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Osmium(III)–Osmium(II) Electrode Potentials. The Effects of Charge, Conjugation, Coordinated Halide, and Substitution in the Ligand

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Electrode potentials for a variety of osmium(III)–osmium(II) complexes containing pyridine, 2,2′-bipyridine, and 2,2′,2″-terpyridine have been measured in aqueous solution. The effect of lowering the over-all ionic charge has been studied in the $[Os(trpy)(bipy)(py)]^{3+,2+}$, $[Os(bipy)_2(py)_2]^{3+,2+}$, and $[Os(bipy)(py)_4]^{3+,2+}$ couples, by replacing pyridine by a chloride ion. The effect of decreasing the degree of conjugation has been studied by substituting pyridine for bipyridine in the $[Os(bipy)_3]^{3+,2+}$ couple and bipyridine + pyridine for terpyridine in the $[Os(trpy)_2]^{3+,2+}$ couple, and the observed stabilization of osmium(III) of 0.03 to 0.1 v is discussed in terms of metal–ligand π bonding. Potentials for the $[Os(trpy)(bipy)X]^{2+,+}$, $[Os(bipy)_2(py)X]^{2+,+}$, and $[Os(bipy)(py)_3X]^{2+,+}$ couples (X = Cl, Br, I) show an order dependent on the remaining aromatic ligands. Potentials for the series $[Os(trpy)(bipy)(Rpy)]^{3+,2+}$ (R = H, 3-CH_3, 4-CH_3, 4-C_2H_5, 4-*i*-C_3H_7) show an order which is not linearly dependent on the basic strength of the substituted pyridine but is consistent with a hyperconjugative treatment.

Introduction

The most accurate method for measuring electrode potentials of metal complexes requires that the compounds be stable in both oxidation states[2] which means that the potentials lie about the range 0.1 to 0.9 v in aqueous solution. Unfortunately, few complexes have their potentials in this region, and most of those that do are labile with respect to dissociation of their ligands and do not permit extensive alterations of the complex structure either at the metal site or in the surrounding ligands. In order to carry out a precise study of changes in potential resulting from variations in coordination, it is desirable that only the oxidant and reductant species be present in the half-cell and that hydrolysis products be excluded. These requirements limit severely those compounds which are suitable for such studies. For example, the iron(III)–iron(II) tris(phenanthroline), tris(bipyridine), and bis(terpyridine) couples have potentials in the vicinity of 1.1 v, and the iron(III) compound is unstable to reduction in aqueous solution. The potential is then determined by the half-equivalence or potentiometric titration procedures, the accuracy of which depends on the relative rates of establishment of equilibrium at the electrode surface and decay of the unstable state. Moreover, some iron(II) complexes containing only one or two phenanthroline or bipyridine ligands coordinated to the metal disproportionate rapidly in aqueous solutions.

Numerous osmium(III)–osmium(II) systems containing one, two, or three molecules of 1,10-phenanthroline or 2,2′-bipyridine have reduction potentials in the vicinity of 0.8 v, and both valency states can usually be isolated. Moreover, the complexes are kinetically inert with respect to disproportionation or dissociation of their ligands, and the couples are reversible. For these reasons the systems are ideal for a study of the above kind.

The thermodynamic potential $E°$ for an osmium(III)–osmium(II) half-cell measures the standard free energy change for the reaction

$$Os(III)L_x^{(n+1)+} + {}^1/_2H_2 \longrightarrow Os(II)L_x^{n+} + H^+ \qquad (1)$$

since the standard free energy change $\Delta G° = -FE°$ for a one-electron reduction. The contributions to the measured potential and hence to $\Delta G°$ may be considered to be derived from the osmium(II) ionization potential I, the difference in enthalpy of formation of the complexes in the gaseous state $\Delta(\Delta H°_c)$

$$\Delta(\Delta H°_c) = \Delta H°_c[Os(II)] - \Delta H°_c[Os(III)]$$

the difference in the hydration enthalpies of the complex ions $\Delta(\Delta H°_{aq})$

$$\Delta(\Delta H°_{aq}) = \Delta H°_{aq}[Os(II)] - \Delta H°_{aq}[Os(III)]$$

and the partial molar entropy difference $\Delta\bar{S}°$ between the complex ions. For differing osmium(III)–osmium(II) couples these factors can be compared using the expression

$$\Delta G° = -I + \Delta(\Delta H°_c) + \Delta(\Delta H°_{aq}) - T\Delta\bar{S}° + {}^1/_2TS°[H_2(g)] \qquad (2)$$

Since the ionization potential remains a constant factor, changes in electrode potential found for a related series of osmium(III)–osmium(II) couples may be attributed to a combination of $\Delta(\Delta H°_c)$, $\Delta(\Delta H°_{aq})$, and $\Delta\bar{S}°$ factors.

Experimental Section

The half-cells were constructed from 50-ml lipless beakers fitted with treated rubber stoppers. Each stopper was drilled with four holes, two for the etched gold electrodes (1 cm²), one for the N_2 inlet, and one for a saturated KCl salt bridge. The cells were thoroughly cleaned in chromic acid solution and washed with conductivity water many times before use, and the gold electrodes were left in conductivity water when not in use. The maximum difference between the potential measured at the two electrodes was 0.2 mv and polarization effects were found to be negligible. The mean reading was accepted. The solutions and electrodes were equilibrated within 5 min in all instances.

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(1) Deceased.

(2) D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press Inc., New York, N. Y., p 242.

TABLE I

THE TEMPERATURE DEPENDENCE OF THE POTENTIALS OF THE REFERENCE ELECTRODES AND SOME OSMIUM(III)–OSMIUM(II) COUPLES (IN VOLTS)

Temp, °C	Calomel–hydroquinone (mean)	Hydroquione[a] at pH 4.00	Saturated calomel	$[Os(bipy)_3]^{3+,2+}$	$[Os(bipy)_2(py)Cl]^{2+,}$
25 ± 0.005	0.2171	0.4623	0.2452	0.8847	0.4836
30 ± 0.01	0.2122	0.4546	0.2424	0.8817	0.4785
10 ± 0.05	0.2301	0.4854	0.2553	0.8947	0.4959

[a] F. P. Dwyer, personal communication.

The saturated calomel half-cells[3] were prepared 6 months before use and allowed to equilibrate for 2 weeks at each temperature. They were calibrated against the quinhydrone electrode prepared[4] from twice-recrystallized AR quinhydrone in fresh potassium hydrogen phthalate buffer (0.05 *M*). The quinhydrone solution was equilibrated with the gold electrodes in the presence of a slow stream of nitrogen. After 20 min the N_2 was stopped, the KCl salt bridge was dried and inserted, and the potential was measured. The potential could be reproduced to within 0.05 mv, and, using this procedure, the potential of the calomel electrode was found to be constant, ±0.1 mv, when measured frequently during a period of 18 months at 25° (Table I).

The potentials of the cells were measured using a Pye Vernier potentiometer (No. 7568) reading to 0.01 mv. A Scalamp high-resistance galvanometer (Model 7904/S) was used as a null detector to obtain potential balance.

Equimolar quantities of the osmium(II) and osmium(III) complexes[5] were accurately weighed out to make the final solution between 0.00025 and 0.000125 *M* with respect to each complex. The concentration depended on the couple being studied and was usually governed by the solubility of the osmium(II) compound. The corresponding osmium(II) and osmium(III) complexes were placed in a 100-ml standard flask and made up to volume with conductivity water. In those instances where the potential was more positive than 0.6 v, 0.1 ml of 0.1 *M* HNO_3 was added to stabilize the osmium(III) state with respect to the oxygen couple. The oxidation–reduction solution (10 ml) and KCl solution (10 ml) were pipeted into the oxidation–reduction cell and the mixture was equilibrated with the gold electrode in a thermostat under nitrogen. After 20 min the nitrogen was stopped, the salt bridge was inserted, and the potential was measured at the two gold electrodes in turn. The mean value for E (μ) is recorded in the next section. The potentials did not vary by more than 0.02 mv over several hours at the same electrode. Potential measurements repeated on freshly prepared compounds agreed within 0.2 mv, and in those instances where the compounds were prepared by different routes, the same agreement was obtained.

A saturated KCl salt bridge was used to minimize and keep constant the liquid junction potential.[6] The potential values obtained, extrapolated to ionic strength $\mu = 0$, are referred to as $E°$ values although they may contain a small contribution from the junction potential. However, this junction potential is not significant in the present investigation where the values are compared with one another.

Results

The mean E (μ) values listed below are the measured potentials for the couples against the calomel electrode (0.2452 v) at 25°. $E°$ given in Tables III–VI was evaluated from the plot of E against $\sqrt{\mu}/(1 + \sqrt{\mu})$.

$[Os(trpy)(bipy)(py)](ClO_4)_3$–$[Os(trpy)(bipy)(py)](ClO_4)_2$: 0.6033 (0.0272), 0.6050 (0.0222), 0.6072 (0.0170), 0.6101 (0.0123), 0.6112 (0.0098), 0.6131 (0.0071), 0.6158 (0.0048), 0.6186 (0.0022).

$[Os(bipy)_3](ClO_4)_3$–$[Os(bipy)_3](ClO_4)_2$: 0.6199 (0.0222), 0.6219 (0.0170), 0.6244 (0.0125), 0.6258 (0.0098), 0.6278 (0.0071), 0.6293 (0.0048), 0.6325 (0.0022).

$[Os(bipy)_2(py)_2](ClO_4)_3$–$[Os(bipy)_2(py)_2](ClO_4)_2$: 0.5707 (0.0222), 0.5733 (0.0148), 0.5760 (0.0098), 0.5780 (0.0071), 0.5801 (0.0048), 0.5826 (0.0022).

$[Os(trpy)(py)_3](ClO_4)_3$–$[Os(trpy)(py)_3](ClO_4)_2$: 0.5338 (0.0170), 0.5367 (0.0125), 0.5385 (0.0098), 0.5407 (0.0071), 0.5431 (0.0048), 0.5465 (0.0022).

$[Os(bipy)(py)_4](ClO_4)_3$–$[Os(bipy)(py)_4](ClO_4)_2$: 0.5396 (0.0222), 0.5406 (0.0184), 0.5428 (0.0148), 0.5456 (0.0098), 0.5477 (0.0071), 0.5497 (0.0048), 0.5529 (0.0022).

$[Os(trpy)(bipy)Cl]Cl_2$–$[Os(trpy)(bipy)Cl]Cl$: 0.3074 (0.0205), 0.3094 (0.0130), 0.3100 (0.0104), 0.3112 (0.0080), 0.3120 (0.0056), 0.3132 (0.0029), 0.3150 (0.0005).

$[Os(trpy)(bipy)Br](ClO_4)_2$–$[Os(trpy)(bipy)Br]Cl$: 0.3122 (0.0205), 0.3142 (0.0130), 0.3149 (0.0104), 0.3158 (0.0080), 0.3168 (0.0056), 0.3182 (0.0029), 0.3201 (0.0005).

$[Os(trpy)(bipy)I](ClO_4)_2$–$[Os(trpy)(bipy)I]Cl$: 0.3112 (0.0205), 0.3123 (0.0155), 0.3129 (0.0130), 0.3148 (0.0080), 0.3161 (0.0056), 0.3170 (0.0029), 0.3194 (0.0005).

$[Os(bipy)_2(py)Cl](ClO_4)_2$–$[Os(bipy)_2(py)Cl]Cl$: 0.2275 (0.0205), 0.2281 (0.0184), 0.2284 (0.0157), 0.2294 (0.0130), 0.2300 (0.0104), 0.2310 (0.0080), 0.2343 (0.0029), 0.2355 (0.0005).

$[Os(bipy)_2(py)Br](ClO_4)_2$–$[Os(bipy)_2(py)Br]Cl$: 0.2307 (0.0205), 0.2317 (0.0184), 0.2323 (0.0157), 0.2330 (0.0130), 0.2337 (0.0104), 0.2347 (0.0080), 0.2375 (0.0029), 0.2399 (0.0005).

$[Os(bipy)_2(py)I](ClO_4)_2$–$[Os(bipy)_2(py)I]Cl$: 0.2323 (0.0205), 0.2337 (0.0157), 0.2344 (0.0130), 0.2350 (0.0104), 0.2362 (0.0080), 0.2392 (0.0029), 0.2420 (0.0005).

$[Os(bipy)(py)_3Cl](ClO_4)_2$–$[Os(bipy)(py)_3Cl]Cl$: 0.1703 (0.0205), 0.1712 (0.0155), 0.1722 (0.0130), 0.1729 (0.0104), 0.1737 (0.0080), 0.1746 (0.0056), 0.1761 (0.0029), 0.1785 (0.0005).

$[Os(bipy)(py)_3Br](ClO_4)_2$–$[Os(bipy)(py)_3Br]Cl$: 0.1895 (0.0205), 0.1904 (0.0155), 0.1912 (0.0130),

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[3] F. Daniels, J. H. Mathews, and J. W. Williams in "Experimental Physical Chemistry," 3rd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 373.

[4] See ref 3, p 197.

[5] The methods for preparing the complexes used in this study are described in the following publications: D. A. Buckingham, F. P. Dwyer, H. A. Goodwin, and A. M. Sargeson, *Australian J. Chem.*, **17**, 315, 325 (1964); D. A. Buckingham, F. P. Dwyer, and A. M. Sargeson, *ibid.*, **17**, 622 (1964).

[6] E. A. Guggenheim, *J. Am. Chem. Soc.*, **52**, 1315 (1930).

0.1921 (0.0104), 0.1927 (0.0080), 0.1933 (0.0056), 0.1950 (0.0029), 0.1968 (0.0005).

$[Os(bipy)(py)_3I](ClO_4)_2$–$[Os(bipy)(py)_3I]Cl$: 0.1703 (0.0205), 0.1712 (0.0155), 0.1722 (0.0130), 0.1729 (0.0104), 0.1737 (0.0080), 0.1746 (0.0056), 0.1761 (0.0029), 0.1785 (0.0005).

$[Os(bipy)_2(acac)](ClO_4)_2$–$[Os(bipy)_2(acac)](ClO_4)$: 0.0818 (0.0262), 0.0829 (0.0212), 0.0840 (0.0159), 0.0856 (0.0110), 0.0868 (0.0061), 0.0894 (0.0010).

$[Os(trpy)(bipy)(3\text{-}CH_3py)](ClO_4)_3$–$[Os(trpy)(bipy)(3\text{-}CH_3py)](ClO_4)_2$: 0.5993 (0.0272), 0.6010 (0.0222), 0.6032 (0.0170), 0.6045 (0.0148), 0.6059 (0.0123), 0.6074 (0.0098), 0.6094 (0.0071), 0.6116 (0.0048), 0.6146 (0.0022).

$[Os(trpy)(bipy)(4\text{-}C_3H_7py)](ClO_4)_3$–$[Os(trpy)(bipy)(4\text{-}C_3H_7py)](ClO_4)_2$: 0.5934 (0.0272), 0.5953 (0.0222), 0.5975 (0.0170), 0.5985 (0.0148), 0.5998 (0.0123), 0.6015 (0.0098), 0.6031 (0.0071), 0.6055 (0.0048), 0.6083 (0.0022).

$[Os(trpy)(bipy)(4\text{-}C_2H_5py)](ClO_4)_3$–$[Os(trpy)(bipy)(4\text{-}C_2H_5py)](ClO_4)_2$: 0.5918 (0.0272), 0.5937 (0.0222), 0.5960 (0.0170), 0.5970 (0.0148), 0.5983 (0.0123), 0.5998 (0.0098), 0.6014 (0.0071), 0.6039 (0.0048), 0.6064 (0.0022).

$[Os(trpy)(bipy)(4\text{-}CH_3py)](ClO_4)_3$–$[Os(trpy)(bipy)(4\text{-}CH_3py)](ClO_4)_2$: 0.5853 (0.0222), 0.5874 (0.0170), 0.5888 (0.0148), 0.5903 (0.0123), 0.5918 (0.0098), 0.5937 (0.0071), 0.5957 (0.0048), 0.5987 (0.0022).

Discussion

The experiments were designed to determine the effect on $E°$ of (a) the over-all charge on the complex, (b) conjugation in the ligands, (c) substitution at the metal with halide ions, and (d) substitution in the ligand. The results are given in Tables II to VI.

It is desired to relate the $E°$ values to the factors in eq 2, and for this reason some discussion of the magnitude of the entropy term is required. From $E°$ measurements over the temperature range 10–30°, $\Delta\bar{S}°$ for the $[Os(bipy)_3]^{3+,2+}$ couple was calculated as 0.4 ± 1 eu. This is to be compared with the value of 0.8 ± 1 eu calculated by George, Hanania, and Irvine[7] from a previous measurement by Dwyer, *et al.*[8] A similar experiment using the $[Os(bipy)_2(py)Cl]^{2+,+}$ couple gave a value of $\Delta\bar{S}° = -5.1 \pm 1$ eu. Table II compares these results with those of closely related couples. It will be noted that the magnitude of $\Delta\bar{S}°$ decreases rapidly with increasing ionic size and is close to zero for the tris(phenanthroline) and tris(bipyridine) couples of iron, ruthenium, and osmium. It is likely that this decrease is associated with the decrease in surface charge density of the ions and hence with their ability to deform the water structure. It follows that, when comparing couples of similar charge and large size, as in this investigation, the contribution of $\Delta\bar{S}°$ to $\Delta G°$ will be small.

Effect of Charge.—Table III gives $E°$ values arranged such that consecutive couples differ only by Cl^- replacing a pyridine molecule.

TABLE II

PARTIAL MOLAR ENTROPY DIFFERENCES FOR SOME COMPLEX IONS

Couple	$\Delta\bar{S}°$, cal mole^{-1} deg^{-1}
$\bar{S}°[Fe(CN)_6]^{4-} - \bar{S}°[Fe(CN)_6]^{3-}$	-48^a
$\bar{S}°[Fe(H_2O)_6]^{2+} - \bar{S}°[Fe(H_2O)_6]^{3+}$	43^b
$\bar{S}°[Fe(phen)_3]^{2+} - \bar{S}°[Fe(phen)_3]^{3+}$	-5.2 ± 2^a
$\bar{S}°[Fe(bipy)_3]^{2+} - \bar{S}°[Fe(bipy)_3]^{3+}$	-8.2 ± 2^a
$\bar{S}°[Ru(bipy)_3]^{2+} - \bar{S}°[Ru(bipy)_3]^{3+}$	-0.2 ± 2^a
$\bar{S}°[Os(bipy)_3]^{2+} - \bar{S}°[Os(bipy)_3]^{3+}$	0.8 ± 1^a 0.4 ± 1^c
$\bar{S}°[Os(bipy)_2(py)Cl]^{+} - \bar{S}°[Os(bipy)_2(py)Cl]^{2+}$	-5.1 ± 1^c
$\bar{S}°[IrCl_6]^{4-} - \bar{S}°[IrCl_6]^{3-}$	-19.6^a

[a] See ref 7. [b] W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., p 221. [c] This work.

TABLE III

ELECTRODE POTENTIALS OF OSMIUM(III)–OSMIUM(II) COUPLES AT 25°: THE EFFECT OF CHARGE

Couple (2.5×10^{-4} *M*)	Exptl slope, mv/$\frac{0.1\sqrt{\mu}}{1+\sqrt{\mu}}$	$E°$, v	$\Delta E°$, v
$[Os(trpy)(bipy)(py)](ClO_4)_3$–$[Os(trpy)(bipy)(py)](ClO_4)_2$	16.4	0.8713	
			−0.3085
$[Os(trpy)(bipy)Cl]Cl_2$–$[Os(trpy)(bipy)Cl]Cl$	8.3	0.5628	
$[Os(bipy)_2(py)_2](ClO_4)_3$–$[Os(bipy)_2(py)_2](ClO_4)_2$	15.1	0.8345	
			−0.3509
$[Os(bipy)_2(py)Cl](ClO_4)_2$–$[Os(bipy)_2(py)Cl]Cl^a$	8.9	0.4836	
$[Os(bipy)(py)_4](ClO_4)_3$–$[Os(bipy)(py)_4](ClO_4)_2$	16.0	0.8052	
			−0.3797
$[Os(bipy)(py)_3Cl](ClO_4)_2$–$[Os(bipy)(py)_3Cl]Cl^a$	8.1	0.4255	
$[Os(bipy)_3](ClO_4)_3$–$[Os(bipy)_3](ClO_4)_2$	15.2	0.8847	
			−0.7317
$[Os(bipy)_2(acac)](ClO_4)_2$–$[Os(bipy)_2(acac)](ClO_4)^{a,b}$	7.3	0.1530	

[a] 1.25×10^{-4} *M*. [b] acac = 2,4-pentanedione.

The two largest contributions to $E°$, excluding the ionization potential, are $\Delta H°_{aq}$ and $\Delta H°_c$. The first term may be estimated from the Born charging expression

$$\Delta H°_{aq} = \frac{-Z^2e^2}{2r}\left(1 - \frac{1}{D}\right) + T/D^2\left(\frac{dD}{dT}\right)_P$$

where D is the continuous medium dielectric constant and r the radius of a spherical cavity bearing a charge Ze. If complex ions are regarded as charged spheres, this expression reduces to $\Delta H°_{aq} = -167Z^2/r$ kcal/mole at 25° in water. In the absence of experimental values for the ionic radii for these large complex ions $\Delta(\Delta H°_{aq})$ cannot be directly calculated. However, it is likely that $r[Os(II)] \geq r[Os(III)]$ making $\Delta(\Delta H°_{aq})$ positive (eq 2); that is, the osmium(III) state is stabilized. If the over-all charge is now reduced by 1 unit while keeping the ions essentially spherical, as in the [Os-

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(7) P. George, G. I. H. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 2548 (1959).

(8) G. T. Barnes, F. P. Dwyer, and E. C. Gyarfas, *Trans. Faraday Soc.*, **48**, 269 (1952).

$(bipy)_2(py)Cl]^{2+,+}$ couple, the magnitude of $\Delta(\Delta H^\circ_{aq})$ will be reduced since it is dependent on the square of the charges. That is, the $\Delta(\Delta H^\circ_{aq})$ contribution to ΔG° should make E° of the $[Os(bipy)_2(py)Cl]^{2+,+}$ couple *more* positive than that for the $[Os(bipy)_2(py)_2]^{3+,2+}$ couple.

It is convenient to divide the $\Delta(\Delta H^\circ_c)$ term of expression 2 into two contributions—the ligand field stabilization energy difference, $\Delta(\Delta H^\circ_{LF})$, and $\Delta(\Delta H^\circ_{c'})$, the enthalpy change if no ligand field effect is present

$$\Delta(\Delta H^\circ_c) = \Delta(\Delta H^\circ_{LF}) + \Delta(\Delta H^\circ_{c'}) \qquad (3)$$

The $\Delta(\Delta H^\circ_{c'})$ term will include all electrostatic, covalent, polarization, and steric effects not present in $\Delta(\Delta H^\circ_{LF})$ and will be the major contribution to $\Delta(\Delta H^\circ_c)$. Unfortunately, there is no experimental information on the magnitude of $\Delta H^\circ_{c'}$ factors for osmium compounds, but if we assume an electrostatic picture of complex formation, the $\Delta(\Delta H^\circ_{c'})$ terms should parallel the difference $3/r^2[Os(III)] - 2/r^2[Os(II)]$, where r is in this case the radius of the gaseous metal ion. This would predict positive $\Delta(\Delta H^\circ_{c'})$ contributions to ΔG° with a consequent stabilization of the osmium(III) state. From this purely electrostatic picture the interaction of a Cl^- ion with the metal will be greater than the interaction of pyridine which in turn will make $\Delta(\Delta H^\circ_{c'})$ for the $[Os(bipy)_2(py)Cl]^{2+,+}$ couple positive in sign but less numerically than the corresponding value for the $[Os(bipy)_2(py)]^{3+,2+}$ couple. The $\Delta(\Delta H^\circ_{c'})$ factor will then make E° *more negative* on substituting Cl^- for pyridine. The covalent and steric factors should also be included in estimating the magnitude of $\Delta H^\circ_{c'}$, but we conclude that such considerations will not change the above order.

The ligand field term $\Delta(\Delta H^\circ_{LF})$ is small in comparison to $\Delta(\Delta H^\circ_{c'})$ even though the Cl^- ion has a ligand field stabilization energy appreciably different from that of pyridine. If this term contributes at all to ΔG°, it probably does so through a slight destabilization of the osmium(II) state on substituting a Cl^- ion for pyridine.

The above discussion then predicts that, on lowering the over-all charge on the complex ions, the $\Delta(\Delta H^\circ_{c'})$ and $\Delta(\Delta H^\circ_{LF})$ terms will make ΔE° negative while $\Delta(\Delta H^\circ_{aq})$ will have the opposite effect, tending to make ΔE° positive. $\Delta \bar{S}^\circ$ was found (Table II) to be about 5 eu or -0.07 v so that purely ΔH factors will be obtained if this contribution is subtracted from the ΔE° observed. In every case ΔE° was found to be negative (Table III) so we must conclude that the $\Delta(\Delta H^\circ_{c'})$ plus $\Delta(\Delta H^\circ_{LF})$ factors are larger than $\Delta(\Delta H^\circ_{aq})$, with $\Delta(\Delta H^\circ_{c'})$ probably making the greatest contribution.

A similar change in potential was observed for the bromo and iodo couples $[Os(bipy)_2(py)X]^{2+,+}$ (X = Br, I), Table V, and also for the case where bipyridine was replaced by acetylacetone, Table III. The larger negative ΔE° found for the latter couple is in keeping with the known ability of bipyridine compared with acetylacetone in stabilizing low-valency states, particularly spin-paired d^6 systems. We have observed that the potential for the $[Os(bipy)_2Cl_2]^{+,0}$ couple $E \sim -0.1$ v is similar to that found for the $[Os(bipy)_2(acac)]^{2+,+}$ couple.

Effect of Chelation.—Table IV lists E° values for three sets of couples in which the ligand conjugation has been successively decreased.

TABLE IV

ELECTRODE POTENTIALS FOR OSMIUM(III)–OSMIUM(II) COUPLES AT 25°: THE EFFECT OF CONJUGATION

Couple (2.5×10^{-4} *M*)	Exptl slope, $\text{mv}\Big/\dfrac{0.1\sqrt{\mu}}{1+\sqrt{\mu}}$	E°, v	ΔE°, v
$[Os(bipy)_3](ClO_4)_3$–$[Os(bipy)_3](ClO_4)_2$	15.2	0.8847	
			−0.0502
$[Os(bipy)_2(py)_2](ClO_4)_3$–$[Os(bipy)_2(py)_2](ClO_4)_2$	15.1	0.8345	
			−0.0293
$[Os(bipy)(py)_4](ClO_4)_3$–$[Os(bipy)(py)_4](ClO_4)_2$	16.0	0.8052	
$[Os(trpy)_2](ClO_4)_3$–$[Os(trpy)_2](ClO_4)_2$[a]	16.6	0.9866	
			−0.1153
$[Os(trpy)(bipy)(py)](ClO_4)_3$–$[Os(trpy)(bipy)(py)](ClO_4)_2$	16.4	0.8713	
			−0.0714
$[Os(trpy)(py)_3](ClO_4)_3$–$[Os(trpy)(py)_3](ClO_4)_2$	18.0	0.7999	
$[Os(trpy)(bipy)Cl]Cl_2$–$[Os(trpy)(bipy)Cl]Cl$	8.3	0.5628	
			−0.0792
$[Os(bipy)_2(py)Cl](ClO_4)_2$–$[Os(bipy)_2(py)Cl]Cl$	8.9	0.4836	
			−0.0581
$[Os(bipy)(py)_3Cl](ClO_4)_2$–$[Os(bipy)(py)_3Cl]Cl$	8.1	0.4255	

[a] F. P. Dwyer and E. C. Gyarfas, *J. Am. Chem. Soc.*, **76,** 6320 (1954).

For each series of couples given in Table IV the ionic size and charge of the osmium(II) and osmium(III) ions remain unaltered. The $\Delta(\Delta H^\circ_{aq})$ contribution to ΔG° will therefore remain essentially constant and $\Delta \bar{S}^\circ$ small and constant. Changes in potential resulting from changes in conjugation in the ligands must therefore reside in $\Delta(\Delta H^\circ_{c'})$ and $\Delta(\Delta H^\circ_{LF})$ factors.

The stability constants of pyridine, bipyridine, and terpyridine complexes cannot be correlated with the basic strength of these ligands and hence with the availability of σ electrons at the donor nitrogen atoms, and it is almost certainly the π-bonding properties of these ligands which account for the stability of their complexes. Further, in these osmium(III)–osmium(II) couples the electron involved in oxidation comes ultimately from a filled π-bonding orbital based mainly on osmium(II), that is, primarily a metal t_{2g} orbital involved in π bonding with the ligand. It is therefore to be expected that E° for such couples will be strongly dependent on the degree of stabilization of these π orbitals and this will be greater for osmium(II) than osmium(III), which has one less electron. The decrease in conjugation, terpyridine > bipyridine + pyridine > three pyridines, may be correlated with a decreasing ability to form metal-to-ligand π bonds and a consequent destabilization of this level. This would result in a relative stabilization of osmium(III) as terpyridine is successively substituted by bipyridine and pyridine and is in agreement with the observed potential order.

The $\Delta(\Delta H^\circ_{c}{}')$ terms are not easy to assess for these couples, but, if we assume that the cumulative polarizability of three pyridines is less than terpyridine and that osmium(III) is a "harder" acid than osmium(II), then osmium(II) would be stabilized for terpyridine, and its potential would tend to be the more negative. This is in agreement with the observed potential order.

Effect of Halide Substitution.—The three sets of complexes containing coordinated Cl^-, Br^-, and I^- showed a variation in E° which depended on the remaining ligands (Table V).

TABLE V

ELECTRODE POTENTIALS OF OSMIUM(III)–OSMIUM(II) COUPLES AT 25°: THE EFFECT OF COORDINATED HALIDE

Couple (1.25×10^{-4} *M*)	Exptl slope, mv$\Big/\dfrac{0.1\sqrt{\mu}}{1+\sqrt{\mu}}$	E°, v	ΔE°, mv
$[Os(trpy)(bipy)Br](ClO_4)_2$–$[Os(trpy)(bipy)Br]Cl$	8.1	0.5675	
			−0.9
$[Os(trpy)(bipy)I](ClO_4)_2$–$[Os(trpy)(bipy)I]Cl$	8.4	0.5666	
			−3.8
$[Os(trpy)(bipy)Cl]Cl_2$–$[Os(trpy)(bipy)Cl]Cl$[a]	8.3	0.5628	
$[Os(bipy)_2(py)I](ClO_4)_2$–$[Os(bipy)_2(py)I]Cl$	9.1	0.4888	
			−1.7
$[Os(bipy)_2(py)Br](ClO_4)_2$–$[Os(bipy)_2(py)Br]Cl$	8.9	0.4871	
			−3.5
$[Os(bipy)_2(py)Cl](ClO_4)_2$–$[Os(bipy)_2(py)Cl]Cl$	8.9	0.4836	
$[Os(bipy)(py)_3I](ClO_4)_2$–$[Os(bipy)(py)_3I]Cl$	7.3	0.4508	
			−7.1
$[Os(bipy)(py)_3Br](ClO_4)_2$–$[Os(bipy)(py)_3Br]Cl$	7.3	0.4437	
			−18.2
$[Os(bipy)(py)_3Cl](ClO_4)_2$–$[Os(bipy)(py)_3Cl]Cl$	8.1	0.4255	

[a] 2.5×10^{-4} *M*.

The system $[Os(trpy)(bipy)X]^{2+,+}$ gave a potential order of Cl < I < Br and $[Os(bipy)_2(py)X]^{2+,+}$ and $[Os(bipy)(py)_3X]^{2+,+}$ gave the order of Cl < Br < I.

There are probably two effects acting here in opposition. The polarizabilities of the halogens tend to stabilize the osmium(III) state for I > Br > Cl, and the d_π–d_π donation of charge from filled osmium(II) or partly filled osmium(III) metal t_{2g} orbitals to the empty d_π orbitals of the halide ion tend to stabilize osmium(II) over-all. The former effect tends to make the iodo potential the least positive while the latter tends to make the iodo potential the most positive. Another factor which must be considered is the π-accepting character of the nitrogen-containing aromatic ligands, greatest for terpyridine and least for pyridine. It would seem from the observed potentials that the π-accepting ability of the halogen determines the potential order except for the $[Os(trpy)(bipy)X]^{2+,+}$ couple, where the large π-accepting ability of terpyridine and bipyridine reduces the d_π–d_π back donation to the halogen and allows the polarizabilities to partially reverse the expected order. A purely electrostatic effect will also be present but will be a factor common to each series. The π-donor abilities of the halogens, although undoubtedly resulting in much mixing of filled ligand p and metal d_π atomic orbitals, apparently contribute very little, if any, net stabilization of osmium(III). This is not unreasonable since osmium(II) has filled t_{2g} orbitals and osmium(III) has one vacancy in these orbitals. It would appear then that these spin-paired osmium(III)–osmium(II) couples are exceedingly sensitive to metal-to-ligand donation of charge and are less sensitive to charge delocalization toward the metal atom.

However, the magnitude of the differences in potential for the Cl^-, Br^-, and I^- couples is very small and it is also possible that these effects may be accounted for by small variations in the hydration and/or entropy terms.

Substitution in the Ligand.—Ligand substituents may affect the oxidation potential by (1) influencing the basicity of the donor atom(s), (2) affecting the π-bonding ability of the ligand, (3) changing the entropy or heat of hydration of the complex ions, or (4) by purely steric effects preventing the ligand from acquiring the most favorable orientation about the central metal ion. The effect of substitution in the ligand on the basicity of the donor atom and hence on the stability of the coordination complex has been extensively studied by observing changes in the potentials of the couples $[M(phen)_3]^{(n+1)+}$–$[M(phen)_3]^{n+}$ and $[M(bipy)_3]^{(n+1)+}$–$[M(bipy)_3]^{n+}$, where M = Fe(III)–Fe(II),[9] Ru(III)–Ru(II),[10] and Cu(II)–Cu(I)[11] and phen and bipy are substituted 1,10-phenanthroline and 2,2′-bipyridine ligands, respectively.

Several authors[12] have suggested that a linear relationship exists between the logarithm of the stability constant β_3 for the series of complex ions of the same metal and the acid dissociation constant pK_a of the ligand of the form

$$\log \beta_3 = a(pK_a) + b \qquad (4)$$

The significance of *a* and *b* has been discussed by Irving and Rossotti,[13] who maintain that only markedly similar ligands would be expected to follow this empirical relationship closely, that is, ligands whose substituents do not hinder complex formation sterically and

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[9] W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949); W. W. Brandt and D. K. Gullstrom, *J. Am. Chem. Soc.*, **74**, 3532 (1952); G. F. Smith and F. P. Richter, *Ind. Eng. Chem.*, **16**, 580 (1944).

[10] F. P. Dwyer, *J. Proc. Roy. Soc., N. S. Wales*, **83**, 134 (1950).

[11] B. R. James and R. J. P. Williams, *J. Chem. Soc.*, 2007 (1961).

[12] G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955); A. E. Martell and M. Calvin in "The Chemistry of the Metal Chelates," Prentice-Hall, Inc., Englewood Cliffs, N. J. 1953, p 76; J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

[13] H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 2904, 2910 (1954); *Acta. Chem. Scand.*, **10**, 72 (1956).

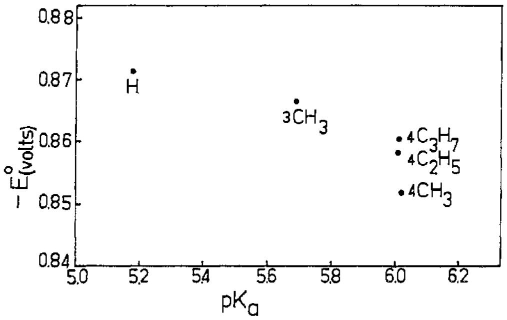

Figure 1.—The reduction potentials $E°$ for $[Os(trpy)(bipy)(Rpy)]^{3+,2+}$ couples *vs.* the pK_a of the substituted pyridine.

which cause no drastic change in the bonding properties of the ligand.

The standard oxidation–reduction potential for any metal complex couple may be related to the corresponding aquo potential, $E°_{aq}$, through the stability constants β_{ox} and β_{red} of the appropriate complex ion; *viz*

$$E° = E°_{aq} + 2.3026\frac{RT}{nF}[\log \beta_{red} - \log \beta_{ox}]$$

If the empirical relationship given by eq 4 holds, then

$$E° = E°_{aq} + 2.3026\frac{RT}{nF}[pK_a(a_{red} - a_{ox}) + (b_{red} - b_{ox})]$$

and a linear relationship should exist between $E°$ and the pK_a of the attached ligand.

Standard potentials for the system $[Os(trpy)(bipy)(Rpy)]^{3+,2+}$ where R = H, 3-CH_3, 4-CH_3, 4-C_2H_5, and 4-*i*-C_3H_7 are given in Table VI. Figure 1 gives a plot of $E°$ against pK_a of the substituted pyridine, and it is seen that no linear relationship exists. This result implies that eq 4 does not hold for these compounds. A similar observation has been made with a series of substituted tris(8-hydroxyquinoline) $Fe^{III,II}$ couples,[14] and other studies[15] show that a linear correlation is obtained only for a series of ligands which are structurally closely related and form similar bonds. It is conceivable that for the osmium complexes recorded here the deviations from the linear relationship or part thereof might be ascribed to hydration and entropy effects. However, if $\Delta(\Delta H°_{aq})$ was of primary importance, a trend could be expected as the size of the substituent increased. Such a correlation was not observed. Furthermore the $\Delta\bar{S}°$ contribution to the $[Os(bipy)_3]^{3+,2+}$ couple is near zero (Table II) and a similar result might be expected for the $[Os(trpy)(bipy)(Rpy)]^{3+,2+}$ couples.

A more plausible explanation may be found in terms of the Baker–Nathan effect. This effect, originally used by Baker and Nathan to explain the order of reactivity of *para*-substituted benzoyl bromides with pyridine[16] and later extended to other reactions,[17] has recently been the center of much discussion and some controversy.[18] Essentially, the observed order of reactivity $CH_3 > C_2H_5 > i\text{-}C_3H_7 > t\text{-}C_4H_9 > H$ is found for reactions that call strongly on the substituent for electron release, and this has been interpreted by some as resulting from a difference in C–H and C–C hyperconjugation in the substituent.[19] Alternatively, Schubert has shown the Baker–Nathan effect to be solvent dependent and suggests that the above sequence is probably due to the influence of the substituent in causing changes in solvation of the ground and transition states.[20] Recent charge-transfer spectral studies are in accord with this latter viewpoint[21] as is a similar study of a series of *para*-alkyl-substituted pyridinium iodides.[22]

Table VI

Electrode Potentials of Osmium(III)–Osmium(II) Couples at 25°: The Effect of Substitution in the Ligand

Couple (2.5×10^{-4} *M*)	Exptl slope, mv $/ \frac{0.1\sqrt{\mu}}{1 + \sqrt{\mu}}$	$E°$, v	$\Delta E°$, mv
$[Os(trpy)(bipy)(py)](ClO_4)_3$–$[Os(trpy)(bipy)(py)](ClO_4)_2$	16.4	0.8713	
			−4.1
$[Os(trpy)(bipy)(3\text{-}CH_3py)](ClO_4)_3$–$[Os(trpy)(bipy)(3\text{-}CH_3py)](ClO_4)_2$	16.4	0.8672	
			−6.3
$[Os(trpy)(bipy)(4\text{-}C_3H_7py)](ClO_4)_3$–$[Os(trpy)(bipy)(4\text{-}C_3H_7py)](ClO_4)_2$	16.0	0.8609	
			−2.2
$[Os(trpy)(bipy)(4\text{-}C_2H_5py)](ClO_4)_3$–$[Os(trpy)(bipy)(4\text{-}C_2H_5py)](ClO_4)_2$	15.3	0.8587	
			−8.1
$[Os(trpy)(bipy)(4\text{-}CH_3py)](ClO_4)_3$–$[Os(trpy)(bipy)(4\text{-}CH_3py)](ClO_4)_2$	15.4	0.8506	

The potential order 4-CH_3 < 4-C_2H_5 < 4-*i*-C_3H_7 < 3-CH_3 < H found in the present study is that expected for the difference between C–H and C–C hyperconjugation and is in accord with the Baker–Nathan series of electron-releasing power and a consequent stabilization of osmium(III). More significantly, the present study is thermodynamic in nature and avoids the uncertain transition state complications inherent in chemical rate studies.

It would therefore seem that a satisfactory explanation of the effect on $E°$ of alkyl-substituted pyridines may be found in $\Delta H°_{c'}$ and $\Delta H°_{LF}$ factors by considering the π-donor properties of the substituents. Such effects do not greatly affect the pK_a of the ligand, and a linear correlation between $E°$ and pK_a would not be expected. Thus, while the 3-CH_3 group is unable to affect the π-electron density on the nitrogen atom and

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(14) J. C. Tomkinson and R. J. P. Williams, *J. Chem. Soc.*, 2010 (1958).

(15) E. Uusitalo, *Ann. Acad. Sci. Fennicae, Ser. AII*, **87**, 1 (1957); J. G. Jones, J. B. Poole, J. C. Tomkinson, and R. J. P. Williams, *J. Chem. Soc.*, 2001 (1958).

(16) J. W. Baker and W. S. Nathan, *ibid.*, 1844 (1935).

(17) E. Berliner, *Tetrahedron*, **5**, 202 (1959).

(18) M. J. S. Dewar in "Hyperconjugation," Modern Concept in Chemistry Series, The Ronald Press Co., New York, N. Y., 1962.

(19) R. S. Mulliken, *Tetrahedron*, **5**, 253 (1959); **17**, 247 (1962).

(20) W. M. Schubert and W. A. Sweeney, *J. Org. Chem.*, **21**, 119 (1956); *J. Am. Chem. Soc.*, **76**, 4625 (1954).

(21) See W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962), for a review of these data.

(22) E. M. Kosower and J. A. Skorez, *U. S. Dept. Comm., Office Tech. Serv., P. B. Rept.*, **143**, 599 (1959).

consequently shows only a slight inductive stabilization of osmium(III), the 4-CH_3 substituent may enter into ligand π–d_π delocalization and distribute more effectively the positive charge. This will be better for osmium(III) and will therefore stabilize this ion. Alternatively, the effect may be considered in terms of a reduction in metal-to-ligand π bonding. This metal-to-ligand π bonding will be more effective for osmium(II) than for osmium(III) and for the unsubstituted pyridine than for the 4-CH_3 derivative, resulting in a stabilization of osmium(III) in the latter couple. On replacing the 4-CH_3 by a 4-C_2H_5 group the stabilization of osmium(III) will now be somewhat reduced owing to a reduction in hyperconjugation of the substituent and a consequent reduction in π-electron density in the pyridine ring. $\Delta(\Delta H^\circ{}_{c}')$ and $\Delta(\Delta H^\circ{}_{LF})$ will be reduced and the osmium(II) ion stabilized. A similar explanation can be given for the further stabilization of osmium(II) found in the $R = i\text{-}C_3H_7$ couple.

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Heteropoly Blues. I. Reduction Stoichiometries and Reduction Potentials of Some 12-Tungstates

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The reduction of five isostructural polytungstates, the heteropolyanions, $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, $[Fe^{III}W_{12}O_{40}]^{5-}$, $[Co^{II}W_{12}O_{40}]^{6-}$, and the isopolymetatungstate anion, $[H_2W_{12}O_{40}]^{6-}$, has been studied by polarographic and potentiometric methods. Each anion can accept two electrons without decomposition. Further electrons can be added in acidic solutions where protonation can accompany reduction and keep the over-all ionic charge low. In neutral solutions, reduction proceeds until the charge on the reduced species is −8. Formal reduction potentials for the initial one-electron reductions vary with the ionic charge in a manner consistent with a simple electrostatic model for the electron affinities of these approximately spherical polyanions.

Introduction

Heteropoly blues, the reduction products of certain heteropoly molybdates and -tungstates, particularly those 1:12 anions with the Keggin structure,[1] have received little fundamental study, although empirical analytical applications of such compounds are well-known.[2] Polarographic[3-6] and potentiometric[7] studies have indicated, with some conflicting results, that Keggin-structure anions can accept a limited number of electrons (*e.g.*, four) without decomposition, and in some cases the reduced compounds have been isolated.[8-12] It seems probable that the formation of heteropoly blues may be formally compared with the reduction of polynuclear aromatic hydrocarbons to the corresponding anions.

The formation, properties, and structural features of various heteropoly blues are currently being studied in this laboratory with a view to elucidating further the stabilities and bonding of nonreduced polyanions. This paper reports the reduction stoichiometries and potentials of five Keggin-structure polytungstate anions whose over-all charges range from −3 to −6. Chemical, spectral, and magnetic properties of the heteropoly blues derived from these anions will be discussed in subsequent papers.

Experimental Section

Preparation and Analysis of Compounds.—Sodium 12-tungstophosphate was precipitated with sodium chloride from a concentrated solution of the free acid, which was prepared according to Wu.[8] The salt was recrystallized from dilute (~0.5 *M*) sulfuric acid. *Anal.* Calcd for $Na_3[PW_{12}O_{40}]\cdot 10H_2O$: P, 0.99; W, 70.57. Found: P, 0.98; W, 70.42.

Potassium 12-tungstosilicate was prepared similarly from 12-

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(1) The general formula for such anions is $[A^{n+}X_{12}O_{40}]^{(8-n)-}$ where A can be one of several representative or transition elements and X is either Mo(VI) or W(VI). The main features of this structure were first elucidated in Keggin's X-ray study of $H_3PW_{12}O_{40}\cdot 5H_2O$ [*Proc. Roy. Soc.* (London), **A144**, 75 (1934)].

(2) See, for example, F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. II, 3rd ed, D. Van Nostrand Co., Inc., Princeton, N. J., 1949, pp 196, 233, 660, 695.

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(12) (a) H. Hahn and F. Hahn, *Naturwissenschaften*, **49**, 539 (1962); (b) H. Hahn and G. Schmidt, *ibid.*, **49**, 539 (1962); (c) H. Hahn and W. Becker, *ibid.*, **49**, 513 (1962); (d) H. Hahn and W. Becker, *ibid.*, **50**, 402 (1963).