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trans-Dichlorooxo(2-propoxido)bis-(triphenylphosphine)rhenium(V)

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Abstract

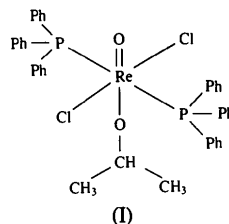
The title compound crystallizes with discrete [ReOCl₂-(C₃H₇O)(C₁₈H₁₅P)₂] units. The coordination sphere of the metal atom is approximately octahedral with the bulky phosphine ligands *trans* with respect to each other. The O=Re—O unit is nearly linear with an angle of 174.25 (9)°. Both Re—Cl bond lengths, as well as both Re—P lengths, are equal within their standard deviations.

Comment

[ReOX₃(Ph₃P)₂] complexes are frequently used as precursors for the synthesis of new rhenium(V)-oxo complexes. The structure of the chloro complex has recently been reported (Lebuis & Beauchamp, 1993). The chloro ligand *trans* to the oxo ligand is only weakly coordinated because of the strong structural *trans* influence of the π-donating oxo ligand and can easily be replaced.

In the course of our studies of the coordination behaviour of tellurium-containing organic ligands, we attempted the reaction of [ReOCl₃(Ph₃P)₂] with bis(2,4,6-

triphenylphenyl)ditelluride. We could not isolate a rhenium species with Re—Te bonds. However, large violet blocks of [ReOCl₂(C₃H₇O)(Ph₃P)₂], (I), were obtained after attempted recrystallization of the brown crude product from CH₂Cl₂/2-propanol solution.



The coordination sphere of the Re atom is approximately octahedral (Fig. 1). Deviations from idealized geometry are found for the O(1)—Re—P angles of 86.7 (1) and 87.5 (1)°. These values are somewhat smaller than those obtained for the related complexes [ReOX₂(OEt)(Ph₃P)₂] (X = Cl, Br) (Graziani, Casellato, Rossi & Marchi, 1985; Lebuis, Roux & Beauchamp, 1993; Lebuis & Beauchamp, 1993), which range between 89.0 (1) and 91.55 (3)°. The differences can be explained by the requirements of the more bulky 2-propoxido ligand *trans* to the oxo ligand. In contrast to the ethoxo ligands in [ReOCl₂(OEt)(Ph₃P)₂] (Graziani, Casellato, Rossi & Marchi, 1985) and [ReOBr₂(OEt)(Ph₃P)₂] (Lebuis, Roux & Beauchamp, 1993; Lebuis & Beauchamp, 1993), no disorder could be detected for the alkoxy group in the title compound.

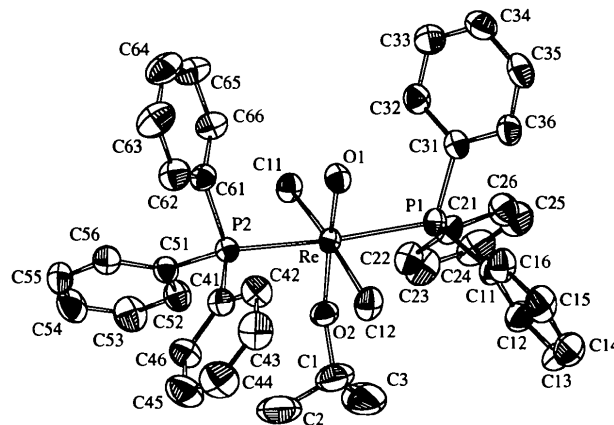


Fig. 1. ORTEP (Johnson, 1976) plot of [ReOCl₂(C₃H₇O)(Ph₃P)₂] along with the atomic numbering scheme (displacement ellipsoids represent 40% probability).

The Re—O(1) bond distance of 1.698 (2) Å comes very close to the mean value for Re—O bonds in monooxo-rhenium(V) complexes (1.69 Å). In agreement with the situation in the comparable complexes [ReO(OR)X₂(Ph₃P)₂] (R = Et, Me; X = Cl, Br, I)

(Graziani, Casellato, Rossi & Marchi, 1985; Lehuis, Roux & Beauchamp, 1993; Lehuis & Beauchamp, 1993; Ciani, D'Alfonso, Romiti, Sironi & Freni, 1983), the Re—O(2) distance is remarkably short [1.890 (2) Å], which may reflect some multiple-bond character, as discussed by Ciani, D'Alfonso, Romiti, Sironi & Freni (1983).

Experimental

Crystal data

[ReOCl₂(C₃H₇O)(C₁₈H₁₅P)₂] **Mo K α radiation**
M_r = 856.73 **λ = 0.71073 Å**
 Triclinic **Cell parameters from 25**
*P*1 **reflections**
a = 9.594 (5) Å **θ = 8–14°**
b = 12.430 (5) Å **μ = 3.754 mm⁻¹**
c = 16.893 (9) Å ***T* = 213 (2) K**
 α = 109.71 (2)° **Column**
 β = 99.13 (3)° **0.5 × 0.25 × 0.2 mm**
 γ = 105.90 (3)° **Violet**
V = 1753 (2) Å³
Z = 2
D_x = 1.624 Mg m⁻³

Data collection

Enraf–Nonius CAD-4 ***R*_{int} = 0.0164**
 diffractometer **θ_{max} = 27°**
 $\omega/2\theta$ scans ***h* = -12 → 12**
 Absorption correction: ***k* = -15 → 15**
 empirical via ψ scan ***l* = 1 → 21**
*T*_{min} = 0.896, *T*_{max} = 0.999 **3 standard reflections**
 8360 measured reflections **monitored every 200**
 7580 independent reflections **reflections**
 7115 observed reflections **intensity decay: 2.3%**
I ≥ 2 σ (*I*)

Refinement

Refinement on *F*² **$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2$**
R(*F*) = 0.0207 **+ 0.8269*P*]**
wR(*F*²) = 0.0509 **where *P* = (*F*_o² + 2*F*_c²)/3**
S = 1.108 **(Δ/σ)_{max} < 0.001**
 7580 reflections **$\Delta\rho_{max}$ = 0.685 e Å⁻³**
 535 parameters **$\Delta\rho_{min}$ = -0.638 e Å⁻³**
 All H-atom parameters **Atomic scattering factors**
 refined **from *International Tables***
for *X-ray Crystallography*
(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Re	0.1676 (1)	0.2282 (1)	0.2465 (1)	0.021 (1)
P(1)	0.0812 (1)	0.3838 (1)	0.2092 (1)	0.023 (1)
P(2)	0.2258 (1)	0.0603 (1)	0.2807 (1)	0.023 (1)
Cl(1)	0.2112 (1)	0.1485 (1)	0.1053 (1)	0.028 (1)
Cl(2)	0.1559 (1)	0.3231 (1)	0.3941 (1)	0.037 (1)

O(1)	-0.0171 (2)	0.1389 (2)	0.2160 (1)	0.029 (1)
O(2)	0.3708 (2)	0.3350 (2)	0.2917 (1)	0.031 (1)
C(1)	0.4842 (4)	0.4295 (3)	0.3682 (2)	0.053 (1)
C(2)	0.5797 (5)	0.3777 (4)	0.4101 (3)	0.074 (1)
C(3)	0.5682 (6)	0.5307 (4)	0.3490 (4)	0.094 (2)
C(11)	0.0809 (3)	0.5094 (2)	0.3034 (2)	0.028 (1)
C(12)	0.1845 (4)	0.6271 (3)	0.3320 (2)	0.038 (1)
C(13)	0.1876 (5)	0.7181 (3)	0.4085 (2)	0.052 (1)
C(14)	0.0890 (4)	0.6932 (4)	0.4567 (2)	0.051 (1)
C(15)	-0.0134 (4)	0.5771 (3)	0.4282 (2)	0.046 (1)
C(16)	-0.0171 (4)	0.4859 (3)	0.3531 (2)	0.037 (1)
C(21)	0.1843 (3)	0.4593 (2)	0.1499 (2)	0.027 (1)
C(22)	0.3245 (3)	0.4539 (3)	0.1440 (2)	0.035 (1)
C(23)	0.4057 (4)	0.5179 (3)	0.1024 (2)	0.044 (1)
C(24)	0.3488 (4)	0.5870 (3)	0.0681 (2)	0.047 (1)
C(25)	0.2093 (4)	0.5918 (3)	0.0729 (2)	0.046 (1)
C(26)	0.1258 (4)	0.5283 (3)	0.1133 (2)	0.039 (1)
C(31)	-0.1128 (3)	0.3098 (2)	0.1393 (2)	0.027 (1)
C(32)	-0.1476 (3)	0.2010 (3)	0.0668 (2)	0.032 (1)
C(33)	-0.2926 (4)	0.1390 (3)	0.0126 (2)	0.038 (1)
C(34)	-0.4072 (3)	0.1815 (3)	0.0318 (2)	0.039 (1)
C(35)	-0.3748 (3)	0.2887 (3)	0.1029 (2)	0.040 (1)
C(36)	-0.2277 (3)	0.3543 (3)	0.1561 (2)	0.034 (1)
C(41)	0.2543 (3)	0.0830 (2)	0.3952 (2)	0.028 (1)
C(42)	0.1365 (4)	0.0954 (3)	0.4326 (2)	0.036 (1)
C(43)	0.1526 (4)	0.1162 (3)	0.5196 (2)	0.045 (1)
C(44)	0.2838 (5)	0.1234 (4)	0.5701 (2)	0.053 (1)
C(45)	0.4008 (5)	0.1125 (4)	0.5349 (2)	0.054 (1)
C(46)	0.3881 (4)	0.0932 (3)	0.4475 (2)	0.039 (1)
C(51)	0.3851 (3)	0.0210 (2)	0.2504 (2)	0.027 (1)
C(52)	0.4955 (3)	0.1010 (3)	0.2330 (2)	0.034 (1)
C(53)	0.6210 (4)	0.0731 (3)	0.2144 (2)	0.043 (1)
C(54)	0.6347 (4)	-0.0349 (3)	0.2125 (2)	0.044 (1)
C(55)	0.5232 (4)	-0.1168 (3)	0.2269 (2)	0.040 (1)
C(56)	0.3977 (3)	-0.0899 (3)	0.2456 (2)	0.035 (1)
C(61)	0.0652 (3)	-0.0833 (2)	0.2236 (2)	0.027 (1)
C(62)	0.0155 (4)	-0.1603 (3)	0.2645 (2)	0.039 (1)
C(63)	-0.1036 (4)	-0.2703 (3)	0.2185 (3)	0.049 (1)
C(64)	-0.1707 (4)	-0.3039 (3)	0.1316 (3)	0.049 (1)
C(65)	-0.1218 (4)	-0.2290 (3)	0.0899 (2)	0.045 (1)
C(66)	-0.0040 (3)	-0.1182 (3)	0.1360 (2)	0.035 (1)

Table 2. Selected geometric parameters (Å, °)

Re—O(1)	1.698 (2)	Re—P(1)	2.5208 (11)
Re—O(2)	1.890 (2)	O(2)—C(1)	1.436 (4)
Re—Cl(2)	2.4071 (14)	C(1)—C(3)	1.463 (6)
Re—Cl(1)	2.4076 (13)	C(1)—C(2)	1.476 (6)
Re—P(2)	2.5201 (11)		
O(1)—Re—O(2)	174.25 (9)	O(1)—Re—P(1)	87.51 (7)
O(1)—Re—Cl(2)	90.38 (8)	O(2)—Re—P(1)	92.21 (7)
O(2)—Re—Cl(2)	83.88 (7)	Cl(2)—Re—P(1)	89.34 (4)
O(1)—Re—Cl(1)	96.59 (8)	Cl(1)—Re—P(1)	91.26 (4)
O(2)—Re—Cl(1)	89.16 (7)	P(2)—Re—P(1)	174.14 (2)
Cl(2)—Re—Cl(1)	173.03 (3)	C(1)—O(2)—Re	145.3 (2)
O(1)—Re—P(2)	86.66 (7)	O(2)—C(1)—C(3)	111.6 (4)
O(2)—Re—P(2)	93.53 (7)	O(2)—C(1)—C(2)	110.5 (3)
Cl(2)—Re—P(2)	90.12 (4)	C(3)—C(1)—C(2)	114.2 (4)

Data collection and cell refinement: *CAD-4 Software* (Enraf–Nonius, 1989). Cell reduction: *SDP* (Frenz, 1983). Structure solution and refinement: *SHELXS86* (Sheldrick, 1985) and *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a packing diagram, have been deposited with the IUCr (Reference: JZ1019). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(diethylenetriamine-*N'*-acetato)-di- μ -hydroxo-dicobalt(III) Perchlorate

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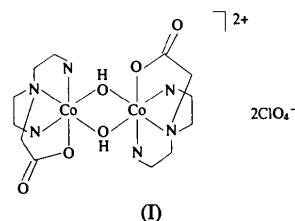
Abstract

The complex cation of the title compound, bis[bis(2-aminoethyl)aminoacetato]-di- μ -hydroxo-dicobalt(III), [Co₂(C₆H₁₄N₃O₂)₂(μ -OH)₂](ClO₄)₂, has a dinuclear structure, with two OH bridges. Each Co atom is octahedrally surrounded by a bis(2-aminoethyl)aminoacetate tripodal structure and two OH groups. In the crystal structure, intermolecular O—H...O hydrogen bonds form infinite chains of molecules, which significantly stabilizes the dinuclear structure; the Co...Co distance is 2.863 (1) Å.

Comment

The crystal and molecular structure and also the properties of metal–amino acid complexes are of continu-

ing interest to both coordination chemists and molecular biologists. In some cases, these compounds provide adequate model systems for metalloproteins and metalloenzymes (Freeman, 1973). Diethylenetriamine-*N'*-acetic acid (dtmaH) is a synthetic amino acid having a tripodal structure and studies of its complexes with metal ions (Cu, Zn, Ni) have been helpful in understanding the spectroscopic properties of Cu, Zn-superoxide dismutase and the magnetic properties of μ -carboxylate complexes (Mao, Yu, Chen, Han, Sui & Tang, 1993; Mao, Fu, Hang, Tang & Yu, 1993). In this paper, the structure of the complex [(dtma)Co(μ -OH)₂Co(dtma)](ClO₄)₂, (I), is reported.



The crystal structure consists of dimeric cations and perchlorate anions. The complex cation has an inversion centre located at the middle of the dimer. The coordination of Co^{III} is roughly octahedral and the bridging unit, Co(OH)Co(OH), is strictly planar with O—Co—O and Co—O—Co angles of 82.43 (8) and 97.57 (8)°, respectively. The Co...Co distance is 2.863 (1) Å and the Co—O distances are 1.902 (3) and 1.904 (2) Å. These bond lengths agree well with corresponding distances in [(edda)Co(OH)₂Co(en)₂]²⁺ (edda is ethylenediaminediacetate and en is ethylenediamine) (Okamoto, Hidaka, Ama & Yasui, 1991). The fragments N1N4O7O7', N4N5O8O7' and N1N5O7O8 are nearly

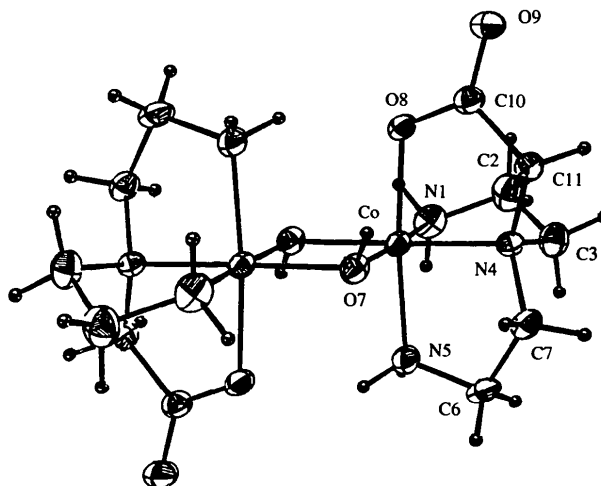


Fig. 1. Displacement ellipsoid representation (ORTEP; Johnson, 1965) of the title cation with the atomic numbering scheme. Ellipsoids are plotted at the 50% probability level.