The Structure of *trans*-Dibromooxo(*N*-phenylsalicylideneiminato)-(triphenylphosphine)rhenium(V)

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Abstract

$C_{31}H_{25}Br_2NO_2PRe$, $M_r = 820 \cdot 5$, $P2_1/a$; $a = 15 \cdot 608$ (4), $b = 11 \cdot 469$ (3), $c = 16 \cdot 413$ (3) Å, $\beta = 92 \cdot 32$ (2)°, $Z = 4$, $D_c = 1 \cdot 86$ Mg m⁻³, μ(Mo $K\alpha$) = 6·69 mm⁻¹. The crystal structure has been determined and refined from 3817 diffractometer data to an R value of 0·037. The coordination around the Re atom is approximately octahedral and the two O and two Br atoms are *trans* to each other. The deformations from octahedral geometry are interpreted in terms of the different repulsion exerted by the oxo group on the *cis* ligands, and the conformation of the PPh_3 ligand is discussed in terms of nonbonded intramolecular potential energy.

Introduction

Reaction of *trans*-[ReOX$_3$(PPh$_3$)$_2$] ($X = $ Cl or Br) with N-substituted salicylideneimines (*R*-salH) is known to give rise to two different series of quasi-octahedral complexes of Re^V, namely [Re^{V}OX$_2$(PPh$_3$)(*R*-sal)] and [Re^{V}OX(*R*-sal)$_2$] (Mazzi, Roncari, Rossi, Bertolasi, Traverso & Magon, 1980). In this latter class of complexes we have recently reported (Gilli, Sacerdoti, Bertolasi & Rossi, 1982) the crystal and molecular structure of [Re^{V}OCl(Me-sal)$_2$], while the only complex of known molecular structure belonging to the first class is [Re$_2^V$O$_2$Cl$_4$(PPh$_3$)$_2$(salen)] [salen = *N,N'*-ethyl-enebis(salicylideneiminato)], where 'salen' behaves as a bisbidentate ligand connecting, by means of the ethylene chain, two quasi-octahedral coordination polyhedra (Bombieri, Mazzi, Gilli & Hernández-Cano, 1978). Both *cis* and *trans* isomers of the type [ReOX$_2$(PPh$_3$)(*R*-sal)] can be obtained according to the reaction conditions (solvent, PPh$_3$ concentration, time and temperature) and the present paper reports the crystal and molecular structure of the yellow-brown reaction product of [ReOBr$_3$(PPh$_3$)$_2$] with (Ph-salH)

(Mazzi, Roncari, Rossi, Duatti & Magon, 1981), which was found to be *trans*-[Re^{V}OBr$_2$(PPh$_3$)(Ph-sal)].

Intensities were collected on an automatic Siemens AED diffractometer (Zr-filtered Mo $K\alpha$ radiation,

Table 1. *Positional* (×10⁴) *and thermal* (Å² ×10³) *parameters* (*Hamilton*, 1959) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}
Re	2354·9 (2)	481·3 (3)	1816·9 (2)	31·2 (2)
Br(1)	2387 (1)	2292 (1)	2731 (1)	51 (1)
Br(2)	2596 (1)	−1161 (1)	804 (1)	49 (1)
P	2759 (1)	−831 (2)	2958 (1)	35 (1)
O(1)	1308 (3)	181 (4)	1911 (3)	40 (3)
O(2)	3543 (3)	849 (4)	1634 (3)	39 (3)
N	2121 (4)	1566 (5)	745 (4)	35 (4)
C(1)	2690 (5)	1922 (6)	241 (5)	42 (5)
C(2)	3602 (5)	1725 (7)	322 (5)	40 (5)
C(3)	4101 (6)	2107 (7)	−324 (5)	51 (6)
C(4)	4976 (6)	1908 (8)	−296 (6)	59 (6)
C(5)	5357 (6)	1357 (8)	377 (5)	55 (6)
C(6)	4891 (5)	998 (7)	1037 (5)	43 (5)
C(7)	4005 (5)	1189 (6)	1009 (5)	35 (4)
C(8)	1235 (5)	1755 (7)	502 (6)	49 (6)
C(9)	698 (6)	2327 (8)	1010 (6)	65 (7)
C(10)	−150 (7)	2492 (11)	750 (10)	104 (11)
C(11)	−456 (8)	2111 (14)	5 (12)	129 (13)
C(12)	91 (9)	1515 (12)	−491 (10)	117 (12)
C(13)	948 (6)	1331 (8)	−250 (7)	72 (8)
C(14)	3917 (5)	−891 (7)	3075 (5)	42 (5)
C(15)	4353 (6)	−149 (8)	3616 (6)	64 (7)
C(16)	5237 (7)	−157 (10)	3677 (7)	82 (8)
C(17)	5688 (7)	−869 (10)	3185 (7)	76 (8)
C(18)	5280 (6)	−1605 (9)	2647 (6)	68 (7)
C(19)	4390 (6)	−1614 (8)	2583 (5)	52 (6)
C(20)	2355 (5)	−457 (7)	3943 (4)	38 (4)
C(21)	2720 (6)	−893 (7)	4671 (5)	55 (6)
C(22)	2353 (8)	−674 (8)	5415 (6)	74 (8)
C(23)	1620 (8)	−24 (8)	5438 (7)	77 (8)
C(24)	1233 (6)	381 (8)	4724 (6)	62 (6)
C(25)	1592 (5)	171 (6)	3978 (5)	43 (5)
C(26)	2372 (5)	−2324 (6)	2830 (5)	37 (5)
C(27)	2812 (7)	−3273 (7)	3169 (6)	70 (6)
C(28)	2452 (8)	−4373 (8)	3136 (7)	91 (9)
C(29)	1650 (8)	−4546 (8)	2775 (6)	71 (7)
C(30)	1197 (7)	−3617 (8)	2456 (6)	66 (7)
C(31)	1559 (6)	−2508 (7)	2477 (5)	52 (6)

$\omega/2\theta$ scan, $\theta \leq 26°$) from a crystal of dimensions 0·30 × 0·20 × 0·20 mm in the [100], [011] and [0$\bar{1}$1] directions respectively. Of 5758 independent reflections, 3817 having $I_o \geq 3\sigma(I_o)$ were considered to be observed. Absorption correction was applied by geometrical methods. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and computations were carried out by means of the *SHELX* 76 system of programs (Sheldrick, 1976). The structure was solved by Patterson and Fourier methods and refined by blocked-matrix (two blocks) least squares in the anisotropic mode for all non-hydrogen atoms. H atoms were assigned calculated positions (C—H distance 1·08 Å) and isotropic temperature factors 10% greater than those of the bonded atoms. Weights were given according to the formula $k_1/w = \sigma^2(F_o) + k_2|F_o|^2$, where k_1 and k_2 are constants to be determined. The final discrepancy factors $R = \sum |\Delta| / \sum |F_o|$ and $R_w = \sum w^{1/2}|\Delta| / \sum w^{1/2}|F_o|$ were 0·037 and 0·032 respectively. Positional and thermal parameters are given in Table 1.*

Discussion

A general view of the molecule is shown in Fig. 1 and bond distances and angles are listed in Tables 2 and 3. The crystal is built up of monomeric units and the only intermolecular contacts shorter than the sum of the van der Waals radii (Bondi, 1964) are those between H(27) and C(5) at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ [2·68 (2) Å], between

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36221 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
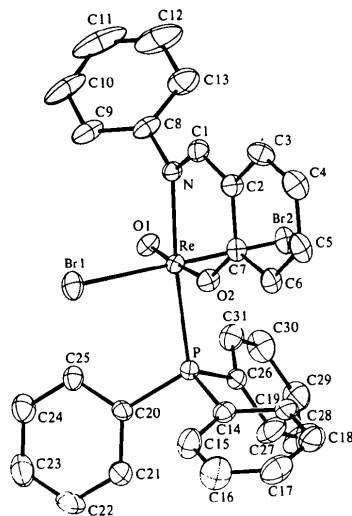

Fig. 1. An *ORTEP* (Johnson, 1971) view of the molecule showing the thermal ellipsoids at 40% probability.

Table 2. *Interatomic distances* (Å) *with e.s.d.'s in parentheses*

Re—Br(1)	2·562 (1)	C(10)—C(11)	1·37 (2)
Re—Br(2)	2·550 (1)	C(11)—C(12)	1·38 (2)
Re—P	2·465 (2)	C(12)—C(13)	1·39 (2)
Re—O(1)	1·683 (5)	C(14)—C(15)	1·39 (1)
Re—O(2)	1·937 (5)	C(14)—C(19)	1·39 (1)
Re—N	2·173 (6)	C(15)—C(16)	1·38 (1)
P—C(14)	1·812 (8)	C(16)—C(17)	1·36 (2)
P—C(20)	1·809 (8)	C(17)—C(18)	1·36 (2)
P—C(26)	1·824 (7)	C(18)—C(19)	1·39 (1)
O(2)—C(7)	1·336 (9)	C(20)—C(21)	1·40 (1)
N—C(1)	1·30 (1)	C(20)—C(25)	1·39 (1)
N—C(8)	1·44 (1)	C(21)—C(22)	1·39 (1)
C(1)—C(2)	1·44 (1)	C(22)—C(23)	1·37 (2)
C(2)—C(3)	1·41 (1)	C(23)—C(24)	1·38 (2)
C(2)—C(7)	1·41 (1)	C(24)—C(25)	1·39 (1)
C(3)—C(4)	1·38 (1)	C(26)—C(27)	1·39 (1)
C(4)—C(5)	1·38 (1)	C(26)—C(31)	1·39 (1)
C(5)—C(6)	1·39 (1)	C(27)—C(28)	1·38 (1)
C(6)—C(7)	1·40 (1)	C(28)—C(29)	1·38 (2)
C(8)—C(9)	1·37 (1)	C(29)—C(30)	1·37 (1)
C(8)—C(13)	1·38 (1)	C(30)—C(31)	1·39 (1)
C(9)—C(10)	1·39 (1)		

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

Br(1)—Re—Br(2)	168·8 (1)	O(2)—C(7)—C(6)	119·5 (7)
Br(1)—Re—P	93·0 (1)	C(2)—C(7)—C(6)	120·2 (7)
Br(1)—Re—O(1)	96·2 (2)	N—C(8)—C(9)	120·4 (8)
Br(1)—Re—O(2)	85·3 (1)	N—C(8)—C(13)	117·9 (8)
Br(1)—Re—N	90·5 (2)	C(9)—C(8)—C(13)	121·7 (8)
Br(2)—Re—P	90·2 (1)	C(8)—C(9)—C(10)	118·4 (10)
Br(2)—Re—O(1)	94·5 (2)	C(9)—C(10)—C(11)	121·8 (12)
Br(2)—Re—O(2)	83·8 (1)	C(10)—C(11)—C(12)	118·9 (13)
Br(2)—Re—N	85·4 (2)	C(11)—C(12)—C(13)	121·0 (14)
P—Re—O(1)	91·4 (2)	C(8)—C(13)—C(12)	118·2 (11)
P—Re—O(2)	91·9 (2)	P—C(14)—C(15)	120·4 (6)
P—Re—N	173·7 (2)	P—C(14)—C(19)	120·8 (6)
O(1)—Re—O(2)	176·3 (2)	C(15)—C(14)—C(19)	118·7 (8)
O(1)—Re—N	93·4 (2)	C(14)—C(15)—C(16)	120·4 (9)
O(2)—Re—N	83·1 (2)	C(15)—C(16)—C(17)	120·0 (10)
Re—P—C(14)	109·1 (3)	C(16)—C(17)—C(18)	121·1 (10)
Re—P—C(20)	116·5 (3)	C(17)—C(18)—C(19)	119·6 (9)
Re—P—C(26)	114·3 (3)	C(14)—C(19)—C(18)	120·3 (8)
C(14)—P—C(20)	107·3 (7)	P—C(20)—C(21)	122·4 (6)
C(14)—P—C(26)	107·5 (4)	P—C(20)—C(25)	119·2 (6)
C(20)—P—C(26)	101·5 (4)	C(21)—C(20)—C(25)	118·0 (7)
Re—O(2)—C(7)	137·1 (5)	C(20)—C(21)—C(22)	121·2 (9)
Re—N—C(1)	126·6 (5)	C(21)—C(22)—C(23)	119·8 (9)
Re—N—C(8)	116·1 (5)	C(22)—C(23)—C(24)	119·9 (10)
C(1)—N—C(8)	116·6 (6)	C(23)—C(24)—C(25)	120·9 (9)
N—C(1)—C(2)	126·0 (7)	C(20)—C(25)—C(24)	120·1 (8)
C(1)—C(2)—C(3)	117·1 (7)	P—C(26)—C(27)	122·1 (6)
C(1)—C(2)—C(7)	123·2 (7)	P—C(26)—C(31)	118·9 (6)
C(3)—C(2)—C(7)	119·7 (7)	C(27)—C(26)—C(31)	118·4 (7)
C(2)—C(3)—C(4)	119·9 (8)	C(26)—C(27)—C(28)	120·4 (9)
C(3)—C(4)—C(5)	119·5 (9)	C(27)—C(28)—C(29)	120·6 (9)
C(4)—C(5)—C(6)	122·4 (8)	C(28)—C(29)—C(30)	119·9 (9)
C(5)—C(6)—C(7)	118·3 (7)	C(29)—C(30)—C(31)	119·9 (9)
O(2)—C(7)—C(2)	120·3 (6)	C(26)—C(31)—C(30)	120·8 (8)

C(24) and C(9) at $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ [3·49 (1) Å] and between Br(2) and H(11) at $(-x, -y, -z)$ [2·79 (1) Å].

The coordination around the Re atom is approximately octahedral with the two O atoms occupying the apical positions and the two Br atoms in the equatorial plane and *trans* to each other. The chelate ring is not planar: atoms C(1) through C(7) lie on a plane within experimental errors ($\chi^2 = 21·0$) and the O(2) atom is displaced from this plane by only 0·031 Å, but the N

and Re atoms are definitely out of plane, their displacements being -0.127 and -0.430 Å respectively. All remaining phenyl groups show no significant displacement from planarity.

The conformation of the triphenylphosphine ligand is such that the P—C(14) bond eclipses, almost exactly, the Re—O(2) bond and it would be of interest to establish whether this arrangement is produced by the simple balance of the nonbonded interactions. This can be accomplished by minimizing the nonbonded intra-molecular potential energy of the free molecule by using semi-empirical atom–atom potentials (Giglio, 1969) and the steepest-descent method. Some addition-al assumptions are needed owing to the lack of proper potentials for P, Br and Re atoms. If it is taken into account that the analytical form of the atom–atom potentials is mainly determined by the van der Waals radii of the atoms involved, potentials pertaining to S and the methyl group can be used for P and Br, as $r_w(S) = r_w(P) = 1.70$ Å (Bondi, 1964) and molecular volumes of Br and $-CH_3$ in organic molecules are similar (Kitaigorodsky, 1973; Dunitz, 1979). Finally, the Re atom was assigned potentials pertaining to C, the only justification being the small van der Waals radius usually associated with metals in metal organic compounds (Bondi, 1964) and also the fact that the Re atom probably has a weak influence on the ligand conformation owing to its central position. In spite of the approximations, the results are fairly good, showing that the ligand adopts the expected conformation of minimum nonbonded energy; the experimental values of the four relevant torsion angles O(2)–Re–P–C(14), Re–P–C(14)–C(15), Re–P–C(20)–C(21) and Re–P–C(26)–C(27) of -1.9, 93.5, -160.7 and $150.2°$ are fairly well matched by the values obtained after minimization, i.e. 3.7, 95.3, -164.8 and $147.0°$ respectively.

In general, the agreement between the present bond distances and those observed in other Re^V quasi-octahedral oxo complexes is good. The Re—O(1) distance of 1.683 (5) Å is indicative of the formation of a Re—O_{oxo} triple bond, in agreement with the diamagnetic properties of this compound, and is strictly comparable with the values of 1.680 (4), 1.69 (1), 1.68 (1) and 1.685 (8) Å found in [ReOCl(Me-sal)$_2$] (Gilli, Sacerdoti, Bertolasi & Rossi, 1981), [ReOCl$_2$(PPh$_3$)(acac)] (Lock & Che'ng Wan, 1975), [Re$_2$O$_2$Cl$_4$(PPh$_3$)$_2$(salen)] (Bombieri, Mazzi, Gilli & Hernández-Cano, 1978) and [ReOCl$_2$(PPh$_3$)-{Ph(O)CNNCMe$_3$}] (Hursthouse, Jayaweera & Quick, 1979). The Re—P distances found in the last two complexes [2.466 (4) and 2.472 (4); 2.472 (2) Å] also compare well with the corresponding value in the present structure [2.465 (2) Å]. Few data are available on Re—Br distances in octahedral Re^V complexes and the present distances of 2.562 (1) and 2.550 (1) Å can be compared only with the rather inaccurate values

reported by Cotton & Lippard (1965, 1966) in [ReOBr$_4$(H$_2$O)]$^-$ [2.51 (1) Å] and [ReOBr$_4$(CH$_3$CN)]$^-$ [ranging from 2.43 (3) to 2.51 (3) Å].

In a previous paper (Gilli, Sacerdoti, Bertolasi & Rossi, 1982) we have reviewed the crystal structures of quasi-octahedral oxorhenium(V) complexes with oxy-genated bidentate ligands and found that the geom-etries of their coordination polyhedra are consistent with the following two rules. First, there appears to be a clear preference for the trans O≡Re—OR con-figuration and this arrangement has been explained by admitting that it corresponds to a minimum of trans-weakening caused by the multiple Re≡O$_{oxo}$ bond. Second, the repulsion exerted by the O$_{oxo}$ atom in view of the very short Re≡O$_{oxo}$ distance (or, alternatively, the increased space occupied by the localized π orbitals of the oxo group) causes a compression field which tends to increase the mean O$_{oxo}$≡Re—L_{cis} angle beyond 90°, the actual value of each single angle not being related to the distances of closest approach (sums of van der Waals radii) of the second neighbors but following the order $R_3P < R=N-R' \ll Cl^- < O^-$, as far as the nature of L_{cis} is concerned. Typical O$_{oxo}$≡Re—L_{cis} angles, as averaged from the few crystal structures so far determined, were 86 ± 2, 88 ± 1, 99 ± 2 and $103°$ respectively.

The present compound complies with the first rule, as the two O atoms are found to be trans to each other. Moreover, the Re—O(2) single-bond distance of 1.937 (5) Å is shorter than the Re—O_{cis} distances found in [ReOCl(Me-sal)$_2$] and [ReOCl$_2$(PPh$_3$)(acac)], i.e. 1.995 (4) and 1.99 (1) Å respectively, confirming the absence, for this ligand, of trans-weakening caused by the oxo group.

As for the deformation of the coordination poly-hedron, the relevant angular values are O(1)–Re–P = 91.4 (2), O(1)–Re–N = 93.4 (2), O(1)–Re–Br(1) = 96.2 (2) and O(1)–Re–Br(2) = 94.5 (2)°. They appear to follow the expected order (P < N < Br$^-$) and the higher values of the two angles involving N and P, when compared with the mean values previously reported for chloro complexes, can be ascribed to a rearrangement of the strains as a consequence of the fact that the O$_{oxo}$≡Re—L_{cis} angle is nearly 4° smaller for bromo than for chloro derivatives. In general, the experimental data, taken as a whole, seem to be consistent with the idea that the repulsion exerted by the oxo group on the equatorial ligands increases in the order P < N(imino) < Br$^-$ < Cl$^-$ < O$^-$, an order which is not meaningless from a chemical point of view as it corresponds to that of increasing hardness of the ligand as a base. The principle of HSAB [hard and soft acids and bases (Pearson, 1963; Pearson & Songstad, 1967)], already applied in relation to Re^V complexes for interpreting the rearrangement of the Re—N and Re—O distances as a function of the oxidation number of the central atom (Gilli, Sacerdoti, Bertolasi & Rossi, 1982),

also seems to be applicable in interpreting the distortions of the coordination polyhedron. As the increasing hardness of the base can be interpreted in terms of increasing ionic character of the bond between the base itself and the hard acid Re^V, it may be expected that the harder atom ligands gain steric hindrance (increase their van der Waals radius) as a consequence of the higher population of their orbitals, in keeping with the observed deviations from the ideal octahedral geometry.

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The Structure of (2-Dimethylaminoethanolato)(trifluoroacetato)copper(II) Tetramer

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Abstract

$[Cu_4(C_2F_3O_2)_4(C_4H_{10}NO)_4]$, $C_{24}H_{40}Cu_4F_{12}N_4O_{12}$, $M_r = 1058·8$, monoclinic, $P2_1/c$, $a = 14·073$ (3), $b = 21·379$ (5), $c = 14·201$ (3) Å, $\beta = 104·65$ (2)°, $Z = 4$, $D_m = 1·70$, $D_c = 1·701$ Mg m^{-3}, μ (Mo $K\alpha$) = 2·22 mm^{-1}. Final $R = 0·087$ for 3584 reflections. The Cu and bridging ethanolato O atoms form a cubane-type Cu_4O_4 core in which the short Cu–O(ethanolato) bonds form an eight-membered ring folded in a boat-like conformation. The Cu–Cu distances range from 3·154 (2) to 3·813 (2) Å. Each Cu^{II} atom has a distorted octahedral environment; two ethanolato O atoms, a carboxyl O atom and an amino N atom form the equatorial coordination plane with Cu–O bonds of 1·914 (9)–1·968 (9) Å and a Cu–N bond of 2·052 (12)–2·062 (13) Å. The axial sites are occupied by a carboxyl O atom and an ethanolato O atom with Cu–O distances of 2·663 (11)–2·847 (11) Å. The trifluoroacetate groups are bidentate, bridging in a *syn–syn* configuration from an equatorial coordination site of one Cu atom to an axial site of another.

Introduction

As part of our studies on the effects of halogeno substitution of the carboxylate ligand on structures of transition-metal complexes we have prepared several copper(II) carboxylate complexes with 2-dialkyl-aminoethanols. Copper(II) acetate forms with 2-diethylaminoethanol a novel centrosymmetric hexa-