.0005(10)	0 0 0.0015(2) 0.0055(14)
Atom	×	y	Z	B, A ²	Atom	×	>	2	B, A ²
C11	0.1224(5)	0.1627(5)	0.0868(9)	3.9(2)	C24	0.3003(5)	(7)267070	-0.0203(10)	7.7(4)
C12 C13	0.1833(4) $0.1905(3)$	0.2351(6)	0.1494(10) $0.2401(9)$	4.4(2) 5.2(3)	C25	0.2462(6)	-0.0992(6)	0.0581(11)	8.7(5)
C14	0.1363(5)	0.2867(5)	0.2681(9)	5.4(3)	C31	0.1058(8)	-0.0313(7)	0.054/(11)	6.3(4)
C15	0.0751(4)	0.2763(5)	0.2055(10)	5.3(3)	C32	0.0961(9)	0.0833(7)	-0.2905(17)	11.0(8)
C16	0.0682(3)	0.2143(6)	0.1148(9)	5.8(3)	C33	0.0935(6)	0.1234(10)	-0.4071(13)	11.4(9)
(2)	0.2377(6)	0.0160(7)	0.02/1(10)	4.0(2)	C34	0.1004(8)	0.2091(10)	-0.4133(13)	11.0(8)
C23	0.2961(5)	-0.0124(7)	-0.1023(11) -0.1021(11)	7.3(5)	C38	0.1101(9) $0.1128(6)$	0.2547(7) $0.2146(10)$	-0.3029(17) -0.1836(13)	10.5(8)
The form of	the anisotropic	thermal parameter	^a The form of the anisotropic thermal parameter is: $\exp(-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl))$	$-B(2,2)k^2 + B(3,$	$(3)l^2 + B(1,2)hk + 1$	B(1,3)hl + B(2,3)kl);			

package on a PDP 11/34 computer; computations for compounds I and III were performed on a UNIVAC 1100/80 computer using local programs. The data were corrected for Lorentz and polarization effects. To data of compound II an empirical absorption correction, based on ψ -scan of suitable reflections, with χ close to 90°, was applied, the maximum, minimum and average relative transmission factors being 1.00, 0.89 and 0.96 respectively. No decay of the samples of II and III was observed during the collection, while compound I showed a total decay, at the end of the collection, of ca. 16%; a correction for this effect was applied.

The structure solutions were based on Patterson and Fourier methods. The complexes in I and II are in general positions, while in III it was found to lie in special position, with the Re and I atoms on a two-fold crystallographic axis. Benzene molecules of solvation were found in I, one in a general position and a second one about an inversion centre, coincident with the centre of the molecule. Chloroform molecules of solvation were found in II. The refinements were carried out assigning anisotropic thermal factors to all atoms of the complexes, except for the phenyl carbon atoms. Block-matrix least-squares were used in the case of compounds I and III, with the phenyl rings treated as rigid bodies $(D_{6h}$ symmetry, C-C 1.392 Å). For the non-centrosymmetric compound III both the structure enantiomorphs were refined, keeping in account the anomalous scattering effects, the final solution giving slightly lower agreement indices. Compound II was refined by full-matrix least-squares, without constraints. The hydrogen atoms were not considered.

Weights were assigned for compounds I and III according to the formula $w = 1/(A + BF_o + CF_o^2)$, where, in the final cycles A, B and C, had values 176.7, -2.31, 0.0088 (for I) and 10.2, -0.20, 0.0047 (for III), respectively, and were chosen on the basis of an analysis of $\Sigma w \Delta^2$. In the case of II the weighting formula was $w = 1/[\sigma(F_o)]^2$ where the σ of the reflections were corrected by a factor of 0.03 F_o^2 .

The scattering factors for structures I and III were taken from ref. 10, corrected for the real and imaginary part of the anomalous dispersion [11]. The results of the refinements are reported in Tables II—IV. Lists of observed and computed structure factors moduli can be obtained on application to the authors.

Results and Discussion

The complex ReI₂O(OEt)(PPh₃)₂ (I), when suspended in acetone, reacts with methanol giving metathesis of the alkoxo group, according to reaction 1

Data
Resonance ^b
Magnetic
Nuclear
and Nuc
Infrared
>
TABLE V.
_

No.	No. Compound	ν Re-O (cm ⁻¹)	Other bands	TH & ppm	Assignment	³1P δ ppm	Assignment
_	Rel ₂ O(OC ₂ H ₅)[P(C ₆ H ₅) ₃] ₂	945(ms)	910(vs) δ (OCH ₂)	7.98m, 7.38m	-C ₆ H ₅	-11.1s	P(C ₆ H ₅) ₃
				1.51q	CH ₂		
				-0.26t	-CH ₃		
П	ReI ₂ O(OCH ₃)[P(C ₆ H ₅) ₃] ₂	930(s)		8.00m, 7.42m	$-C_6H_5$	-9.39s	$P(C_6H_5)_3$
				0.89s	-CH3		
Ш	$ReIO_2[P(C_6H_5)_3]_2$	923(s), 843(s)		7.62m, 7.42m	$-C_6H_5$	4.578	$P(C_6H_5)_3$

^bN.M.R. spectra were recorded on a Bruker-80 spectrometer ^aInfrared spectra were performed on nujol mulls and recorded on a Perkin-Elmer model 781 spectrophotometer. in deuterochloroform solution at 35 °C, Me₄Si as internal standard. ³¹P to 85% H₃PO₄ external.

C₁₂₁, C₁₁₁, C₁₃₁

C₂₁₁, C₁₁₁, C₁₃₁

C₂₁₁, C₁₃₁

C₂₁₁, C₁₃₁

C₂₁₁, C₂₃₁

C₂₁₁, C₂₃₁

Fig. 1. A view of the complex ReI₂O(OEt)(PPh₃)₂.

$$ReI_{2}O(OEt)(PPh_{3})_{2} (I) + MeOH \xrightarrow{acctone}$$

$$ReI_{2}O(OMe)(PPh_{3})_{2} (II) + EtOH$$
 (1)

The process can be reversed by suspending (II) in ethanol. It seems very probable that these substitutions take place because of the presence of a large excess of the alcohol which furnishes the entering OR group. Compound II was previously obtained in a different way [2, 3].

I.R. and ¹H and ³¹P N.M.R. spectra are reported

I.R. and ¹H and ³¹P N.M.R. spectra are reported in Table V. The Re-O(oxide) stretching frequencies of I and II fall in the usual range 1000-900 cm⁻¹. An interesting feature concerns their ¹H NMR spectra, which were not previously reported: the signals of the ethyl and methyl hydrogens of the alkoxo groups are found at anomalously high field.

The reaction of ReI₂O(OR)(PPh₃)₂ with water in acetone occurs as previously described [8], according to reaction 2:

$$ReI_{2}O(OR)(PPh_{3})_{2} + H_{2}O \xrightarrow{\text{acetone}}$$

$$ReIO_{2}(PPh_{3})_{2} (III) + ROH + HI$$
 (2)

Since the violet product III appeared rather surprising, (because five-coordinate species are unusual in the chemistry of Re(V)), we have reinvestigated the reaction. The formulation of III, based essentially

Re(V) Oxide Complexes 35

TABLE VI. Selected Bond Distances and Angles within the Compound ReI₂O(OEt)(PPh₃)₂·3/2C₆H₆ (I).

Distances (Å)	Angles (deg.)	
Re-I1	2.806(1)	$I_1 - Re - I_2$	169.8(1)
Re-I2	2.772(1)	$I_1 - Re - P_1$	89.1(1)
Re-P ₁	2.528(5)	I_1-Re-P_2	92.8(1)
$Re-P_2$	2.519(5)	I_1-Re-O_1	93.7(4)
$Re-O_1$	1.715(9)	I_1-Re-O_2	84.1(4)
Re-O ₂	1.880(9)	I_2-Re-P_1	90.4(1)
$P_1 - C_{111}$	1.841(12)	$I_2 - Re - P_2$	88.0(1)
$P_1 - C_{121}$	1.835(13)	$I_2 - Re - O_1$	96.5(4)
$P_1 - C_{131}$	1.839(12)	I_2-Re-O_2	85.7(4)
$P_2 - C_{211}$	1.850(11)	$P_1 - Re - P_2$	177.6(1)
$P_2 - C_{221}$	1.817(10)	P_1-Re-O_1	90.4(5)
$P_2 - C_{231}$	1.852(12)	$P_1 - Re - O_2$	91.5(4)
O_2-C_1	1.41(2)	P_2-Re-O_1	88.0(5)
C_1-C_2	1.56(3)	P_2-Re-O_2	90.1(4)
		$O_1 - Re - O_2$	177.1(5)
		$Re-O_2-C_1$	176.2(14)
		$O_2 - C_1 - C_2$	108.4(16)

Distances (Å)	Angles (deg.)	
Re-I ₁	2.764(1)	I_1 -Re- I_2	166.89(2)
Re-l ₂	2.800(1)	$I_1 - Re - P_1$	90.91(5)
$Re-P_1$	2.525(2)	$I_1 - Re - P_2$	88.47(5)
Re-P ₂	2.512(2)	$I_1 - Re - O_1$	97.2(2)
Re-O ₁	1.698(5)	$I_1 - Re - O_2$	83.8(2)
$Re-O_2$	1.859(5)	I_2-Re-P_1	90.57(5)
$P_1 - C_{111}$	1.835(8)	$I_2 - Re - P_2$	90.63(5)
$P_1 - C_{121}$	1.824(8)	I_2-Re-O_1	95.9(2)
$P_1 - C_{131}$	1.818(8)	$I_2 - Re - O_2$	83.1(2)
$P_2 - C_{211}$	1.808(7)	$P_1 - Re - P_2$	177.31(7)
$P_2 - C_{221}$	1.840(7)	$P_1 - Re - O_1$	88.5(2)
$P_2 - C_{231}$	1.832(8)	$P_1 - Re - O_2$	91.0(2)
$O_1 - C_1$	1.497(12)	P_2-Re-O_1	89.0(2)
C-C (phen	yl) 1.35(1)-	$P_2 - Re - O_2$	91.5(2)
1.43(1) (m	ean 1.40)	$O_1 - Re - O_2$	178.9(2)
C-C1 (chlo	roform)	$Re-O_2-C_1$	168.4(7)
1.73(1)-1.	.78(1)		

TABLE VII. Selected Bond Distances and Angles within

the Compound ReI₂O(OMe)(PPh₃)₂·CHCl₃ (II).

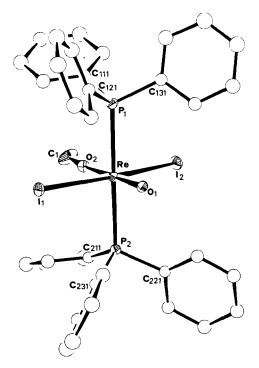


Fig. 2. A view of the complex ReI₂O(OMe)(PPh₃)₂.

on elemental analysis and I.R. spectra [8], has now been confirmed by X-ray investigation.

Description of the Structures

The structures of the hexa-coordinate species trans-ReI₂O(OR)(PPh₃)₂ are illustrated in Figs. 1 (I) and 2 (II). Bond distances and angles are listed in Tables VI and VII. The stereochemistries are very similar, with a trans disposition of the two phosphines, of the two iodide ligands and of the two oxygen donor ligands. While the two PPh3 groups are almost exactly trans between themselves, with P-Re-P angles of $177.6(1)^{\circ}$ (I) and $177.31(7)^{\circ}$ (II), some distorsions of the octahedral coordination are present within the other four ligands. In particular, the two iodides exhibit a bent I-Re-I interaction of $169.8(1)^{\circ}$ (I) and $166.89(2)^{\circ}$ (II), with larger I-Re-O (oxide) angles (mean values 95.1° (I) and 96.5° (II) than the I-Re-O(alkoxo) ones (mean values 84.9° (I) and 83.5° (II)). These distortions are related to the higher bond order associated to the Re-O(oxide) vs. the Re-O(alkoxo) bond.

The Re-P bond lengths (mean 2.523 Å (I) and 2.518 Å (II)), although slightly longer, are comparable with similar interactions e.g. 2.45-2.48 Å in ReCl₃O(PEt₂Ph)₂ [5], 2.41-2.43 Å in Re-(CO)₂(HCS₂)(PPh₃)₂ [12], 2.45 Å in ReCl₂N(PPh₃)₂ [13] and 2.44-2.49 Å in ReCl₂N(PEt₂Ph)₃ [14].

The Re-I interactions (mean 2.789 Å (I) and 2.782 Å (II)) are similar to the corresponding Re-I-(terminal) bonds in $[Re_3H_3I(CO)_{11}]^-$ (2.839(4) Å) [15] and in $[Re_4H_4I(CO)_{15}]^-$ (2.813(2) Å) [16]. The values, however, are somewhat longer than

TABLE VIII. Interatomic Distances and Angles within the Complex ReIO₂(PPh₃)₂ (III).

Distances (A))	Angles (deg.)	_
Re-I	2.664(2)	I-Re-P	96.4(1)
ReP	2.488(3)	I−Re–O	110.6(4)
Re-O	1.742(11)	P-Re-P'	167.2(1)
$P-C_{11}$	1.832(10)	P-Re-O	85.4(3)
P-C ₂₁	1.832(12)	P-Re-O'	90.1(3)
$P-C_{31}$	1.814(15)	O-Re-O'	138.7(6)
$P \cdots O$	2.921(10)	$Re-P-C_{11}$	116.7(3)
P····O'	3.038(11)	$Re-P-C_{21}$	115.1(4)
$O \cdot \cdot \cdot \cdot C_{31}$	3.22(2)	$Re-P-C_{31}$	108.6(5)
		$C_{11}-P-C_{21}$	105.8(5)
		$C_{11} - P - C_{31}$	104.9(6)
		$C_{21}-P-C_{31}$	104.6(7)

expected, when compared with the Re-I (terminal) intramolecular bond contacts in Re₃I₉, 2.580(5)–2.744(3) Å [17] and with the Re(V)-Br bond lengths, e.g. 2.51(1) Å in [ReBr₄O(H₂O)]⁻ [6], keeping into account the different covalent radii of Br and I, $1.11 \, \nu s. \, 1.28 \, \text{Å}.$

The values of the rhenium—oxygen bonds are discussed below.

The coordination geometry of the alkoxo groups is almost linear (Re-O-C angles of 176.2(14)° (I) and 168.4(7)° (II)). These M-O-C interactions are dictated by intramolecular and, possibly, intermolecular non-bonding contacts, and exhibit a variety of values (see *e.g.* a bent interaction of 149° in NbCl₂O(OEt)(bipy) [18]). Differently coordinated alcohols show considerably smaller M-O-C angles, as, for instance, in [ReBr₄(NO)(EtOH)]⁻ (Re-O-C 132.1(13)°) [19].

The five-coordinate species ReIO₂(PPh₃)₂ (III) possesses a rigorous C₂ crystallographic symmetry, the two-fold axis passing through the Re and I atoms. In contrast with the suggested square-pyramidal geometry of the anion [ReOBr₄]⁻ [20], this complex shows a stereochemistry intermediate between the trigonal-bipyramidal and the square-pyramidal one, as in the case of the nitrido species ReCl₂N(PPh₃)₂ [13]. The structure of ReIO₂(PPh₃)₂ is illustrated in Fig. 3 and the bond distances and angles are reported in Table VIII.

It resembles more a trigonal-bipyramid, the major deviations being the value of the P-Re-P' angle of the two axial phosphines, 167.2(1)°, and the difference between the bond angles involving the equatorial I and O ligands, I-Re-O 110.6(4)° and O-Re-O' 138.7(6)°. The two axial PPh₃ groups are bent toward the oxide ligands (I-Re-P 96.4(1)° vs. O-Re-P (mean) 87.7°). The Re-P bonds are

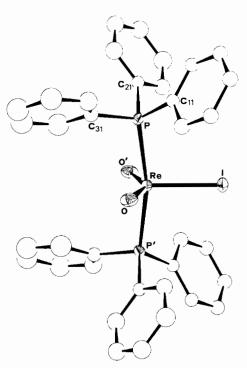


Fig. 3. A view of the complex $ReIO_2(PPh_3)_2$. A two-fold crystallographic axis passes through atoms Re and I.

only slightly shorter than in the six-coordinate species, while the Re-I interaction is quite shorter (of ca. 0.12 Å, on average). Analogous Re-ligand shortenings were previously observed in ReCl₂-N(PPh₃)₂ vs. ReCl₂N(PEt₂Ph)₃ and were attributed to steric factors on passing from the six-coordinate to the five-coordinate species [13].

The Rhenium-Oxygen Bond

The previous suggestions of a considerable triplebond character in the rhenium-oxygen interactions for terminal oxides in Re(V) species [4, 20] have been confirmed by the Re-O (oxide) bond lengths found in the six-coordinate species ReI2O(OR)-(PPh₃)₂, 1.715(9) Å (I) and 1.698(5) Å (II), values more reliable than the much too short bond of 1.60 A reported for the similar species ReCl₃O(PEt₂Ph)₂ [5]. The Re-O bond order exceeds two since both the px and py oxygen orbitals overlap with the rhenium d_{xz} and d_{yz} orbitals (z axis in the Re-O direction). This fact accounts also for the diamagnetism of the compounds, the two d electrons of the metal occupying the non-bonding d_{xy} orbital. Similar arguments were used to explain the diamagnetism of the square-pyramidal [ReOBr₄] anion [20]. Rheniumoxygen bond contacts were found in the range 1.60-2.32 Å. A rationalization of the bond orders was previously attempted [7, 13], assigning to Re-O single, double and triple bonds the theoretical values of 2.04, 1.86 and 1.75 Å, respectively. On that basis,

TABLE IX. Rhenium-Oxide (terminal) Bond Lengths in Mononuclear Re(V) Species.

Compound	Distance (Å)	Ref.
ReCl ₃ O(PEt ₂ Ph) ₂	1.60	5
$[ReBr_4O(H_2O)]^{-1}$	1.71(4)	6
[ReBr ₄ O(MeCN)]	1.73(6)	7
Rel ₂ O(OMe)(PPh ₃) ₂	1.698(5)	this work
$ReI_2O(OEt)(PPh_3)_2$	1.715(9)	this work
$[ReO_2(py)_4]^+$	1.76(3)	21
$\left[\text{ReO}_2(\text{CN})_4\right]^{3-1}$	1.773(8)	22
•	1.781(3)	23
RelO ₂ (PPh ₃) ₂	1.742(11)	this work

however, not only the Re–O(oxide) bonds reported here must be considered triple, but also the Re–O(alkoxo) interactions, 1.880(9) Å (I) and 1.859(5) Å (II), must have a considerable double bond character. Rhenium—oxide bond lengths in Re(V) species are reported in Table IX. As can be seen, the Re—oxide bonds are longer in dioxide species, close to the values expected for double bonds, probably as a consequence of a certain competition in the Re–O π -bonding.

It is interesting to note that ReIO₂(PPh₃)₂ is unique, showing the two oxide ligands not in *trans* positions between themselves.

The relatively lower values of the Re-O interactions in III, with respect to the other dioxide species, can be explained by taking into account the five-coordination of the compound (see above).

Acknowledgement

We thank the Italian Ministero della Pubblica Istruzione for financial support.

References

- 1 G. Rouschias, Chem. Rev., 74, 531 (1974).
- 2 J. Chatt and G. A. Rowe, J. Chem. Soc., 4019 (1962).
- 3 N. P. Johnson, C. J. L. Lock and G. Wilkinson, *J Chem. Soc.*, 1054 (1964).
- 4 J. Chatt, J. D. Garforth, N. P. Johnson and G. A. Rowe, J. Chem. Soc., 1012 (1964).
- 5 H. W. W. Elrhich and P. G. Owston, J. Chem. Soc., 4368 (1963).
- 6 F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 4, 1621 (1965).
- 7 F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 5, 416 (1966).
- 8 M. Freni, D. Giusto, P. Romiti and G. Minghetti, *Gazz. Chim. It.*, 99, 286 (1969).
- 9 See footnote to: G. Ciani, M. Manassero and A. Sironi, J. Organomet. Chem., 199, 271 (1980).
- D. T. Cromer and J. B. Mann, Acta Crystallogr. A24, 321 (1968).
- 11 'International Tables for X-Ray Crystallography', Vol. 4, Kynoch Press, Birmingham (1974).
- Y. G. Albano, P. L. Bellon and G.Ciani, J. Organomet. Chem., 31, 75 (1971).
- 13 R. J. Doedens and J.A. Ibers, *Inorg. Chem.*, 6, 204 (1967).
- 14 P. W. R. Corfield, R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).
- 15 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, J. Organomet. Chem., 220, C11 (1981).
- 16 G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, J. Organomet. Chem., 170, C15 (1979).
- 17 M. J.Bennett, F. A. Cotton and B. M. Foxman, *Inorg. Chem.*, 8, 1563 (1968).
- 18 B. Kamenar and C. K. Prout, J. Chem. Soc. (A), 2379 (1970).
- 19 G. Ciani, D. Giusto, M. Manassero and M. Sansoni, J. Chem. Soc. Dalton, 2156 (1975).
- F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 5, 9 (1966).
- 21 C. Calvo, N. Krishnamachari and C. J. L. Lock, J. Cryst. Mol. Struct., 1, 161 (1971).
- 22 R. H.Fenn, A. J.Graham and N. P. Johnson, J. Chem. Soc. (A), 2880 (1971).
- 23 R. K. Murmann and E. O. Schlemper, *Inorg. Chem.*, 10, 2352 (1971).