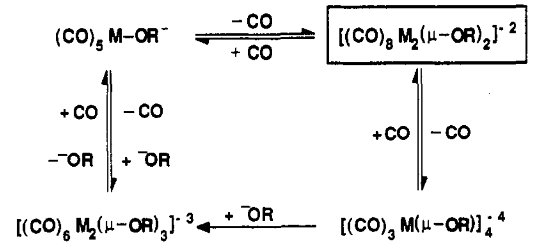
Scheme I



phenoxide dimer, $[Et_4N]_3[W_2(CO)_6(\mu\text{-}OPh)_3]$,[3] where the average W–O length is 2.222 (5) Å, and the W–O bond lengths of the triple-bridged hydroxy dimer $[K]_3[W_2(CO)_6(\mu\text{-}OH)_3]$, where the average W–O bond length is 2.16 (2) Å.[8] The W–CO distances range from 1.90 (3) to 1.95 (1) Å, with an average distance of 1.93 (3) Å. The geometry at each metal center is that of a distorted octahedron, where the W–O–W bond angle of the W_2O_2 core is 107.8 (5)°. This angle is significantly more obtuse than either the triple-bridged hydroxy or phenoxy dimers, 97 (1) and 96.7 (3)°, respectively. Furthermore, this angle is significantly more open than the W–S–W angle of the tungsten dimer, $[Et_4N]_2[W_2(CO)_8(\mu\text{-}SPh)_2]$, of 103.1°.[9a]

Acknowledgment. The financial support of this research by the National Science Foundation (Grant 88-17873) is greatly appreciated.

Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters, and H atom coordinates and isotropic displacement parameters for $[PPN]_2[W_2(CO)_8(CH_2CF_3)_2]$ (6 pages). Ordering information is given on any current masthead page.

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Received November 21, 1989

Molecular Structure of $[(O)_2Re(bpy)(py)_2](ClO_4)$: An Unusual Example of a d^2 Metal Complex with a *cis*-Dioxo Ligand Configuration

Dioxo rhenium(V) species, especially with pyridyl-type ligands, have attracted significant interest recently—on account of both their electrochemical properties[1] and their photophysical and photochemical reactivity characteristics.[2,3] We have been examining these species from the point of view of multielectron-transfer kinetics (i.e. Re(V) ⇄ Re(III) and Re(V) ⇄ Re(II)), especially at electrochemical interfaces.[4] In the course of those studies we have had occasion to introduce relatively minor modifications to the ligand environment. One of these—the replacement of a pair of pyridine(py) ligands by 2,2′-bipyridine(bpy) in the prototypical complex, *trans*-$(O)_2Re(py)_4^+$—had profound chemical consequences. Formal potentials shifted by up to 600 mV, photophysical activity disappeared, and a rare display of three-electron redox chemistry emerged at high pH's. Furthermore, the kinetics of the multielectron electrochemical reduction were greatly accelerated. Finally, there were marked changes in NMR, Raman, UV-vis, and infrared spectra.[4]

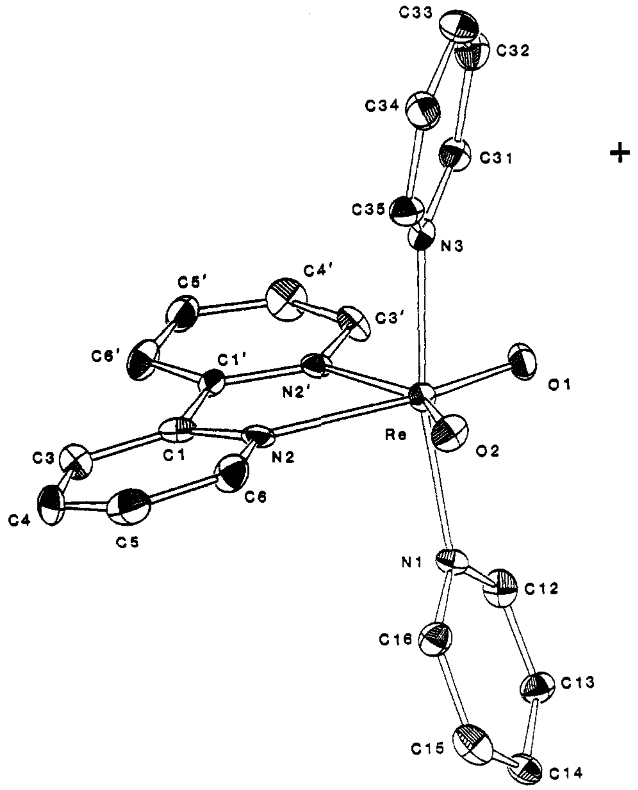

Figure 1. ORTEP drawing of *cis*-$(O)_2Re(bpy)(py)_2^+$.

On the basis of extensive circumstantial evidence we were forced to conclude that the changes were brought about by trans to cis isomerization upon bpy substitution. (The conclusion was particularly attractive, however, because it could account for the rather remarkable kinetic effects.) It was noted, nevertheless, that a rigorous structural assignment was impossible based upon either magnetic or vibrational spectroscopy—the reason being that both *cis*- and *trans*-$(O)_2Re(bpy)(py)_2^+$ would possess C_{2v} symmetry.[4,5] Furthermore, there were theoretical reasons to doubt the cis geometry.[6]

We now report, on the basis of X-ray crystal structure investigations,[7] that the product of bipyridyl substitution at *trans*-$(O)_2Re(py)_4^+$ is indeed *cis*-$(O)_2Re(bpy)(py)_2^+$. To our knowledge this is one of only two confirmed examples of a hexacoordinate d^2 metal complex with a *cis*-dioxo structure.[8,9] (It should be noted,

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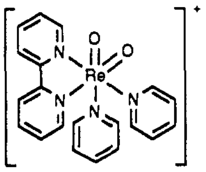
(1) Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256.

(2) (a) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1371. (b) Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1985**, *24*, 346. (c) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889. (d) Thorp, H. H.; Kumar, C. V.; Turro, N. J.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 4364.

(3) Newsham, M. D.; Giannelis, E. P.; Pinnavia, T. J.; Nocera, D. E. *J. Am. Chem. Soc.* **1988**, *110*, 3885.

(4) Ram, M. S.; Johnson, C. S.; Blackbourn, R. L.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 238.

(5) NMR studies did, however, enable us to rule out an even lower symmetry cis structure:



(6) Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29.

(7) Crystal data: formula = $[ReO_2(py)_2(bpy)]ClO_4\cdot0.33(pyH)ClO_4\cdot0.33(CH_3)_2CO$, M = 711.25, rhombohedral, space group $R\bar{3}$ (No. 148), a = 24.627 (5) Å, c = 19.748 (5) Å, V = 10,372 (7) Å^3, Z = 18. The structure was solved by Patterson and Fourier techniques and refined to $R(F)$ and $R_w(F)$ of 0.052 and 0.070, respectively. A total of 2260 absorption-corrected reflections with $I > 3\sigma(I)$ were measured on an Enraf-Nonius CAD4 diffractometer up to $2\theta_{max}$ = 55° (Mo Kα radiation, λ = 0.71069 Å).

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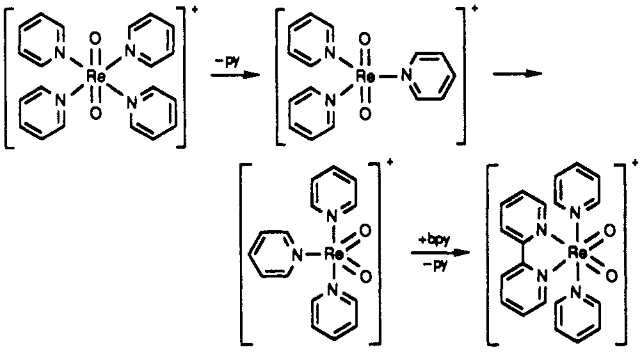
however, that two additional examples have been proposed by Meyer and co-workers[10,11] on the basis of polypyridyl complexation of oxidation state VI of either osmium or ruthenium. The osmium complex is moderately stable and has been isolated as a perchlorate salt;[10] the Ru species displays only a transient solution existence.[11] Neither has been confirmed by crystallographic measurements. Nevertheless, in view of the present findings the earlier structural assignments almost certainly are correct.)

For the current work a powdered sample of *cis*-[$(O)_2$Re(bpy)$(py)_2$](ClO_4) was prepared and purified as described by Ram et al.[4] Red crystals of X-ray quality (ca. 0.4 mm diameter) were obtained (~3 days) by dissolution of the powder in an acetone/ethyl acetate mixture, followed by cooling to -30 °C.[12]

An ORTEP drawing of the complex cation is shown in Figure 1. The Re atom is present within a distorted octahedral environment. The *cis*-$(O)_2$Re moiety is characterized by Re═O bond lengths of 1.733 (8) and 1.736 (7) Å and an O═Re═O bond angle of 121.4 (4)°. The Re═O bond lengths are only slightly shorter than those found in the d^2 trans complexes [$(O)_2$Re$(py)_4$]Cl and [$(O)_2$Re(ethylenediamine)$_2$]Cl.[13] They also compare very well to those found in a trigonal bipyramidal *cis*-$(O)_2$Re species.[14] The O═Re═O angle, however, is much smaller in $(O)_2$Re(bpy)$(py)_2$ than in the five-coordinate structure (138.7 (6)°).[14] On the other hand, it is appreciably larger than in most d^0 *cis*-dioxo complexes.[15,16] The bipyridine N1-Re-N1′ "bite" angle is 70.6 (3)°, a quite typical value for bpy complexes. Likewise the inter-ring "twist" of 7.2° is typical of transition-metal bpy complexes.[17] Finally, it is worth noting that the pyridyl ligands are tilted significantly towards the *cis*-$(O)_2$Re moiety. Thus the dihedral angles between the $(O)_2$Re plane and the N1 and N3 rings are 74.6 and 74.8° respectively. (The N1-Re-N3 angle itself is 169.0 (3)°.) At present, we have no explanation for this peculiar geometry.

In view of Mingos' work,[6] the cis configuration is probably not the most stable form thermodynamically for $(O)_2$Re(bpy)$(py)_2^+$. Evidence of *chemical* instability comes from solution studies[4] and from the detection of $pyH^+ClO_4^-$ in the sample. Obviously, the appearance of the cis structure at the expense of the trans must reflect a kinetic preference at some stage in the substitution process. Although we have not pursued the issues of substitution kinetics or mechanism, one simple sequence that might account for the isomerization would be the following:



The crucial second step presumably would be driven by the need to relieve steric crowding at the α-sites on adjacent pyridine ligands.

Acknowledgment. We thank the Office of Naval Research for support of this work.

Supplementary Material Available: A summary of the X-ray crystallographic study of the title compound, tables of crystal data, positional parameters, thermal parameters, interatomic distances, and bond angles for the Re cation, and a table of interatomic distances for the disordered perchlorate and acetone (9 pages); a table of structure factors (16 pages). Ordering information is given on any current masthead page.

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Received February 14, 1990

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(8) The sole previous example is potassium tris(acetato)dioxoosmate(VI). Here the trans acetato ligands are monodentate while the remaining acetate is bidentate. It has been argued that the *cis*-dioxo configuration is obtained because the molecule effectively conforms to pseudo-trigonal-bipyramidal (tbp) symmetry, with the bidentate acetate effectively occupying only one coordination site. (Genuinely pentacoordinate *cis*-dioxo species are well-known.[15]) Pseudo tbp symmetry was also invoked to explain the rather large O═Os═O bond angle (125°) (Behling, T.; Capparelli, M. V.; Skapski, A. C.; Wilkinson, G. *Polyhedron* **1982**, *1*, 840). Our results for the more nearly octahedral rhenium complex would seem to be at variance with these "geometrical" explanations.

(9) For a review of this area, see: Holm, R. H. *Chem. Rev.* **1987**, 1401.

(10) Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2357.

(11) Dobson, J. C.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3283.

(12) Identical IR spectra were obtained in the metal-oxo stretching region for crystalline and powdered samples.

(13) Lock, C. J. L.; Turner, G. *Acta Crystallogr.* **1978**, *B34*, 923.

(14) Ciani, G. F.; D'Alfonso, G.; Romiti, P. F.; Sironi, A.; Freni, M. *Inorg. Chim. Acta* **1983**, *72*, 29.

(15) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley and Sons: New York, 1988.

(16) Bond angles for the latter almost always fall in the 102-112° range.[15]

(17) See, for example: Ghosh, M.; Siddhartha, R. *Acta Crystallogr.* **1983**, *C39*, 1367.

(18) The studies by Meyer and co-workers[10,11] of $(O)_2Ru(bpy)_2^{2+}$ and $(O)_2Os(bpy)_2^{2+}$ clearly support this contention. A reviewer has pointed out, however, that in $(O)_2$Re(bpy)$(py)_2^+$ the π-donating oxo ligands might be sufficiently stabilized by the π-accepting bipyridyl ligand in a trans configuration (relative to the oxo groups) to render the cis dioxo species the more stable isomer. Obviously, a definitive resolution will require the synthesis of one or both trans isomers—a goal that has thus far proven elusive.

(19) A reviewer has argued (based on the work of Kashani and Murmann (*Int. J. Chem. Kinet.* **1985**, *17*, 1005)) that a six-coordinate intermediate, $Re(py)_3(H_2O)(O)_2^+$, is more likely. (It is worth noting that neither intermediate has been isolated.) While we have no strong feelings on this point, we are inclined to favor the five-coordinate pathway. One piece of evidence in support of isomerization via a pentacoordinate species is a recently discovered route to *cis*-$(O)_2$Re(bpy)$(py)_2^+$ through a known[20] five-coordinate precursor, $(O)_2Re(py)_3I$ (Ram, M. S. Unpublished work).

(20) Freni, M.; Giusto, D.; Romiti, P.; Minghetti, G. *Gazz. Chim. Ital.* **1969**, *99*, 286.