

magnetic moment. As we did not succeed in locating the H atom, we do not know whether the π bond is actually formed by the d_{xy} or d_{xz} AO's, although the observed deformations in the coordination polyhedron seem to indicate that the last AO is more probably used. In fact the greater repulsion exerted by oxygen towards the P atoms, which could not be explained by the balance of the intramolecular contacts, can be understood in terms of increased angular space occupied by the π MO in the P(1)–Re–P(2) plane.

A comparison of the Re–P and Re–Cl distances observed in the present compound with those found in oxo complexes of Re^V is reported in Table 4. The mean Re–P distance of 2.47 Å agrees well with that observed in the other molecules studied, with the exception of [ReOCl₂(PPh₃)(acac)], where this distance was found significantly shorter (2.43 Å). The Re–Cl distances deserve more attention. Data of Table 4 show that Re–Cl distances are systematically longer when the Cl atom is *trans* to a ligand known to exert a relevant *trans* influence (like thiourea or PR₃) and that a similar lengthening of the Re–Cl bond *trans* to the multiply bonded O atom is observed in the compound under examination. However, whether or not such an effect can be interpreted in terms of *trans* weakening remains controversial, as Bright & Ibers (1969) believe that the weakening of bonds *trans* to multiply bonded nitrido or imino ligands is essentially caused by steric repulsion of other ligands, while Shustorovich, Porai-Koshits & Buslaev (1975) uphold with theoretical arguments and structural data the point of view of a true *trans* influence exerted by a multiple metal–ligand bond.

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Structure of Chlorobis(*N*-methylsalicylideneiminato)oxorhenium(V)

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Abstract

C₁₆H₁₆ClN₂O₃Re, $M_r = 505.9$, is monoclinic, space group *I2/c*; $a = 20.731(4)$, $b = 11.949(3)$, $c = 13.578(3)$ Å, $\beta = 94.13(2)^\circ$, $Z = 8$, $D_c = 2.00$ Mg

0567-7408/82/010100-05\$01.00

m^{-3} , $\mu(\text{Mo } K\alpha) = 7.08 \text{ mm}^{-1}$. The crystal structure has been determined and refined to an *R* value of 0.028 for 2767 observed reflections. The coordination around the Re atom is approximately octahedral. The two bidentate ligands are mutually orthogonal and the oxygen of

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one of them is *trans* to the multiply bonded O_{oxo} atom. The reasons for this arrangement are discussed in terms of the *trans* influence of the Re≡O bond.

Introduction

Re^v is known to give three different classes of complexes with multiple Re–X bonds, *i.e.* nitrido-, imino- and oxo-rhenium derivatives. In all these compounds Re–X stretching frequencies, magnetic properties, X-ray-determined bond distances and AO symmetry considerations seem to agree in indicating the formation of a strong triple Re≡X bond. Recently some of us have been interested (Mazzi, Roncari, Rossi, Bertolasi, Traverso & Magon, 1980) in the reaction of [ReOX₃(PR₃)] (X = Cl or Br) with substituted salicylideneimine 'R-salH' (R = Me, Ph) and have shown that the reaction leads to two different classes of oxo derivatives of Re^v, having the formula [ReOX₂(PR₃)(R-sal)] or [ReOX(R-sal)₂] and whose configurations were determined mainly by IR and ¹H NMR spectroscopy. At the same time the crystal-structure determinations of some of them were undertaken and the present paper reports the structure of [ReOCl(N-methylsalicylideneiminato)₂] {hereafter [ReOCl(Me-sal)₂]}, which belongs to the class of the [ReOX(R-sal)₂] derivatives. No other crystal structure has been reported so far in this class of compounds, while a single structure determination is known of compounds having the general formula [ReOX₂(PR₃)(R-sal)], namely that of [Re₂O₂Cl₄(PPh₃)₂(salen)] (Bombieri, Mazzi, Gilli & Hernández-Cano, 1978). In this complex the 'salen' ligand [salen = N,N'-ethylenebis(salicylideneiminato)] was found to bridge two Re atoms which present a distorted octahedral coordination with the O_{oxo} *trans* to the O of the ligand itself.

It will be shown here that this configuration (R–O–*trans* to O_{oxo}) is the most common in this class of complexes and can be justified on the grounds of simple theoretical arguments and, moreover, that the deformations from the octahedral coordination are not casual but follow a general scheme, which is common to Re^v nitrido complexes.

Experimental

Intensity data have been collected by means of an automatic Siemens AED diffractometer using Zr-filtered Mo K α radiation and an $\omega/2\theta$ scan technique ($\theta \leq 26^\circ$). The dimensions of the crystal used were 0.4 × 0.1 × 0.1 mm in the [001], [110] and [110] directions respectively. Out of 3290 reflections measured, 2767 having $I_o \geq 3\sigma(I_o)$ were used in the refinement. Irradiated crystals were stable during the data-collection time. Polarization and Lorentz corrections were

Table 1. *Positional* ($\times 10^4$) and *thermal* ($\text{\AA}^2 \times 10^3$) parameters with *e.s.d.'s* in parentheses

U_{eq} according to Hamilton (1959).				
	x	y	z	U_{eq}
Re	3246.4 (1)	4148.5 (2)	4953.7 (2)	36.4 (2)
Cl	3920 (1)	3057 (2)	3956 (1)	52 (1)
O(1)	3217 (2)	3289 (4)	5928 (3)	53 (3)
O(2)	3292 (2)	5402 (4)	4009 (3)	42 (2)
O(3)	2501 (2)	3628 (4)	4060 (3)	44 (2)
N(1)	4103 (2)	4886 (5)	5609 (4)	48 (3)
N(2)	2651 (2)	5262 (5)	5673 (3)	43 (3)
C(1)	3545 (3)	6422 (5)	4048 (4)	43 (3)
C(2)	3293 (4)	7209 (6)	3371 (6)	59 (5)
C(3)	3568 (4)	8269 (7)	3388 (7)	73 (6)
C(4)	4083 (5)	8526 (7)	4050 (8)	82 (6)
C(5)	4329 (4)	7763 (7)	4713 (6)	68 (5)
C(6)	4058 (3)	6682 (6)	4733 (5)	51 (4)
C(7)	4331 (3)	5868 (7)	5417 (5)	54 (4)
C(8)	4476 (3)	4204 (8)	6355 (6)	71 (5)
C(9)	1934 (3)	4167 (5)	3903 (4)	39 (3)
C(10)	1513 (3)	3730 (6)	3137 (5)	48 (4)
C(11)	915 (3)	4219 (6)	2913 (5)	56 (3)
C(12)	727 (3)	5151 (7)	3425 (6)	61 (4)
C(13)	1139 (3)	5586 (6)	4170 (5)	54 (4)
C(14)	1747 (3)	5104 (6)	4428 (2)	46 (4)
C(15)	2100 (3)	5576 (5)	5291 (5)	47 (4)
C(16)	2878 (3)	5758 (6)	6631 (5)	58 (4)

applied as usual; absorption correction was applied by geometrical methods. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and computations were mainly carried out by means of the *SHELX 76* (Sheldrick, 1976) system of crystallographic programs.

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares with anisotropic temperature factors for all the non-H atoms. H atoms were assigned calculated positions (C–H bond length of 1.08 Å) and isotropic temperature factors 10% greater than the average U_H 's of the bonded atoms. Weights were given according to the scheme $k_1/w = \sigma^2(F_o) + k_2|F_o|^2$, where k_1 and k_2 are constants to be determined. In the last cycle $R (= \sum |A|/\sum |F_o|)$ and $R_w [= (\sum |A|^2/\sum w|F_o|^2)^{1/2}]$ were respectively 0.028 and 0.038. It may be of interest to remark that the geometrical absorption correction reduced R from 0.049 to its current value (0.028). Final values of the positional parameters and U_{eq} (Hamilton, 1959) are given in Table 1.*

Discussion

The structure consists of a van der Waals packing of single molecules without significantly short inter-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36153 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

molecular contacts. An *ORTEP* (Johnson, 1971) view of the molecule is shown in Fig. 1 and bond distances and angles are reported in Table 2.

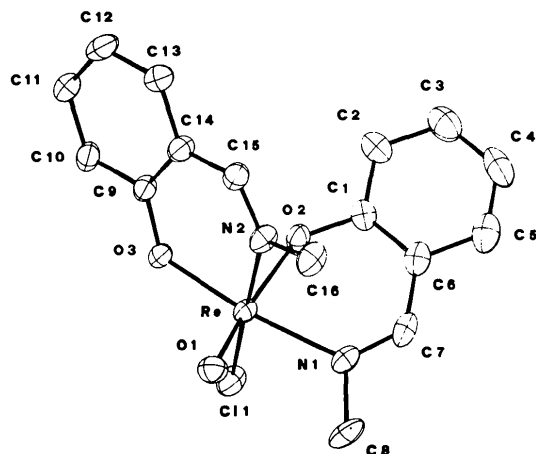


Fig. 1. An *ORTEP* (Johnson, 1971) view of the molecule showing the thermal ellipsoids at 40% probability.

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

Re—Cl	2.399 (2)	C(1)—C(6)	1.40 (1)
Re—O(1)	1.680 (4)	C(2)—C(3)	1.39 (1)
Re—O(2)	1.979 (4)	C(3)—C(4)	1.38 (1)
Re—O(3)	1.995 (4)	C(4)—C(5)	1.35 (1)
Re—N(1)	2.120 (5)	C(5)—C(6)	1.41 (1)
Re—N(2)	2.103 (5)	C(6)—C(7)	1.43 (1)
O(2)—C(1)	1.326 (7)	C(9)—C(10)	1.41 (1)
O(3)—C(9)	1.343 (7)	C(9)—C(14)	1.40 (1)
N(1)—C(7)	1.298 (9)	C(10)—C(11)	1.38 (1)
N(1)—C(8)	1.475 (8)	C(11)—C(12)	1.38 (1)
N(2)—C(15)	1.276 (8)	C(12)—C(13)	1.38 (1)
N(2)—C(16)	1.476 (8)	C(13)—C(14)	1.41 (1)
C(1)—C(2)	1.39 (1)	C(14)—C(15)	1.45 (1)
Cl—Re—O(1)	99.7 (2)	O(2)—C(1)—C(2)	117.8 (6)
Cl—Re—O(2)	89.3 (1)	O(2)—C(1)—C(6)	120.7 (6)
Cl—Re—O(3)	86.8 (1)	C(2)—C(1)—C(6)	121.4 (6)
Cl—Re—N(1)	87.6 (1)	C(1)—C(2)—C(3)	118.2 (8)
Cl—Re—N(2)	172.3 (1)	C(2)—C(3)—C(4)	120.7 (9)
O(1)—Re—O(2)	168.5 (2)	C(3)—C(4)—C(5)	121.3 (8)
O(1)—Re—O(3)	102.6 (2)	C(4)—C(5)—C(6)	120.0 (8)
O(1)—Re—N(1)	90.1 (2)	C(1)—C(6)—C(5)	118.4 (7)
O(1)—Re—N(2)	88.0 (2)	C(1)—C(6)—C(7)	121.8 (6)
O(2)—Re—O(3)	85.0 (2)	C(5)—C(6)—C(7)	119.7 (7)
O(2)—Re—N(1)	83.1 (2)	N(1)—C(7)—C(6)	127.7 (6)
O(2)—Re—N(2)	83.1 (2)	O(3)—C(9)—C(10)	115.4 (6)
O(3)—Re—N(1)	166.9 (2)	O(3)—C(9)—C(14)	125.0 (5)
O(3)—Re—N(2)	91.4 (2)	C(10)—C(9)—C(14)	119.6 (6)
N(1)—Re—N(2)	92.6 (2)	C(9)—C(10)—C(11)	120.2 (7)
Re—O(2)—C(1)	135.0 (4)	C(10)—C(11)—C(12)	120.7 (6)
Re—O(3)—C(9)	125.4 (4)	C(11)—C(12)—C(13)	119.3 (6)
Re—N(1)—C(7)	126.7 (4)	C(12)—C(13)—C(14)	121.7 (7)
Re—N(1)—C(8)	116.1 (5)	C(9)—C(14)—C(13)	118.5 (6)
C(7)—N(1)—C(8)	117.2 (6)	C(9)—C(14)—C(15)	125.6 (6)
Re—N(2)—C(15)	122.3 (4)	C(13)—C(14)—C(15)	115.7 (6)
Re—N(2)—C(16)	120.2 (4)	N(2)—C(15)—C(14)	126.8 (6)
C(15)—N(2)—C(16)	117.4 (6)		

The coordination around the Re atom is approximately octahedral and a stereographic projection of the coordination polyhedron with the O_{oxo} located at the south pole is reported in Fig. 2. It shows that the two chelate rings are almost mutually orthogonal, one ligand bridging an equatorial and an apical position and the other two equatorial ones. Accordingly the molecule is chiral and both enantiomers are contained in the centrosymmetric crystal. That shown in Fig. 1 corresponds to the *A* absolute configuration.

Re, N(1) and N(2) define a plane which is nearly equatorial, the angle between this plane and the Re— O_{oxo} line being actually 88.0° . The Cl and O(3) atoms are out of the plane by 0.32 and 0.43 Å respectively and the Re—O(2) line is displaced from its normal by 10.0° . It is seen that O(1) repels the *cis* ligands in the order $O(3) > \text{Cl} > \text{N}(1) \approx \text{N}(2)$. The O(3) and Cl atoms, which are pushed upwards out of the equatorial plane, displace the O(2) atom from the vertical, causing a compression field which reduces the bite of the ligand bridging the equatorial and apical positions, as can be seen from the O(2)—N(1) distance of 2.720 (4) Å and O(2)—Re—N(1) angle of $83.1(2)^\circ$, when compared with the corresponding values for the other ligand, 2.933 (4) Å and $91.4(2)^\circ$ respectively. The different repulsion exerted by O(1) on the equatorial atoms cannot be accounted for on the grounds of the sums of the van der Waals radii (Bondi, 1964) of the neutral atoms; in fact such a sum is 0.36 and 0.42 Å greater than the intramolecular contact distances for O(1)—N(1) and O(1)—N(2), while it is only 0.17 and 0.12 Å greater for O(1)—O(3) and O(1)—Cl respectively.

Nevertheless, the observed deformation is not accidental and data of Table 3 show that the O_{oxo} —Re— X_{cis} angle is systematically larger for $X = \text{O}^-$ or Cl^- than for $X = \text{P}$ or N and that a similar effect occurs in octahedral or square-pyramidal Re^{V} nitrido complexes. To all appearances the π electron density associated with the multiple $\text{Re} \equiv \text{O}$ or $\text{Re} \equiv \text{N}$ bond repels more ligands connected by formally covalent $L^- \rightarrow M^+$ than donor—acceptor $L: \rightarrow M$ bonds and this could be interpreted in terms of increased steric

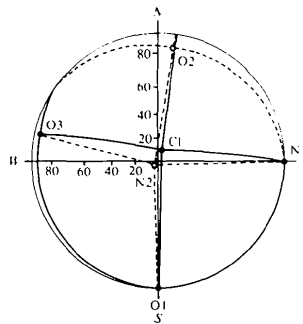


Fig. 2. Stereographic projection of the coordination polyhedron. The O_{oxo} is located at the south pole.

Table 3. Selected bond distances (Å) and angles (°) in octahedral or square-pyramidal oxo- and nitrido-complexes of Re^V

Ref.	Coord.	Re≡(O/N)	<i>X</i> _{trans}	Re- <i>X</i> _{cis} and (O/N)≡Re- <i>X</i> _{cis}									
				Re- <i>X</i> _{trans}	<i>X</i> _{cis} = N	P		Cl ⁻		-O ⁻			
[ReOCl(Me-sal) ₂]	<i>a</i>	oct	1.680 (4)	O	1.979 (4)	2.120 (5)	90.1 (2)			2.399 (2)	99.7 (2)	1.995 (4)	102.6 (2)
[ReOCl ₂ (PPh ₃ (acac))]	<i>b</i>	oct	1.69 (1)	O	2.10 (1)	2.103 (5)	88.0 (2)	2.431 (4)	85.5 (3)	2.376 (7)	97.0 (5)	1.99 (1) ^{tp}	108.6 (5) [*]
[Re ₂ O ₂ Cl ₄ (PPh ₃) ₂]	<i>c</i>	oct	1.68 (1)	O	1.92 (1)	2.15 (1)	87.7 (3)	2.466 (4)	87.9 (3)	2.339 (6)	96.7 (5)		
		oct	1.68 (1)	O	1.93 (1)	2.15 (1)	87.9 (4)	2.472 (4)	87.8 (3)	2.416 (4) ^{tp}	98.0 (3)		
[ReOCl ₂ (PPh ₃)- {Ph(O)CNCMe ₃ }]	<i>d</i>	oct	1.685 (8)	O	2.013 (7)	2.13 (1)	94.9 (4) [*]	2.472 (2)	83.7 (2)	2.367 (3)	98.8 (3)		
										2.409 (4) ^{tp}	96.3 (3)		
[ReNCl ₃ (PPh ₃) ₂]	<i>e</i>	spy	1.60 (1)					2.448 (2)	98.4 (1)	2.365 (3)	98.8 (3)		
[ReNCl ₃ (PPhEt ₂) ₂]	<i>f</i>	oct	1.79 (1)	Cl	2.563 (4)			2.490 (5)	91.8 (4)	2.388 (3) ^{tp}	101.1 (2)		
								2.442 (4)	95.6 (4)	2.344 (4)	103.9 (3)		
								2.469 (5)	89.1 (4)	2.377 (2)	109.7 (1)		
										2.454 (4) ^{tp}	99.2 (4)		

References: (a) present work; (b) Lock & Che'ng Wan (1975); (c) Bombieri *et al.* (1978); (d) Hursthouse, Jayaweera & Quick (1979); (e) Doedens & Ibers (1967); (f) Corfield, Doedens & Ibers (1967). tp = ligand *trans* to phosphorus.

* Angle possibly affected by the small bite of the ligand bridging the equatorial and apical positions.

hindrance of the more electronegative substituents in consequence of the increased population of their orbitals.

It has to be remarked that the model given here for the distortion of the coordination polyhedron is widely inconsistent with the model proposed by Bright & Ibers (1969), who suggested that the stereochemical configurations of this class of compounds were mainly determined by intramolecular packing forces. However, two main criticisms can be made of this latter theory. First, it is prevalently based on structures of overcrowded molecules, where steric effects likely override any other factor and, secondly, it leads to a purely steric explanation of the lengthening of the Re-*L* bond *trans* to the multiply bonded ligand which, as will be shown later, does not fit all the experimental data.

Neither 'Me-sal' ligand is planar. Atoms C(1)-C(7) define a plane ($\chi^2 = 8.0$), from which the O(2), N(1) and C(8) atoms are displaced by 0.04, -0.14 and -0.08 Å respectively; the Re atom is out of this plane by -0.47 Å. A similar plane through the other ligand [atoms C(9)-C(15)] has a χ^2 as large as 173 and the O(3), N(2), C(16) and Re atoms are displaced from it by 0.05, -0.09, -0.38 and 0.33 Å respectively.

The most important bond distances are reported in Table 3, together with the corresponding values found in other similar complexes of Re^V.

The Re-Cl distance of 2.399 (2) Å is somewhat longer than that observed in other oxo complexes in the absence of a *trans* influence (2.36 ± 0.02 Å). The Re-O(1) distance is 1.680 (4) Å; it agrees with the values found in other oxo complexes of Re^V and is, by itself, indicative of triple bonding, as the Re-O single-bond distance is found to be in the range 1.90-2.10 Å, and that of a double bond, determined only once in [Re(IV)(OH)Cl₃(PPhEt₂)₂] (Sacerdoti,

Bertolasi, Gilli & Duatti, 1982), is 1.795 (4) Å. The most convincing proof of the existence of a real triple R≡O bonding in Re^V octahedral oxo complexes is given, however, by their magnetic properties. In fact, the π overlapping of two of the *t*_{2g} orbitals with the two doubly filled *p*_x and *p*_y AO's of the oxygen (if the *z* axis is pointing in the Re-O direction), giving a total of two bonding, one non-bonding and two antibonding orbitals occupied by six electrons, remains the best way for explaining the diamagnetism of the *d*² Re^V complexes.

The single bond Re-O [Re-O(2) = 1.979 (4) and Re-O(3) = 1.995 (4) Å] and Re-N distances [Re-N(1) = 2.120 (5) and Re-N(2) = 2.103 (5) Å] are in good agreement with those reported in Table 3. The Re-N bond is significantly longer than the Re-O bond (on average 0.12 Å) and this effect is known to occur only in complexes of metal ions in high oxidation state, *e.g.* [Ti(IV)Cl₂(salen)] (Gilli, Cruickshank, Beddoes & Mills, 1972), [Fe(III)Cl(salen)] (Gerloch & Mabbs, 1967) and [Re₂(V)O₂Cl₄(PPh₃)₂(salen)] (Bombieri *et al.*, 1978), where the difference between the *M*-N and *M*-O bonds is 0.25, 0.20 and 0.22 Å respectively; it can be understood in terms of Pearson's hard-soft acid-base theory (Pearson, 1963), as hard Lewis acids Re^V, Ti^{IV} and Fe^{III} must form stronger bonds with oxygen rather than with the comparatively softer base nitrogen.

The fact that the Re-O(2) bond, which is *trans* to the oxo ligand, is slightly shorter than the *cis* Re-O(3) bond definitely excludes *trans* weakening due to the strong π bonding of the oxo group. This was observed also in [Re₂O₂Cl₄(PPh₃)₂(salen)] (Bombieri *et al.*, 1978) and is in apparent agreement with Bright & Ibers (1969) theory that *trans* lengthening in this class of compounds can be observed only in the case of relevant steric hindrance of the *cis* ligands. This theory, however, is unable to explain why in all known quasi-octahedral Re^V oxo complexes with oxygenated

bidentate ligands (see Table 3) the $R-O^-$ group has been found to be *trans* to the $Re=O_{oxo}$ multiple bond. There appears to be a definite gain in energy associated with such a configuration and this has been confirmed by recent studies (Mazzi, Roncari, Rossi, Duatti & Magon, 1981) on the reaction between *trans*- $[Re(V)OCl_3(PPh_3)_2]$ or $[Re(V)OBr_3(PPh_3)_2]$ and 'salH' derivatives, where all final products were shown to correspond to the *trans* $O=Re^+-O^-R$ arrangement, most likely as a consequence of the chelate-ring closure in a first substitution product of PPh_3 by imino nitrogen. It is evident that the observed behavior of these compounds can be more easily understood by admitting a definite *trans* influence (and therefore a *trans* weakening) caused by the $Re=O_{oxo}$ bond, which increases according to the *trans* ligand, L , in the order $RO^- < Cl^-$, $Br^- < R_3N$. This hypothesis is supported by several different arguments, the first being that the suggested sequence corresponds, in inverse order, to the expected strength sequence of the bonds formed with L by hard acid Re^V , fitting the intuitive idea that the *trans* weakening is greater, the weaker the $M-L$ bond. In general, the most convincing proof of the *trans* influence exerted by multiply bonded ligands (X) in quasi-octahedral MXL_5 transition-metal complexes has been collected by Shustorovich, Porai-Koshits & Buslaev (1975). They came to the conclusion, based on structural data as well as on theoretical arguments, that the *trans* influence caused by the $M-X$ bond increases according to X in the sequence $R-N\equiv < O\equiv < N\equiv$ and, which is more important here, is much greater for neutral ($L = H_2O, NR_3, CH_3CN, etc.$) than for anionic ligands ($R-O^-, Cl^-, Br^-, etc.$). A final point in favor of the idea that the *trans* $O=Re^+-O^-R$ configuration is preferred in that it corresponds to a minimum of *trans* weakening is given by the absence of any *trans* elongation in the $Re-O$ single bond when compared with the small but unquestionable elongation observed for the $Re-Cl$ bond (see data reported by Shustorovich *et al.*, 1975).

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