Contribution from the Department of Biochemistry, College of Agricultural and Life Sciences, University of Wisconsin—Madison, Madison, Wisconsin 53706, and Department of Chemistry, University of Maryland, College Park, Maryland 20742

Crystal Structure and Molecular Conformation of P^1,P^2-Bidentate Tetraammine(methylenediphosphato)cobalt(III) Hydrochloride (CoPCP): $CoH_2P_2O_6CH_2(NH_3)_4^+Cl^-$

TULI P. HAROMY,[†] WILSON B. KNIGHT,[‡] DEBRA DUNAWAY-MARIANO,*[‡] and M. SUNDARALINGAM*[†]

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The title compound (CoPCP) is a cobalt(III) complex of a pyrophosphate analogue that has a methylene group in the bridge oxygen position. The methylene ATP analogue adenylyl methylenediphosphonate (AMP-PCP), with the methylene group between the β- and γ-phosphate groups, is an inhibitor of various enzyme reactions. The X-ray structure of CoPCP has provided geometrical data that help to understand enzyme inhibition by β,γ-bidentate metal AMP-PCP. The complex was studied under acidic conditions to investigate the effect of enzyme-mediated acid catalysis. The complex crystallizes in the monoclinic space group $P2_1/c$ ($Z = 4$ with cell dimensions $a = 9.259$ (2) Å, $b = 8.586$ (1) Å, $c = 14.448$ (2) Å, and $\beta = 126.23$ (1)°. The structure was solved by the heavy-atom technique and refined to an R index of 0.045 for 2044 reflections. The six-membered chelate ring, which resists HCl cleavage, is found in the half-chair conformation. The P–C bonds (1.789 (5) and 1.799 (5) Å) are considerably longer than the bridge P–O bonds (1.601 and 1.627 Å) of the corresponding Co(III) pyrophosphate complex (CoPP). The P–C–P angle (116.4 (3)°) is much smaller than the P–O–P angle (127°) in CoPP. The geometrical differences may contribute to the lower binding affinity of metal AMP-PCP to polyphosphate processing enzymes.

Introduction

Analogues of adenosine triphosphate (ATP) that are structurally similar to ATP although resistant to enzymatic hydrolysis can be of significant utility to the in vivo and in vitro study of enzyme mechanism and regulation. The ATP analogue AMP-PCP, which has a methylene group substituted for the distal bridge oxygen atom, is resistant to bond cleavage between the β- and γ-phosphate groups but may replace ATP as a substrate for enzymes that catalyze cleavage between the α- and β-phosphate groups.[1,2] AMP-PCP may act as an inhibitor by competing for the ATP binding site on the enzyme. With some ATP-dependent enzymes, AMP-PCP does not serve as a substrate, effector, or inhibitor. Thus some enzymes recognize structural differences that exist between AMP-PCP and ATP, while others do not.

The ionization constant of the last phosphonate hydrogen of AMP-PCP is smaller than that of the phosphate hydrogen of ATP ($pK_a = 8.5$ vs. $pK_a = 7$).[3] Thus, the net charge of the two nucleotides over the pH 6.5–9.0 range will differ, thereby contributing to binding or reactivity differences. However, in the presence of metal ions, which are typically required as cofactors by ATP-dependent enzymes, both nucleotides would be complexed and fully ionized and, therefore, isoelectronic.

Previous studies have shown that while solutions of metal(2+)/ATP consist principally of three equilibrating structural isomers (γ-monodentate, β,γ-bidentate, and α,β,γ-tridentate), a given enzyme will recognize only one structural form as substrate or effector.[6,7] The nature of the P–X–P linkage will control the geometrical features of the structural isomers and may also affect the population of these isomers in solution.[7-9] The nature of the P–X–P linkage may also contribute to the preferred conformation of the chelate ring both in solution and at the enzyme-active site.

The present X-ray study was carried out in order to determine the differences in the structures of the chelate rings formed from ATP and AMP-PCP. Co(III), a metal ion that forms exchange-inert coordination complexes, was complexed to methylene diphosphonate (PCP), the basic P–X–P unit of AMP-PCP. The X-ray structure of CoPCP is compared to the structures of the related complexes: P^1,P^2-bidentate tetraammine(pyrophosphato)cobalt(III) (CoPP)[10] and P^1,P^2-bidentate tetraammine(imidodiphosphato)cobalt(III)-(CoPNP).[11]

Table I. Crystallographic Parameters for CoPCP

formula	$Co(NH_3)_4H_2P_2O_6CH_2^+Cl^-$
space group	$P2_1/c$
cell constants	$a = 9.259$ (2) Å
	$b = 8.586$ (1) Å
	$c = 14.448$ (2) Å
	$\beta = 126.23°$
wavelength (Cu Kα)	1.5418 Å
cryst dimens	0.3 mm × 0.1 mm × 0.05 mm
abs coeff	17.0 mm^{-1}
extinction param	$2.6\ (4) \times 10^{-6}$
2θ limit	155°
octants collcd	$+h,+k,\pm l$
unique reflcns	2419
intensities > $2\sigma(I)$ (used for struct anal.)	2044
final R index	0.045
final weighted R index	0.064

Experimental Section

$[Co(NH_3)_4CO_3]NO_3$[12] was dissolved in a 10% excess of 1 M HCl and the solution then diluted to a final concentration of 10 mM. This solution was combined with an equal volume of 10 mM methylenediphosphonate, and the resulting solution was then adjusted to pH 3, heated at 80 °C for 10 min, and cooled to 4 °C. The reaction solution was absorbed onto a Dowex 50-X2 (H^+) column, which was then washed with deionized water at 4 °C until a rose-colored band

[†] University of Wisconsin.
[‡] University of Maryland.

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Table II. Fractional Positional Parameters for All Atoms of Tetraammine(methylenediphosphato)cobalt(III) Hydrochloride[a]

atom	x	y	z	B_{eq} or B, Å²
Co	2505 (1)	6840 (1)	4445 (0)	1.25 (2)
P(1)	714 (1)	4623 (1)	2981 (1)	1.46 (2)
P(2)	4004 (1)	4754 (1)	2974 (1)	1.48 (2)
O1(P1)	909 (3)	5796 (3)	3757 (2)	1.96 (5)
O2(P1)	284 (4)	5454 (3)	2043 (2)	2.61 (7)
O3(P1)	-451 (3)	3428 (3)	3142 (2)	2.08 (5)
C	2373 (5)	3620 (4)	2818 (3)	1.90 (9)
O1(P2)	4012 (3)	5675 (3)	3873 (2)	1.85 (5)
O2(P2)	3901 (4)	5882 (4)	2125 (2)	3.35 (8)
O3(P2)	5298 (4)	3710 (4)	2954 (2)	2.66 (7)
N(1)	4032 (4)	7906 (4)	5153 (2)	1.94 (7)
N(2)	1039 (4)	8001 (4)	5037 (2)	1.98 (7)
N(3)	2479 (4)	5217 (4)	5394 (2)	2.22 (7)
N(4)	2559 (4)	8505 (4)	3523 (2)	1.89 (7)
Cl	2541 (1)	11459 (1)	5091 (1)	2.58 (3)
H(O2P1)	35 (6)	637 (6)	204 (4)	4.1 (14)
H1(C)	233 (6)	307 (7)	221 (4)	3.9 (14)
H2(C)	252 (5)	286 (6)	330 (4)	2.8 (12)
H(O2P2)	432 (8)	656 (7)	217 (5)	7.4 (21)
H1(N1)	369 (6)	886 (7)	529 (4)	3.8 (13)
H2(N1)	482 (5)	796 (5)	485 (3)	1.7 (9)
H3(N1)	433 (6)	752 (7)	565 (4)	3.3 (12)
H1(N2)	16 (5)	795 (6)	463 (4)	2.9 (12)
H2(N2)	79 (7)	778 (7)	554 (4)	4.7 (15)
H3(N2)	137 (5)	889 (5)	512 (3)	1.2 (8)
H1(N3)	172 (7)	523 (8)	575 (5)	6.7 (19)
H2(N3)	327 (7)	499 (9)	573 (5)	8.0 (22)
H3(N3)	229 (7)	425 (9)	522 (5)	6.1 (18)
H1(N4)	347 (5)	858 (5)	323 (3)	1.7 (10)
H2(N4)	252 (5)	946 (6)	380 (3)	1.9 (10)
H3(N4)	195 (5)	837 (5)	312 (3)	2.1 (11)

[a] Values are multiplied by 10^4 for non-hydrogen atoms and 10^3 for hydrogen atoms.

appeared below the monovalent-cation band. The resin of the rose band was removed to a second column and carefully eluted with 0.3 M aniline. The eluate was immediately extracted with ether, at which point crystallization occurred (yield 30%; ^{31}P NMR (10% D_2O at isoionic pH) singlet, 26.7 ppm downfield from external 0.1 M D_3PO_4). These crystals, which were too small and thin for X-ray data collection, were dissolved in an excess of 0.2 M HCl. Upon evaporation to dryness over a period of several days, dark red crystals of CoPCP·HCl, suitable for X-ray analysis, were obtained.

X-ray intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using Ni-filtered Cu Kα radiation. Crystallographic parameters are presented in Table I. The data were corrected for decay, absorption (empirical φ-curve correction), Lorentz, and polarization effects.

The cobalt position was found from a three-dimensional Patterson map. From the phases computed with the cobalt atom, the phosphorus atoms could be clearly identified in a subsequent Fourier map. Several additional cycles of structure factor and Fourier calculations revealed all of the remaining non-hydrogen atoms. These atoms were refined by the full-maxtrix least-squares technique using anisotropic temperature factors. A weighting scheme based on counting statistics was used with the weights proportional to $1/[\sigma^2(F) + (0.02F_o)^2]$. Subsequent difference Fourier syntheses revealed all the hydrogen atoms.

The non-hydrogen atoms were further refined with the contribution of the hydrogen atoms included in the structure factors. The positions of the hydrogen atoms were subsequently refined by using isotropic temperature factors, yielding a final R index of 0.045. At the conclusion of refinement, the maximum shift/error ratio was 0.13 for non-hydrogen atoms and 0.53 for hydrogen atoms.

Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber[13] while those for hydrogen atoms are from Stewart, Davidson, and Simpson.[14] The anomalous scattering components for non-hydrogen atoms were taken from ref.[15] Calculations were performed on a PDP 11/35 computer using locally developed programs.[16]

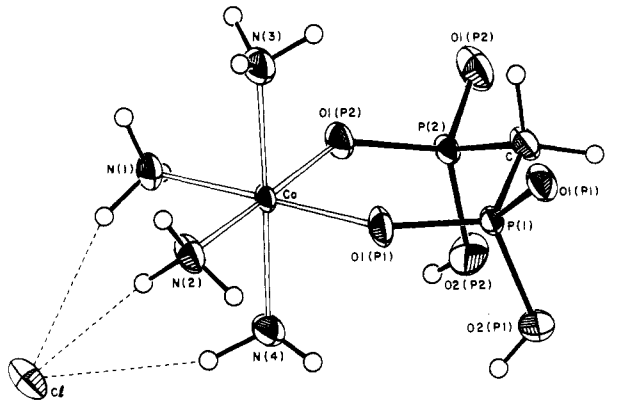

Figure 1. ORTEP drawing of the title compound showing atom numbering. Non-hydrogen atoms are represented by 50% probability ellipsoids and hydrogen atoms are represented by spheres of arbitrary size.

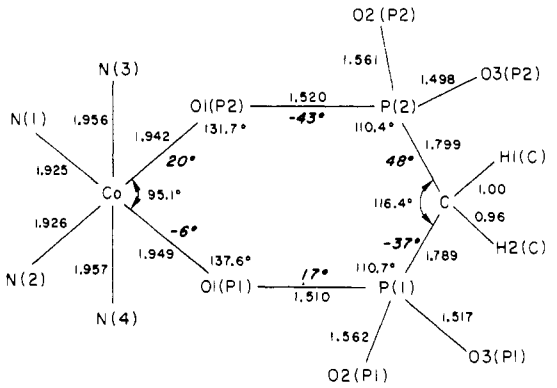

Figure 2. CoPCP bond lengths, ring bond angles, and torsion angles (in italics). The estimated standard deviations are 0.004 Å for lengths and 0.3° for bond angles and torsion angles.

Table III. Comparison of Conformational and Geometrical Parameters for the Title Compound and Related Structures

	bridge bond lengths, Å		bridge bond angle P1–X–P2, deg	ring pucker		
	P1–X	P2–X		Q, Å	θ, deg	φ, deg
CoPCP·HCl	1.789	1.799	116.4	0.42	46	208
CoPNP, neutral	1.670	1.657	124.2	0.41	175	17
CoPNP·2HCl	1.638	1.647	122.7	0.61	84	227
CoPP	1.601	1.627	127.1	0.62	87	108
uncomplexed PCP	1.79	1.79	117			
uncomplexed PNP	1.678	1.678	127.2			
uncomplexed PP	1.612	1.612	130.2			

Results

Fractional atomic coordinates for the title compound are given in Table II. An ORTEP[17] drawing is presented in Figure 1. Non-hydrogen bond lengths, as well as bond angles and torsion angles for the six-membered chelate ring, are given in Figure 2. The important conformational and geometrical differences between the title compound and related structures are presented in Table III.

Chelate Ring Pucker. The six-membered chelate ring, formed by the bidentate coordination between the pyro-

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Table IV. List of Hydrogen Bonds for $Co(NH_3)_4H_2P_2O_6CH_2^+Cl^-$

hydrogen bond A-H···B	symm code[a]	translation x	y	z	dist, Å A-H	H···B	A···B	angle A-H···B, deg
N(1)-H1(N1)···O2(P2)	2	0	1	0	0.90	2.66	3.043	107
N(1)-H1(N1)···Cl	1	0	0	0	0.90	2.48	3.347	160
N(1)-H2(N1)···Cl	3	1	2	1	0.88	2.49	3.260	147
N(1)-H3(N1)···O2(P2)	2	0	1	0	0.82	2.58	3.043	116
N(1)-H3(N1)···O3(P2)	3	1	1	1	0.82	2.28	3.096	169
N(2)-H1(N2)···Cl	3	0	2	1	0.98	2.61	3.341	132
N(2)-H2(N2)···O3(P1)	3	0	1	1	0.80	2.21	2.983	164
N(2)-H3(N2)···Cl	1	0	0	0	0.83	2.46	3.278	170
N(3)-H1(N3)···O3(P1)	3	0	1	1	0.90	2.35	3.136	147
N(3)-H2(N3)···O3(P2)	3	1	1	1	0.88	2.51	3.192	135
N(3)-H3(N3)···Cl	1	0	−1	0	0.88	2.42	3.257	160
N(4)-H1(N4)···O3(P2)	4	1	0	0	0.97	2.12	3.006	152
N(4)-H2(N4)···Cl	1	0	0	0	0.91	2.53	3.401	159
N(4)-H3(N4)···O3(P1)	4	0	0	0	0.79	2.22	3.005	168
O2(P1)-H(O2P1)···O3(P1)	4	0	0	0	0.79	1.79	2.573	172
O2(P2)-H(O2P2)···O3(P2)	4	1	0	0	0.70	1.89	2.543	155

[a] Symmetry codes: (1) x, y, z; (2) $x, {}^1/_2 - y, {}^1/_2 + z$; (3) $-x, -y, -z$; (4) $-x, {}^1/_2 + y, {}^1/_2 - z$.

phosphate moiety and the cobalt atom, assumes the half-chair conformation. The chelate ring pucker can be described by three parameters: Q, θ, and ϕ,[18] where Q measures the amplitude of ring puckering, θ measures the degree of chair ($\theta = 0$ or 180° equivalent to the poles of a sphere of radius Q) vs. boat character ($\theta = 90°$ on the equator), and ϕ is the angle of pseudorotation between the various boat and twist-boat (TB) conformations (0° = boat, 30° = TB, 60° = boat, 90° = TB, ...). These parameters for the Co–O1(P1)–P(1)–C–P(2)–O1(P2) ring are $Q = 0.42$ (1) Å, $\theta = 46(1)°$, and $\phi = 208$ (1)°. The ring pucker is flatter than that observed for CoPP ($Q = 0.62$ Å). The θ value for CoPCP lies nearly midway between the ideal chair conformation and the boat/twist-boat pseudorotation path. The pseudorotation parameter ϕ for CoPCP is close to the meridian at $\phi = 210°$ defining the perfect half-chair. CoPP, which has $\theta = 87°$, has a ϕ value of 108° thus exhibiting a conformation that is intermediate between the boat and twist-boat conformations.

Bond Lengths and Angles. The P–C bond lengths of 1.789 (5) and 1.799 (5) Å are approximately 0.18 Å longer than the average P to bridge oxygen bond length of 1.61 Å observed for the cobalt pyrophosphate structure.[10] The P–C–P bond angle of 116.4 (3)° is not as far removed from the ideal tetrahedral angle (109.47°) as the P–O–P angle of the CoPP complex (127.1°). The Co–O–P angles of 137.6 (2) and 131.7 (2)° are significantly wider than the corresponding angles of 126.1 and 127.0° for the CoPP complex. The ammonia ligand coordination distances are nearly identical with those observed for COPP. The P–C distance is 0.13 Å longer than the average P–N distance of 1.66 Å in neutral CoPNP and 0.15 Å longer than the corresponding distance of 1.64 Å in CoPNP·2HCl.[11] The P–C–P angle is smaller than the P–N–P angles of 124.2 and 122.7° observed for the neutral and hydrochloride forms of CoPNP, respectively.

Hydrogen Bonding. The structure is stabilized by a large number of hydrogen bonds, six of which involve the chloride counterion (Table IV). The two strongest hydrogen bonds (2.543 (5) and 2.573 (4) Å) are between oxygen atoms of symmetry-related methylenediphosphonate groups. The remaining hydrogen bonds are mediated by the ammonia ligands. Those between ammonia groups and phosphate oxygen atoms have N to O distances ranging from 2.983 (4) to 3.192 (5) Å while the weaker N to Cl hydrogen bonds have distances ranging from 3.260 (4) to 3.401 (3) Å. Both H1(N1) and H3(N1) are engaged in bifurcated hydrogen bonding with each having one strong primary hydrogen-bonding interaction and a weaker secondary interaction. H1(N1) interacts strongly with the chloride ion while having a weaker interaction with O2(P2) of a symmetry-related molecule. H3(N1) forms a strong hydrogen bond with O3(P2) of one symmetry-related molecule and a weaker interaction with O2(P2) of a different molecule. As expected, the methylene protons are not involved in the hydrogen-bonding scheme.

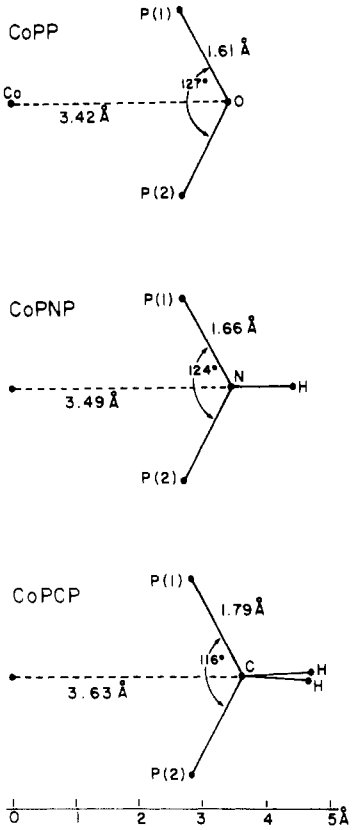

Figure 3. Graphic comparison of the geometry about the P–X–P linkage for CoPP, CoPNP, CoPNP·2HCl, and CoPCP·HCl. The Co to bridge-atom distance is given below each compound label while the average P–X distances and P–X–P angles are given next to the appropriate bonds. The diagrams for the neutral and hydrochloride forms of CoPNP are nearly identical; therefore, only the former is shown.

Discussion

There is no known enzyme capable of cleaving the P–C–P linkage and therefore capable of utilizing AMP-PCP as a substrate in reactions that require cleavage between the β- and

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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, α = 103.17 (2)°, β = 99.64 (2)°, γ = 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

† Corporate Research Science Laboratories.
‡ Analytical Division.

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