TABLE I

PHYSICAL AND ANALYTICAL DATA FOR COMPLEXES

Starting materials					Mol. wt.		Calculated		Found	
Metal compound	Olefin	Formula of complex	Yield, %	M.p., °C.	Calcd.	Found	% C	% H	% C	% H
K_2PdCl_4	1,5-COD	$(C_8H_{12})PdCl_2$	85	205 dec.	235.5	280	33.66	4.23	33.80	4.25
K_2PdCl_4	1,3-COD	$(C_8H_{12})PdCl_2$	58	205 dec.	235.5	280	33.66	4.23	33.74	4.25
K_2PdBr_4	1,5-COD	$(C_8H_{12})PdBr_2$	80	207 dec.	374.4	384	25.66	3.23	25.69	3.25
K_2PdBr_4	1,3-COD	$(C_8H_{12})PdBr_2$	74	207 dec.	374.4	388	25.66	3.23	25.66	3.24
K_2PtCl_4	1,5-COD	$(C_8H_{12})PtCl_2$	58	270 dec.	374.2	390	25.68	3.24	25.65	3.23
K_2PtCl_4	1,3-COD	$(C_8H_{12})PtCl_2$	24	270 dec.	374.2	386	25.68	3.24	25.62	3.25
K_2PtBr_4	1,5-COD	$(C_8H_{12})PtBr_2$	20	280 dec.	463.1	470	20.74	2.61	20.82	2.65
K_2PtBr_4	1,3-COD	$(C_8H_{12})PtBr_2$	18	280 dec.	463.1	480	20.74	2.61	20.80	2.65

Frohlich.[2] Recent papers by Hüttel and co-workers,[3] by Rinehart and Lasky,[4] and by Robinson and Shaw[5] indicate that 1,3-cyclooctadiene yields different products with palladium(II) than does the 1,5- isomer. Research in this laboratory concerning the synthesis of the palladium(II) and platinum(II) complexes of 1,3-cyclooctadiene has produced excellent evidence of rearrangement of the ligand to the 1,5- isomer. Preparation of $(C_8H_{12})PdCl_2$, $(C_8H_{12})PdBr_2$, $(C_8H_{12})PtCl_2$, and $(C_8H_{12})PtBr_2$ with both isomers yielded compounds identical in appearance and melting point and with the same infrared spectra. Recovery of cycloolefin by decomposition of the supposed 1,3- complex yielded in every case a compound identical with the 1,5- isomer. Treatment of the 1,3- complex with potassium cyanide or dimethyl sulfoxide yielded pure 1,5-cyclooctadiene exclusively as established by vapor phase chromatography. This rearrangement appears to be identical with that reported by Rinehart and Lasky[4] *via* the rhodium(I) complex.

Experimental

The cycloolefins used in this research were obtained from Cities Service Research and Development Co. and from K and K Laboratories. Each olefin was carefully redistilled in an efficient column; the middle fraction was retained and was stored over Drierite in the dark. Vapor phase chromatographic analysis of the retained fraction showed the purity of the 1,3-cyclooctadiene to be 98.7 mole %, and the purity of the 1,5-isomer to be 99.9 mole %. Vapor phase chromatograms showed that the 1,3-cyclooctadiene did not contain any 1,5- isomer as an impurity. Infrared spectra of the purified cycloolefins were made and were compared with those in the literature; all showed the characteristic strong absorbance at 1630 cm.$^{-1}$. The palladium(II) and platinum(II) halogenides were obtained from K and K Laboratories and were used without further purification.

The platinum(II) complexes were prepared according to the method of Chatt[1] involving the reaction of the potassium (better, sodium) salt of the type K_2PtX_4 with the cycloolefin in either methanol or 1-propanol. The palladium(II) complex using K_2PdCl_4 was prepared by displacement of the appropriate benzonitrilo complex with the cycloolefin in benzene as in the method of Kharasch.[6] A modification of this technique as reported by Frye, Kuljian, and Viebrock[7] was used to prepare the corresponding bromide. Synthetic procedures are given in the last named paper and are not repeated here. The benzonitrilo intermediates were recrystallized from benzene and benzonitrile, respectively, and were characterized by means of infrared spectra and elemental analyses. The crystals were vacuum filtered, washed with petroleum ether, and stored over Drierite at atmospheric pressure; reduced pressure tended to pump off benzonitrile.

The platinum(II) complexes were crystallized directly from the methanol or 1-propanol reaction mixtures; palladium(II) complexes were obtained by allowing purified bis(benzonitrilo)-palladium(II) halogenide to react with cycloolefin in benzene. In each case good crystalline products were obtained which were carefully recrystallized from the appropriate solvent and were subsequently characterized by means of infrared and ultraviolet–visible spectra and elemental analyses. Molecular weight determinations by the Rast method using bromoform as solvent were made on all complexes. Data concerning the physical and analytical properties of the various complexes are presented in Table I.

Infrared spectra of the 1,5-cyclooctadiene complexes were checked with the rather sparse data in the literature. The infrared spectra of the complexes prepared with 1,3-cyclooctadiene were identical with those of the 1,5- analogs. The spectra were obtained using potassium bromide tablets. Ultraviolet–visible spectra were likewise identical.

Recovery of the cycloolefin by means of replacement of the ligand with cyanide ion or dimethyl sulfoxide yielded a material in all cases that was identical with the 1,5- isomer as established by means of infrared spectrophotometry and vapor phase chromatography. Absence of the strong absorbance at 1630 cm.$^{-1}$ indicated π bonding in the complex; the peak reappeared in the recovered cycloolefin, of course. Yield data for the various complexes are given in Table I.

The observed rearrangement is doubtless due to the more favorable placement for π bonding of the double bonds in the *cis-cis* (tub) form of the 1,5-cyclooctadiene; thus the rearrangement occurs in spite of the fact that the conjugated 1,3- isomer is the more stable olefin. Rinehart and Lasky[4] suggested a mechanism for the rearrangement *via* π complex formation followed by hydrogen transfer; this mechanism is, in our opinion, a valid one and is preferable to that proposed by Harrod and Chalk.[8]

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CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
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Lattice Constants of Some Alkali Metal Actinyl(V) Compounds[1]

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Over the past few years, several new compounds have been reported which contain the doubly oxygen-

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ated XO_2^+ species of a pentavalent actinyl(V) element. However, with the exception of $KAmO_2F_2$, which had been known for some time,[2] no structure data had been given for any other fluoride containing an actinyl(V) species. The preparation of and lattice constants for several 1:1 rubidium (and one ammonium) actinyl(V) fluorides are described in the present note.

One recent publication[3] reported lattice constants for the series $KNpO_2CO_3$, $KPuO_2CO_3$, and $KAmO_2CO_3$. As a continuation of that work, similar data are given for $CsAmO_2CO_3$.

All pentavalent actinyl(V) species undergo disproportionation and are relatively easy to reduce. Therefore, considerable care must be exercised in the preparation of these compounds, especially those involving PuO_2^+, to maintain the actinyl(V) ion in its pentavalent state. The conditions described in the following section were found to be effective in preparing the actinyl(V) compounds in good yield.

Experimental

$CsAmO_2CO_3$.—Cesium americyl(V) carbonate was prepared by treating a slurry of pink $Am(OH)_3$ in *ca.* 0.5 *M* $CsHCO_3$ with ozone (5% O_3 in O_2) at 92° for 1 hr. The resulting tan precipitate was washed with small amounts of water, methyl alcohol, and acetone and air dried.

$RbNpO_2F_2$.—Rubidium neptunyl(V) fluoride was prepared by injecting a chilled solution of NpO_2^+ in ~0.1 *M* HNO_3 *into* a chilled saturated solution of rubidium fluoride (*ca.* 12 *M*) at 0°. The gray-green precipitate which formed was centrifuged rapidly, washed with small amounts of water, methyl alcohol, and acetone, and air dried. It was important to work as rapidly as possible during the precipitation step because of disproportionation of pentavalent neptunium.

$RbPuO_2F_2$.—Rubidium plutonyl(V) fluoride also required rapid manipulation for successful preparation. A solution of PuO_2^+ was injected into a solution of saturated rubidium fluoride at 0° at pH 6. The PuO_2^+ solution was prepared by addition of a 50% excess of hydrogen peroxide to a solution of PuO_2^{2+} according to the equation: $PuO_2^{2+} + {}^1/_2H_2O_2 \rightarrow PuO_2^+ + H^+ + {}^1/_2O_2$. This reduction is most conveniently carried out at pH 3 at 0°; the light green color of PuO_2^{2+} disappears within 5 min. with evolution of O_2. The reduction is quantitative and the absence of PuO_2^{2+} and Pu^{4+} was checked on a Cary spectrophotometer. The brilliant lavender-colored PuO_2^+ is reported stable up to 0.01 *M* PuO_2^+ at pH values of *ca.* 3.[4] Adjustment of the pH to 6 (with RbOH) was made *after* the reduction of PuO_2^{2+} to PuO_2^+. The PuO_2^+ solution was then combined rapidly with the RbF solution; the lavender precipitate was washed with a minimum amount of water, methyl alcohol, and acetone and air dried.

$NH_4PuO_2F_2$.—Ammonium plutonyl(V) fluoride was formed by adding solid NH_4F to a solution of PuO_2^+ at pH 6 prepared as above except that NH_4OH was used to adjust the pH. The addition of NH_4F was made at 0°. The lavender precipitate was treated in the same manner as the others.

$RbAmO_2F_2$.—Rubidium americyl(V) fluoride was made by addition of saturated RbF solution to AmO_2^+ in 0.01 *M* HCl. As with the other preparations, the precipitation was carried out at 0° although the rapid centrifugation and manipulations were not as necessary as with the neptunyl(V) and plutonyl(V) compounds. The tan rubidium americyl(V) precipitate was likewise washed with small amounts of water, methyl alcohol, and acetone and air dried.

X-Ray samples were prepared from the dried powders. The data from the X-ray films were treated as described elsewhere[3,5] to calculate lattice parameters and their standard deviations. Table I lists the lattice constants that were obtained for these compounds.

TABLE I

LATTICE DIMENSIONS OF ALKALI METAL ACTINYL(V) COMPOUNDS

Rhombohedral, Space Group $R\bar{3}m\text{-}D_{3d}^5$, $Z = 1$

Compound	a_0, Å.	α, deg.	Hexagonal dimensions a_0, Å.	 c_0, Å.
$RbNpO_2F_2$	6.814 ± 0.008	36.18	4.245 ± 0.005	19.07 ± 0.02
$RbPuO_2F_2$	6.796 ± 0.008	36.17	4.232 ± 0.005	19.02 ± 0.02
$RbAmO_2F_2$	6.789 ± 0.006	36.15	4.224 ± 0.004	19.00 ± 0.02
$NH_4PuO_2F_2$	6.817 ± 0.006	36.16	4.243 ± 0.004	19.08 ± 0.03

Hexagonal, Space Group $C6/mmc\text{-}D_{6h}^4$, $Z = 2$

Compound	a_0, Å.	c_0, Å.
$CsAmO_2CO_3$	5.123 ± 0.001	11.538 ± 0.007

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The Infrared Spectra of Some Compounds of Zirconium(IV) and Hafnium(IV) Tetrahalides and Ligands Containing Group V Donor Atoms

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Preparations of a number of complexes of zirconium(IV) halides and hafnium(IV) chloride have been reported previously together with studies of their infrared spectra in the 4000–650 cm.$^{-1}$ region. However, only one published work on the important 550–200 cm.$^{-1}$ region has appeared to date.[1] It is in this region that metal–ligand stretching frequencies should occur.

Pyridine and nitriles,[2] some secondary and tertiary amines,[3,4] and *o*-phenylenebisdimethylarsine[5] have been shown to form adducts with zirconium(IV) chloride and bromide. Infrared spectra have been recorded for some of the adducts,[4,6] but emphasis was placed upon investigation of the effect of coordination on the ligand modes themselves.

The present work deals with the preparation of complexes of ZrX_4 and HfX_4 (where X = Cl, Br) with donor molecules containing nitrogen, phosphorus, and arsenic and describes the effect of change of ligand and

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