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# CONTRIBUTION TO THE COORDINATION CHEMISTRY OF OSMIUM

## II. CHELATES OF BIVALENT AND TERVALENT OSMIUM WITH BIGUANIDE DERIVATIVES

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SUMMARY

An investigation has been made into the tendency of osmium(II) and osmium(III) to form di- and tri- chelates with some substituted biguanide derivatives, *viz.*, with $[Os(RBig)_3]X_2$, $[Os(RBig)_3]X_3$, $[Os(RBig)_2X_2]X$, hwere RBig = $N^1$,$N^1$-dimethylbiguanide, $N^1$-morpholinbiguanide and $N^1$-*p*-chlorophenyl-$N^5$-isopropylbiguanide. Chemical methods, resolution of optical antipodes, magnetic susceptibility methods and absorption spectra have been used for the characterisation of the compounds.

### INTRODUCTION

Earlier work on the tendency of osmium to form biguanide compounds is limited to the work of M. M. RÂY[1] who, in 1964, reported briefly on osmium(VI) compounds of the type $[OsO_2(Big)_2]$, $[OsO_2(BigH)_2]SO_4.H_2O$ and $[OsO_2(BigH)Cl_2]$ in addition to two mixed compounds. Work carried out in these laboratories[2] has led to the preparation of biguanidonium salts of osmium(IV) hexahalogenacids of the form $(HRBig)_2[OsX_6]$, where X = Cl or Br. The chemical structure of these biguanidonium salts was confirmed by thermal decomposition and spectrophotometry. On heating, the biguanidonium hexabromosmiates in aqueous solution undergo autoxidation accompanied by the separation of $[Os(RBig)_3]Br_2$.

The present paper is concerned with the tendency of osmium(II) and osmium(III) to form tri- and di-chelates of the type $[Os(RBig)_3]X_2$, $[Os(RBig)_3]X_3$ and $[Os(RBig)_2X_2]X$, with some substituted derivatives of biguanide. The new compounds have been characterised by chemical methods, resolution into optical antipodes, absorption spectra and by magnetic susceptibility methods.

### EXPERIMENTAL

$OsO_4$ p.a. was used as starting material for the preparation of $K_2[OsCl_6]2H_2O$, $(NH_4)_2[OsCl_6]$ and $(NH_4)_2[OsBr_6]$, the reduction of the $OsO_4$ being carried out either with ethanol or with $FeCl_2$, as described in the literature[3-6]. The following biguanide derivatives were used: $N^1$,$N^1$-dimethylbiguanide ($Me_2Big$), $N^1$-morpholinobiguanide (MorphBig) and $N^1$-*p*-chlorophenyl-$N^5$-isopropylbiguanidide (pald). Micromethods were used for the analysis of the compounds. Osmium was determined by one of the methods previously described[7]. Methanol, absolute ethanol and dimethylformamide (DMF) were used as solvents; these were dried by molecular sieves.

Magnetic susceptibility measurements were carried out by the Gouy method, using mercury(II)tetrathiocyanocobaltate(II) for calibration. The effective magnetic moments were calculated from the expression $\mu_{eff} = 2.84\,(\chi_m \times T)^{\frac{1}{2}}$. Resolution of optical antipodes was carried out by a chemical method, the rotation being measured by means of a polarimeter with sodium light to ±0.02°.

Ultraviolet and visible absorption spectra were measured in aqueous and methanol solution by means of a Zeiss Universal $VSU_1$ spectrophotometer.

### *Preparation of* $[Os(RBig)_3]X_2$

On mixing aqueous solutions of $(NH_4)_2[OsBr_6]$ and the hydrochlorides of the biguanide derivatives in a molar ratio of 1:3, red $(HRBig)_2[OsBr_6]$ separated at first; this dissolved after heating for some time. The solution became a dark violet colour on boiling for one hour the rate of this reaction being increased by the addition of metallic osmium. The filtered solution contained $[Os(RBig)_3]Br_2$ from which, by double decomposition in solution, $[Os(RBig)_3]X_2$ compounds were obtained.

### *Resolution of* $[Os(pald)_3]^{2+}$ *into optical antipodes*

The aqueous solution containing racemic $[Os(pald)_3]Br_2$ was stirred with a small excess of silver *d*-antimonyl tartrate and the solution filtered. The violet precipitate was washed on a filter with methanol until only AgBr remained. The dark violet filtrate was concentrated on a water bath until fine crystals of *l*-$[Os(pald)_3](SbOC_4H_4O_6)_2$ appeared, and then cooled. This product was filtered off, washed with cold water and dried under vacuum; the *d*-antimonyl tartrate of tripaludrineosmium(II) separated from the filtrate on standing for some time. The *laevo* and *dextro* antimonyl tartrates, respectively, were converted into the iodides by treatment with potassium iodide in aqueous solution. The polarimeter measurements were carried out with 0.5% aqueous solutions, using a 20 cm tube.

$\alpha = -1.80°$ $[\alpha]_D = -1800°$ $[M]_D = -2169°$

$\alpha = +1.90°$ $[\alpha]_D = +1900°$ $[M]_D = +2289°$

### *Preparation of* $[Os(pald)_3]X_3$

These compounds may be obtained either in aqueous solution by the gentle oxidation of $[Os(pald)_3]Br_2$ with air or a dilute solution of hydrogen peroxide, or in DMF solution by heating, under reflux, a mixture of (pald).HCl and $(NH_4)_2[OsCl_6]$ in a molar ratio of 1:3 until the solution becomes reddish-brown in colour. After cooling, 20 ml of 20% HCl solution ($\sim 2\ M$) are added and the mixture cooled on ice and then filtered. The product remaining on the filter is washed with cold water until the filtrate begins to change to a green colour. It is then washed with ether and dried under vacuum.

*Preparation of* $[Os(pald)_2X_2]X$

$K_2[OsCl_6]$ or $(NH_4)_2[OsBr_6]$ and paludrine are dissolved, in a molar ratio of 1:2, in anhydrous DMF and the solution refluxed for 1 h when fine crystals of potassium or ammonium halide separate from the brown solution. After cooling on ice these are filtered off and HX added in a small excess to the solution, which is kept cool. Brown, very pure, compounds separate; these are immediately filtered off, washed with a little cold water and ether and then dried under vacuum over phosphoric oxide. Analyses of these compounds are given in Table I.

TABLE I

ANALYTICAL DATA

| *Compounds* | *Elements (%)* | |
|---|---|---|
| | *Os* | *N* |
| $[Os(C_4H_{11}N_5)_3]I_2$ | | |
| found: | 22.69 | 25.13 |
| calcd.: | 22.88 | 25.27 |
| $[Os(C_6H_{13}N_5O)_3]I_2$ | | |
| found: | 19.71 | 21.80 |
| calcd.: | 19.87 | 21.94 |
| $[Os(C_{11}H_{16}N_5Cl)_3]I_2$ | | |
| found: | 15.83 | 17.23 |
| calcd.: | 15.78 | 17.44 |
| $[Os(C_{11}H_{16}N_5Cl)_3](SbOC_4H_4O_6)_2$ | | |
| found: | 12.18 | 13.62 |
| calcd.: | 12.49 | 13.80 |
| $[Os(C_{11}H_{16}N_5Cl)_3]Br_3$ | | |
| found: | 16.10 | 17.67 |
| calcd.: | 15.97 | 17.64 |
| $[Os(C_{11}H_{16}N_5Cl)_3]Cl_3$ | | |
| found: | 18.04 | 19.91 |
| calcd.: | 17.98 | 19.86 |
| $[Os(C_{11}H_{16}N_5Cl)_2Cl_2]Cl$ | | |
| found: | 23.85 | 17.23 |
| calcd.: | 23.65 | 17.42 |
| $[Os(C_{11}H_{16}N_5Cl)_2Br_2]Br$ | | |
| found: | 20.01 | 14.92 |
| calcd.: | 20.29 | 14.97 |

## DISCUSSION

Osmium(II) trichelates of the type $[Os(RBig)_3]Br_2$ are formed by the reduction of a mixture of $(NH_4)_2[OsBr_6]$ and RBig.HCl by metallic osmium in aqueous solution. This method of synthesis is general in character and is independent of the nature of the radical in the substituted biguanide.

Stable, deep violet solutions are formed; the stability of the compounds in solution, which may extend to as much as 10 days, increases from $Me_2Big \rightarrow MorphBig \rightarrow$ pald.

The $[Os(RBig)_3]^{2+}$ cations may be combined with bulky anions, resulting in the separation of crystalline compounds which have the form $[Os(RBig)_3]X_2$, where $X = I^-$, $CNO^-$, $CNS^-$, $N_3^-$, $[B(C_6H_5)_4]^-$, $S_2O_3^{2-}$, $S_2O_4^{2-}$, $H_2PO_2^-$, $[Fe(CN)_5NO]^{2-}$, tartrate, antimonyl tartrate etc. Some of these compounds have been resolved into optical antipodes.

The deep violet aqueous solutions, on treatment with various oxidants such as $Ce^{4+}$, $S_2O_8^{2-}$, $H_2O_2$, $ClO_2^-$ lose their colour, becoming light yellow, after passing through green. This enables one to assume that in the violet solutions the osmium is in the oxidation state 2+

$$\underset{\text{violet}}{[Os^{II}(RBig)_3]^{2+}} \rightarrow \underset{\text{green}}{[Os^{III}(RBig)_3]^{3+}} \rightarrow \underset{\text{yellow}}{Os(IV)}$$

The $d^2sp^3$ structure of the complexes is confirmed by their behaviour towards oxidants, by the diamagnetic character of the respective tartrates and iodides and also by the ability of $[Os(pald)_3]Br_2$ to be resolved into optical antipodes. The experimental data show that $[Os(pald)_3]^{2+}$ is sufficiently stable to permit this resolution into optically active *l* and *d* forms, the molecular rotations $[M]_D$ of the respective iodides being $-2169°$ and $+2289°$.

We suggest that $[Os(pald)_3]Br_2$ may be used in quantitative analysis, either for the direct titration of oxidants or as a redox indicator. For example, $Fe^{2+}$ could be determined with $K_2Cr_2O_7$ in $H_2SO_4$ and $H_3PO_4$ medium in the presence of this indicator, the transition from violet to green being quite clear.

TABLE II

MAGNETIC MOMENTS FOR OCTAHEDRAL COMPOUNDS

| *Compounds* | *Temperature (°K)* | *μ eff (BM)* | *References* |
|---|---|---|---|
| $[Os\ pald_3]Cl_3$ | 293 | 2.45 | |
| $[Os\ pald_3]Br_3$ | 293 | 2.20 | |
| $[Os\ pald_2\ Cl_2]Cl$ | 294 | 1.60 | |
| $[Os\ pald_2\ Br_2]Br$ | 294 | 1.68 | |
| $[Os(NH_3)_6]Br_3$ | 300 | 2.05 | 8 |
| $[Os(NH_3)_6]I_3$ | 300 | 2.20 | 9 |
| $[Os\ en_3]I_3$ | 298 | 1.60 | 10 |

$[Os(pald)_3]^{3+}$ may be formed, either by the oxidation of an osmium(II) trichelate in aqueous solution, or from $(NH_4)_2[OsCl_6]$ and paludrine in DMF, which acts as a reducing agent. The $[Os(pald)_3]X_3$ compounds, where $X = Cl^-$, $Br^-$, $CNO^-$, $CNS^-$, $N_3^-$, $[B(C_6H_5)_4]^-$, $NO_2^-$, $[Cr(SCN)_6]^{3-}$ or $[Cr(NH_3)_2(SCN)_4]^-$ are green crystalline powders, sparingly soluble in water but soluble in ethanol. The solutions are stable.

The behaviour of the respective aqueous solutions towards oxidants, as well as towards some reducing agents, confirms that the osmium is in the 3+ oxidation state. Thus, in the presence of $Ce^{4+}$ or $S_2O_8^{2-}$ the solutions become yellow, which is characteristic of osmium(IV), whilst in the presence of $H_3PO_2$ they become violet, indicating the formation of the $[Os(pald)_3]^{2+}$ cation.

The determination of the magnetic susceptibility of the above trichelates has confirmed the presence of the osmium in the 3+ oxidation state.

An analysis of the absorption spectra of the trichelates of osmium(II) and

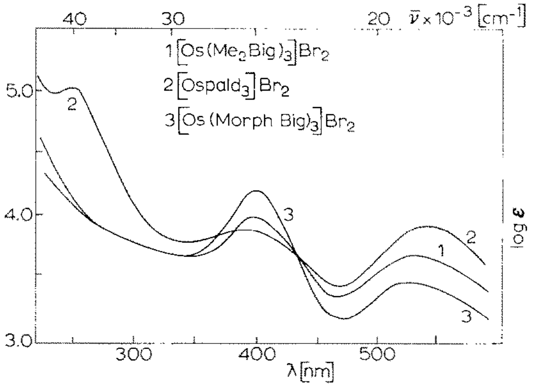

Fig. 1. The visible and ultraviolet spectra for complexes of Os(II) with biguanide derivatives.

TABLE III

ABSORPTION MAXIMA ($\lambda_{max}$) AND MOLECULAR EXTINCTION COEFFICIENT (LOG $\varepsilon_{max}$)

| *Compounds* | $\lambda_{max}$ *(nm)* | $\nu_{max}$ *(cm$^{-1}$)* | *log ε* | *References* |
|---|---|---|---|---|
| $[Os(Me_2Big)_3]Br_2$ | 530 | 18,870 | 3.671 | |
| | 406 | 24,630 | 3.995 | |
| $Me_2Big \cdot HCl$ | 240 | 41,670 | 4.448 | |
| $[Os(MorphBig)_3]Br_2$ | 530 | 18,870 | 3.462 | |
| | 406 | 24,630 | 4.180 | |
| $MorphBig \cdot HCl$ | 240 | 41,670 | 4.243 | |
| $[Os\ pald_3]Br_2$ | 540 | 18,520 | 3.924 | |
| | 398 | 25,130 | 3.915 | |
| | 252 | 39,680 | 4.995 | |
| $pald \cdot HCl$ | 259 | 38,610 | 4.447 | |
| | 232 | 43,100 | 4.267 | |
| $[Os\ pald_3]Br_3$ | 565 | 17,700 | 3.825 | |
| | 432 | 23,150 | 4.122 | |
| | 256 | 39,060 | 4.520 | |
| $[Os\ bipy_3]I_2 \cdot 3H_2O$ | 483 | 20,700 | | 11 |
| | 437 | 22,880 | | |
| $[Os\ bipy_3](ClO_4)_3$ | 458 | 21,820 | | |
| | (450) | (22,220) | | 12 |
| | (420) | (23,810) | | |
| $[Os\ pald_2Cl_2]Cl$ | 420 | 23,810 | 3.580 | |
| | 256 | 39,060 | 4.314 | |
| $[Os\ pald_2Br_2]Br$ | 438 | 22,830 | 3.771 | |
| | (320) | (31,250) | 3.880 | |
| | 254 | 39,370 | 4.275 | |
| $[Os\ bipy_2Cl_2]Cl \cdot 2H_2O$ | 407 | 24,570 | 3.778 | |
| | 287 | 34,800 | 4.556 | 13 |
| | 245 | 40,800 | 4.255 | |
| $[Os\ bipy_2Br_2]Br \cdot 2H_2O$ | 408 | 24,510 | 3.908 | |
| | (325) | (30,800) | | |
| | 290 | 34,500 | 4.544 | 13 |
| | 240 | 41,600 | 4.398 | |

osmium(III) with biguanide derivatives (Fig. 1, Table III), indicates the transfer of intramolecular energy from the $\pi$-electron system of the ligand to the $5d$-electron system of the osmium. Each *tris*-R-biguanidide osmium(II) exhibits a similar absorption spectrum which consists of a strong ligand band $\pi$–$\pi^x$ (log $\varepsilon \sim 5$) between 50,000–30,000 cm$^{-1}$ and two marked charge-transfer bands (CT)$^1A_{1g}$–$^1(d\text{-}\pi^x)$ (log $\varepsilon \sim 4$) at 25,000 cm$^{-1}$ and (log $\varepsilon \sim 3.8$) at 18,800 cm$^{-1}$.

The presence of the charge transfer band is in agreement with recent data given in the literature concerning osmium(II) trichelates with 2,2′-bipyridyl, 1,10-phenanthroline and bis(2,2′,2″-terpyridyl)[14,15].

Paludrine dichelates of osmium(III), of the type $[Os(pald)_2X_2]X$ are formed either by the pyrolysis of the quaternary ammonium salts $(paldH)_2[OsX_6]$ where $X = Cl^-$ or $Br^-$, at 150°C, which leads to a raw product of $[Os(pald)_2X_2]$ and $[Os(pald)_2X_2]X$, or by the refluxing of a mixture of paludrine and $M_2[OsX_6]$, where $M = K^+$, $NH_4^+$, in DMF, which leads to a product of high purity.

Osmium(III) dichelates are brown powders, sparingly soluble in water, and soluble in methanol, ethanol and DMF. These solutions are easily reduced by sodium dithionite to $[Os(pald)_2X_2]$ and became dark violet in colour. The behaviour towards $Ce^{4+}$ or $H_2O_2$, which is accompanied by the appearance of the yellow coloration, implies the transition of osmium from valence 3 to valence 4. The determination of the magnetic susceptibility (Table II) confirms this assumption. The magnetic moments range from 1.60 to 1.68 B.M. EPR spectra of polycrystalline powders at room temperature have also been examined and a signal without any hyperfine structure found. Ultraviolet and visible absorption spectra are given in Table III.

The stability of $[Os(pald)_2X_2]^+$ in solution without the occurrence of disproportionation into mono- and trichelates is also noteworthy. Paludrine is not removed from the complex ion by the presence of other organic bases such as pyridine, ethylenediamine, 1,10-phenanthroline and 2,2′-bipyridyl; only the halogens are replaced, followed by the separation of mixed compounds. Thus, on refluxing $[Os(pald)_2X_2]X$ in a pyridine–ethanol or ethylenediamine–ethanol mixture, $[Os(pald)py_2]X_3$ or $[Os(pald)_2en]X_3$ green-brown compounds separate. A later note will give some data concerning the structures of these compounds and their resolution into optical antipodes.

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