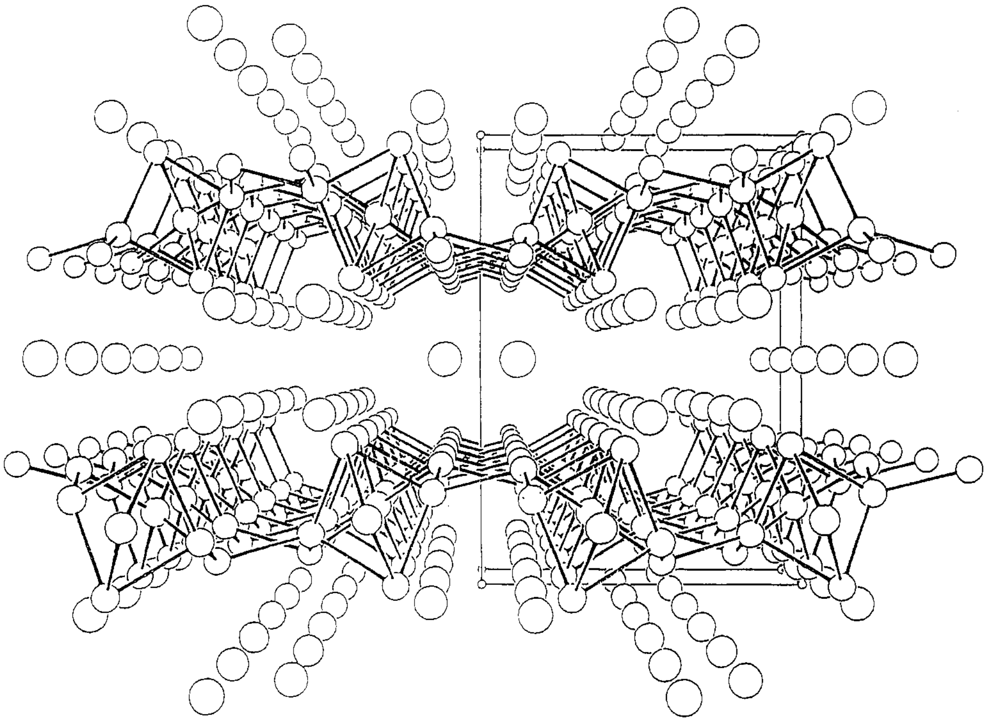

Figure 2. Structural diagram showing the layered nature of the gallium arsenide sheets insulated by potassium sheets.

unit in the unit cell is illustrated in Figure 1. Selected bond distances and angles are listed in Table III.

The structure of $K_3Ga_3As_4$ is composed of layers of K^+ ions and covalently bonded sheets of $[Ga_3As_4{}^{3-}]_\infty$ alternating in the *b* direction (Figure 2). Within the anionic sheets, each Ga atom is bonded to four As atoms at the corners of a distorted tetrahedron. Three $GaAs_4$ tetrahedra, one centered at Ga(1) and two centered at Ga(2) atoms, share a common edge [As(1)–As(1)]. Corner sharing links groups of three tetrahedra together in both the *a* and *c* directions, forming the infinite two-dimensional anionic sheet. The average Ga–As bond distance is 2.497 Å compared with 2.448 Å with GaAs. The average As–Ga–As angle is 108.4° although there is substantial variation from the average, most noticeably in the angles to the shared edge, which are 90.66 (7) and 89.42 (7)°.

The As atoms are bonded to three Ga atoms in an orientation that directs the filled lone-pair orbitals approximately perpendicular to the sheet and toward the layer of K^+ ions. The average K···As contact distance is 3.36 Å compared with average distances of 3.46 Å in K_2SiAs_2 and KSi_3As_3 and 3.47 Å in KAs.

The gross structure of the $[Ga_3As_4{}^{3-}]_\infty$ sheets can also be described in two different ways, depending on the angle at which the structure is viewed. When viewed parallel to the layers, the structure appears to contain trigonal-bipyramidal clusters with As atoms occupying the axial positions and Ga atoms occupying the equatorial positions. These $Ga_3As_2{}^{3+}$ clusters are structurally similar to the $Bi_5{}^{3+}$ and $Pb_2{}^{2-}$ Zintl ions. Each equatorial Ga atom in the cluster is linked to two other clusters through a bridging As atom.

When the structure is viewed perpendicular to the layers, a two-dimensional network of six-membered rings is apparent. This type of structure is well-known, appearing in materials such as metallic arsenic and Zintl phases such as $CaSi_2$[21] and KSnAs.[25] In $K_3Ga_3As_4$ pairs of six-membered rings are "tied together" by bridging As atoms. A similar structure has been observed for $M_2Al_2Sb_3$ (M = Na, K), in which the six-membered rings are bridged by As_2 moieties.[29]

Zintl phase materials are formally classified as semiconductors. $K_3Ga_3As_4$ has the appearance of a semiconductor: it is a dark metallic gray solid and opaque in appearance. The resistivity measurements on pressed pellets of $K_3Ga_3As_4$ indicate that the activation energy for elevation of electrons into the conduction band is sufficiently large that a calibrated current ($i \geq 0.1$ mA at V = 1 mV) may not be passed through the material at room temperature and the material behaves as a semiconductor with a band gap ≥2 eV.

We are in the process of preparing and characterizing a variety of I–III–V Zintl phase materials and will report on their structural and resistivity properties.

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Supplementary Material Available: Tables of anisotropic thermal parameters and complete crystal data (2 pages); a listing of observed and calculated stucture factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Water Oxidation by $[(bpy)_2(O)Ru^{V}ORu^{V}(O)(bpy)_2]^{4+}$. An Oxygen-Labeling Study

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Introduction

The complex $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ can be oxidized chemically or electrochemically to the [V,V] state, which undergoes autoreduction to the [III,IV] state, in water, accompanied by the appearance of dioxygen.[1-3] In order to understand

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Table I. Mass Spectral Peak Heights for Vapor-Phase Samples from the Oxygen-Labeling Studies

	peak height at the masses indicated					production ratio	
sample	28	32	32[a]	34	36	$^{18}O_2/^{18}O^{16}O$	$^{16}O_2/^{18}O^{16}O$
bkgd	50	8.9		0	0		
run 1[b]	3330	785	190	35.7	3.1	0.087	5.3
run 2[b]	195	48.6	14	41.1	7.9	0.192	0.34
run 3[c]	203	52.0	16	42.1	8.0	0.190	0.38
run 4[c]	1140	239	36	41.7	9.2	0.221	0.86

[a] Corrected for adventitious oxygen. [b] Solution A: [III,III] complex. [c] Solution B: [III,IV] complex.

the mechanism of this reaction, we have labeled the aqua groups of the [III,III] and [III,IV] states with ^{18}O, oxidized them to the [V,V] state in water of normal isotopic composition, and determined the ratios of $^{18}O_2$, $^{18}O^{16}O$, and $^{16}O_2$ that were produced.

Experimental Section

Materials. Water was purified by the Nanopure system (Millipore, Inc.) and was of specific resistance >16 M Ω cm. Trifluoromethanesulfonic acid (HTFMS) was diluted with water to give the monohydrate, which was vacuum-distilled and stored as the solid. The salt $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2](ClO_4)_4$ was prepared by the literature method[1] and recrystallized before use.

Procedure. Two solutions, A and B, each containing 26.2 mg (0.020 mmol) of $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2](ClO_4)_4$ in 1.00 mL of 95% ^{18}O-enriched water (Isotec) were prepared. The complex in each solution was allowed to equilibrate with the ^{18}O-enriched water by sitting overnight. To solution B was added a drop of HTFMS and 11.0 mg (0.020 mmol) of ceric ammonium nitrate in order to oxidize the complex to the [III,IV] state. For each run, half (0.500 mL) of each solution was deoxygenated with helium and injected into a helium-deoxygenated solution containing 9.50 mL of 0.100 M HTFMS and 0.0274 g (0.050 mmol) or 0.0219 g (0.040 mmol) of ceric ammonium nitrate for solution A or B, respectively. After 1 h, the vapor phase above each solution was drawn into an evacuated glass bulb and subjected to mass spectrometric analysis. In addition, the background mass spectrum was recorded.

Results

For each gas sample, the heights of the mass spectral peaks at 28, 32, 34, and 36 amu were obtained from the spectrometer chart. No significant differences between the samples and the background were noted at any other mass numbers. Peak heights are listed in Table I for the results of representative experiments. Problems in these experiments were encountered from occasional air leakage into the apparatus used.

By using the background ratio of the 28- and 32-amu peaks, which are attributable to nitrogen and oxygen, the observed heights of the 32-amu peaks can be corrected for adventitious air. These corrected values and the ratios of the isotopic forms of dioxygen that were produced are also tabulated in Table I.

On the basis of the height of the 28-amu peak, it can be seen that runs 1 and 4 were contaminated with air, presumably by leakage into the collecting bulb. The heights of the 34- and 36-amu peaks are very consistent except for the low value of the 36-amu peak in run 1. The results of run 1 are thus dubious, and the value of the corrected height in run 4 is obviously of low accuracy. The value of the $^{18}O_2/^{18}O^{16}O$ ratio is consistent in runs 2–4, and the $^{16}O_2/^{18}O^{16}O$ ratio is consistent in runs 2 and 3, where contamination by air was not a problem. On the basis of the results of runs 2 and 3, the yields of the three forms of O_2 were 13% $^{18}O^{18}O$, 64% $^{18}O^{16}O$, and 23% $^{16}O^{16}O$.

Discussion

In the experiments described here, the oxidation of the ^{18}O-labeled [III,III] complex $[(bpy)_2(^{18}OH_2)RuORu(^{18}OH_2)(bpy)_2]^{4+}$ by 5 equiv of Ce(IV) or the oxidation of the labeled [III,IV] complex by 4 equiv of Ce(IV) was carried out in a solution that, after mixing, contained about 4.8 atom % $H_2{}^{18}O$. Following oxidation in either case, the final product was the [III,IV] complex, as shown by spectrophotometric measurements.[1a]

The isotopic ratios in the dioxygen product were essentially the same when the starting complex was in either the [III,III] or [III,IV] state. The $^{18}O_2/^{18}O^{16}O$ ratio was consistently about 0.20, and the $^{16}O_2/^{18}O^{16}O$ ratio was about 0.36 in the runs not contaminated by air.

The [III,III] and [III,IV] complexes have considerably different properties toward substitution, with the [III,III] complex being more labile.[4] Since the same labeling result was obtained with either, it can be inferred that (1) initial exchange of bound water with the ^{18}O-enriched water in the bulk solution was complete and (2) mixing with normal water containing Ce(IV) resulted in the oxidation of either the [III,III] or [III,IV] complexes to [V,V] before either underwent significant water exchange with bulk water.

Several conclusions can be drawn from the labeling results that relate to the mechanism of water oxidation:

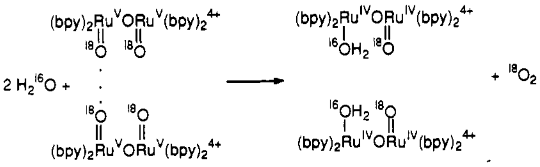
(1) Water oxidation is undoubtedly occurring, as adventitious oxygen cannot account for the labeled product.

(2) The mechanism of water oxidation does *not* involve primarily the oxidation of uncoordinated water. This would produce 0.2% $^{18}O_2$, 9% $^{18}O^{16}O$, and 91% $^{16}O_2$. The oxygens initially bound to the [III,III] or [III,IV] complexes must be involved in the mechanism.

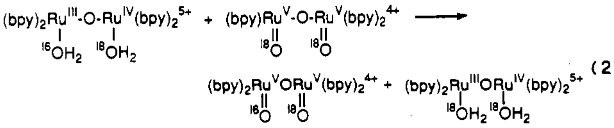
(3) The data appear to rule out, at least as a sole pathway, a mechanism involving direct attack of solvent water on a ruthenyl site, as this would lead primarily to a singly labeled product. The $^{18}O_2/^{18}O^{16}O$ ratio could not exceed 0.048 for this mechanism. The experimental ratio was 0.20.

(4) A mechanism in which coupling occurs between the two oxygens present as aqua groups in the initial complexes may be operative, but not as the sole pathway. This would lead primarily to $^{18}O_2$ as the product. Some $^{16}O_2$ and 4.8% as much $^{18}O^{16}O$ would also be produced if the dimer, which had reacted and incorporated bulk water, were reoxidized to the [V,V] state by electron exchange. The labeling result could be accommodated by this mechanism if partial exchange of oxygen between the solvent and the oxo groups of the [V,V] state occurs on the time scale for water oxidation. Oxygen exchange is known to be slow for an oxo complex of Ru(IV).[6]

One may conclude from the observed results that direct O–O coupling could be involved or that there is a competition between two or more mechanisms. A single mechanism that might account for the results without invoking oxygen exchange between solvent and ruthenyl would involve the coupling of the ruthenyl oxygens on two separate [V,V] molecules (reaction 1). Initially, this reaction would produce primarily $^{18}O_2$. However, with each cycle of the reaction, one of the oxygen atoms of the dimer exchanges with the solvent. It is known from electrochemical studies that both the [IV,V] and [IV,IV] states are unstable with regard to disproportionation into [V,V] and [III,IV] under the conditions of the experiments.[1a] Disproportionation and electron exchange (reaction 2) would allow the monolabeled complex to reattain the [V,V] state and engage in subsequent oxidation cycles. They would lead to the production of both mono- and dilabeled oxygen.



(1)



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It is not clear that this mechanism can rationalize the observed results exactly.

The results of initial kinetic studies based on spectrophotometric monitoring have shown that the mechanism of water oxidation is complex kinetically and may involve more than one pathway and at least one discernible intermediate. Additional studies will be required before distinctions can be drawn among the various mechanistic possibilities.

Comparison to Photosynthesis. The ruthenium complex may or may not serve as a model for the oxygen-evolving complex (OEC) of photosystem II. Only one oxygen-labeling study has addressed directly the question of the source of the oxygen atoms that are coupled to the production of dioxygen in photosynthesis.[5] In the study, chloroplasts in the S_1 state were equilibrated with ^{18}O-labeled or unlabeled water for several minutes at 11 °C, and were preflashed once or twice to achieve the S_2 or S_3 states. The samples were then diluted with unlabeled water for approximately 1 min and flashed sequentially, with the isotopic yield of dioxygen determined mass spectrometrically. Only unlabeled dioxygen was observed in all cases. On the basis of these results, either (1) the OEC in S_1 chloroplasts does not exchange water at all in several minutes, (2) the S_2 and S_3 chloroplasts exchange completely with water in 1 min, or (3) the oxidation of water by the OEC does not involve bound water. Although the results for the OEC appear to differ considerably from those obtained for the ruthenium complex, the mechanisms could be the same. The difference between the two could lie in differences in available exchange pathways rather than in a difference in oxidation mechanism.

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Novel Ambidentate and Chelate Complexes of Ruthenium with Methylenebis(1,3,2-dithiaphospholane) and (Methylimino)bis(1,3,2-dithiaphospholane) as Ligands

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Diphosphorus compounds having either a single methylene group or an amino group between the two phosphorus nuclei have been variously used as chelating and bridging ligands to transition-metal centers.[1] A research area of growing importance is the use of these complexes in photochemical reactions and catalysis.[2] A potential drawback to such applications is the possibility that either the ground or excited state of the complex can undergo irreversible cyclometalation with functional groups at the ligand periphery.[3] A plausible approach to the use of diphosphorus ligands in these complexes, while minimizing the likelihood of cyclometalation side reactions, is to employ small rings as peripheral substituents at phosphorus. In this note, we report the synthesis of several new ligands of this type and show how, in complexation with ruthenium(II), chelation via phosphorus and a ring heteroatom can occur to circumvent ring strain.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. The compounds $CH_2(PCl_2)_2$, $CH_3N(PCl_2)_2$, and $RuCl_2(PPh_3)_3$ were synthesized according to the literature procedures.[4] All solvents were dried and distilled under nitrogen. Ethylene glycol was purified by distillation and catechol by sublimation. Ethanedithiol and DABCO were used as received from Aldrich. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained on a Brucker AC200 spectrometer. The NMR simulation for $RuCl_2(pcps)_2$ was performed by using the PANIC software routine.[5] Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Methylenebis(1,3,2-dioxaphospholane), $CH_2(POCH_2CH_2O)_2$. To a stirred solution of $CH_2(PCl_2)_2$ (0.15 mL, 1 mmol) and DABCO (0.45 g, 4 mmol) in dichloromethane (50 mL) was added dropwise a solution of ethylene glycol (0.14 mL, 2 mmol) in dichloromethane (10 mL) at 0 °C. After being stirred for 10 min, the solution was filtered to remove the white precipitate of DABCO·HCl. The solution volume was reduced to 10 mL and *n*-hexane (30 mL) added. Additional DABCO·HCl precipitated, and it was removed by filtration. The filtrate was kept under vacuum for 24 h to give the product as a pale yellow liquid. Yield: 0.078 g (40%).

(Methylimino)bis(1,3,2-dioxaphospholane), $CH_3N(POCH_2CH_2O)_2$. Using a similar procedure as for $CH_2((POCH_2CH_2O)_2$ with $CH_3N(PCl_2)_2$ (0.14 mL, 1 mmol) and the other reagents in the same stoichiometric ratios gave the compound as a pale yellow liquid. Yield: 0.084 g (40%).

Methylenebis(benzo-1,3,2-dioxaphospholane), $CH_2(POC_6H_4O)_2$. To a stirred solution of $CH_2(PCl_2)_2$ (0.15 mL, 1 mmol) and DABCO (0.45 g, 4 mmol) in dichloromethane (50 mL) was added dropwise a solution of catechol (0.22 g, 2 mmol) in dichloromethane (10 mL) at 0 °C. After being stirred for 10 min, the solution was filtered to remove the white precipitate of DABCO·HCl. The solution volume was reduced to 10 mL and *n*-hexane (30 mL) added. The solvent was removed from the filtrate under vacuum to give the product as a pale yellow liquid. Yield: 0.158 g (54%).

(Methylimino)bis(benzo-1,3,2-dioxaphospholane), $CH_3N(POC_6H_4O)_2$. Using a similar procedure as for $CH_2(POC_6H_4O)_2$ with $CH_3N(PCl_2)_2$ (0.14 mL, 1 mmol) and the other reagents in the same stoichiometric ratios gave the compound as a pale yellow liquid. Yield: 0.184 g (60%).

Methylenebis(1,3,2-dithiaphospholane), $CH_2(PSCH_2CH_2S)_2$. To a stirred solution of 1,2-ethanedithiol (0.17 mL, 2 mmol) was added dropwise a solution of $CH_2(PCl_2)_2$ (0.15 mL, 1 mmol) in dichloromethane (10 mL) at ambient temperature. After the mixture was stirred for 2 h, the volume of solvent was reduced to 20 mL under vacuum and methanol (40 mL) added. The colorless crystals were filtered immediately and washed with a small portion of cold methanol. The compound (pcps) was recrystallized from dichloromethane and *n*-hexane as a solvate containing half of a molecule of dichloromethane. Yield 0.195 g (75%). mp 63–64°, Anal. Calcd for $C_{5.5}H_{11}ClP_2S_2$: C, 21.8; H, 3.66. Found: C, 21.3; H, 3.99.

(Methylimino)bis(1,3,2-dithiaphospholane), $CH_3N(PSCH_2CH_2S)_2$. To a stirred solution of 1,2-ethanedithiol (0.17 mL, 2 mmol) and DABCO (0.45 g, 4 mmol) in dichloromethane (50 mL) was added dropwise a solution of $CH_3N(PCl_2)_2$ (0.14 mL, 1 mmol) in dichloromethane (10 mL) at 0 °C. The solution was stirred for 2 h while it was allowed to warm to ambient temperature. The white precipitate of DABCO·HCl was filtered, and the solution volume was reduced under vacuum to 20 mL. Methanol (40 mL) was added, and the colorless crystals were filtered immediately and washed with a small portion of cold methanol. The compound (pnps) was recrystallized from dichloromethane and *n*-hexane. Yield: 0.192 g (70%). Mp: 142–145 °C. Anal. Calcd for $C_5H_{11}NP_2S_2$: C, 21.8; H, 4.03; N, 5.09. Found: C, 21.7; H, 4.07; N, 5.05.

***trans*-Dichlorobis(methylenebis(1,3,2-dithiaphospholane))ruthenium(II), $RuCl_2(pcps)_2$.** To a stirred solution of $RuCl_2(PPh_3)_3$ (0.18 g, 0.2 mmol) in dichloromethane (20 mL) was added dropwise a solution of pcps (0.1 g, 0.4 mmol) in dichloromethane (10 mL). The color of the solution changed from brown to yellow. The solution was stirred for 30 min, and the volume of the solution changed from brown to yellow. The solution was stirred for 30 min, the volume of the solution reduced to 15 mL under vacuum, and *n*-hexane (40 mL) added to give a yellow precipitate. The yellow complex was filtered, recrystallized from dichloromethane and *n*-hexane, and dried in vacuo. Yield: 0.093 g (82%). Anal.

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