Osmium dithiophosphates. Synthesis, X-ray crystal structure, spectroscopic and electrochemical properties

Prateek U. Jain, Himadri Paul, Pradip Munshi, Mrinalini G. Walawalkar, Goutam Kumar Lahiri *

Department of Chemistry, Indian Institute of Technology, Bombay, Powai, Mumbai 400076, India

Abstract

The reactions of ammonium salt of dialkyldithiophosphate ligands, $(RO)_2PS_2^-NH_4^+$ (R = Me/Et) with $(NH_4)_2Os^{IV}Br_6$ in methanol solvent and under dinitrogen atmosphere result in one-electron paramagnetic tris complexes, {(RO)₂PS₂}₃Os^{III} (1a-1b) in the solid state. The molecular structure of one complex (1a) has been determined by single-crystal X-ray diffraction. It shows the expected pseudo-octahedral geometry with reasonable strain due to the presence of four-membered chelate rings. The reflectance spectra of the solid complexes display two broad bands in the range 552-484 nm and in the solid-state complexes exhibit one isotropic EPR signal at 77 K. Although the complexes 1a-1b are found to be stable in the solid state, in solution state the complexes are transformed selectively into the diamagnetic and electrically non-conducting metal-metal bonded dimeric species [{(RO)₂PS₂}₃Os^{III}-Os^{III}{S₂P(OR)₃}. The formation of dimeric species in the solution state is authenticated by the electrospray mass spectrum of one representative complex where R = Et (1b). In dichloromethane solution the complexes show two moderately strong sulfur to osmium charge-transfer transitions in the visible region and two strong ligand based transitions in the UV region. The complexes exhibit successive two oxidations correspond to Os^{IV}-Os^{IV}/Os^{III}-Os^{III} and Os^V-Os^V/Os^{IV}-Os^{IV} processes near 0.8 and 1.9 V versus SCE, respectively. One reductive couple corresponds to the Os^{III}–Os^{III}/Os^{II}–Os^{II} couple has been observed near -0.6 V. Electrochemically generated oxidized species $[\{(RO)_2PS_2\}_3Os^{IV}-Os^{IV}\{S_2P(OR)_2\}_3]^{2+}$ display lowest energy ligand to metal charge-transfer transition near 550 nm which has observed to be reasonably red shifted as compared to that of the parent trivalent species. On the other hand electrochemically generated reduced species [$\{(RO)_2PS_2\}_3Os^{II}$ - $Os^{II}{S_2P(OR)_2}_3^{2-}$ are found to be unstable even on coulometric time scale.

Keywords: Osmium dithiophosphates; X-ray crystal structures; Spectroscopic properties

1. Introduction

Despite considerable research activity in the area of osmium dithiocarbamate and dithiocarbonate complexes over the last several years [1-15] relatively little progress has been made so far in the direction of corresponding osmium dithiophosphate chemistry [16-18]. The versatile bonding, structural features as well as fascinating chemical and electrochemical reactivities of

osmium dithiocarbamate and dithiocarbonate complexes have prompted us to make a systematic study of osmium dialkyldithiophosphate complexes. The present study indicates that the osmium tris dithiophosphates $\{(RO)_2PS_2\}_3Os^{III}$ (1), generated from the reaction of ammonium salt of dialkyldithiophosphates $[(RO)_2P(S)S^-NH_4^+]$ and the osmium precursor $(NH_4)_2Os^{IV}Br_6$, are stable only in the solid state. However, in solution state, the tris complexes 1 predomiexist in dimeric form of the nantly type $[\{(RO)_2PS_2\}_3Os^{III}-Os^{III}\{S_2P(OR)_2\}_3]$. Herein we describe the solid-state characterization of the tris complexes 1 including the single-crystal X-ray structure of one complex (1a) and the solution spectroscopic and electron-transfer properties of the complexes.

2. Experimental

2.1. Materials

Osmium tetroxide was obtained from Johnson Matthey, London. The starting osmium complex, $(NH_4)_2Os^{IV}Br_6$ was prepared by following the reported procedure [19]. The ligands NH_4L^{1-2} were synthesized according to the literature method [20]. Other chemicals and solvents were reagent grade and used as received. Silica gel (60–120 mesh) used for chromatography was of BDH quality. For spectroscopic and electrochemical studies HPLC grade solvents were used. Commercial tetraethyl ammonium bromide was converted into pure tetraethyl ammonium perchlorate by following an available procedure [21].

2.2. Physical measurements

UV-Vis spectra were recorded by using a Shimadzu-2100 spectrophotometer. FTIR spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. Magnetic susceptibility was checked with a PAR vibrating sample magnetometer. NMR spectra were obtained with a 300 MHz Varian FT spectrometer. Cyclic voltammetric, differential pulse voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. Platinum wire working and auxiliary electrodes and an aqueous saturated calomel reference electrode (SCE) were used in a three electrode configuration. The supporting electrolyte was [NEt₄][ClO₄] and the solute concentration was ~ 10^{-3} M. The half-wave potential E°_{298} was set equal to $0.5(E_{\rm pa}+E_{\rm pc})$, where $E_{\rm pa}$ and $E_{\rm pc}$ are anodic and cathodic cyclic voltammetric peak potentials, re-

Table 1 Crystallographic data for complex **1a**

Formula	$C_6H_{18}O_6P_3S_6Os$
$f_{\rm w}$	661.67
Crystal symmetry	monoclinic
Space group	Cc
Unit cell dimensions	
a (Å)	14.138(12)
b (Å)	11.228(4)
<i>c</i> (Å)	12.970(14)
β (°)	96.988(10)
$U(Å^3)$	2043.6(8)
Ζ	4
$D_{\rm calc}$ (Mg m ⁻³)	2.151
$\mu ({\rm mm}^{-1})$	7.105
R_1	0.0358
wR_2	0.0902

spectively. A platinum wire-gauze working electrode was used in coulometric experiments. All experiments were carried out under a dinitrogen atmosphere and were uncorrected for junction potentials. The electrospray mass spectrum was recorded on a Micromass Quattro II triple quadrupole mass spectrometer. The elemental analyses were carried out with Carlo–Erba elemental analyzer. The EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). The spectra were calibrated by using tetracyanoethylene (tcne) (g = 2.0023).

2.3. Preparation of complexes

The complexes (1a and 1b) were synthesized by following a general procedure. Details are given for the complex 1a. Yields vary in the range 65-70%.

Tris(dimethyldithiophosphate)osmium(III) (1a). 2.3.1. The precursor $(NH_4)_2Os^{IV}Br_6$ (100 mg, 0.14 mmol) was dissolved in 15 ml of methanol solvent and a stream of nitrogen was flushed through the solution for a period of 15 min. The ligand NH₄L¹ (98 mg, 0.56 mmol) was then added to the metal solution and the reaction mixture was stirred magnetically under nitrogen atmosphere for 12 h. The solvent was removed under reduced pressure and the solid product thus obtained was purified by using a silica gel column. On elution with benzene, one yellow colored band was separated out leaving behind a dark mass at the top of the column which did not move even on using methanol. On removal of benzene under reduced pressure dark crvstalline solid complex 1a was obtained in the pure solid state. Yield: 66 mg (70%).

2.4. X-ray structure determination

Single crystals of complex 1a were grown by slow diffusion of dichloromethane solution of the complex into hexane followed by slow evaporation. Cell parameters were determined by least-squares fit of 25 ($2\theta =$ 10-17°) machine centered reflections. Data were collected by ω -scan technique in the range $4.62 \le 2\theta \le$ 49.86° on a Nonius MACH 3 four-circle diffractometer with graphite-monochromated Mo K α radiation ($\lambda =$ 0.7013 Å) at 293 K. Significant crystal data and data collection parameters are listed in Table 1. Absorption correction was done by performing psi-scan measurement [22]. The data reduction was done by using MAXUS and structure solution and refinement using the programs of SHELXS-93 and SHELXL-97, respectively [23]. The metal atom was located from the Patterson map and the other non-hydrogen atoms emerged from successive Fourier synthesis. The structure was refined



by full-matrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions.

3. Results and discussion

3.1. Synthesis

The reaction of osmium precursor $(NH_4)_2Os^{IV}Br_6$ with the ammonium salt of dialkyl dithiophosphates NH_4L^{1-2} in methanol solvent under dinitrogen atmosphere at room temperature for 12 h results in a yellow solution. Chromatographic purification of the yellow solution on a silica gel column, using benzene as eluant, yields pure tris complex, $Os^{III}{S_2P(OR)_2}_3$ (1) in the solid state (Scheme 1).

3.2. Solid-state characterization

In the solid state the complexes **1a** and **1b** are found to be stable and one-electron paramagnetic in nature (low-spin Os^{III}, Table 2) [24]. Microanalytical data of the complexes match well with the calculated values (Table 2). The molecular structure of one complex (**1a**) has been determined by single-crystal X-ray diffraction technique. The crystal structure of **1a** is shown in Fig. 1. Selected bond lengths and angles are listed in Table 3. The complex is monomeric and the lattice consists of one type of molecule where the dimethyldithiophosphate ligands are in bidentate S,S mode. The RuS₆ coordination sphere is distorted octahedral as can be seen from the angles subtended at the metal (Table 3). The observed distortion from the perfect octahedral

Table 2 Microanalytical ^a reflectance ^b magnetic moment



Fig. 1. Crystal structure of complex 1a.

symmetry has originated from the constraints due to the four-membered chelate rings in which the average S-Os-S bite angle is $81.31(5)^\circ$ (Table 3). A similar effect of ring constraints on the molecular geometry has been also observed earlier [25–28].

The Os^{III}–S distances are unequal, the longer and shorter distances are 2.455(6) and 2.404(7) Å, respectively. The Os^{III}–S distances in the present complex are slightly longer than the Os^{III}–S distances observed in the dimeric complex $[Os_2^{III}(S_2CNEt_2)_3-(S_3CNEt_2)_2]BPh_4$ (average Os^{III}–S distance is 2.36(1) Å) [9].

The distances within the dithiophosphate ligands agree well with those found in structurally characterized dithiophosphate complexes of other metal ions [29–31].

To the best of our knowledge the present work demonstrates the first crystal structure of osmium complex incorporating dithiophosphate ligand and also the first crystal structure of osmium tris chelate having dithioacid based ligands.

Compound	Elemental analysis (%)		Reflectance λ (nm)	Magnetic moments μ_M (BM)	EPR (g)
	C	Н			
1a	11.01 (10.89)	2.65 (2.72)	552, 484	1.828	2.203
1b	19.48 (19.32)	4.16 (4.05)	548, 492	1.877	2.183

Microanalytical ^a, reflectance ^b, magnetic moment ^b and EPR data ^c

^a Calculated values are in parentheses.

^b In the solid state at 298 K.

^c In the solid state at 77 K.

The reflectance spectra of the solid complexes 1a-1b exhibit two broad bands in the visible region (Fig. 2, Table 2). The band profiles look similar for both the complexes, but the band maxima are observed to be sensitive to the nature of the 'R' groups present in L.

Consistent with the low-spin configuration, the complexes $[Os^{III}L_3]$ (low-spin d⁵-Os^{III}, S = 1/2) display one isotropic broad EPR signal in the solid state (Table 2) [24,32]. No anisotropic pattern has been observed even at liquid N₂ temperature (77 K).

3.3. Solution properties of the complexes

The solid complexes (1a and 1b) are fairly soluble in non-polar solvents like dichloromethane, chloroform, benzene. In dichloromethane, acetonitrile the complexes are non-conducting, diamagnetic and consequently EPR silent even at chloroform-toluene glass temperature (77 K, liquid N₂). The observed change in magnetic properties of the complexes while moving from the solid state (one-electron paramagnetic) to solution state (diamagnetic) indicates that the solid tris

Table 3 Selected bond distances (Å) and bond angles (°) and their e.s.d. values for **1a**

Os-S(1)	2.426(7)
Os–S(2)	2.427(6)
Os–S(3)	2.415(7)
Os–S(4)	2.455(6)
Os–S(5)	2.415(7)
Os–S(6)	2.404(7)
P(1)–S(1)	2.012(8)
P(1)–S(2)	1.989(10)
P(2)–S(3)	2.025(10)
P(2)–S(4)	1.999(8)
P(3)–S(5)	2.014(11)
P(3)–S(6)	1.989(11)
P(1)–O(1)	1.567(15)
P(1)–O(2)	1.563(19)
P(2)–O(3)	1.597(15)
P(2)–O(4)	1.589(18)
P(3)–O(5)	1.580(15)
P(3)–O(6)	1.557(16)
S(1)–Os–S(2)	81.1(2)
S(1)–Os–S(4)	95.09(9)
S(2)–Os–S(4)	92.8(2)
S(3)–Os–S(1)	92.4(2)
S(3)–Os–S(2)	170.95(7)
S(3)–Os–S(4)	81.5(2)
S(3)–Os–S(5)	95.5(2)
S(5)–Os–S(1)	170.3(3)
S(5)–Os–S(2)	91.7(2)
S(5)–Os–S(4)	91.7(2)
S(6)–Os–S(1)	92.9(3)
S(6)–Os–S(2)	95.9(2)
S(6)–Os–S(3)	90.6(2)
S(6)–Os–S(4)	168.9(2)
S(6)–Os–S(5)	81.32(10)

complexes undergo molecular reorganization in the solution state and which eventually leads to the formation of a different species having diamagnetic in nature.

Electrospray mass spectrum of one representative complex (1b) has been recorded in dichloromethane solvent. The maximum molecular peak is observed at m/z, 1492 (Fig. 3) which corresponds to the molecular ion $[{(EtO)_2PS_2)}_3Os^{III}-Os^{III}{S_2P(OEt)_2}_3]$ (calculated molecular weight, 1491.8). Thus the tris complexes 1 in the solid state have been transformed selectively into the metal-metal bonded dinuclear species as shown in Scheme 2. The conversion of the solid tris complexes $[(RO)_2PS_2)$ ₃Os^{III}] (1) to the metal-metal bonded dimeric $[(EtO)_2PS_2)$ $_3Os^{III} - Os^{III} \{S_2P(OEt)_2\}_3]$ species in solution state can account for the observed change in magnetic behavior, i.e. one-electron paramagnetic in the solid state and diamagnetic in the solution state (the unpaired electron in each Os^{III} center gets paired up antiferromagnetically through the metal-metal bond formation) [33].

It may be noted that the tris dithiocarbamato osmium complex, $Os^{III}(dtc)_3$ (dtc = diethyldithiocarbamate) is known to exhibit a monomer-dimer equilibrium $[Os^{III}(dtc)_3 \rightarrow Os_2^{IV} (dtc)_6^{2+}]$ in solution state at low-temperature, where each osmium is effectively seven coordinated [8]. Therefore the general tendency of dimerization of osmium dithioacid based complexes and to form higher coordination numbers (>6) in solution state [8,9] might be playing a crucial role here as well in forming the dimeric species in the solution state. In case of the ruthenium-dthiocarbamate complex the formation of seven coordinated metal-metal bonded species is also known [10].

The ¹H NMR spectra of the ligands NH_4L^{1-2} and the complexes are recorded in D₂O and CDCl₃, respectively. The free ligand, NH_4L^1 exhibits two singlets at 3.663 and 3.615 ppm due to two inequivalent $-OCH_3$ groups and similarly NH_4L^2 displays two quartets (3.93 and 3.76 ppm) and two triplets (1.17 and 1.12 ppm) due to two inequivalent $-OC_2H_5$ groups. The ¹H NMR spectrum of **1a** incorporating $R = CH_3$ exhibits one singlet corresponding to $-OCH_3$ groups at 3.70 ppm and for **1b** ($R = C_2H_5$) one quartet and one triplet at 4.18 and at 1.28 ppm, respectively, due to $-OC_2H_5$ groups as internal symmetry makes all the ligands equivalent.

The decoupled ³¹P NMR spectra of the complexes **1a** and **1b** in CDCl₃ solvent display one signal at 121.9 and 120.6 ppm, respectively.

In dichloromethane solvent the complexes display two moderately intense bands in the visible region. The higher energy band is associated with a shoulder at a further higher energy part of the spectra (Table 4, Fig. 2). Since osmium ion is in the +3 oxidation state in the complexes, the bands are therefore believed to be ligand to metal charge-transfer transitions from sulfur to the



Fig. 2. Electronic spectrum of 1a in dichloromethane. The inset shows the reflectance spectrum of 1a.



Fig. 3. Electrospray mass spectrum of [{(EtO)₂PS₂}₃Os^{III}-Os^{III}{S₂P(OEt)₂}₃] (1b) in dichloromethane.

metal ion [1,24]. The direct comparison of the solidstate reflectance spectra of **1a** and **1b** with the corresponding solution absorption spectra (Fig. 2, Tables 2 and 4) reveals that the bands have been reasonably blue shifted while moving from solid to solution state. The observed shift in band maxima on switching from solid to solution state provides an additional support in favor of the presence of different species in the solution state as shown in Scheme 2.



Scheme 2.

The UV region strong bands (Fig. 2, Table 4) might be due to ligand centered transitions as the free ligands also exhibiting a strong band in the same region (NH_4L^1 , 236 nm and NH_4L^2 , 237 nm in H_2O).

Electron-transfer properties of the complexes have been studied in dichloromethane solvent by cyclic voltammetry using a platinum working electrode in the range ± 2.0 V versus saturated calomel electrode (SCE) at 298 K (tetraethyl ammonium perchlorate as electrolyte). Representative voltammograms are shown in Fig. 4 and the reduction potentials data are set in Table 4. The complexes display two reversible couples (couple-II and couple-III) and the separation between the two $E_{1/2}$ values is found to be ~ 1.4 V (Fig. 4, Table 4). The reduction potentials vary depending on the nature of the 'R'groups present in L and it follows the order **1b** < **1a**. The two-electron nature of the oxidative cou-

Table 4				
Electronic	spectral $^{\rm a}$	and	electrochemical b	data



Fig. 4. Cyclic voltammograms of 1a in dichloromethane at 298 K.

ple near 0.8 V (couple-II, Fig. 4) is confirmed with the help of constant-potential coulometry (Table 4) whereas the two-electron nature of the reductive couple near -0.6 V (couple-III, Fig. 4) has been confirmed by comparing its differential pulse voltammetric current height with that of the previous oxidative couple near 0.8 V. The responses at the positive (couple-II) and negative potentials (couple-III) are assigned to be simultaneous oxidations and reductions of the osmium(III) centers, respectively, Eqs. (1) and (2), since the free ligands (NH_4L^{1-2}) do not show any redox activities within the reported potential range. Here the difference in potential between the two successive electron-transfer processes (couple-II–couple-III) is found to be ~ 1.4 V (Table 4) which is in good agreement with the potential differences (1.3-1.4 V) between the two successive reduction processes of Os^{IV/III}-Os^{III/II} observed in other complexes [24].

$$[\{(RO)_{2}PS_{2}\}_{3}Os^{IV}-Os^{IV}\{S_{2}P(OR)_{2}\}_{3}]^{2+}+2e^{-}$$

$$\rightarrow [\{(RO)_{2}PS_{2}\}_{3}Os^{III}$$

$$-Os^{III}\{S_{2}P(OR)_{2}\}_{3}]$$
(1)

Compound	λ (nm) (ε (M ⁻¹ cm ⁻¹))	Os ^{IV} –Os ^{III} couple	n ^c	$Os^{V} – Os^{IV}$	Os ^{III} –Os ^{II} couple	
		E°_{298} (V) ($\Delta E_{\rm p}$ (mV))	_	$E_{\rm pa}{}^{\rm d}$	E°_{298} (V) ($\Delta E_{\rm p}$ (mV))	
1a 1b	438(2634), 362(2568), 330(1807), 246(18074) 442(2403), 365(2431), 333(1621), 246(16460)	0.86(92) 0.83(90)	2.13 2.07	1.89 1.82	-0.58(110) -0.63(90)	
1a ²⁺ 1b ²⁺	533, 430, 363 540, 427, 360					

^a In dichloromethane at 298 K.

^b Condition: solvent, dichloromethane; supporting electrolyte, NEt₄ClO₄; reference electrode, SCE; solute concentration, 10^{-3} M; working electrode, platinum. Cyclic voltammetric data: scan rate, 50 mV s⁻¹; $E^{\circ}_{298} = 0.5(E_{pc} + E_{pa})$ where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively.

 $^{c}n = Q/Q'$ where Q' is the calculated Coulomb count for a two-electron transfer and Q that found after exhaustive electrolysis of $\sim 10^{-2}$ mol of solute.

 $^{\rm d}E_{\rm pa}$ is considered for irreversible nature of the responses.



Fig. 5. Electronic spectrum of coulometrically oxidized complex of $[\{(MeO)_2PS_2\}_3Os^{IV}-Os^{IV}\{S_2P(OMe)_2\}_3]^{2+}$ (1a²⁺) in dichloromethane.

$$[\{(RO)_{2}PS_{2}\}_{3}Os^{III} - Os^{III}\{S_{2}P(OR)_{2}\}_{3}] + 2e^{-}$$

$$\rightarrow [\{(RO)_{2}PS_{2}\}_{3}Os^{II}$$

$$-Os^{II}\{S_{2}P(OR)_{2}\}_{3}]^{2-}$$
(2)

The complexes also exhibit an irrevesible oxidation near 1.9 V (couple-I, Fig. 4, Table 4). No significant response on scan reversal in cyclic voltammetry is observed (Fig. 4). The oxidized species thus decomposes rapidly on the cyclic voltammetric time-scale. Although the anodic current height (i_{pa}) of this irrevesible process is ~ 1.5 times that of the previous reversible osmium(III)-osmium(IV) process, the differential pulse voltammogram shows the second oxidation wave to have the same height as that of the first, implying a two-electron process (Fig. 4). This irreversible oxidation is therefore considered to be $Os^{IV}-Os^{IV} \rightarrow Os^{V}-Os^{V}$ oxidation process. It may be noted that osmium(IV) \rightarrow osmium(V) oxidation process has also been detected in dithiocarbamate system as well [6].

Electrochemical oxidation (constant-potential coulometry) of the complexes (1a and 1b) at 1.0 V versus SCE in dichloromethane solvent using a platinum gauze-working electrode under a dinitrogen atmosphere results in a sharp color change from yellow to purple. The observed Coulomb counts correspond to two-electron transfer (Table 4). The resulting oxidized species $[\{(RO)_2PS_2\}_3Os^{IV}-Os^{IV}\{S_2P(OR)_2\}_3]^{2+1}$ display the voltammograms which are superimposable on those of the corresponding starting (Os^{III}–Os^{III}) complexes, which imply that the oxidations here may be stereoretentive in nature [34,35]. When the same oxidized solutions are rereduced coulometrically at a potential 200 mV negative to the corresponding E_{pc} of the Os^{IV}/Os^{III} couple, the starting yellow colored trivalent complexes are formed quantitatively. The oxidized species are not stable enough to be isolated in the solid state at 298 K, however, we have managed to record the qualitative absorption spectra. In dichloromethane solvent, the complexes display two sulfur to metal charge transfer transitions in the visible region (Fig. 5, Table 4) [36] and ligand based transitions in the UV region (Table 4). The lowest energy charge-transfer bands have been red shifted approximately 100 nm while moving from Os^{III}-Os^{III} to Os^{IV}-Os^{IV} center. Coulometric reductions of the complexes (1a and 1b) at -0.7 V versus SCE result in unstable reduced species $[\{(RO)_2PS_2\}_3Os^{II}-Os^{II}\{S_2P(OR)_2\}_3]^2$ -. In contact with a slight amount of air the complexes immediately get oxidized to the starting trivalent species, therefore no further study is made in this direction. The low Os^{III/II} potentials (~ -0.60 V) and the dianionic nature of the reduced species might be responsible for their spontaneous aerial oxidation to the higher congeners.

Further investigations are in progress in the direction of isolating the oxidized dimeric species, $[{(RO)_2PS_2}_3Os^{IV}-Os^{IV}{S_2P(OR)_2}_3]^{2+}$, particularly at low temperature in order to have direct evidence in favor of the observed monomer-dimer equilibrium in the solid-solution states, respectively.

4. Conclusions

We have observed that the one-electron paramagnetic osmium tris-dithiophosphate complexes, $[Os^{III}{(RO)_2PS_2}_3]$ (1a and 1b), generated from the reaction of dialkyldithiophosphate ligands (NH_4L^{1-2}) and $(NH_4)_2OsBr_6$, are stable only in the solid state. However, in the solution state the tris complexes have been transformed selectively into the diamagnetic $[\{(RO)_2PS_2\}_3Os^{III}-Os^{III}\{S_2P$ complexes dimeric $(RO)_{2}_{3}$ where the paramagnetic osmium(III) centers are antiferromagnetically coupled. The trivalent dinuclear complexes are susceptible to undergo stereoretentive electrochemical oxidations and reductions to the corresponding tetravalent and bivalent dinuclear congeners $[{(RO)_2PS_2}_3Os^{IV}-Os^{IV}{(S_2P(RO)_2)_3}]^2 +$ and $[\{(RO)_2PS_2\}_3Os^{II}-Os^{II}\{S_2P(RO)_2\}_3]^2^{-1}$, respectively. The bivalent species are found to be unstable whereas the tetravalent complexes are stable on the coulometric time scale but the isolation of the oxidized tetravalent species in the pure solid state has not been succeeded so far.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 148040 for 1a. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK Financial support received from the Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR), New Delhi, India are gratefully acknowledged. We also thank the DST for establishing a National Single Crystal Diffractometer Facility at the Indian Institute of Technology, Bombay. Special acknowledgement is made to the Regional Sophisticated Instrumental Center, RSIC, Indian Institute of Technology, Bombay for providing NMR and EPR facilities.

References

- A. Pramanik, N. Bag, D. Ray, G.K. Lahiri, A. Chakravorty, Inorg. Chem. 30 (1991) 410.
- [2] A. Pramanik, N. Bag, G.K. Lahiri, A. Chakravorty, J. Chem. Soc., Dalton Trans. (1992) 101.
- [3] A. Pramanik, N. Bag, D. Ray, G.K. Lahiri, A. Chakravorty, J. Chem. Soc., Chem.Commun. (1991) 139.
- [4] B.K. Santra, P. Munshi, G. Das, P. Bharadwaj, G.K. Lahiri, Polyhedron 18 (1999) 617.
- [5] W.P. Griffith, in: G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, vol. 4, Pergamon, Oxford, 1987, p. 603.
- [6] A.H. Dix, J.W. Diesveld, J.G.M. van der Linden, Inorg. Chim. Acta 24 (1977) L51.
- [7] P.B. Critchlow, S.D. Robinson, J. Chem. Soc., Dalton Trans. (1975) 1367.
- [8] S.H. Wheeler, L.H. Pignolet, Inorg. Chem. 19 (1980) 972.
- [9] L.J. Maheu, L.H. Pignolet, Inorg. Chem. 18 (1979) 3626.
- [10] K.W. Given, S.H. Wheeler, B.S. Jick, L.J. Maheu, L.H. Pignolet, Inorg. Chem. 18 (1979) 1261.
- [11] T. Behling, G. Wilkinson, T.A. Stephenson, D.A. Tocher, M.D. Walkinshaw, J. Chem. Soc., Dalton Trans. (1983) 2109.
- [12] L.J. Maheu, L.H. Pignolet, J. Am. Chem. Soc. 102 (1980) 6346.

- [13] L.J. Maheu, G.L. Miessler, J. Befy, M. Burow, L.H. Pignolet, Inorg. Chem. 22 (1983) 405.
- [14] D. Coucouvanis, Prog. Inorg. Chem. 26 (1979) 301.
- [15] A.M. Bond, L. Martin, Coord. Chem. Rev. 54 (1984) 23.
- [16] R.N. Mukherjee, V.S. Vijaya, Indian J. Chem. Sect. A 21 (1982) 427.
- [17] N.V. Tkachev, L.O. Atovmyan, S.A. Shchepinov, Bull. Acad. Sci. USSR Div. Chem. Sci. (1977) 2011.
- [18] D.J. Cole-Hamilton, T.A. Stephenson, J. Chem. Soc., Dalton Trans. (1976) 2396.
- [19] A.P. Dwyer, J.W. Hogarth, Inorg. Synth. 5 (1957) 204.
- [20] J.L. Lefferts, K.C. Mollouy, J.J. Zuckerman, I. Haituc, C. Guta, D. Ruse, Inorg. Chem. 19 (1980) 1662.
- [21] D.T. Sawyer, A. Sobkowick, J.L. Roberts, Jr., Electrochemistry for Chemists, second ed., Wiley, New York, 1995.
- [22] A.C.T. North, D.C. Phillips, F.S. Mathews, Acta Crystallogr., Sect. A 24 (1968) 351.
- [23] G.M. Sheldrick, SHELXTL, Version 5.03, Siemens Analytical X-ray Instruments Inc, Madison, WI, 1994.
- [24] G.K. Lahiri, S. Bhattacharya, B.K. Ghosh, A. Chakravorty, Inorg. Chem. 26 (1987) 4324.
- [25] B.K. Santra, M. Menon, C.K. Pal, G.K. Lahiri, J. Chem. Soc., Dalton Trans. (1997) 1387.
- [26] S.L. Lawton, Inorg. Chem. 10 (1971) 328.
- [27] D.F. Lewis, S.J. Lippard, J.A. Zubieta, Inorg. Chem. 11 (1972) 823.
- [28] S.R. Fletcher, A.C. Skapski, J. Chem. Soc., Dalton Trans. (1972) 635.
- [29] S.L. Lawton, G.T. Kakotailo, Inorg. Chem. 8 (1969) 2410.
- [30] J.F. McConnell, V. Kastalsky, Acta Crystallogr. 22 (1967) 853.
- [31] K. Kirschbaum, U. Bonnighausen, E. Gesing, K. Greiwe, U. Kuhlmann, H. Strasdeit, B. Krebs, G. Henkel, Z. Naturforsch., Teil B. 45 (1990) 245.
- [32] R. Hariram, B.K. Santra, G.K. Lahiri, J. Organomet. Chem. 540 (1997) 155.
- [33] R. Samanta, P. Munshi, B.K. Santra, N.A. Lokanath, M.A. Sridhar, J.S. Prasad, G.K. Lahiri, J. Organomet. Chem. 581 (1999) 311.
- [34] S. Chakraborty, M.G. Walawalkar, G.K. Lahiri, J. Chem. Soc., Dalton Trans. (2000) 2875.
- [35] B. Mondal, S. Chakraborty, P. Munshi, M.G. Walawalkar, G.K. Lahiri, J. Chem. Soc., Dalton Trans. (2000) 2327.
- [36] B.K. Santra, G.K. Lahiri, J. Chem. Soc., Dalton Trans. (1997) 129.