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Note

Oxalato complexes of Re(V). Synthesis and structural characterization of [ReO(OCH_3)(ox)(L)] (L = bipy, dppe and dppee)

Raúl Chiozzone [a], Ricardo González [a], Carlos Kremer [a,*], Giovanni De Munno [b], Juan Faus [c]

[a] *Cátedra de Química Inorgánica, Facultad de Química, CC 1157 Montevideo, Uruguay*
[b] *Dipartimento di Chimica, Università degli Studi della Calabria, 87030 Arcavacata di Rende, Cosenza, Italy*
[c] *Departamento de Química Inorgánica, Facultad de Química de la Universidad deValencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain*

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Abstract

Three novel neutral complexes containing the $[ReO]^{3+}$ core have been prepared starting from K_2ReBr_6. Complexes with general formula [ReO(OCH_3)(ox)(L)] (ox = oxalate; L = 2,2′-bipyridine (bipy), 1,2-bis(diphenylphosphino)ethane (dppe) or *cis*-1,2-bis-(diphenylphosphino)ethylene (dppee)) have been obtained and characterized. The molecular structures of [ReO(OCH_3)(ox)(bipy)] and [ReO(OCH_3)(ox)(dppe)] have been determined of single-crystal X-ray analysis. The structure of the complexes consists of a six-coordinated rhenium atom bonded to two *trans*-oxygen atoms, one of the $[ReO]^{3+}$ core and one from a methoxy group. One oxalate ligand and a neutral diamine or diphosphine make the equatorial plane.

Keywords: Rhenium; Re(V) complexes; Oxalate; Crystal structures; Oxo complexes

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1. Introduction

The interest in the coordination chemistry of rhenium has been increased due to the expanding role in therapeutic applications in Nuclear Medicine [1]. Taking into account the success of the ^{186}Re(Sn)-HEDP as a therapeutic agent for the palliation of bone pain, new Re complexes are been currently designed and evaluated for the treatment of cancers and other therapies [2].

Although different kinds of ligands have been used and assayed to stabilize Re complexes, oxalato complexes have been only scarcely studied. The first report was of a brown solid obtained by reaction of ReO_2 with oxalic acid [3,4]. This diamagnetic solid was later identified as the dimer $K_4[(ox)Re(\mu\text{-}O)_2Re(ox)]\cdot 3H_2O$ (ox = oxalate) [5]. Recently, $(As\phi_4)_2[Re^{IV}Cl_4(ox)]$ ($As\phi_4$ = tetraphenylarsonium cation) was prepared and characterized by X-ray diffraction [6]. No other reports can be found in the literature with this simple ligand.

The situation is not very different with the congener Tc. The tris oxalato compound $[Tc(ox)_3]^{2-}$ [7], the dimer $[(ox)Tc(\mu\text{-}O)_2Tc(ox)]^{4-}$ [8] analogous to the above Re(IV) compound and also a neutral Tc(II) complex $[Tc(ox)(dppe)_2]$ [9] have been fully characterized.

No Re(V) or Tc(V) oxalato complexes have been reported. Re(V) is normally stabilized by oxo groups, forming very stable cores like $[ReO_2]^+$ and $[ReO]^{3+}$ [10,11]. It is assumed that the major factor of the formation of these cores is the lowering of the high positive formal charge by bonding with a hard base. Then, the coordination sphere is usually completed by soft bases like amines or phosphines. This seems to be the reason why oxalato complexes of Re(V) or Tc(V) appears so difficult to obtain.

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[*] Corresponding author. Fax: + 598-2-924 1906.
E-mail address: ckremer@bilbo.edu.uy (C. Kremer).

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As a part of our investigation to develop new Re-oxalato compounds, we have prepared neutral complexes with the general formula [ReO(OCH$_3$)(ox)(L)] starting from K$_2$Re^{IV}Br$_6$; L represents a didentate ligand like 2,2′-bipyridine (bipy), 1,2-bis(diphenylphosphino)ethane (dppe) or *cis*-1,2-bis(diphenylphosphino)ethylene (dppee). The general structure of these complexes shows a [ReO]$^{3+}$ core with a methoxy group in a *trans* position and the oxalate anion occupying two equatorial sites. The other didentate ligand completes a distorted octahedral coordination geometry around the metal ion.

2. Experimental

2.1. Materials

All chemicals were of reagent grade and used as received. K$_2$ReBr$_6$ was prepared using the previously reported method [12].

2.2. Physical measurements

IR spectra were recorded as KBr pellets on a Bomen MB FT-IR spectrophotometer and UV–Vis spectra on a Spectronic 300 instrument. Elemental analysis was accomplished on a Carlo Erba model 1108 elemental analyzer.

2.3. Synthesis of the complexes

2.3.1. Solution A

A mixture of K$_2$ReBr$_6$ (70 mg, 0.094 mmol), H$_2$C$_2$O$_4$·2H$_2$O (100 mg, 0.793 mmol), tris(hydroxymethyl)aminomethane (96 mg, 0.793 mmol) and 4 ml of methanol was stirred in a water bath at 60 °C. After 30 min, a deep green solution was obtained. A white solid was also formed, which was filtered off and discarded. The green solution was used to prepare the following compounds.

2.3.2. [ReO(OCH$_3$)(ox)(bipy)] (**1**)

Bipy (15 mg, 0.096 mmol) was added to solution A. The mixture was allowed to react in a water bath at 45 °C for a few minutes, until the imine was dissolved and the solution turned to dark brown. Then, the solution was kept at room temperature (r.t.) for 20 h. Dark green crystals were collected by filtration and washed with DMF (2 × 1 ml), water (5 × 1 ml) and acetone (3 × 1 ml). Yield: 65–70%. Some of the crystals were suitable for X-ray diffraction studies. IR (cm^{-1}): bands associated to the oxalato ligand appear at 1723 (vs), 1680 (vs) and 1334 (s); 1111 ($\nu_{O–CH_3}$, s), 955 ($\nu_{Re–O}$, s); bands associated to the aromatic rings appear at 855 (s), 811(s) and 726 (s). *Anal.* Calc. for C$_{13}$H$_{11}$N$_2$O$_6$Re: C, 32.7; H, 2.3; N, 5.9; O, 20.1. Found: C, 32.6; H, 2.3; N, 5.9; O, 19.6%.

2.3.3. [ReO(OCH$_3$)(ox)(dppe)] (**2**)

Dppe (37 mg, 0.093 mmol) was added to solution A. The mixture was allowed to react in a water bath at 40 °C for 30 min. The solution turned dark orange. Then, the solution was kept at r.t. for 20 h. Dark orange crystals were collected by filtration and washed with methanol (5 × 2 ml), DMF (2 × 1 ml) and acetone (3 × 1 ml). Yield: 45–50%. Some of the crystals were suitable for X-ray diffraction studies. IR (cm^{-1}): bands associated to the oxalato ligand appear at 1713 (vs), 1682 (vs), 1344 (vs) and 796 (vs); 1436 ($\nu_{P–\phi}$, s), 1123 ($\nu_{O–CH_3}$, s), 947 ($\nu_{Re–O}$, vs). *Anal.* Calc. for C$_{29}$H$_{27}$O$_6$P$_2$Re: C, 48.4; H, 3.8; O, 13.3. Found: C, 47.9; H, 3.8; O, 13.3%.

2.3.4. [ReO(OCH$_3$)(ox)(dppee)] (**3**)

Dppee (37 mg, 0.096 mmol) was added to solution A. The mixture was allowed to react in a water bath at 60 °C for 20 min. The solution turned brown. Brown crystals were obtained and filtered upon slow evaporation of the solvent and washed with CH$_2$Cl$_2$ (5 × 2 ml). Yield: 30–35%. IR (cm^{-1}): bands associated to the oxalato ligand appear at 1715 (vs), 1683 (vs), 1347 (vs) and 798 (vs); 1436 ($\nu_{P–\phi}$, s); 1118 ($\nu_{O–CH_3}$, s), 946 ($\nu_{Re–O}$, vs). *Anal.* Calc. For C$_{29}$H$_{25}$O$_6$P$_2$Re: C, 48.5; H, 3.5; O, 13.4. Found: C, 48.1; H, 3.4; O, 13.6%.

2.4. Crystallographic measurements and structure determinations

Crystals of dimensions 0.28 × 0.22 × 0.15 (**1**) and 0.30 × 0.35 × 0.38 mm (**2**) were mounted on a Bruker R3m/V automatic four-circle diffractometer and used for data collection. Diffraction data were collected at r.t. by using graphite monochromated Mo-Kα: radiation ($\lambda = 0.71073$ Å) with the $\omega–2\theta$ scan method. The unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the 2θ range of 15–30°. Information concerning crystallographic data collection and structure refinements is summarized in Table 1. Examination of two standard reflections, monitored after every 98 reflections, showed no sign of crystal deterioration. Lorentz-polarization and absorption corrections were applied to the intensity data [13]. The maximum and minimum transmission factors were 0.267 and 0.086 for **1**, 0.264 and 0.185 for **2**. 3373 (**1**) and 5422 (**2**) reflections were measured in the 2θ range 3–54° with index ranges $0 \leq h \leq 10$, $0 \leq k \leq 24$ and $-11 \leq l \leq 10$ (**1**), $0 \leq h \leq 12$, $0 \leq k \leq 22$ and $-17 \leq l \leq 17$ (**2**).

The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The refinement was performed on F^2 using 3023 for **1** and 5005 for **2**. Models reached convergence with values of the R and R_w indices listed in Table 1. Solutions and refinements were performed with the SHELXTL PLUS system [14]. The graphical manipulations were performed using the XP utility of the SHELXTL PLUS system. Main interatomic bond distances and angles are listed in Table 2 (**1**) and Table 3 (**2**).

Table 1
Crystal data and structural refinement parameters for compounds **1** and **2**

	1	**2**
Chemical formula	$C_{13}H_{11}N_2O_6Re$	$C_{29}H_{27}O_6P_2Re$
Formula weight	477.44	719.65
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	8.411(2)	10.350(2)
b (Å)	19.176(6)	18.762(3)
c (Å)	8.705(2)	14.709(3)
β (°)	101.00(2)	99.27(1)
V (Å^3)	1378.2(6)	2819.0(9)
Z	4	4
D_{calc} (g cm^{-3})	2.301	1.696
F(000)	904	1416
μ (cm^{-1})	88.49	44.65
Reflections, unique/observed	3023/2670	5005/4334
R [a]	0.0378	0.0333
R_w [b]	0.1229	0.0994
S [c]	1.068	0.868

Details in common: $T = 25$ °C.

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

[b] $R_w = [\Sigma\, w(F_o{}^2 - F_c{}^2)^2/\Sigma\, w(F_o{}^2)^2]^{1/2}$.

[c] Goodness-of-fit $= [\Sigma\, w(F_o{}^2 - F_c{}^2)^2/(N_o - N_p)]^{1/2}$.

Table 2
Selected bond distances (Å) and bond angles (°) for compound **1**

Bond distances	
Re(1)–O(5)	1.699(5)
Re(1)–O(6)	1.886(5)
Re(1)–O(1)	2.057(6)
Re(1)–O(2)	2.037(5)
Re(1)–N(l)	2.126(6)
Re(1)–N(2)	2.131(5)
Bond angles	
O(5)–Re(1)–O(6)	170.1(2)
O(1)–Re(1)–O(2)	80.3(2)
O(1)–C(11)–C(12)	114.8(8)
O(2)–C(12)–C(11)	114.4(6)
O(5)–Re(1)–O(1)	97.1(3)
O(5)–Re(1)–O(2)	98.1(2)
O(6)–Re(1)–O(1)	89.4(2)
O(6)–Re(1)–O(2)	90.3(2)
O(5)–Re(1)–N(1)	89.0(2)
O(5)–Re(1)–N(2)	88.6(3)
O(6)–Re(1)–N(1)	82.3(2)
O(6)–Re(1)–N(2)	84.7(2)
Re(1)–O(6)–C(13)	146.9(5)

Table 3
Selected bond distances (Å) and bond angles (°) for compound **2**

Bond distances	
Re(1)–O(5)	1.691(5)
Re(1)–O(6)	1.875(4)
Re(1)–O(1)	2.094(4)
Re(1)–O(2)	2.082(4)
Re(1)–P(1)	2.432(2)
Re(1)–P(2)	2.427(1)
Bond angles	
O(5)–Re(1)–O(6)	174.2(2)
O(1)–Re(1)–O(2)	79.0(1)
O(1)–C(1)–C(2)	115.9(4)
O(2)–C(2)–C(1)	114.7(4)
O(5)–Re(1)–O(1)	95.3(2)
O(5)–Re(1)–O(2)	96.6(2)
O(6)–Re(1)–O(1)	87.9(2)
O(6)–Re(1)–O(2)	88.8(2)
O(5)–Re(1)–P(1)	90.7(1)
O(5)–Re(1)–P(2)	88.65(13)
O(6)–Re(l)–P(1)	90.74(14)
O(6)–Re(1)–P(2)	88.34(16)

3. Results and discussion

The reaction of K_2ReBr_6 with an excess of oxalic acid in the presence of equivalent amounts of a base like tris(hydroxymethyl)aminomethane, produces a green solution characterized by a strong absorption at 640 nm. This solution is stable for periods up to 2 days, then it turns to brown and finally ReO_4^- is evident in solution. This decomposition product can be precipitated as $As\phi_4ReO_4$ and identified by IR spectroscopy.

Addition of bulky cations (like $As\phi_4^+$) to the green solution only yields small amounts of a green powder which could not been fully characterized. The IR spectrum of this solid shows the presence of coordinated oxalate (1707, 1670 and 788 cm^{-1}) and $As\phi_4^+$ (1439, 1081, 997, 741 and 688 cm^{-1}). A strong band at 971 cm^{-1} reveals the presence of a $[ReO]^{3+}$ core. The position of this signal is similar with those seen for monooxo Re(V) complexes [15]. The characteristic band of the $-OCH_3$ group (around 1100 cm^{-1}) is not detected. Electron microprobe chemical analysis on the solid shows a 1:1 rhenium–arsenic ratio. Magnetic measurements indicate that this solid is diamagnetic, as expected for a Re(V) complex [16]. In conclusion, during this first stage of the synthesis, the Re(IV) atom of the precursor seems to be oxidized to Re(V) forming an anionic Re(V) oxo complex containing oxalate in the coordination sphere. The formula $As\phi_4[ReO(ox)_2]$ is consistent with all the experimental data.

When a didentate ligand L is added to the green solution, solids with composition [ReO(OCH$_3$)(ox)(L)] are obtained. This composition is consistent with the elemental analysis. IR spectra of complexes **1**–**3**, show a very intense band around 950 cm^{-1} due to the presence of a [ReO]$^{3+}$ core. Moreover, this position is in line with those previously reported for other *trans*-[O–Re–OCH$_3$] complexes [15]. In addition, characteristic bands of the oxalate and methoxy groups are evident (see Section 2).

Single crystals were obtained for compounds **1** and **2**. Both structures contain discrete, monomeric, neutral monooxorhenium(V) units. Perspective drawings of the complexes are shown in Figs. 1 and 2.

The rhenium atom is in a distorted octahedral environment with apical positions occupied by the oxo group O(5) and the methoxy group O(6). The equatorial plane of the octahedron is formed by the oxalate and the neutral ligand (bipy or dppe). Oxygen atoms are not aligned with the metal. O–Re–O angles are 170.1(2) (**1**) and 174.2(2)° (**2**). The short Re–O(5) distance is consistent with other Re(V) complexes with an uninegative oxygen *trans* to the oxo group [15,17]. Anionic charge of the methoxy and oxalate groups produces the elongation of the Re–O distance compared with the expected mean value [18]. In addition, the presence of a negative charged equatorial ligand originates an important distortion in the geometry. High electron density of the oxalate causes the apical groups to be pushed away towards the neutral ligand.

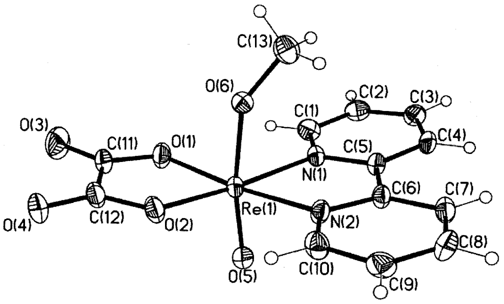

Fig. 1. Perspective drawing of complex **1** showing the atom numbering. Thermal ellipsoids are plotted at 30% probability level.

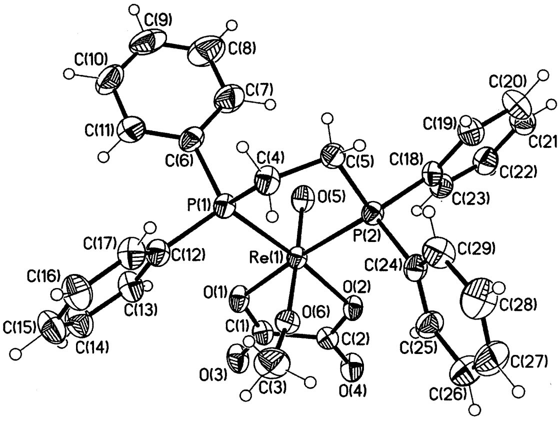

Fig. 2. Perspective drawing of complex **2** showing the atom numbering. Thermal ellipsoids are plotted at 30% probability level.

The atoms that constitute the equatorial plane around Re(1) in **1** [O(1), O(2), N(1), N(2)] and **2** [O(1), O(2), P(l), P(2)] deviate from planarity, the largest deviation being 0.013(6) (**1**) and 0.070(4) Å (**2**) for O(1). The Re(1) atom is 0.721(1) (**1**) and 0.112(1)(**2**) Å out of this plane. The values of the dihedral angle between this mean plane and that of the oxalate are 3.6(2)° (**1**) and 4.9(1)° (**2**). The corresponding value with bipy in **1** is only 1.3(2)°.

The Re(1) atom constitutes, with N(1), C(5), C(6) and N(2) atoms in **1**, an almost planar ring. On the contrary, the corresponding ring containing the P(1), C(4), C(5) and P(2) atoms in **2** is very distorted from the planarity.

The pyridyl rings of the bipy ligand in **1** are planar as expected, the maximum deviation from the mean planes being 0.017(8) Å at the C(2) atom. The ligand as a whole is also planar, the dihedral angle between the two pyridyl rings being of 2.7(2)°. The values of the angle subtended at the metal atom by the chelating bipy (average 76.2(2)°) is significantly reduced with respect to the ideal value of 90°. The carbon–carbon and carbon–nitrogen bond distances within the bipy ligand are in agreement with those reported for the coordinated bipy molecule.

The phosphorus atoms in **2** show the expected tetrahedral geometry with angles in the range 104.3(3)–115.6(2)°.

4. Conclusions

The reaction of K$_2$ReBr$_6$ with oxalic acid produces a new kind of mixed-ligand Re(V) complexes. As far as we know, these are the first examples of Re(V) complexes with oxalate. Usually, Re(V) oxo-methoxy complexes are prepared starting from other Re(V) precursors: [ReOCl$_3$(PPh$_3$)$_2$], [ReOCl$_4$]$^-$, [ReO$_2$I-(PPh$_3$)$_2$], etc. According to our results, [Re^{IV}Br$_6$]$^{2-}$ can be a good alternative for complexes with such core.

The basic structural framework for these complexes is provided by the rhenium-oxo-methoxy core and the oxalate ligand. The two remaining positions can be occupied by a neutral didentate coligand. These results open the possibility to prepare and study a new series of neutral complexes by changing the coligand.

5. Supplementary material

Crystallographic data for the structural analyses and complete atom coordinates, thermal parameters and bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 167907 and 167908 for compounds **1** and **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033: e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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