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μ-Oxo-bis{{2,2′-[2,2-dimethylpropane-1,3-diylbis(nitrilomethylidyne)]-diphenolato}oxorhenium(V)}

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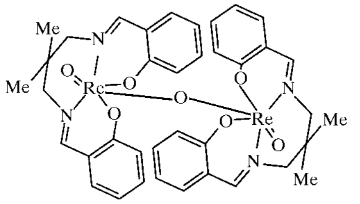
The title compound, $[\text{Re}_2\text{O}_3(\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2)_2]$, is a hexacoordinate complex containing an $[\text{Re}_2\text{O}_3]^{4+}$ core with a linear O=Re—O—Re=O bridge. The distorted octahedral coordination of the Re^{V} atom is achieved by an N_2O_2 donor set from the tetradentate imine–phenol ligand. The overall charge of the compound is neutral due to deprotonation of the phenol groups, and the terminating and bridging O atoms. The Re=O and Re—O bond distances of the $[\text{Re}_2\text{O}_3]^{4+}$ core are 1.699 (4) and 1.911 (1) Å, respectively. The Re—O and Re—N bond distances of the equatorial plane are in the ranges 2.024 (4)–2.013 (4) and 2.128 (5)–2.120 (5) Å, respectively.

Comment

Rhenium, being a congener to technetium in Group VIIa, might be expected to form complexes that have structural and biological similarities to the corresponding technetium complexes. With β-emitter characters, both ^{188}Re and ^{186}Re have potential utility in radiotherapy. Recent focus has been on the design and preparation of new rhenium complexes in order to optimize the biodistribution of the potential radiopharmaceuticals. Interest is aroused in exploring the coordination chemistry of the rhenium complexes with tetradentate N_2O_2 ligands (Luo *et al.*, 1995; Tisato *et al.*, 1990; Mazzi *et al.*, 1986). We describe here the synthesis and characterization of the title compound, (I).

The title compound forms a dinuclear complex, the Re atom being hexacoordinated to two imine N, two phenol O and two axial O atoms. The dinuclear structure, with a linear O=Re—O—Re=O bridge, is very similar to those of the μ-oxo-dioxotechnetium(V) or μ-oxo-dioxorhenium(V) complexes reported in the literature (Middleton *et al.*, 1979; Bandoli & Nicolini, 1984; Pietzsch *et al.*, 1995; Pillai *et al.*, 1990, 1994). The compound consists of two independent ReO–dmpn(sal) {dmpn(sal) is *N*,*N*′-2,2-dimethylpropane-1,3-diylbis(salicylideneimine) or 2,2′-[2,2-dimethylpropane-1,3-diylbis(nitrilomethylidyne)]diphenolate} units bridged by an O atom and the tetradentate Schiff base occupies the four planar coordination sites of an octahedron. The structure of ReO–dmpn(sal), with an N_2O_2 donor set in the same plane perpendicular to the Re=O bond, is different from the configuration of chloro{1,3-[*N*,*N*′-bis(salicylidene)diamino]-2,2-dimethylpropyl}oxorhenium(V) [(II); Herrmann, Rauch & Artus, 1996]. It was reported that substitution reactions on the MO^{3+} (M = Tc, Re) core with N_2O_2 Schiff base ligands might lead to three types of complex, $[MOX(\text{N}_2\text{O}_2)]$ (X = Cl, Br), $\{[MO(\text{N}_2\text{O}_2)]_2\text{O}\}$ and $[MO(\text{OH}_2)(\text{N}_2\text{O}_2)]^+$ (Herrmann, Rauch & Artus, 1996; Herrmann, Rauch & Roesky, 1996; Bandoli & Nicolini, 1984). The title compound, $\{[MO(\text{N}_2\text{O}_2)]_2\text{O}\}$, was facile to form in the solution containing water. The other two types of the compound were presumably formed but the product isolated was the most stable (Bandoli & Nicolini, 1984).



(I)

The Re=O bond length [1.699 (4) Å] is similar to the mean value (1.691 Å, σ = 0.025 Å) for a large sample of monooxo Re^{V} (Mayer, 1988). The Re—N(imine) distance [2.128 (5) Å] observed is similar to that of (II) (Herrmann, Rauch & Artus, 1996). The O2—Re1—N1 and O2—Re1—N2 angles deviate by less than 2.0° from the ideal value of 90°. The *trans*-O3—Re1—N2 and *trans*-O4—Re1—N1 angles are 171.5 (2) and 169.7 (2)°, respectively. The compression of both *trans*-O—Re—N angles from 180° indicates a marked level of tetrahedral distortion from square-planar geometry around the Re^{V} atom. The least-square-planes data shows that the Re atom is approximately 0.14 Å out of the plane defined by the coordinated atoms of tetradentate ligand toward the terminal O atoms.

Experimental

The ligand *N*,*N*′-2,2-dimethylpropane-1,3-diylbis(salicylideneimine) was prepared by condensation of salicylaldehyde (50 mmol) and 1,3-diamino-2,2-dimethylpropane (25 mmol) in absolute ethanol (100 ml). Refluxing was continued for 6 h and the resultant product was placed in a freezer for 24 h. The yellow precipitate which appeared was collected by filtration and washed with cold ethanol (95%). After recrystallization, yellow crystals were harvested and dried *in vacuo*. $\text{Bu}_4\text{NReOCl}_4$ was synthesized following the previous report of Cotton & Lippard (1966). Bu_4NCl (2 *M*, 20 ml) was added to NH_4ReO_4 (20 mmol) in distilled water. The white precipitate, Bu_4NReO_4, were collected, dried and purged with dry HCl in dry ethanol (100 ml). The brown precipitate were collected and dried. *N*,*N*′-2,2-Dimethylpropane-1,3-diylbis(salicylideneimine) (0.84 mmol) was added to solid $\text{Bu}_4\text{NReOCl}_4$ (0.42 mmol) in dry ethanol.

The reaction mixture was refluxed for 3 h and then stirred for 24 h at room temperature. The green solution was concentrated until dark-green crystals of the Re complex formed. The crystals were then dissolved in 95% ethanol at 348 K and the resulting solution was allowed to stand at room temperature for a few days whereupon crystals suitable for X-ray analysis were formed.

Crystal data

$[Re_2O_3(C_{19}H_{20}N_2O_2)_2]$
M_r = 1037.14
Monoclinic, $P2_1/c$
a = 11.2427 (2) Å
b = 13.3736 (2) Å
c = 12.4932 (2) Å
β = 108.109 (1)°
V = 1785.38 (5) $Å^3$
Z = 2

D_x = 1.929 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6635 reflections
θ = 2.5–25.0°
μ = 6.830 mm^{-1}
T = 293 (2) K
Tabular, green
0.21 × 0.20 × 0.06 mm

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical from equivalent data (Sheldrick, 1991)
T_{min} = 0.274, T_{max} = 0.664
10 934 measured reflections

4225 independent reflections
3266 reflections with $I > 2\sigma(I)$
R_{int} = 0.0559
θ_{max} = 28.79°
$h = -14 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -16 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.084
S = 1.013
4225 reflections
232 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.19 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.79 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Re1—O2	1.697 (4)	Re1—N2	2.123 (5)
Re1—O1	1.9114 (2)	Re1—N1	2.126 (5)
Re1—O4	2.015 (4)	N1—C7	1.292 (7)
Re1—O3	2.025 (4)	N2—C11	1.279 (7)
O2—Re1—O1	171.76 (14)	O4—Re1—N2	91.43 (16)
O2—Re1—O4	98.06 (18)	O3—Re1—N2	171.54 (15)
O1—Re1—O4	89.75 (12)	O2—Re1—N1	91.05 (18)
O2—Re1—O3	94.71 (19)	O1—Re1—N1	81.39 (12)
O1—Re1—O3	88.86 (12)	O4—Re1—N1	169.80 (16)
O4—Re1—O3	82.77 (15)	O3—Re1—N1	91.95 (18)
O2—Re1—N2	92.19 (19)	N2—Re1—N1	92.80 (18)
O1—Re1—N2	84.94 (12)		

Symmetry code: (i) $-x, -y, 1 - z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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