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Structure of μ-Oxo-bis[dichlorobis(1-methylimidazole-N^3)oxorhenium(V)], [{$ReOCl_2(C_4H_6N_2)_2$}$_2$O]

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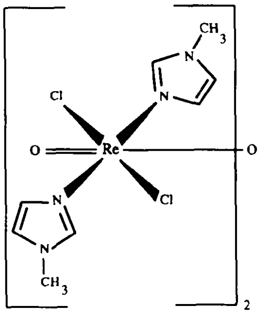
Abstract

The crystals contain dinuclear molecules in which all-*trans* octahedral $ReCl_2(O)_2$(1-methylimidazole)$_2$ units share an O-atom apex. The O=Re—O—Re=O backbone is linear by symmetry and the bonds in the $ReCl_2N_2$ planes of the two units are staggered. The main bond lengths are: Re—O = 1.913 (1), Re=O = 1.703 (8), Re—Cl = 2.415 (2) and Re—N = 2.132 (6) Å.

Comment

The title compound (I) was obtained from the [$ReCl_3$(1-Meim)$_2${$P(C_6H_5)_3$}] monomer by replacing pyridine with 1-methylimidazole (1-Meim) in the procedure used by Rouschias & Wilkinson (1967) to obtain [$ReCl_3py_2${$P(C_6H_5)_3$}]. Blue crystals appeared after several days upon recrystallization in acetone and were found to contain the oxo-bridged [{$ReCl_2O$(1-Meim)$_2$}$_2$O] molecule shown in Fig. 1. It is not clear whether oxygen originates from the solvent or air leaking into the argon-filled closed flask. A related [{$ReCl_2Opy_2$}$_2$O] dimer, in which the pyridine ligands are *cis* to one another, has been prepared by Lock & Turner (1978) from [$ReCl_3$-O{$P(C_6H_5)_3$}$_2$] and pyridine in benzene.



(I)

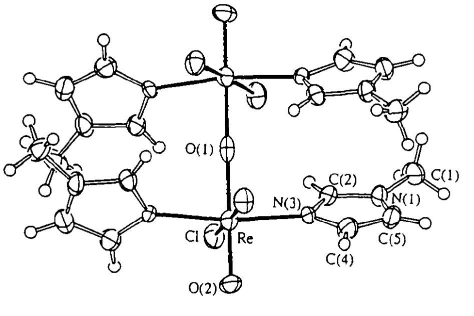


Fig. 1. *ORTEP* drawing of the [{$ReOCl_2(C_4H_6N_2)_2$}$_2$O] molecule. Ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary size.

The bridging O atom occupies a site of crystallographic 222 symmetry. The Re and terminal O atoms also lie on one of these twofold axes, making the O=Re—O—Re=O backbone perfectly linear. The bridging Re—O(1) and terminal Re—O(2) bond distances [1.913 (1) and 1.703 (8) Å, respectively] are similar to those obtained with related compounds containing the O=Re—O—Re=O backbone (Lock & Turner, 1978; Backes-Dahmann & Enemark, 1987). The Re—N distances determined here are in agreement with these studies. The Re—Cl bonds, *trans* to each other, are significantly longer [2.415 (2) Å] than those of the pyridine analogue (2.356–2.390 Å, σ = 0.005 Å), where they are in *cis* positions. The octahedron is appreciably distorted, with the four equatorial ligands being displaced away from the Re=O bond. The effect is small for the Cl atoms [Cl—Re—O(2) = 91.3 (2), Cl—Re—O(1) = 88.7 (1)°], but more important for the N atoms [N(3)—Re—O(2) = 94.1 (3), N(3)—Re—O(1) = 85.9 (2)°]. The N(3)—Re—Cl angle [90.2 (2)°] is normal.

The molecule adopts a staggered conformation in which the $ReCl_2N_2$ planes are mutually rotated by 29° about the O=Re—O—Re=O axis. The imidazole ring makes an angle of 42° with the $ReCl_2N_2$ plane and the parallel arrangement of the two 1-Meim ligands on the same side of the molecule favours intramolecular stacking interactions.

The imidazole ring is planar, but the methyl C(1) atom is displaced by 0.088 (11) Å from the plane, whereas the Re atom is displaced on the same side by 0.091 (1) Å. The bond distances and angles within the ring are comparable with those of other compounds containing 1-methylimidazole (Therrien & Beauchamp, 1993; Wang & Craven, 1979).

The molecules are packed with the O=Re—O—Re=O backbone along the *b* axis (Fig. 2) and are thus oriented so that the 1-Meim ligands are grouped in layers parallel to the *ab* face at *z* = 0 and $\frac{1}{2}$. Within these layers, all the rings are parallel and interact by normal van der Waals contacts.

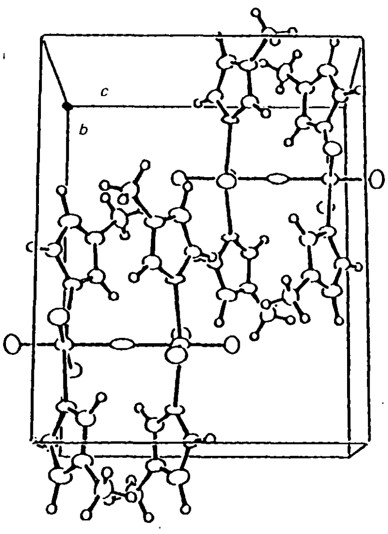


Fig. 2. View of the unit cell down the *a* axis. The origin corresponds to the black dot and the *b* and *c* axes, lying in the plane of the figure, are oriented vertically and to the right, respectively. Atoms can be identified by comparison with Fig. 1.

Experimental

Crystal data

$[Re_2Cl_4(O)_3(C_4H_6N_2)_4]$
$M_r = 890.64$
Orthorhombic
Pnnn
$a = 9.307$ (2) Å
$b = 10.561$ (4) Å
$c = 13.241$ (2) Å
$V = 1301.4$ (6) Å^3
$Z = 2$
$D_x = 2.273$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 20\text{-}25.0°$
$\mu = 21.44$ mm^{-1}
$T = 210$ K
Elongated prism
0.280 × 0.068 × 0.054 mm
Blue

Data collection

Enraf-Nonius diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
$T_{min} = 0.15$, $T_{max} = 0.42$
4583 measured reflections
1248 independent reflections
710 observed reflections
$[I \geq 3\sigma(I)]$

$R_{int} = 0.051$
$\theta_{max} = 70°$
$h = -11 \rightarrow 0$
$k = -12 \rightarrow 0$
$l = -16 \rightarrow 0$
5 standard reflections
frequency: 60 min
intensity variation: 1%

Refinement

Refinement on F
$R = 0.0253$
$wR = 0.0301$
$S = 1.06$
710 reflections
77 parameters
H-atom parameters not refined

$w = 1/\sigma^2(F) + 0.0001F^2$
$(\Delta/\sigma)_{max} = 0.138$
$\Delta\rho_{max} = 0.78$ e Å^{-3}
$\Delta\rho_{min} = -1.80$ e Å^{-3}
Extinction correction: none

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Re	0.2500	0.5689 (1)	0.7500	0.0300 (1)
Cl	−0.0012 (2)	0.5739 (3)	0.7958 (2)	0.0360 (6)
O(1)	0.2500	0.7500	0.7500	0.032 (4)
O(2)	0.2500	0.4077 (8)	0.7500	0.039 (3)
N(1)	0.0837 (8)	0.6469 (9)	0.4594 (5)	0.033 (2)
N(3)	0.1937 (8)	0.5833 (7)	0.5944 (5)	0.025 (2)
C(1)	−0.0144 (12)	0.7172 (9)	0.3950 (7)	0.043 (4)
C(2)	0.0870 (10)	0.6519 (10)	0.5601 (6)	0.030 (3)
C(4)	0.2621 (14)	0.5331 (9)	0.5131 (7)	0.035 (3)
C(5)	0.1914 (11)	0.5714 (11)	0.4291 (7)	0.037 (3)

Table 2. *Geometric parameters* (Å, °)

Re—O(2)	1.703 (8)	N(3)—C(2)	1.311 (12)
Re—O(1)	1.913 (1)	N(3)—C(4)	1.358 (12)
Re—Cl	2.415 (2)	N(1)—C(1)	1.452 (13)
Re—N(3)	2.132 (6)	N(1)—C(2)	1.335 (11)
C(4)—C(5)	1.355 (14)	N(1)—C(5)	1.343 (13)
Cl—Re—N(3)	90.2 (2)	N(3)—C(4)—C(5)	107.9 (9)
Cl—Re—O(1)	88.7 (1)	N(1)—C(2)—N(3)	110.0 (8)
Cl—Re—O(2)	91.3 (2)	C(2)—N(3)—C(4)	107.3 (8)
N(3)—Re—O(1)	85.9 (2)	C(2)—N(1)—C(5)	107.7 (8)
N(3)—Re—O(2)	94.1 (3)	C(1)—N(1)—C(5)	126.7 (8)
Cl—Re—Cl^i	177.5 (1)	C(2)—N(1)—C(1)	125.5 (8)
N(3)—Re—N(3)^i	171.8 (3)	Re—N(3)—C(2)	124.1 (6)
N(1)—C(5)—C(4)	107.1 (9)	Re—N(3)—C(4)	128.5 (6)

Symmetry code: (i) $\frac{1}{2} - x, y, \frac{3}{2} - z$.

The data were corrected for Lp effects. The space group *Pnnn* was identified unambiguously from the orthorhombic Laue symmetry absences ($0kl$, $k + l \neq 2n$; $h0l$, $h + l \neq 2n$; $hk0$, $h + k \neq 2n$). The structure was solved by the heavy-atom method. Non-H atoms were refined anisotropically by full-matrix least-squares methods (*SHELX76*; Sheldrick, 1976). Local programs (Authier-Martin & Beauchamp, 1977) were used for the remaining calculations. H-atom positions were fixed: C—H = 0.95 Å, $U_{iso} = 0.04$ (ring) and 0.07 Å^2 (methyl). Atomic scattering factors were taken from Cromer & Mann (1968) (non-H atoms), Stewart, Davidson & Simpson (1965) (H atoms), and Cromer & Liberman (1970) (real and imaginary coefficients for anomalous dispersion, Re and Cl)

We wish to thank M. Simard and F. Bélanger-Gariépy for assistance in collecting the X-ray data.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71410 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1046]

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Chloronitrosylbis[*o*-phenylenebis(dimethylarsine)]technetium(I) Chloride–Tetrabutylammonium Chloride (1/1)

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Abstract

The complex $[TcCl(NO)(C_{10}H_{16}As_2)_2]^+$ lies on a crystallographic inversion centre with disordering of the *trans* chloro and nitrosyl ligands. The coordination about Tc is close to octahedral with Tc—As distances of 2.479 (1) and 2.502 (2) Å. The As—C mean distance is 1.924 (15) Å and the angles at As are within 10° of tetrahedral.

Comment

The title compound, in which Tc is in the monovalent state, was prepared (Hildreth, 1992) in the context of a search for low-oxidation-state Tc complexes as potential radiopharmaceuticals (Cheah, Newman, Nowotnik & Thornback, 1987).

Although the presence of the nitrosyl ligand is indicated by IR spectroscopy and fast-atom bombardment mass spectrometry (Hildreth, 1992), the X-ray results do not show separate Cl and nitrosyl groups as a result of packing disorder. The Tc atom lies on a centre of symmetry with the chloro and nitrosyl substituents equivalent and indistinguishable on Fourier difference maps. A large peak at *ca* 2.3 Å from Tc was taken to represent $\frac{1}{2}$(Cl + NO). The postions of the N and O atoms were calculated using the known covalent radii of the elements involved, such that the Tc—N—O angle was close to 180°. Atomic coordinates are given in Table 1 and Fig. 1 shows the atomic numbering scheme.

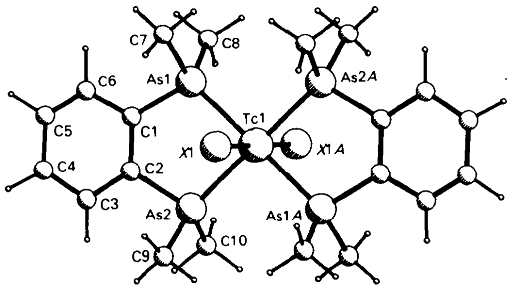

Fig. 1. The complex cation showing the atomic numbering scheme. *X*1 and *X*1*A* represent $\frac{1}{2}$(Cl + NO).

The overall coordination about Tc is close to octahedral; as a result of symmetry requirements the four As atoms and the central Tc are precisely coplanar. Selected bond lengths and angles are shown in Table 2. The Tc—As distances reported here represent the first determination of such a bond involving Tc^I. They are a little shorter than those found in the perchlorate and chloride salts of dichlorobis[*o*-phenylenebis(dimethylarsine)]Tc^{III} (Elder, Whittle, Glavan, Johnson & Deutsch, 1980), where the mean Tc—As length is 2.512 Å, compared to 2.491 Å in the present structure. The Tc—Cl distance [2.391 (15) Å] is some 0.02–0.07 Å greater than those found in a Tc^{II} complex [mean 2.357(5) Å (Brown, Newman, Thornback & Davison, 1987)], a Tc^{III} complex [mean 2.322 (17) Å (Elder *et al.*, 1980)] and a Tc^{IV} complex [mean 2.373 (11) Å (Bush, Hamor, Hussain, Jones, McCleverty & Rothin, 1987)]. There is no obvious correlation between the Tc oxidation state and the Tc—Cl length. However, because of the disorder involving Cl and NO, the Tc—Cl distance in the present structure is probably more uncertain than indicated by the calculated e.s.d.

The valence angles at arsenic are in the range 99.8–118.7°. The pattern of variation from the ideal tetrahedral value [large Tc—As—C_{methyl} angles of mean 117.8 (4)° and small C_{phenyl}—As—C_{methyl} angles of mean 101.8 (7)°] is also observed in the dichlorobis[*o*-phenylenebis(dimethylarsine)]technetium(III) cation [the corresponding mean values are 118.3 (8) and 103.3 (15)°, respectively].

The tetrabutylammonium cation lies on the twofold axis at $x = 0$, $y = \frac{1}{4}$, with two of the atoms C(13) and C(16) disordered, each partially occupying two sites. These 'half atoms' were refined with isotropic temperature factors. A number of other atoms have very large thermal parameters, possibly indicative of some degree of disorder also at these sites. Considering the unprimed sites for the disordered atoms (Table 1), the butylammonium chains are in the extended antiperiplanar–antiperiplanar conformation.