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Sym-cis-Dioxo(2,2'-bipyridine)bis(pyridine)rhenium(V) Hexafluorophosphate, *Sym-cis*-$[(O)_2Re(bpy)(py)_2](PF_6)$

by

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The complex *sym-cis*-(bpy)(py)$_2$Re(O)$_2^+$ has recently been synthesized and its structure has been determined. The complex represents the first confirmed hexacoordinate *cis*-dioxo complex of rhenium and is one of only a handful of d^2 metal complexes known to possess the *cis*-dioxo ligand configuration. The dioxo complexes of rhenium(V) are of interest in general because of their multielectron electrochemical behavior, persistent (in some instances) photophysical activity, and possible redox catalytic activity. The unusual geometry for the (bpy)(py)$_2$Re(O)$_2^+$ species exerts a profound influence upon all of these properties. We report here an improved procedure for its synthesis. The method appears to be general for synthesizing various substituted pyridyl and bipyridyl complexes. (The earlier method[1] was notably deficient in this respect.) The new synthesis also represents a considerable savings in total time and in effort needed to achieve purification. The current synthesis can be considered complementary to the synthesis of *trans*-terakis(pyridine) dioxorhenium(V) and *trans*-bis(ethylenediamine)dioxorhenium(V) complexes which have been previously described in Inorganic Synthesis.[10,11]

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Introduction

The complex *sym-cis*-$(bpy)(py)_2Re(O)_2^+$ has recently been synthesized[1] and its structure has been determined.[2] The complex represents the first confirmed hexacoordinate *cis*-dioxo complex of rhenium and is one of only a handful of d^2 metal complexes known to possess the *cis*-dioxo ligand configuration.[3-5] The dioxo complexes of rhenium(V) are of interest in general because of their multielectron electrochemical behavior,[1,6] persistent (in some instances) photophysical activity,[7-9] and possible redox catalytic activity.[6,9] The unusual geometry for the $(bpy)(py)_2Re(O)_2^+$ species exerts a profound influence upon all of these properties. We report here an improved procedure for its synthesis. The method appears to be general for synthesizing various substituted pyridyl and bipyridyl complexes. (The earlier method[1] was notably deficient in this respect.) The new synthesis also represents a considerable savings in total time and in effort needed to achieve purification. The current synthesis can be considered complementary to the synthesis of *trans*-terakis(pyridine)dioxorhenium(V) and *trans*-bis(ethylenediamine)dioxorhenium(V) complexes which have been previously described in Inorganic Synthesis.[10,11]

Procedure

The total time required for the synthesis is ~two days. For steps 4 and 5 (only) the time required is about 3 hours. The net yield of the purified complex (steps 1-5) is ~15%.

Step 1. Synthesis of $ReOCl_3(PPh_3)_2$

$$ReO_4^- + 3Ph_3P + 3Cl^- + 4H^+ \longrightarrow ReOCl_3(PPh_3)_2 + Ph_3PO + 2H_2O \qquad (1)$$

The complex was prepared by the method described by Wilkinson, et al.[12] (To a boiling solution of 10 g perrhenic acid plus 10 ml of concentrated HCl in 100 ml ethanol was added 50 g triphenylphosphine (Ph_3P) dissolved in 150 ml refluxing ethanol. The mixture was boiled for three minutes (with swirling), cooled to about 50° C and filtered. The complex was thoroughly washed with toluene and dried.) The green product was used without purification.

Step 2. Synthesis of *trans*-$[(py)_4Re(O)_2](Cl)$

$$ReOCl_3(Ph_3P)_2 + 6py + H_2O \longrightarrow (py)_4Re(O)_2^+ + 2\ Ph_3P + 2\ pyH^+ + 3Cl^- \qquad (2)$$

Although there are other methods of synthesis for this complex[10,12-14], we find the following method, a *modification* of Wilkinson's procedure,[12] the most convenient. 6 g of $ReOCl_3(PPh_3)_2$ was mixed with 12 ml pyridine and 6 ml water in 120 ml acetone. The mixture was refluxed for 90 minutes and cooled in ice-water for 30 minutes. The orange yellow complex (which precipitates even while refluxing) is collected by filtration (porous glass frit), washed with two 20 ml portions of toluene and two 20 ml portions of ether. Yield 3.7 g (90%). In our hands this procedure proved to be superior (with respect to time and yields) to those described in references 10 and 12.

Step 3. Synthesis of $Re(O)(OEt)(I)_2(py_3P)_2$

$$[Re(O)_2(py)_4](Cl) + 3\ HI + EtOH \longrightarrow$$

$$Re(O)(OEt)(py)_2(I)_2 + 2\ pyH^+ + Cl^- + I^- + H_2O \qquad (3)$$

This complex is prepared according to a literature method,[14] but again with a slight modification. 2.0 g of *trans*-$[(py)_4Re(O)_2](Cl)$ was dissolved in 60 ml of refluxing ethanol. 3 ml of 57% HI was added to the solution. The

mixture was then refluxed with stirring for 15 minutes followed by cooling in ice water for 45 minutes. The precipitated green complex was collected by filtration, washed with three 20 ml portions of ethanol and dried. Yield 1.16 g (50%)

Step 4. Synthesis of *sym-cis*-[(bpy)$(py)_2Re(O)_2$](I)

$$Re(O)(OEt)(I)_2(py)_2 + H_2O \longrightarrow Re(O)_2(py)_2I + EtOH + HI \qquad (4)$$

$$Re(O)_2(py)_2(I) + bpy \longrightarrow \textit{sym-cis}\text{-}[(bpy)(py)_2Re(O)_2](I) \qquad (5)$$

1.15 g (1.7 mmoles) of the green complex obtained in step 3 was mixed with 2.6 g (~17 mmoles) of 2,2'-bipyridine (bpy) and 2 ml water in 60 ml acetone. The mixture was stirred at room temperature for 1 h, and then rotary evaporated (at 35° C) until the volume was 10 ml. To complete the precipitation of the complex, 200 ml of ether was added (with stirring). The purple black solid was filtered with a medium porosity frit and washed with 2 x 10 ml portions of ether. Yield 0.85 g (73%)

Step 5. Synthesis of *sym-cis*-[(bpy)$(py)_2Re(O)_2$](PF_6)

0.85 g of the iodide salt of the complex was dissolved in 130 ml water (ultrasonication dissolved most of the complex). 5 ml of a saturated aqueous solution of NH_4PF_6 was then added to precipitate the *sym-cis*-[(bpy)$(py)_2Re(O)_2$](PF_6). (The addition of 10 ml of saturated $NaClO_4$ solution likewise gives the crude *sym-cis*-[(bpy)$(py)_2Re(O)_2$](ClO_4) salt. The perchlorate salt is advantageous because of its relatively high aqueous solubility. The purification of this material follows the same procedure as for the PF_6^- salt.)

CAUTION: *Perchlorates of heavy metal ions with organic ligands are potentially explosive. It is advisable to handle or store < 50 mg of this material, and then also with the usual precautions to avoid mixing with concentrated acids or EtOH. Furthermore, it should not be subjected to mechanical or thermal stress.*

The complex was collected on a medium glass frit, washed with 2 x 2 ml water and with 2 x 10 ml of ether containing 10% acetone. Crude yield 0.5 g (57%). The complex is easily purified by adsorbing onto a Brockmann I, neutral alumina (Aldrich) column (about 30 ml volume) containing CH_2Cl_2 as solvent. Elution of the desired purple band is accomplished with 30% 2-propanol/70% CH_2Cl_2solution. The complex is precipitated from the eluent solution by addition of 200 ml ether (with stirring), then filtered with a medium frit and washed with 2 x 10 ml portions of ether containing 10% acetone. The solid is dried at ~40° C in a vacuum oven overnight. Yield 0.35 g (70%); Analysis: Found: C 35.1%, H 2.72%, N 8.05%; Calc: C 35.4%, H 2.65%, N 8.26%.

Properties

The *sym-cis*-$[(bpy)(py)_2Re(O)_2]^+$ complex is burgundy red in color. The perchlorate salt is fairly highly soluble in water (~5 mM) as is the iodide. (The iodide salt is not particularly useful, however, for oxidative electrochemical studies). Both the perchlorate and the hexaflurophosphate salts are highly soluble in polar organic solvents. The complex decomposes significantly (~10%) in two hours in water and more slowly in other solvents. With excess pyridine in acetonitrile as solvent, it rapidly reverts to *trans*-tetrakis(pyridine)dioxorhenium(V). The complex has a solvent-dependent

electronic absorption spectrum. In water four absorption maxima (ϵ, M^{-1} cm^{-1}) are seen: 498 nm (4.2×10^3), 383 nm (8.3×10^3), 300 nm (1.64×10^4) and 245 nm (1.45×10^4). In acetonitrile the two longer wavelength transitions move to 527 nm and 406 nm. Symmetric and asymmetric O=Re=O stretches were observed by both IR and resonance Raman at 845 cm^{-1}(s) and 906 cm^{-1}(s). The δ values (in ppm with respect to CD_3COCHD_2 at 2.04 ppm as reference) for the proton magnetic resonances are as follows: 10.87 (d, 2H), 8.70 (d, 2H), 8.44 (d, 4H), 7.99 (t, 2H), 7.88 (t, 2H), 7.69 (m, 6H). The electrochemical behavior is quite distinctive. At pH 7 in water, a reversible oxidation to Re(VI) occurs at 0.63 V (vs. SCE). A quasi-reversible V/III couple exists at -0.63 V with a III/II couple at -0.91 V. At pH 13, the VI/V potential is unchanged. The reductive processes coalesce, however, to give an unusual three electron transformation (V/II) at -0.98 V.

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