15054-01-0; $C_2O_4^{2-}$, 338-70-5; $HC_2O_4^-$, 920-52-5.

References and Notes

(1) Abbreviations used in this paper are as follows: ox = $C_2O_4^{2-}$; en = $NH_2CH_2CH_2NH_2$; enH = $-NH_2CH_2CH_2NH_3^+$; bpy = 2,2′-bipyridine; *o*-phen = 1,10-phenanthroline.

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(24) Pertinent molar absorptivities at 394 nm: $Cr(ox)(en)(H_2O)_2^+$, 62.2 $M^{-1}\ cm^{-1}$; $Cr(ox)_2(en)^-$, 100.0 $M^{-1}\ cm^{-1}$; $Cr(ox)_2(enH)(H_2O)$, 66.6 $M^{-1}\ cm^{-1}$; and $Cr(ox)_3^{3-}$, 83.2 $M^{-1}\ cm^{-1}$.

(25) $k(3) \simeq k(2) = 5 \times 10^{-5}\ s^{-1}$ at 35.0 °C,[18] while $k(4) = 3.0 \times 10^{-4}\ s^{-1}$ at 35.0 °C and an oxalate formality of 0.250 F.[10]

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Monomer–Dimer Phenomena in Oxoosmium(VI) Complexes

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Both monomeric and dimeric forms of the oxoosmium(VI) complexes formed by reaction between oxoosmium(VI) species and *N,N,N′,N′*-tetramethylethylenediamine have been isolated and characterized by elemental analysis, by IR, UV, and NMR spectroscopy, and by molecular weight determinations. Equilibrium constants have been measured as a function of temperature. The rate of the dimer to monomer conversion has been measured as a function of pH. Corresponding 1,10-phenanthroline complexes have also been isolated and partially characterized largely through study of their IR spectra since, in this case, the equilibrium and solubility characteristics make studies in solution difficult.

Wintrebert[1] prepared an oxoosmium(VI) complex by reaction of potassium nitrite with potassium osmate or with osmium tetroxide. The complex was originally formulated as the pentacoordinate monomeric species $K_2[OsO_3(NO_2)_2]$. Atovmyan and D'yachenko[2] established by X-ray crystallography that the structure was, in fact, the hexacoordinate dioxo-bridged dimer $K_4[Os_2O_6(NO_2)_4]$. Criegee[3] prepared a related nonionic complex by reaction between osmium tetroxide and pyridine in the presence of a reducing agent which he formulated as $OsO_3(py)_2$. Griffith and Rossetti[4] found good spectroscopic evidence to show that this complex was also dimeric in the solid state. Solution studies[5] suggested the existence of a monomer–dimer equilibrium for the pyridine complex, but contrary evidence has also appeared.[6] We and others have been particularly interested in oxoosmium(VI) complexes with tertiary amines as ligands because of their synthetic utility in preparing oxoosmium(VI) esters of biologically important molecules[7] and because of the ease with which their properties can be altered by variation in the structure of the ligand.[8]

We show in this paper that the *N,N,N′,N′*-tetramethylethylenediamine (TMEN) and 1,10-phenanthroline (phen) oxoosmium(VI) complexes can be isolated in the solid state either as dimers or as monomers.

Results

Synthesis of the Oxoosmium(VI)–*N,N,N′,N′*-Tetramethylethylenediamine Complexes. The standard preparation of oxoosmium(VI) ligand complexes involves reduction of osmium tetroxide in alkaline solution in the presence of the ligand. When this procedure is carried out with the ligand *N,N,N′,N′*-tetramethylethylenediamine, a 60% yield of green crystals of the dimeric form of the complex can be isolated. If, on the other hand, the complex is made in neutral solution, the monomeric form of the complex is the principal product. However, the best procedure we have found for preparation of the monomer is by ligand exchange with the corresponding oxoosmium(VI)–bis(pyridine) complex. The complexes differ markedly in solubility properties. Both complexes are quite soluble in water and methanol, but only the monomer is soluble in acetone, chloroform, and *tert*-butyl alcohol.

Monomer–Dimer Interconversion.[25] The monomer–dimer interconversion can be conveniently followed in aqueous solution by NMR techniques. If the proton NMR spectrum of the dimer is observed soon after dissolution in D_2O, pD 6, only the expected pair of singlets corresponding to the methyl and

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Table I. Equilibrium Data for the TMEN Monomer–Dimer System in D_2O, 35 °C

wt,[a] mg	$[D]_0$[b]	$[D]_{eq}$[c]	$[M]_{eq}$[c]	K_{eq}[d]
40.9	0.109	0.0507	0.1182	0.276
20.0	0.0537	0.0183	0.0708	0.274
19.4	0.0521	0.0178	0.0686	0.266
9.6	0.0258	0.0063	0.0390	0.245
6.1	0.0164	0.0030	0.0268	0.244
2.3	0.0062	~0.0006	0.0112	~0.2

[a] Weight of dimer dissolved in 0.5 mL of D_2O. [b] Mol wt is 745. [c] Equilibrium concentrations after 2 h at 35 °C. [d] $K_{eq} = [M]^2/[D]$; M = monomer, D = dimer.

Table II. Equilibrium Data for the TMEN Monomer–Dimer System in Phosphate-Buffered D_2O, pD 7.5, as a Function of Temperature

temp, °C	$[D]_{eq}$[a]	$[M]_{eq}$[a]	K_{eq}, M
28	0.0299	0.0854	0.244 ± 0.007
38	0.0278	0.0896	0.289 ± 0.02
48	0.0259	0.0934	0.337 ± 0.04
75	0.0232	0.0988	0.421 ± 0.02

[a] Key: D = dimer, M = monomer.

Table III. Apparent Molecular Weight of the TMEN Monomer–Dimer System as a Function of Concentration, 60 °C, H_2O

	mol wt	
wt,[a] mg	calcd[b]	found[c]
7.451	389	392
22.432	414	420
45.459	442	460
74.290	456	465

[a] The complex was added as the dimer dihydrate, mol wt 745, dissolved in water to a final volume of 1 mL, and equilibrated at 60 °C for 30 min before the measurement. [b] From the data of Table II using $K_{eq} = 0.37$ and the assumed molecular weights of the monomer = 372, dimer = 709 (anhydrous weight). [c] Galbraith Laboratories by vapor-phase osmometry.

Table IV. Kinetics for the Conversion of the TMEN Dimer to the TMEN Monomer[a]

pH	medium	μ	k_{obsd}, min^{-1}	k_{cor}[d]
5.76	0.1 M phosphate	0.11	0.1996	0.1865
5.82		0.6[b]	0.2475	0.1709
5.85		0.5[b]	0.2128	0.1563
5.88		0.4[b]	0.2170	0.1696
5.92		0.3[b]	0.1964	0.1632
6.02		0.13	0.1803	0.1664
6.54		0.16	0.1075	0.0975
6.98	0.001 M phosphate	0.3[c]	0.0544	
7.06	0.01 M phosphate	0.3[c]	0.0562	
7.06	0.1 M phosphate	0.22	0.0659	
7.15		0.3[c]	0.0617, 0.0624	
8.00		0.3[c]	0.0604	
8.50	0.01 M phosphate	0.6[c]	0.0447	
8.58		0.6[c]	0.0550	
8.92		0.03	0.0509	
9.08	0.1 M phosphate	0.3[c]	0.0642	
9.77		0.3[c]	0.0665	
10.79		0.3	0.0553	
~8.5	1 × 10^{-4} M NaOH	~0	0.0503	
8.5		~0	0.0493	
10.51	1 × 10^{-3} M NaOH	0.001	0.0596	
10.53			0.0689	
11.53	1 × 10^{-2} M NaOH	0.01	0.2081	
11.73			0.1939	
11.86		0.1[c]	0.1967	
11.88		0.6[c]	0.1902	
11.92		0.3[c]	0.2047	
12.55		0.05	0.4576	

[a] General conditions: 30 °C, initial dimer concentration = $(1.5-2) \times 10^{-4}$ M, μ = ionic strength. [b] μ adjusted with KCl. [c] μ adjusted with NaCl. [d] Corrected according to the equation $\log k_{cor} = \log k_{obsd} - 0.268\mu$.

Table V. Kinetics of the TMEN Dimer–Monomer Conversion, 0.1 M Phosphate, pH 7

$10^4[D]_0$,[a] M	T, °C	k, min^{-1}
1.74	40	0.262
1.87	33	0.131
1.90	30.1	0.06
1.74	25.3	0.0427
1.86	19.6	0.0159

[a] D = dimer.

methylene groups of complexed TMEN at δ 2.65 and 2.92, respectively, are observed in the ratio 3:1. Free TMEN shows these resonances at δ 2.22 and 2.45. Compare ref 9. There rapidly appear, however, two additional resonances at δ 2.72 and 3.08 which grow at the expense of the original resonances. These new resonances are also in the ratio 3:1. After some time, a steady state is reached. If one starts with the monomer, the initial resonances are at δ 2.72 and 3.08. These diminish with time and the resonances at δ 2.65 and 2.92 grow. The same equilibrium state is reached from either direction. The assumption that these new resonances represent a monomer–dimer interconversion can be tested by integration of the spectra and calculation of an equilibrium constant, $K_{eq} = M^2/D$, as one varies the initial concentration of the dimer (Figure 1). Table I shows data treated in this way. A reasonably constant value for $K_{eq} = 0.261 \pm 0.016$ M is obtained over a sevenfold initial concentration range. The point determined at the lowest concentration was excluded from this average since the quantity of dimer at this high dilution at equilibrium was hard to measure. We have also determined the dependence of K_{eq} on temperature (Table II). An Arrhenius plot of these data gives $\Delta H° = 2.4 \pm 0.3$ kcal mol^{-1}, $\Delta S° = 5.3 \pm 1$ cal mol^{-1} deg^{-1}, and $\Delta G°_{301\text{ K}} = 0.8 \pm 0.3$ kcal mol^{-1}.

The dimer–monomer equilibrium is established too rapidly to allow a molecular weight determination for either the monomer or dimer alone. However, molecular weight determinations on equilibrium mixtures should show apparent molecular weights which would depend upon the initial concentrations in accordance with the equilibrium constants just discussed. Table III shows a set of such data. The calculated and experimental values are in good agreement. Furthermore, extrapolation of these data to infinite dilution gives a monomeric molecular weight of 375 in excellent agreement with the weight 372 calculated for $OsO_2L(OH)_2$, where L = TMEN.

This formulation of the structure of the monomer is supported by the NMR spectrum of the monomer in $CDCl_3$. Immediately upon dissolving the monomer, one observes in addition to the methyl and methylene singlets centered at δ 3.1, a broad resonance at about δ 3.7. After the solution is allowed to stand, the dimer precipitates. When the mixture is filtered and reexamined, the methyl and methylene resonances have decreased in intensity, as expected, while the broad resonance has moved upfield. It comes to rest after about 30 h at 35 °C at about δ 2.1, the position of the H_2O resonance in $CDCl_3$. These observations are in accord with the assignment of the downfield broad resonance to OsO–H. This moves upfield as it becomes equilibrated with H_2O produced by dimerization according to equation

$$2M(OH)_2 \rightleftharpoons D + 2H_2O$$

This also implies exchange of these protons at a rate faster than 150 s^{-1}.

Kinetics of the Monomer–Dimer Interconversion. The kinetics of this reaction were most conveniently followed by

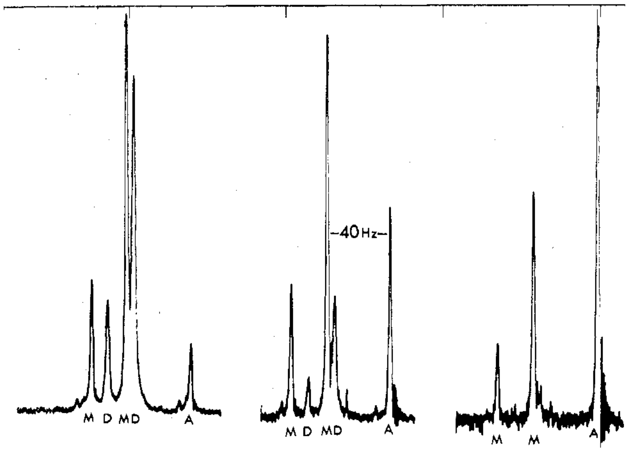

Figure 1. Proton NMR spectra (60 MHz) of the TMEN–oxo-osmium(VI) complex in D_2O at three concentrations, 35 °C, expressed as molarity of dimer (from left to right): 0.11 M, 0.026 M, and 0.0062 M; M = monomer, D = dimer. In each case, the high-field singlet is internal acetone (A).

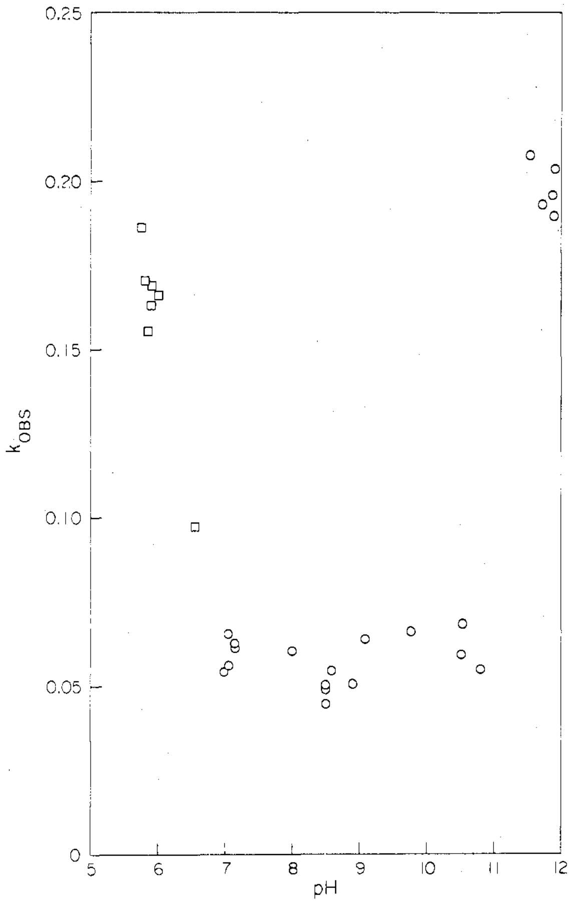

Figure 2. Rate constant for monomerization of the TMEN dimer as a function of pH. Initial dimer concentration (1.5–2) × 10^{-4} M. The rate was followed by measurement of the absorbance at 305 nm, 30 °C.

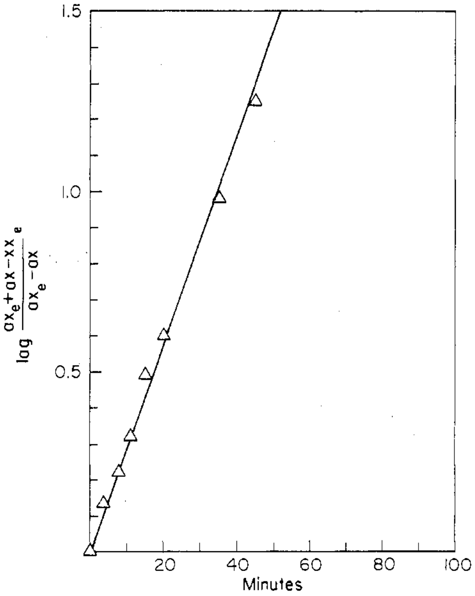

Figure 3. The kinetics of the TMEN monomer–dimer reaction at an initial dimer concentration of 0.054 M, 35 °C. The rate was followed by integration of the monomer and dimer resonances in the NMR spectrometer. See Experimental Section. The rate constant, k_f, for this run was 0.00612 min^{-1}. The equilibrium constant was 0.272 M.

Table VI. Kinetics of the Conversion of the TMEN Dimer to Monomer in the Presence of Added TMEN[a]

[added TMEN], M	k_{obsd}, min^{-1}	[added TMEN], M	k_{obsd}, min^{-1}
0	0.2167	0.0166	0.0769
0.0033	0.1423	0.0332	0.0553
0.0066	0.1138	0.0663	0.0415

[a] General conditions: initial [TMEN dimer] = (1.8–2.20) × 10^{-4} M, carbonate buffer pH 10.85, $T = 40$ °C.

observing the decrease in absorption at 305 nm due to conversion of the dimer to the monomer in solutions sufficiently dilute that the back-reaction was negligible. Under these conditions the reaction is first order in dimer. Tables IV and V present our results. Figure 2 shows the pH dependence of the reaction. The plot of log k_{obsd} vs. pH is linear with a slope of −1 in the pH range 5.75–7.0 and essentially invariant with pH in the range 7.0–11. There is a relatively unimportant base-catalyzed pathway above pH 11 complicated by decomposition of the complex to osmate ions at pH values above 13. The observed kinetic behavior as a function of pH in the range 5.75–11.0 is consistent with the rate law

$$\text{rate} = k_0[D] + k_H[D][H^+] + k_{OH}[D][OH^-]$$

Thus, under pseudo-first-order conditions, $k_{obsd} = k_0 + k_H[H^+] + k_{OH}[OH^-]$. The values of these constants at 30 °C are $k_0 = 5 \times 10^{-2}$ min^{-1}, $k_{H^+} = 1 \times 10^5$ M^{-1} min^{-1}, and $k_{OH^-} = 45$ M^{-1} min^{-1}. We estimate the error in these values at about ±8%.

We observe a small positive ionic strength effect in the acid range. The data can be expressed by the equation $\log k_{\mu=0} = \log k_{obsd} - -0.27\mu$. Above pH 7, variation of the ionic strength from about 0.01 to 0.6 M has no significant effect. There is no appreciable specific catalysis by phosphate.

The temperature dependence of the rate of conversion of dimer to monomer was measured at pH 7 in phosphate buffer over the temperature range 19–40 °C. The derived activation parameters are $E_a = 25 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 9 \pm 6$ eu.

A few kinetic runs were carried out at higher initial concentrations. A single run at an initial dimer concentration of 6.8×10^{-3} M was made by following the decrease in absorbance of the dimer at 450 nm. Good first-order kinetics were still observed, but the rate constant was about 10% lower than that measured under the more dilute conditions. Finally a few runs were made under conditions where the back-reaction cannot be ignored. At an initial dimer concentration of 5×10^{-2} M, the reaction can be monitored by integration of the monomer and dimer resonances in D_2O by NMR techniques. The kinetics were treated according to the method described

Table VII. Infrared Data, cm^{-1}

Os(VI) complex	assignments: δ(OsO-H) [δ(OsO-D)]	O=Os=O	Os_2O_2	ν(Os-OH) [ν(Os-OD)]	other observns
TMEN monomer	1015 [730]	845		560 [550]	900
TMEN dimer		840	620		885
phen monomer, brown	960 [740]	825		608, 585 [595, 560]	no δ 1640, ν(OsO-H) 3480, 3398 ν(OsO-D) 2580, 2520
phen monomer, copper-colored	1060 [800]	850		560 [580]	
phen dimer		830	640		

in the Experimental Section. A plot of such a run is shown in Figure 3. The good linearity which was observed confirms that the reaction is of the form

$$\mathrm{D} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\mathrm{M}$$

The rate constant for the forward reaction calculated for this run is, however, almost 3 times less than that measured spectrophotometrically in D_2O at 1/250th the concentration of dimer. We do not know the origin of this difference, but it may be an activity effect.

Table VI shows the effect of added excess ligand on the rate of the dimer to monomer conversion. The rate is decreased with an apparent order of –0.4 as shown by the slope of a plot of log k_{obsd} vs. log [TMEN]. In NMR observations of this kind of experiment, we see separate resonances for free ligand as well as for the two forms of complexed ligand. This is in accord with the observations of Marzilli et al.[9] and in contrast to the analogous case for pyridine as ligand when the exchange is fast on the NMR time scale.

The Phenanthroline Complexes. The analogous 1,10-phenanthroline complexes can also be isolated in the solid state either as the dimer or as the monomer which, in turn, exists in two forms.[10] Reaction between equimolar quantities of 1,10-phenanthroline and potassium osmate in water gave a brown solution which deposited copper-colored crystals of a monomer mixed with an amorphous light green precipitate of the dimer. Formation of the monomer is favored by low temperatures. The monomer and the dimer are easily separated from each other by differential solubility. Saturated solutions in water at 25 °C are about 1×10^{-3} M (monomer) and 1×10^{-6} M (dimer). When crystals of the copper-colored monomer are dried or when they are washed with acetone, they are converted to a different, still crystalline, brown monomeric complex. This brown complex is reconverted to the copper-colored complex by dissolution and recrystallization from water. The monomer is quantitatively converted to the dimer by boiling in water for a few hours or, more rapidly and consistent with the acid catalysis observed for the TMEN system, by boiling for 15 min in water acidified with a few drops of acetic acid. A molecular weight determination (vapor-phase osmometry, Galbraith Laboratories) on the monomer under conditions during which some conversion to the dimer probably took place (water, 60 °C, 10 min) gives 545 ± 100 (theory 436). The low precision is due to low solubility. The dimer is too insoluble to allow a molecular weight determination.

The oxidation state of osmium in the phenanthroline complexes was measured by reaction with 8 M HBr at 100 °C and titration of the liberated bromine with hydrazine at 25 °C.[11] The dimer, the monomer, and potassium osmate each showed a two-electron reduction. Reaction with iodide ions[12] gave a normal reduction of the dimer to Os^{IV} but reduction of the monomer to Os^{III}. Reduction with hydrazine in 1 M KOH at 70 °C gave three-electron reductions for both the dimer and the monomer. Stabilization of the lower valent states of the transition-metal ions by neutral aromatic ligands is a well-known phenomenon.[13]

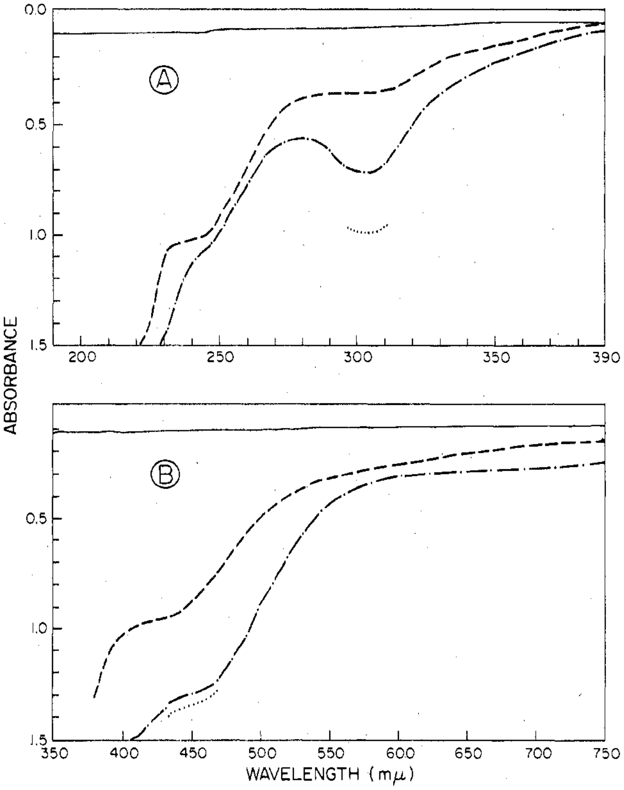

Figure 4. Panel A: (–·–) electronic spectrum of the TMEN dimer (1.53×10^{-4} M) in water recorded 30 min after dissolution; (···) extrapolated time-zero spectrum of the dimer in the vicinity of 305 nm, ϵ_{305nm} 5900 ± 400; (– – –) electronic spectrum of the monomer in water recorded 8 h after dissolving the dimer, ϵ_{305nm} 1000 ± 30. Panel B: (–·–) spectrum of the dimer in phosphate buffer, pH 7 (5.78×10^{-3} M); (···) extrapolated time-zero spectrum of the dimer in the vicinity of 450 nm, ϵ_{450nm} 180; (– – –) spectrum of the monomer recorded 2 h after dissolving the dimer, ϵ_{450nm} 60.

Infrared Spectra. Griffith[14] and his co-workers have established those features of the IR spectra which are useful in characterizing oxoosmium(VI) species. These are a very strong band around 830 cm^{-1} due to the asymmetric stretch of the O=Os=O group, a strong band around 640 cm^{-1} characteristic of the Os_2O_2 bridge system, a band of moderate intensity near 1000 cm^{-1} for the OsO–H bending frequency, and a band around 570 cm^{-1} due in part to the Os–OH stretch. Of these, the first two show no shift upon deuterium substitution. The OsO–H bending frequency shows a characteristically large shift on deuteration, $\nu_H/\nu_D = 1.34$, while the Os–OH stretch shows a small and variable deuterium shift. Table VII lists the observed characteristic bands for both the TMEN and the phen complexes together with the isotopic shifts upon deuterium substitution. For reproductions of these spectra, see ref 10.

UV–Visible Spectra. Both TMEN complexes show maxima at 305 nm and at about 450 nm. This latter band is actually a shoulder on a long tail extending past 750 nm. The spectra are given in Figure 4. Table VIII compares the data for both

Table VIII. UV-Visible Spectra of Oxoosmium(VI) Complexes

complex	medium	λ_{max}, nm (ϵ)
phen monomer (coppery)	water solution	347 sh (870), 425 sh (130), 540 sh?
phen monomer (coppery)	water suspension	355 sh, 420 sh, 535 sh
phen monomer (brown)	Nujol suspension	350 sh
phen dimer	water suspension	350 sh, 440 sh, 605, 690
phen dimer	Nujol suspension	400 sh
TMEN monomer	water solution	305 (1000), 445 sh (60)
TMEN dimer	water solution	305 (5900), 455 sh (180)

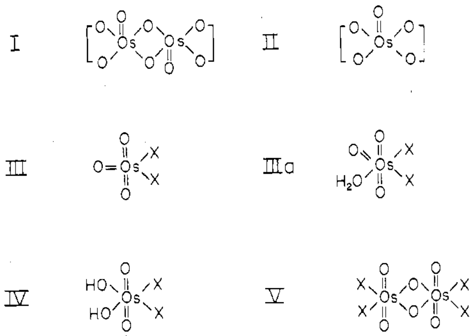

Figure 5. Structures of oxoosmium species.

the TMEN and phen complexes.

Electrophoresis. The TMEN complexes were subjected to electrophoresis at several pH values in order to determine the net charge. No movement was observed following electrophoresis at pH 6.9 (phosphate buffer) or at pH 10 (carbonate buffer).

Discussion

Griffith and his colleagues[15] have shown that the oxoosmium(VI) esters formed by reaction between osmium tetroxide and olefins, long thought to be monomeric species, are in fact dimeric bridged structures, I (Figure 5), although bridged diesters of the type II can be formed under some circumstances. See also Marzilli et al.[9] This tendency of oxoosmium(VI) species to exist as oxo-bridged dimers seems to extend also to the compounds long known as oxyosmyl salts. Wintrebert's formulation was as the monomeric pentacoordinate species III. Griffith,[16] on the basis of vibrational spectroscopy, argued for the monomeric dihydroxo complex of this structure, IV. However, the one structure in this series that has been looked at by X-ray crystallographic techniques,[2] Wintrebert's nitrite complex, is dimeric in the solid state, V. There is some evidence that the simplest member of this general type, potassium osmate, although monomeric in the solid state, undergoes dimerization in solution.[17]

Which form or forms predominate appears to depend on the electron-donating properties or basicity of X. For X = OH^-, the monomeric form IV appears most stable; for X = $^1/_2$ TMEN, both types IV and V have approximately equal stability; for X = $^1/_2$ phen the dimer is strongly favored. This also appears to be true for X = $^1/_2$ bpy. It will be of interest to reinvestigate Wintrebert's complexes for X = Cl, Br, $^1/_2$ oxalate as well as to examine a wider range of nonionic complexes of this sort.

The structures of the TMEN complexes follow without much uncertainty from the empirical formulas, the molecular weight determinations as a function of concentration, the NMR evidence supporting the monomer–dimer relationship, the direct observation of the OsO–H resonance in the NMR, and the IR evidence which is fully in accord with literature data on similar complexes. We therefore propose structures of type IV and V for the monomeric and dimeric TMEN complexes, respectively. Empirical formulas for both the brown phenanthroline monomer and the TMEN monomer require the presence of water in addition to OsO_3L. This can be accommodated either as lattice water with a pentacoordinate complex (III), as coordinated water (IIIa), or as the dihydroxo complex (IV). For the brown phenanthroline monomer, the absence of an IR band near 1645 cm^{-1} is strong evidence in favor of the dihydroxo complex IV.

All three monomeric complexes show two bands characteristic of the OsOH group: the OsO–H bend around 1000 cm^{-1} which shifts to lower frequencies by a factor of about 0.75 upon deuterium substitution and the Os–OH stretch around 570 cm^{-1} which shows a small and variable shift upon deuterium substitution. The recognition of these bands is not easy since the range has not been established for a sufficiently broad variety of complexes. For example, the OsO–H bending frequency for the phen brown monomer is rather lower than expected from the few data in the literature. We make this assignment rather than, for example, a terminal Os═O stretch, on the basis of the deuterium shift. The bands are also frequently difficult to observe because of overlap with ligand bands. For example, the 1015-cm^{-1} absorption in the TMEN monomer is overlapped by two sharp ligand bands; it is observable by a change in shape of these bands and by the deuterium-induced shift. Reproductions of the spectra can be found in ref 10.

We propose that the differences between the two monomeric phen complexes lie only in the hydrogen bonding of lattice water for the copper-colored complex, both because of the similarity of their vibrational and electronic spectra and also because of the great ease with which they are interconverted. For the phenanthroline dimer, the dioxo-bridged structure, type V, seems favored by the evidence, particularly by correlation of the complex of bands around 640 cm^{-1} with a similar set of bands in the known dioxo-bridged dimer, X = NO_2.[18] A monooxo-bridged dimer cannot be excluded absolutely, however. The distinction between a mono- and a dioxo bridge in the absence of an X-ray structure is not easy. The problem has been extensively discussed for some analogous molybdenum complexes.[19] By this analogy, we might expect to see an IR absorption around 700 cm^{-1} for a monooxo-bridged species. This has not been observed.

Both monomer and dimeric forms of the TMEN complexes show transitions around 305 and 450 nm. These bands are assigned to a metal–ligand charge-transfer process and to a d → d* transition, respectively. A band near 450 nm with an extinction coefficient in the range 100–200 M^{-1} cm^{-1} is typical of numerous octahedral oxoosmium(VI) complexes which have been previously examined.[20] The structure of some of these is accurately known from X-ray crystallographic studies.[21]

Both monomeric phenanthroline complexes and the dimeric phenanthroline complex also show a weak transition in the range 430–450 nm. We have been able to measure the extinction coefficient only for the copper-colored phenanthroline complex: the brown complex is converted to the copper-colored complex in solution and the green dimer is too insoluble to allow observation of this transition in solution. The position of the maxima (shoulders) has been measured for these latter two complexes as mulls. We can see, also, that the mull and solution spectra of the copper-colored complex are similar thus suggesting similar structures both in the solid state and in solution.

The mechanism of the conversion of the dimer to the monomer can be accounted for as follows: the fact that excess ligand decreases the rate of monomerization of the dimer must mean that there exists a pathway for monomerization which involves a dimer species from which a ligand molecule has been lost. The fact that the order in ligand is –0.4 rather than –1.0 may imply imply that the undissociated complex can also directly undergo monomerization (hydrolysis). These observations on the effect of excess ligand are similar to our previous observations that excess ligand decreases the rate of transesterification of oxoosmium(VI) esters and also decreases the rate of reaction of osmium(VI) complexes with glycol.

Since the monomerization reaction is a hydrolysis, it is not surprising to find acid catalysis of this process. The dependence on hydrogen ion concentration is close to one in the pH range 5.75–7.0. This is consistent with a mechanism in which the dimer is first protonated and then attacked by water.

TMEN appears to be a promising ligand for oxoosmium(VI) complexes in several respects: the ligand and its complexes have good solubility in water, the complexes are quite inert, and, finally, structural modification of the ligand is quite easy in contrast to synthetic manipulations with aromatic bidentate ligands such as 1,10-phenanthroline and 2,2′-dipyridyl.

A few TMEN–oxoosmium(VI) complexes have been briefly reported from several laboratories.[9,22] A comparative study of various ligands for oxoosmium(VI) systems is underway here.

Experimental Section

Chemicals. Potassium osmate, $K_2OsO_2(OH)_4$, was prepared by ethanol reduction of osmium tetroxide in 1 N KOH.[23] $OS_2O_6(py)_4$ was prepared according to Subbaraman et al.[5] All other chemicals were reagent grade and used as obtained from the usual suppliers.

Instrumentation. Ultraviolet and visible spectral measurements were taken on a Perkin-Elmer 202 instrument, infrared spectra on a Perkin–Elmer 237B or 457 instrument, and proton NMR spectra on a Varian Associates T-60 instrument (60 MHz). Elemental analyses were carried out by Galbraith Laboratories.

Di-μ-oxo-tetraoxobis(*N,N,N′,N′*-tetramethylethylenediamine)diosmium(VI). The dimer was prepared by adding 1.78 mL (1.18 g, 0.01 mol) of *N,N,N′,N′*-tetramethylethylenediamine (TMEN) to a solution of 1 g (0.003 93 mol) of osmium tetroxide in 10 mL of cold acetone containing a few drops of ethanol. The light green crystals were collected after 30 min and washed with acetone. Recrystallization was carried out from water containing a few drops of TMEN. These were washed in acetone and dried at 25 °C in vacuo over P_4O_{10}; yield 61%. Anal. Calcd for $Os_2O_6(C_6H_{16}N_2)_2 \cdot 2H_2O$: C, 19.35; H, 4.87; N, 7.52. Found: C, 19.08; H, 4.95; N, 7.44.

Dioxodihydroxo(*N,N,N′,N′*-tetramethylethylenediamine)osmium(VI). The monomer was best prepared by the addition of 2 mL of *N,N,N′,N′*-tetramethylethylenediamine (TMEN) (0.0114 mol) to a solution of 0.46 g (0.0024 mol) of $Os_2O_6(py)_4$ in 200 mL of water. This solution was stirred at 25 °C for 1 h, filtered, and then taken to dryness in vacuo to yield 0.49 g of the crude product (83%). This material was washed with tetrahydrofuran or carbon tetrachloride and then dried in vacuo. Measurement of the absorption of this material at 305 nm showed that it was about 93% monomer and 7% dimer. An analytically clean sample was obtained by dissolving the crude product in chloroform, filtering to remove dimer, and removal of the solvent in vacuo. We note that during purification of the monomer, there forms a small quantity of dark, perhaps polymeric, material which is removable by gel chromatography. Anal. Calcd for $OsO_2(OH)_2(C_6H_{16}N_2) \cdot 1.5H_2O$: C, 18.04; H, 5.30; N, 7.01. Found: C, 18.22; H, 5.50; N, 6.72.

Dioxodihydroxo(1,10-phenanthroline)osmium(VI) (Two Forms). To 1 g of anhydrous 1,10-phenanthroline (0.0055 mol) dissolved in 350 mL of water at 5 °C is added 1.8 g (0.0049 mol) of potassium osmate, $K_2OsO_2(OH)_4$, freshly dissolved in 10 mL of water. The copper-colored crystals which form are collected after 24 h at 5 °C. The yield is about 90%. The complex is recrystallized by heating 1-g portions in 100 mL of water at 95 °C, filtering rapidly to remove traces of the dimer, and cooling. The crystals must be stored damp. Washing with acetone and drying over P_4O_{10}, 25 °C in vacuo, yields the monomer in the form of brown crystals. The brown crystals are reconverted to the copper-colored crystals by recrystallization from water. Ultraviolet data (aqueous solution, pH 7): λ_{max} 223 nm (ϵ 32 300), 272 (28 300), 296 (sh) (1670), 347 (sh) (870), 430 (sh) (130). Anal. Calcd for $C_{12}H_{10}N_2O_4Os$: C, 33.01; H, 2.29; N, 6.42. Found: C, 33.02, 33.23; H, 2.38, 2.51; N, 6.40, 6.47.

Di-μ-oxo-tetraoxobis(1,10-phenanthroline)diosmium(VI). The conversion of the monomer to the dimer is carried out by boiling a solution of the monomer for 15–20 min in water containing a few drops of acetic acid. The dimer precipitates as a pale green powder during this process. It cannot be recrystallized due to its insolubility. It is freed of traces of the monomer by washing repeatedly with hot water. It is finally washed with acetone and dried over P_4O_{10}, 25 °C, in vacuo. Ultraviolet data (aqueous suspension): λ_{max} 226, 267, 289 (sh), 310 (sh), 335 (sh), 353 (sh), 455 (sh) nm. Anal. Calcd for $C_{24}H_{16}N_4O_6Os_2 \cdot 3H_2O$: C, 32.4; H, 2.49; N, 6.28. Found: C, 32.6; H, 2.85; N, 6.82.

The kinetics of the reaction

$$\mathrm{D} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2\mathrm{M}$$

was followed by two methods. At high concentrations (ca. 0.1 M), the reaction was treated as a reversible first- and second-order system according to eq 77

$$\ln \frac{ax_e + x(a - x_e)}{a(x_e - x)} = k_f \frac{(2a - x_e)}{x_e} t$$

given by Frost and Pearson.[24] Concentration changes were monitored by integration of the NMR resonances. For most purposes, however, it was more convenient to follow the reaction at low concentrations (ca. 2 × 10^{-4} M) by the decrease in absorption at 305 nm as the dimer is converted to the monomer. At these concentrations, there is less than 1% dimer at equilibrium and hence the system can be simply treated as an irreversible first-order system. Plots of ln $(A_t - A_\infty)$ were linear with time. The first-order rate constants, k_f, were taken from the slopes of these plots.

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Registry No. TMEN dimer, 69531-94-8; TMEN monomer, 69531-95-9; phen dimer, 69531-96-0; phen monomer, 69531-97-1; OsO_4, 20816-12-0; $Os_2O_6(py)_4$, 38641-68-8; $K_2OsO_2(OH)_4$, 31429-76-2.

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High-Pressure Phase Transformation Studies of $M_{1-x}Rh_xSe_2$ (M = Pd, Pt)

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Members of the system $Pd_{1-x}Rh_xSe_2$, prepared at ambient pressure, consisted of mixtures of $PdSe_2$ and $RhSe_2$. Compositions with $x \geq 0.3$, subjected to a pressure of 50 kbar and 1000 °C, gave a single-phase region crystallizing with the pyrite structure. For the system $Pt_{1-x}Rh_xSe_2$ ($x \leq 0.4$) sample preparation at 1000 °C and ambient pressure yielded a solid solution crystallizing with a CdI_2 structure. A high-pressure phase transformation was not observed for this system at 50-kbar pressure and 1000 °C.

Introduction

A number of transition-metal ditellurides may be induced to undergo a high-pressure phase transformation from a cadmium iodide structure to a pyrite structure by chemical substitution. Among the systems which have been studied are $Ni_{1-x}Fe_xTe_2$[1] and $Pd_{1-x}Rh_xTe_2$.[2] Although $NiTe_2$ undergoes only a partial transformation from a cadmium iodide structure to a pyrite structure at 89 kbar,[3] a single-phase pyrite region may be obtained for the system $Ni_{1-x}Fe_xTe_2$ ($0.4 \leq x \leq 0.8$) at 60-kbar pressure.[1] $PdTe_2$ also crystallizes with the cadmium iodide structure at ambient pressure. However, at 60-kbar pressure a complete transformation to a pyrite phase was obtained for $Pd_{1-x}Rh_xTe_2$ ($x \geq 0.6$).[2]

At ambient pressure $PdSe_2$ crystallizes with a layer structure (space group *Pbca*; $a = 5.741$ Å, $b = 5.866$ Å, $c = 7.691$ Å). Grønvold and Røst[4] have indicated that $PdSe_2$ may be described in terms of an elongated pyrite structure. At pressures as high as 65 kbar, Bither[5] observed only a compression of the structure in the interlayer direction but he did not report a transformation to the pyrite structure. He also noted that high-pressure synthesis of rhodium-substituted $PdSe_2$ yielded a mixture containing a $PdSe_2$ high-pressure orthorhombic phase and a pyrite phase ($a \sim 6.12$ Å). $RhSe_2$ has been reported to adopt either an orthorhombic $IrSe_2$ structure[6] (*Pnam* with $a = 20.91$ Å, $b = 5.951$ Å, $c = 3.709$ Å) at room temperature or a pyrite structure ($a \sim 6.01$ Å, extrapolated value) at high temperature.[7] Comparison of the cell constants for these two pyrite phases indicates that the pyrite phase obtained by Bither[5] for rhodium-substituted $PdSe_2$ contains rhodium.

$PtSe_2$ crystallizes with the CdI_2 structure (space group $P\bar{3}m1$; $a = 3.724$ Å, $c = 5.062$ Å). High-pressure phase transformations for $PtSe_2$ have not been reported.

The systems $M_{1-x}Rh_xSe_2$ (M = Pd, Pt) were investigated both at ambient pressure and under high pressure in order to determine the extent of solid solution and the effect of the rhodium substitution for palladium and platinum on the existence of high-pressure phases.

Table I. Lattice Constants and Densities for $Pd_{1-x}Rh_xSe_2$ Phases Obtained at 50-kbar Pressure and 1000 °C

phase	a_0, Å	ρ_{exptl}, g/cm^3	ρ_{calcd}, g/cm^3
$Pd_{0.7}Rh_{0.3}Se_2$	6.123 (2)	7.5 (1)	7.62
$Pd_{0.6}Rh_{0.4}Se_2$	6.109 (2)	7.6 (1)	7.66
$Pd_{0.4}Rh_{0.6}Se_2$	6.076 (2)	7.7 (1)	7.76
$Pd_{0.2}Rh_{0.8}Se_2$	6.048 (2)	7.8 (1)	7.85
$RhSe_2$	6.018 (2)	7.9 (1)	7.95

Experimental Section

All polycrystalline samples were prepared by reacting stoichiometric quantities of the elements in evacuated silica tubes. The samples were heated for 1 week with several intermittent grindings. At the end of each heat treatment the samples were cooled to room temperature at the rate of 100 °C/h.

The reacted polycrystalline samples were subjected to 1000 °C and 50-kbar pressure for $1^1/_2$ h in a belt apparatus described by Hall.[8] Reactions were not carried out at higher temperatures in order to avoid decomposition of the products. At the end of each experiment, the sample was allowed to cool for 15 min and the pressure was then reduced to 1 atm (ambient pressure).

The phases present in each sample were identified from powder patterns obtained with a Norelco diffractometer equipped with a high-intensity copper source and a graphite monochromator (λ(Cu Kα) 1.5418 Å) located in the diffracted beam. Lattice parameters were calculated from a least-squares refinement using 2θ angles corrected relative to a KCl internal standard. Densities were measured by the hydrostatic technique described by Adams.[9] Perfluoro(1-methyldecalin) served as the density fluid which was calibrated with a high-purity silicon crystal ($\rho = 2.33$ g/cm^3 at 25 °C).

Results

Ambient Pressure. For the system $Pd_{1-x}Rh_xSe_2$ ($0.1 \leq x \leq 0.9$) the products obtained at 750 °C and ambient pressure contained three structure types, namely, $PdSe_2$, $RhSe_2$ ($IrSe_2$ structure), and $RhSe_2$ (pyrite structure).

For the system $Pt_{1-x}Rh_xSe_2$ ($x \leq 0.4$) sample preparation at 1000 °C yielded a single-phase region with the CdI_2

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