γ-phosphate groups of ATP. Unlike CoPP, where the metal chelate ring is broken by addition of HCl,[19] the CoPCP moiety is stable to acid hydrolysis both in solution and at the enzyme-active site. This is due to the saturated methylene carbon atom, which cannot be further protonated. CoPNP, where the bridge nitrogen atom carries a proton, is also stable to acid hydrolysis in solution as well as in most enzymes. However, some enzymes can catalyze the hydrolysis of AMP-PNP by adding a second proton to the bridge nitrogen position.[11]

In many enzyme-catalyzed reactions not requiring cleavage between the β- and γ-phosphate groups of ATP, AMP-PNP has been shown to serve as ligand, substrate, or allosteric effector as effectively as ATP, while AMP-PCP was shown to be ineffective.[2] These results would suggest that this discrimination is based on the differences in the chelate ring geometry found for the P–C–P analogue as compared to the chelate rings formed from the corresponding P–O–P and P–N–P complexes. A grapic representation of the geometrical differences resulting from the substitution of nitrogen or carbon at the bridge position of pyrophosphate is given in Figure 3. Significant differences exist between the chelate ring structures of CoPP and CoPCP especially at the methylene group, which is further removed from the chelating metal (3.626 Å) than is the corresponding bridge oxygen atom (3.425 Å). The long P–C bonds and narrow P–C–P bond angle require that the chelate ring of the $Co(NH_3)_4PCP$ complex be more extended than that of the $Co(NH_3)_4PP$ complex. Enzymes that act on the β,γ-bidentate MgATP complex or P^1,P^2-bidentate MgPP complex bind MgAMP-PNP or MgPNP with nearly equal affinity,[2] while the MgAMP-PCP or MgPCP complexes result in unproductive enzyme binding or binding of lesser affinity. The extended P–C–P chelate ring of metal-coordinated AMP-PCP apparently fails to fit well within the steric constraints of the metal–polyphosphate binding site of most enzymes. In contrast, the chelate ring of metal-coordinated AMP-PNP has a much closer resemblance to the structure of β,γ metal ATP and will therefore readily bind to most ATP-dependent enxymes as a competitive inhibitor.

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Supplementary Material Available: Listings of anisotropic temperature factors for the non-hydrogen atoms and all observed and calculated structure factors for the title compound (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Corporate Research Science Laboratories and Analytical Division,
Exxon Research and Engineering Company, Annandale, New Jersey 08801

Reduction of Re_2O_7 by Triethylphosphine

J. W. JOHNSON,*† J. F. BRODY,† G. B. ANSELL,‡ and S. ZENTZ‡

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Re_2O_7 is reduced by PEt_3 in the presence of L (L = pyridine, 4-methylpyridine, 4-phenylpyridine) to yield the mixed-valent $Re^{5+}Re^{7+}$ salts $ReO_2L_4{}^+ReO_4{}^-$. ReO_3 also reacts directly with pyridine to give the same compound. $ReO_2(4\text{-Mepy})_4ReO_4$ crystallizes in the triclinic space group $P\bar{1}$: $a = 10.180$ (2) Å, $b = 10.695$ (3) Å, $c = 13.261$ (3) Å, $\alpha = 103.17$ (2)°, $\beta = 99.64$ (2)°, $\gamma = 96.47$ (2)°, $Z = 4$. The structure consists of two crystallographically independent centrosymmetric *trans*-$ReO_2L_4{}^+$ cations and tetrahedral $ReO_4{}^-$ anions in general positions.

Introduction

In previous work we have shown that molybdenum(VI) and tungsten(VI) oxides form compounds with pyridine and substituted pyridines that are composed of two-dimensional metal oxide layers separated by the organic ligands, which are covalently bound to the transition-metal atoms within the layers.[1] These layers are held together only by van der Waals contacts. In $MoO_3(py)$ and $WO_3(py)$ the transition-metal ions are in their hexavalent states and have no d electrons. Compounds with a similar structure that process d electrons can be expected to exhibit interesting electronic properties due to two-dimensional d-electron delocalization. Rhenium(VI), which has a d^1 configuration, is a good candidate to form the analogous compound $ReO_3(py)$, since the oxide ReO_3 has a structure similar to that of WO_3, containing the corner-sharing octahedra required by the $MO_3(py)$ structure.

Two synthetic strategies directed toward $ReO_3(py)$ were pursued. In analogy to the preparation of $MoO_3(py)$, pyridine was reacted directly with ReO_3 at elevated temperature. In additional experiments, controlled reduction of solutions of Re_2O_7 in pyridine with triethylphosphine was attempted. Both of these approaches led to a compound of the formula $ReO_3(py)_3$ which was soluble in polar solvents. Further investigation of this compound and its substituted pyridine analogues proved them not to contain Re(VI) at all; they are mixed-valent Re(V)/Re(VII) salts. In the course of this work it was demonstrated that Re_2O_7 is soluble in dry pyridine without reduction of Re(VII), in contrast to a previous report.[2] A molecular adduct, $Re_2O_7{\cdot}3py$, was isolated. Although our initial synthetic goal was not realized, the reduction of Re_2O_7 in pyridine solution by PEt_3 through oxygen atom transfer is of chemical interest, particularly when compared with the inertness of $ReO_4{}^-$ salts under identical conditions. In this report we detail the efficient synthesis of $ReO_2L_4ReO_4$ and describe the crystal structure of $ReO_2(4\text{-Mepy})_4ReO_4$ (4-Mepy = 4-methylpyridine).

Experimental Section

Re_2O_7 was prepared from Re metal by the literature method[3] and transferred directly from the synthesis apparatus to a flowing N_2 drybox. Reagent grade pyridine and 4-methylpyridine were dried by prolonged reflux over BaO, distilled, and stored in the drybox over

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† Corporate Research Science Laboratories.
‡ Analytical Division.

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activated 4A molecular sieves. Periodic Karl Fischer titrations showed water contents in the range 8–36 ppm. ReO_3, 4-phenylpyridine, and triethylphosphine were used as received. Infrared spectra of solid samples were run in KBr pellets on an FT instrument. Solution spectra in pyridine were run in matched KBr cells on a Perkin-Elmer 283 grating instrument. NMR spectra were run on a Varian EM-360L, with chemical shifts referenced to the signal from the residual protons in the deuterated solvent. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Re_2O_7·3py. Dry pyridine was slowly added in portions to Re_2O_7 (0.103 g) until the solid completely dissolved to form a clear, pale yellow solution; 1.07 g of pyridine was required. This solution was then carefully evaporated with a purge of dry N_2 to yield 0.154 g of clear crystalline solid. The ratio of pyridine to Re_2O_7 is 3.03. Evacuation at 100 mtorr for 2 h resulted in additional weight loss to 0.150 g; py/Re_2O_7 = 2.79. When the crystals were handled in air, they immediately turned opaque and crumbled. Infrared spectra of the resulting powder showed it to be pyridinium perrhenate. Re_2O_7 was insoluble in dry dioxane, but addition of 2 equiv of pyridine resulted in complete solution.

$ReO_2(py)_4ReO_4$·2py. Re_2O_7 (2.19 g, 4.53 mmol) was dissolved in dry pyridine (23 g) with warming. The solution was filtered to remove traces of insoluble material and treated with PEt_3 (0.58 g, 4.61 mmol). The solution immediately turned dark red-brown. After the inside of the flask was scratched the solution was allowed to stand for a few days, large well-formed clear red crystals were deposited. The clear red-brown mother liquid was decanted, and the crystals were allowed to dry by evaporation in the drybox to yield 2.29 g (54%) of $ReO_3(py)_3$. Anal. Calcd for $ReO_3(py)_3$: C, 38.21; H, 3.21; N, 8.91; Re, 39.49. Found: C, 38.04; H, 3.22; N, 8.85; Re, 39.20; P, 0.25. The same compound was produced by heating ReO_3 (1.24 g) with pyridine in a sealed tube at 175 °C for 6 days. $ReO_3(py)_3$ (0.091 g) was isolated from the pyridine solution, and ReO_3 (0.976 g) was recovered. Prolonged exposure of $ReO_3(py)_3$ crystals to the atmosphere or evacuation resulted in formation of an orange powder of formula $ReO_3(py)_2$. ^1H NMR ($(CD_3)_2C{=}O$): δ 7.67 m, 2 H; δ 7.90 m, 1 H; δ 9.27 m, 2 H.

$Re_2O_2(py)_4PF_6$. NH_4PF_6 (0.20 g) in H_2O (10 mL) was added to a solution $ReO_2(py)_4ReO_4$ (0.176 g, 0.224 mmol) in acetone (20 mL). The solution was allowed to evaporate for 1 day, and orange needles of $ReO_2(py)_4PF_6$ were deposited (0.132 g, 87%). Anal. Calcd for $ReO_2C_{20}H_{20}N_4PF_6$: C, 35.35; H, 2.97; N, 8.24. Found: C, 34.82; H, 2.94; N, 8.18. Infrared spectrum (KBr): 853 (PF_6^-), 819 (ReO_2^+), 556 cm^{-1} (PF_6^-), and coordinated pyridine bands.

$ReO_2(py)_4BPh_4$. $NaBPh_4$ (0.20 g) in acetone (5 mL) was added to a solution of $ReO_2(py)_4ReO_4$ (0.160 g, 0.204 mmol) in acetone (15 mL) with 2 drops of pyridine. H_2O was added to the resulting solution. The orange precipitate was collected by filtration and suction dried to yield $ReO_2(py)_4BPh_4$ (0.175 g, 100%). This sample was recrystallized from acetone/ether. Anal. Calcd for $ReO_2C_{44}H_{40}N_4B$: C, 61.90; H, 4.72. Found: C, 60.57; H, 4.62. Infrared spectrum: 817 cm^{-1} (ReO_2^+). ^1H NMR ($(CD_3)_2C{=}O$); δ 7.45 m, 2 H; δ 7.68 m, 2 H; δ 7.87 m, 1 H; δ 9.28 m, 2 H.

$ReO_2(4\text{-}Mepy)_4ReO_4$. Re_2O_7 (0.983 g, 2.029 mmol) was dissolved in 4-methylpyridine (6.21 g). Solutions of Re_2O_7 in 4-Mepy darken rapidly at room temperature, so PEt_3 (0.26 g, 2.07 mmol) was added immediately to give a dark brown solution which deposited an orange solid that was separated by decantation and dried under an N_2 flow to yield $ReO_2(4\text{-}Mepy)_4ReO_4$ (1.37 g, 80%). Anal. Calcd for $ReO_3C_{12}H_{14}N_2$: C, 34.28; H, 3.36%; N, 6.66. Found: C, 34.44; H, 3.37; N, 6.31. Infrared spectrum (KBr): 908 (ReO_4^-), 817 cm^{-1} (ReO_2^+). The compound was recrystallized from 4-Mepy to yield X-ray-quality single crystals. The compound is soluble in pyridine and CH_3CN and insoluble in acetone and dioxane.

$ReO_2(4\text{-}Mepy)_4BPh_4$. $NaBPh_4$ (0.3 g) in CH_3CN (5 mL) was added to $ReO_2(4\text{-}Mepy)_4ReO_4$ (0.150 g, 0.179 mmol) in CH_3CN (20 mL). $ReO_2(4\text{-}Mepy)_4BPh_4$ was precipitated by the addition of H_2O (75 mL). The solid was separated by filtration and suction dried to give 0.141 g (87%) of yellow solid. An analytical sample was recrystallized from acetone/ether. Anal. Calcd for $ReO_2C_{48}H_{48}N_4B$: C, 63.36; H, 5.32; N, 6.16. Found: C, 62.22; H, 5.18; N, 6.08. Infrared spectrum: 818 cm^{-1} (ReO_2^+).

Table I. Fractional Atomic Coordinates and Isotropic Thermal Parameters for $ReO_2(4\text{-}Mepy)_4ReO_4$

Atom	x	y	z	B(A2)
RE(1)	0.500	0.000	0.500	3.44(4)
RE(2)	0.000	0.000	0.000	3.07(4)
RE(3)	0.7127(1)	0.3967(1)	0.2605(1)	5.64(4)
O(1)	0.467(1)	0.138(1)	0.457(1)	3.3(4)*
O(2)	-0.148(2)	-0.017(2)	0.048(1)	3.7(4)*
O(3)	0.582(2)	0.457(2)	0.304(2)	8.7(7)*
O(4)	0.748(2)	0.468(2)	0.173(2)	8.5(6)*
O(5)	0.840(3)	0.426(3)	0.362(2)	12.3(9)*
O(6)	0.675(3)	0.239(3)	0.203(2)	11.2(8)*
N(1)	0.707(2)	0.078(2)	0.544(1)	2.7(5)*
N(2)	0.473(2)	0.093(2)	0.655(2)	3.9(5)*
N(3)	-0.104(2)	-0.129(2)	-0.149(1)	3.3(5)*
N(4)	0.059(2)	-0.168(2)	0.051(2)	4.0(5)*
C(1)	0.797(2)	0.020(2)	0.595(2)	3.3(6)*
C(2)	0.936(2)	0.060(2)	0.622(2)	3.7(6)*
C(3)	0.983(3)	0.169(3)	0.596(2)	4.5(7)*
C(4)	0.895(3)	0.231(2)	0.543(2)	3.9(7)*
C(5)	0.764(3)	0.189(3)	0.520(2)	5.1(7)*
C(6)	0.445(2)	0.026(2)	0.721(2)	3.0(6)*
C(7)	0.417(3)	0.077(3)	0.820(2)	6.1(8)*
C(8)	0.432(3)	0.212(2)	0.853(2)	4.1(7)*
C(9)	0.467(2)	0.279(2)	0.786(2)	3.8(7)*
C(10)	0.486(2)	0.224(2)	0.684(2)	3.1(6)*
C(11)	-0.237(2)	-0.151(2)	-0.169(2)	3.6(6)*
C(12)	-0.302(2)	-0.244(2)	-0.259(2)	2.8(6)*
C(13)	-0.242(2)	-0.311(2)	-0.331(2)	3.5(6)*
C(14)	-0.105(2)	-0.280(2)	-0.315(2)	3.3(6)*
C(15)	-0.033(2)	-0.190(2)	-0.223(2)	3.1(6)*
C(16)	-0.018(3)	-0.225(3)	0.109(2)	4.2(7)*
C(17)	0.014(3)	-0.339(3)	0.131(2)	5.2(8)*
C(18)	0.133(3)	-0.386(3)	0.112(2)	4.7(7)*
C(19)	0.207(3)	-0.320(3)	0.056(2)	5.3(8)*
C(20)	0.162(3)	-0.217(3)	0.027(2)	5.2(8)*
C(21)	1.134(3)	0.219(3)	0.626(2)	6.3(8)*
C(22)	0.415(3)	0.277(3)	0.961(3)	9(1)*
C(23)	-0.315(3)	-0.409(3)	-0.433(2)	5.0(7)*
C(24)	0.169(3)	-0.500(3)	0.146(3)	7.5(9)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Crystal Structure of $ReO_2(4\text{-}Mepy)_4ReO_4$. A crystal of approximate dimensions 0.4 mm × 0.4 mm × 0.2 mm was sealed in a glass capillary in a nitrogen atmosphere and mounted on an Enraf-Nonius CAD4 diffractometer. Using Mo Kα radiation (λ = 0.7103 Å), a least-squares refinement of the setting angles of 25 intensities gave a triclinic unit cell of dimensions a = 10.180 (2) Å, b = 10.695 (3) Å, c = 13.261 (3) Å, α = 103.17 (2)°, β = 99.64 (2)°, γ = 96.47 (2)°, V = 1369 Å^3, and Z = 4. On the basis of these data and a formula weight of 840.9, a calculated density of 4.08 g cm^{-3} is obtained. A total of 2112 independent reflections were collected for $0 < \theta < 25°$, with 948 considered observed ($I > 3\sigma(I)$). Three reflections were measured periodically throughout the data collection, and no significant changes in intensity were noted. ψ scans were collected to measure absorption; μ = 180.0 cm^{-1} was used to calculate the necessary corrections with transmission factors varying from 0.89 to 1.00. The structure was solved through Patterson and Fourier techniques. Solution and refinement were performed on a PDP-1160 computer with standard programs.[4] Throughout the final cycles of least-squares refinement, anisotropic thermal parameters were applied to the Re atoms while

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(4) The programs used for data collection and reduction were supplied by Enraf-Nonius. All programs used for structure solution and refinement were part of the Enraf-Nonius Structure Determination Package (SDP). Standard atomic scattering factors and anomalous dispersion factors $\Delta f'$ and $\Delta f''$ were taken from: Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

Table II. Bond Distances and Angles in the Re Coordination Spheres of $ReO_2(4\text{-Mepy})_4ReO_4$

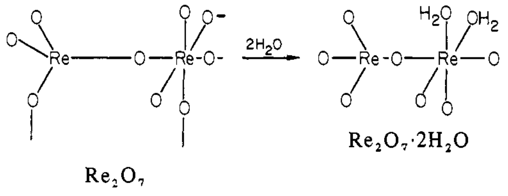
Bond Distances (Å)					
Re(1)-O(1)	1.75 (2)	Re(2)-O(2)	1.74 (2)	Re(3)-O(3)	1.67 (3)
Re(1)-N(1)	2.11 (2)	Re(2)-N(3)	2.15 (2)	Re(3)-O(4)	1.59 (3)
Re(1)-N(2)	2.14 (2)	Re(2)-N(4)	2.16 (2)	Re(3)-O(5)	1.65 (3)
				Re(3)-O(6)	1.65 (3)

Bond Angles (deg)			
O(1)-Re(1)-N(1)	89.9 (8)	O(3)-Re(3)-O(4)	107 (1)
O(1)-Re(1)-N(2)	90.1 (8)	O(3)-Re(3)-O(5)	108 (1)
N(1)-Re(1)-N(2)	89.7 (8)	O(3)-Re(3)-O(6)	112 (1)
O(2)-Re(2)-N(3)	88.9 (8)	O(4)-Re(3)-O(5)	111 (1)
O(2)-Re(2)-N(4)	90.6 (8)	O(4)-Re(3)-O(6)	107 (1)
N(3)-Re(2)-N(4)	88.7 (8)	O(5)-Re(3)-O(6)	111 (2)

isotropic thermal parameters were used for the remaining atoms. H atoms were included in idealized positions. Refinement of the resulting 158 parameters converged at $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.036$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.040$. Final fractional atomic coordinates for non-hydrogen atoms are presented in Table I, and bond lengths and angles, in Tables II and III. Anisotropic thermal parameters, calculated coordinates for H atoms, observed and calculated structure factors, and a diagram of the ReO_4^- anion are included in the supplementary material.

Results

Re_2O_7–Pyridine Adduct. An early report states that Re_2O_7 is soluble in anhydrous dioxane.[3] We find Re_2O_7 insoluble in thoroughly dry dioxane, as others have subsequently noticed.[2] However, in disagreement with these authors, our results show that Re_2O_7 is soluble in dry pyridine to the extent of ~9 wt %. Furthermore, addition of 2 equiv of pyridine to a dioxane suspension of Re_2O_7 results in complete dissolution. The intracrystalline Re–O bonds must be disrupted by the pyridine ligands, much the same as when Re_2O_7 is converted to the molecular hydrate $Re_2O_7{\cdot}2H_2O$.[5]



Re_2O_7

$Re_2O_7{\cdot}2H_2O$

When a solution of Re_2O_7 in dry pyridine is evaporated, clear crystals of $Re_2O_7{\cdot}3py$ are formed. These crystals are extremely sensitive to hydrolysis, giving $pyHReO_4$. Further investigation of the $Re_2O_7{\cdot}3py$ adduct is in progress. Possible formulations include a pyridine solvate of $Re_2O_7{\cdot}2py$ or $ReO_3(py)_3^+ReO_4^-$.

Reduction of Re_2O_7 by PEt_3. A solution of Re_2O_7 in pyridine reacts rapidly with PEt_3 to form $ReO_2(py)_4ReO_4$ according to

$$Re_2O_7 + PEt_3 + 4py \rightarrow ReO_2(py)_4ReO_4 + Et_3P{=}O$$

Table III. Bond Distances and Angles in the 4-Methylpyridine Rings of $ReO_2(4\text{-Mepy})_4ReO_4$

Bond Distances (Å)			
C(1)-N(1)	1.33 (3)	C(6)-N(2)	1.30 (3)
C(5)-N(1)	1.39 (3)	C(10)-N(2)	1.35 (3)
C(1)-C(2)	1.40 (3)	C(6)-C(7)	1.38 (4)
C(2)-C(3)	1.35 (4)	C(7)-C(8)	1.39 (4)
C(3)-C(4)	1.37 (4)	C(8)-C(9)	1.34 (4)
C(4)-C(5)	1.33 (3)	C(9)-C(10)	1.41 (3)
C(3)-C(21)	1.52 (4)	C(8)-C(22)	1.49 (4)
C(11)-N(3)	1.32 (3)	C(16)-N(4)	1.38 (3)
C(15)-N(3)	1.40 (3)	C(20)-N(4)	1.28 (3)
C(11)-C(12)	1.39 (3)	C(16)-C(17)	1.38 (4)
C(12)-C(13)	1.33 (3)	C(17)-C(18)	1.40 (4)
C(13)-C(14)	1.37 (3)	C(18)-C(19)	1.39 (4)
C(14)-C(15)	1.40 (3)	C(19)-C(20)	1.35 (4)
C(13)-C(23)	1.53 (4)	C(18)-C(24)	1.46 (4)

Bond Angles (deg)			
C(5)-N(1)-C(1)	114 (2)	C(10)-N(2)-C(6)	119 (3)
N(1)-C(1)-C(2)	126 (3)	N(2)-C(6)-C(7)	125 (3)
C(1)-C(2)-C(3)	116 (3)	C(6)-C(7)-C(8)	117 (3)
C(2)-C(3)-C(4)	120 (3)	C(7)-C(8)-C(9)	117 (3)
C(3)-C(4)-C(5)	121 (3)	C(8)-C(9)-C(10)	125 (3)
C(4)-C(5)-N(1)	122 (3)	C(9)-C(10)-N(2)	116 (3)
C(2)-C(3)-C(21)	118 (3)	C(7)-C(8)-C(22)	121 (3)
C(4)-C(3)-C(21)	122 (3)	C(9)-C(8)-C(22)	122 (3)
C(15)-N(3)-C(11)	120 (2)	C(20)-N(4)-C(16)	118 (3)
N(3)-C(11)-C(12)	118 (2)	N(4)-C(16)-C(17)	118 (3)
C(11)-C(12)-C(13)	126 (3)	C(16)-C(17)-C(18)	122 (3)
C(12)-C(13)-C(14)	116 (3)	C(17)-C(18)-C(19)	115 (3)
C(13)-C(14)-C(15)	120 (3)	C(18)-C(19)-C(20)	119 (3)
C(14)-C(15)-N(3)	119 (2)	C(19)-C(20)-N(4)	126 (3)
C(12)-C(13)-C(23)	125 (3)	C(17)-C(18)-C(24)	121 (3)
C(14)-C(13)-C(23)	118 (3)	C(19)-C(18)-C(24)	124 (3)

The resulting red-orange $Re^{5+}Re^{7+}$ salt crystallizes from pyridine solution with two pyridine molecules of solvation, giving the crystals the formula $ReO_3(py)_3$. The infrared spectrum of the solid compound exhibits the expected pattern for coordinated pyridine in the 1650–1450-cm^{-1} region,[6] while in the Re–O stretching region strong absorption[7] is present at 907 cm^{-1} for ReO_4^- and at 819 cm^{-1} for the ReO_2^+ group of the cation.[8] The same compound could be produced in low yield by direct reaction of solid ReO_3 with pyridine at 175 °C.

The 4-methylpyridine analogue was also produced by PEt_3 reduction of Re_2O_7. It crystallized without occluded solvent to give $ReO_2(4\text{-Mepy})_4ReO_4$. $ReO_2(py)_4PF_6$, $ReO_2(py)_4BPh_4$, and $ReO_2(4\text{-Mepy})_4BPh_4$ were produced by metathesis reactions with NH_4PF_6 or $NaBPh_4$.

Pyridine solutions of NH_4ReO_4 do not react with PEt_3 at room temperature. This demonstrates that the nature of the solution of Re_2O_7 in pyridine is not merely $pyH^+ReO_4^-$ formed from adventitious moisture. The infrared spectrum of Re_2O_7 in pyridine solution does exhibit an ReO_4^- band at 911 cm^{-1} but also exhibits a band at 824 cm^{-1}, indicating another ReO species as well. No 1540-cm^{-1} band characteristic of pyridinium ion is observed.

Structure of $ReO_2(4\text{-Mepy})_4ReO_4$. Although well-formed, apparently high-quality crystals of the pyridine adduct $ReO_3(py)_3$ diffracted X-rays well, the structure could not be solved. The 4-methylpyridine analogue was then examined. The crystals contain two independent octahedral ReO_2L_4 cations located on inversion centers and tetrahedral ReO_4^- anions in general positions. The cations are nearly equivalent and have approximate 4/*mmm* symmetry with Re–O distances of 1.75 (2) and 1.74 (2) Å. The geometry and atom-labeling scheme are depicted in Figure 1. The bond lengths in the linear ReO_2 group do not differ significantly from those found in dioxobis(ethylenediamine)rhenium(V) chloride (1.769 (7), 1.761 (7) Å) and dioxotetrakis(pyridine)rhenium(V) chloride dihydrate (1.78 (1), 1.75 (1) Å.[9] The range of Re–N bond lengths found in $ReO_2(4\text{-Mepy})_4ReO_4$ (2.11–2.16 Å) are in good agreement with the values of 2.15–2.19 Å found in the two previously mentioned compounds. The bond distances also agree with those in dioxobis(ethylenediamine)rhenium(V) perrhenate, considering the lower precision of that structure,

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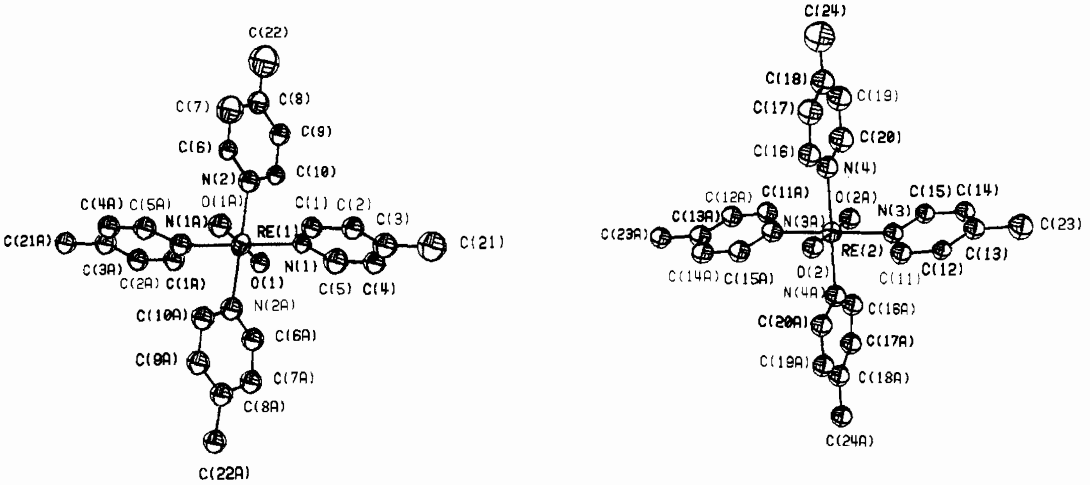

Figure 1. Atomic arrangements and labeling schemes around the octahedrally coordinated Re(1) and Re(2) atoms.

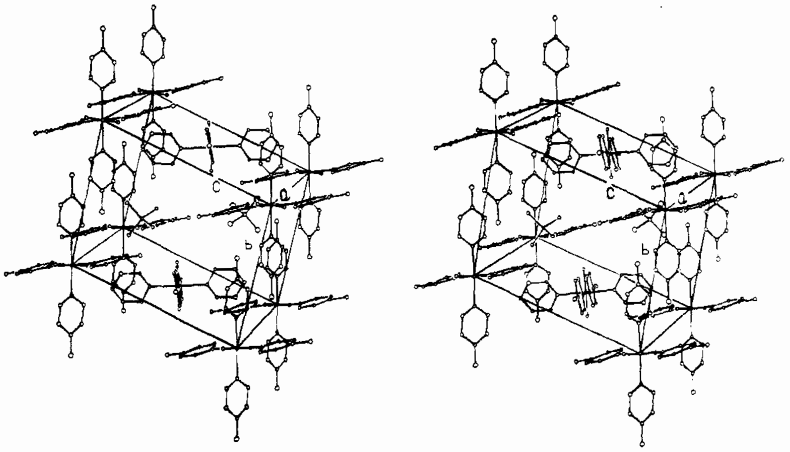

Figure 2. Stereoscopic view showing the packing arrangement of the octahedral cations and tetrahedral anions in the unit cell.

which was determined by using film techniques.[10] The distortion from 4/*mmm* symmetry results mainly from the rotation of the 4-methylpyridine rings about the Re–N bond. The planes of each ring are tilted from the mean ReN_4 plane by angles ranging from 5 to 23°. As shown in Figure 2, the ligand rings form an interwoven three-dimensional network separated by van der Waals distances. The ReO_4^- anions fit into cavities within this network. The four tetrahedral Re–O bond distances range from 1.59 (3) to 1.67 (2) Å and may be compared with Re–O bond lengths of 1.723 (4) Å found in $KReO_4$.[11]

Discussion

The most significant feature of this study is the reduction of Re^{7+} by atom transfer to triethylphosphine to form triethylphosphine oxide. Only half the rhenium is reduced, the balance remaining as Re^{7+} in the ReO_4^- anion. The ReO_4^- anion is inert to reduction by PEt_3 as demonstrated by reactions of Re_2O_7 with excess PEt_3 and also by the absence of reaction of a pyridine solution of NH_4ReO_4 with PEt_3. This inertness of the ReO_4^- anion makes it reasonable to assume that in pyridine solutions of Re_2O_7, half the Re is present as ReO_4^- with the other half in a cationic form, possibly $ReO_3(py)_3^+$. The infrared data seem consistent with this interpretation. This inertness of ReO_4^- in pyridine to reduction by phosphine contrasts to its behavior in hydrochloric acid solution, where perrhenic acid is completely reduced by triphenylphosphine to the Re^{5+} compound $ReOCl_3(PPh_3)_2$.[8,12]

Supplementary Material Available: Tables IV–VI, including anisotropic thermal parameters, calculated coordinates for H atoms, and observed and calculated structure factors, and Figure 3, displaying the tetrahedral ReO_4^- anion (17 pages). Ordering information is given on any current masthead page.

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