[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYDNEY UNIVERSITY]

The Preparation of the Enantiomorphous Forms of the Tris-2,2'-dipyridyl Osmium(III) Ion

BY F. P. DWYER AND E. C. GYARFAS

Tris-2,2'-dipyridyl osmium(II) salts can be oxidized either anodically or by chlorine to the red tris-2,2'-dipyridyl osmium(III) compounds. In this way the enantiomorphous forms of the osmium(III) complex were obtained by oxidation of *d* and *l* $Os(dipy)_3Cl_2$ with chlorine and isolated as the red crystalline perchlorates $Os(dipy)_3(ClO_4)_3\cdot H_2O$ for which $[\alpha]^{20}_{5461}$ was ±250°. This is the first instance of the resolution of a trivalent six covalent osmium complex.

Tris-2,2'-dipyridyl osmium(II) salts were recently prepared and resolved into enantiomorphous forms.[1] The dark green ion $Os(dipy)_3^{++}$ was found to be reversibly oxidized to the red ion $Os(dipy)_3^{+++}$. The potential of the reaction in 0.1 *N* hydrochloric acid was +0.8557 volt.[2] The perchlorate, chloride and nitrate of the trivalent osmium complex have now been prepared and isolated in solid form. The oxidation was carried out either with a slight excess of chlorine or anodically in a partitioned cell. The salts were deep red, dissolving in water to red solutions which became brown in the presence of dust or traces of reducing agents. From the oxidation–reduction potential, it can be predicted that the bromide would be highly unstable and the iodide incapable of existence in solution, and all attempts to isolate them have failed.

The preparation of the enantiomorphous forms of the tris-2,2'-dipyridyl osmium(III) ion was affected by the oxidation of *d* and *l* tris-2,2'-dipyridyl osmium(II) chlorides in aqueous solution at 4° with chlorine. The active forms were then isolated by the addition of sodium perchlorate as the crystalline perchlorates $Os(dipy)_3(ClO_4)_3\cdot H_2O$. This is another example of the method of preparation of optical antipodes by the oxidation of the dextro and levo forms of a lower oxidation state,[3] as well as the first recorded resolution of a trivalent hexacovalent osmium compound. The enantiomorphous forms were optically stable in the solid state and in solution at room temperature, as with the osmium(II) complex, no rotation was observed in the NaD line, this being close to an absorption maximum (Fig. 1), but in the Hg line 5461 Å., $[\alpha]^{20}_{5461}$ was ±250°. Like the corresponding iron(II), ruthenium(II) and -(III) and nickel(II) compounds[4] with 2,2'-dipyridyl and 1,10-phenanthroline it is obvious that this ion has a large abnormal rotatory dispersion. The optical forms were reversibly reduced with persistence of the activity.

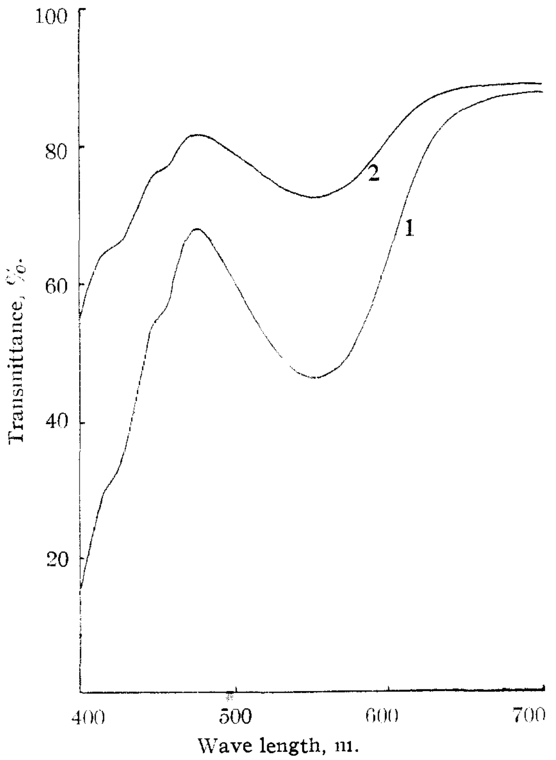

Fig. 1.—Absorption spectrum of $Os(dipy)_3(ClO_4)_3\cdot H_2O$: $c_1 = 5 \times 10^{-4}$ *M*, $c_2 = 1.7 \times 10^{-4}$ *M*.

The isolation of optically and chemically stable salts of the ions $Os(dipy)_3^{++}$ and $Os(dipy)_3^{+++}$ with a single electron difference presents a unique tool for the investigation of the properties of optically active ions in solution by the classical methods of oxidation–reduction potentials. A further use is the study of the electron transfer reaction since both the oxidant and reductant are "tagged" ions owing to their individual abnormal rotatory dispersions.

Experimental

All rotations were measured at 20° in a 1-dm. tube using a mercury vapor lamp with filter as the source of the 5461 Å. line.

***dl*-Tris-2,2'-dipyridyl Osmium(III) Perchlorate Monohydrate.**—*dl*-Tris-2,2'-dipyridyl osmium(III) iodide (0.5 g.) (Burstall, Dwyer and Gyarfas, ref. 1) in hot water (25 ml.) was treated with freshly prepared silver chloride, and the resulting deep green solution of the chloride cooled to 4°. Chlorine gas was led into the solution until the color changed to red, when the passage of the gas was discontinued and the solution warmed to 15–20°. Sodium perchlorate solution (20%) was added until the solution became cloudy. On scratching the sides of the vessel and cooling in ice, the perchlorate crystallized as mulberry-red monoclinic prisms. After filtration through a sintered glass disc, the substance was washed quickly with cold absolute alcohol, in which it is sparingly soluble, then with pure dry ether and dried rapidly in warm air. The absorption spectrum curve was obtained with a General Electric Recording Spectrophotometer and is shown in Fig. 1.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3(ClO_4)_3\cdot H_2O$: Os, 19.51; N, 8.62. Found: Os, 19.6; N, 8.64.

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(2) F. P. Dwyer, N. A. Gibson and E. C. Gyarfas, *J. Proc. Roy. Soc.* (N. S. W.), **84**, 80 (1950).

(3) F. P. Dwyer and E. C. Gyarfas, *Nature*, **163**, 918 (1949); *J. Proc. Roy. Soc.* (*N. S. W.*), **83**, 170 (1949).

(4) F. P. Dwyer and E. C. Gyarfas, *ibid.*, **83**, 232, 263 (1949).

dl-**Tris-2,2'-dipyridyl Osmium(III) Chloride Monohydrate.**—The corresponding osmium(II) complex chloride (0.5 g.) in water (10 ml.) at 4° was treated with chlorine gas until the color changed to red. After filtering through a sintered glass filter, the solution was evaporated to dryness over phosphorus pentoxide in the presence of a little chlorine. The dark red needles of the compound had a green reflex, and were very hygroscopic. On analysis the substance was found to contain adsorbed chlorine, and was purified by solution in methanol and precipitation with acetone. After removal of traces of these solvents in vacuum over phosphorus pentoxide the substance was obtained as green micro needles.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3Cl_3 \cdot H_2O$: Os, 24.29; Cl, 13.58. Found: Os, 24.13; Cl, 13.6.

dl-**Tris-2,2'-dipyridyl Osmium(III) Nitrate Hexahydrate.**—A saturated solution of tris-2,2'-dipyridyl osmium(II) nitrate in water, was oxidized anodically, using a stout platinum spiral as anode, at 6 volts with 0.2 amp. A sintered glass crucible served as the anode compartment and was suspended in a beaker of dilute acid as the cathode chamber and electrolyte. When the oxidation was complete, the red solution was allowed to evaporate in vacuum over solid sodium hydroxide. The red microcrystalline powder was extremely deliquescent and very soluble in methyl alcohol. Solutions in the methanol rapidly became brown and finally green.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3(NO_3)_3 \cdot 6H_2O$: Os, 19.96; N, 13.23. Found: Os, 19.92; N, 13.3.

d-**Tris-2,2'-dipyridyl Osmium(III) Perchlorate Monohydrate.**—Dextro-tris-2,2'-dipyridyl osmium(II) iodide (0.5 g. in 35 ml. of hot water) was transformed to the chloride with silver chloride, oxidized with chlorine at 4° and treated as the *d,l*-perchlorate above, with sodium perchlorate. The mulberry-red prismatic needles of the active perchlorate were more soluble in water than the *d,l*-perchlorate. A 0.02% solution in water gave $\alpha = +0.05°$ (mean value) whence $[\alpha]^{20}_{5461} = +250°$ and $[M]^{20}_{5461} = +2500°$. The substance had no detectable rotation in the NaD line.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3(ClO_4)_3 \cdot H_2O$: Os, 19.51; N, 8.62. Found: Os, 19.6; N, 8.67.

l-**Tris-2,2'-dipyridyl Osmium(III) Perchlorate Monohydrate.**—This was prepared by the same methods as the dextro compound using instead levo tris-2,2'-dipyridyl osmium(II) iodide. The substance crystallized in mulberry-red prismatic needles. A 0.02% solution in water gave $\alpha = -0.05°$ whence $[\alpha]^{20}_{5461} = -250°$ and $[M]^{20}_{5461} = -2500°$.

Anal. Calcd. for $Os(C_{10}H_8N_2)_3(ClO_4)_3 \cdot H_2O$: Os, 19.51; N, 8.62. Found: Os, 19.4; N, 8.62.

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Ionization Constants of Fluorinated Acids

BY ALBERT L. HENNE AND CHARLES J. FOX

Perfluorinated acetic and butyric acids are strong electrolytes. $CF_3CH_2CO_2H$ and $CF_3(CH_2)_2CO_2H$ are weak electrolytes with ionization coefficients of 1×10^{-3} and 7×10^{-5}, respectively; their unfluorinated analogs have coefficients of only 1.3×10^{-5} and 1.5×10^{-5}, respectively. The shielding effect of one methylene group between the fluorinated cluster and the acid function is considerable, but even two methylene groups do not achieve complete shielding; this emphasizes the magnitude of the electronegative induction exerted by CF_3 groups.

The ionization constants of substituted acetic acids have been used to evaluate the electronegative induction of various elements; for instance, CH_3CO_2H, CH_2FCO_2H, CHF_2CO_2H and CF_3CO_2H have values of 1.8×10^{-5}, 2.2×10^{-3}, 5.7×10^{-2} and 0.5, respectively, and the last of these acids acts as a strong electrolyte.[1] Measurements are now presented on compounds in which a CF_3 group is located at increasing distances from the acid function in order to evaluate as quantitatively as possible the loss of inductive effect in relation to distance. Two experimental procedures have been used, namely: (1) determination of the limiting equivalent conductance and (2) determination of the *p*H curve during neutralization. From these experimental measurements, values have been computed for the ionization constants which were found consistent and are listed in Table I.

A direct comparison between strong and weak electrolytes would not be valid, but the weak electrolytes can be contrasted with their unfluorinated analogs. At 25°, propionic and butyric acids have $K_{25} = 1.343 \times 10^{-5}$ and 1.506×10^{-5}, respectively,[2] coefficients which are about $^1/_{70}$th and $^1/_5$th as small as those of $CF_3CH_2CO_2H$ and $CF_3CH_2CO_2H$. The degrees of dissociation α of 0.1 *N* aqueous solutions are: $C_3F_7CO_2H$, 0.878; CF_3CO_2H, 0.877; $CF_3CH_2CO_2H$, 0.0926; $CF_3CH_2CH_2CO_2H$, 0.0263; $C_2H_5CO_2H$, 0.0116 and $C_3H_7CO_2H$, 0.0123; these figures are not absolute constants, but they do give a clear picture of relative acidities.

The above results show how great the electronegative induction of a CF_3 group is, and it is quite consistent to find that it takes two methylene groups to cause an amount of shielding equal to that which a single methylene group causes on less effective groups, as shown by the ionization constants of the monochlorinated butyric acids[3]: $CH_3CH_2CHClCO_2H$, 1.4×10^{-3}; $CH_3CHClCH_2CO_2H$, 8.8×10^{-5} and $C_3H_7CO_2H$, 1.5×10^{-5}.

Experimental

Samples.—Redistilled CF_3CO_2H, b.p. 70.8° (739 mm.), f.p. −15.22° and $C_3F_7CO_2H$, f.p. −19.95° were used. $CF_3CH_2CO_2H$ was taken from a cut b.p. 144.8° (746 mm.), f.p. about 7°; after redistillation with immediate freezing of the distillate, a good sample had: f.p. 9.7°; b.p. 144.8° (746 mm.); d^{27}_4 1.441; n^{27}_D 1.3316; *MR* (obsd.) 18.20 from which AR_F was computed as 1.31, a value agreeing with 1.33 for CF_3CO_2H. $CF_3CH_2CH_2CO_2H$ was similarly purified: f.p. 32.3°; b.p. 78.0° (18 mm.). Previously reported values[4] are: CF_3CO_2H, f.p. −15.55° (a), −15.5° (b); $C_3F_7CO_2H$, f.p. −17° (b); $CF_3CH_2CO_2H$ f.p. +12°, b.p. 146° (c); $CF_3CH_2CH_2CO_2H$, f.p. 33.2°, b.p. 166.6° (d).

Electrical Equipment.—The Wheatstone bridge consisted of a Leeds and Northrup Student Potentiometer No. 7651,

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[1] F. Swarts, *Bull. Acad. Roy. Belg.*, 681 (1896), 624 (1903), and 353 (1922).

[2] D. Belcher, THIS JOURNAL, **60**, 2744 (1938).

[3] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 15.

[4] (a) F. Swarts, ref. 1 (1922); (b) Minnesota Mining and Manufacturing Co.; (c) undescribed sample in documents from I. G. Farben Industrie; (d) E. T. McBee and A. Truchan, THIS JOURNAL, **70**, 2910 (1948).