Synthesis, characterization and electrochemical studies of oximato-bridged binuclear osmium(II)-oxovanadium(IV) complexes

Pradyut K Das, Sutapa Sinha & Barindra K Ghosh*

Department of ·Chemistry, The University of Burdwan, Burdwan 713 104, West Bengal

The. reaction of facial-$[OsA_3]^-$ (3 [A = anion of arylazo oxime (HA, 1)] with $VO(acac)_2$ furnishes hetero-bimetallic complexes of the type $[OsA_3 VO(acac)]$ (4). Replacement of acac by neutral N,N donors (B) like 2,2'-bipyridine and 1,10-phenanthroline gives cationic species of the type $[OsA_3VO(B)]^+$ isolated as perchlorate salt 5. Extrusion of 4 and 5 with NaOH reverts to mononuclear 3. All the complexes have been characterized using their spectroscopic, magnetic and physicochemical results. A 1:1 correspondence in the IR spectra of 4 (A = A^2) and corresponding well-characterized iron-vanadium analogue, $[FeA^2{}_3VO(acac)]$ suggests cognate structure 6. The new binuclear complexes are one-electron paramagnets and VO^{2+} core is EPR-active. The g-values suggest the occupancy of the unpaired electron in d_{xy} orbital. The complexes show a number of charge-transfer transitions in 200-700 nm region and exhibit nearly reversible osmium(III)-osmium(II) couple.

A novel feature[1-6] of recent coordination chemistry has been the appending of pendant arms at appropriate position on basic ligand framework. Such tailoring ensures modified complexation behaviour relative to the corresponding unarmed ligand. Arylazo oximes (HA, 1) bind[7-14] several transition metal ions through azo and oxime nitrogens. The chelate ring 2 thus formed has pendant arm (N→O) on oxime N which can act as further donating site via oxygen. Polynuclear ensembles[7-9,12-14] are reported to form with use of such metal complexes. Anionic tris chelates $[OsA_3]^-$ (3) have the facial geometry[12,13]; the pendant oximato oxygen triad on the same face of the octahedron is correctly disposed to span a triangular face of another polyhedron. In other words, 3 should be able to act as facial O_3 ligand. Trinuclear ensembles[12,13] of the type $[(OsA_3)_2M]^{n+}$ (n = 0 or 1 and M = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II} and the alkaline earths) have been prepared from

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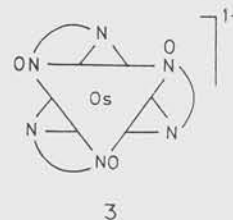
3 via Lewis basicity of these oxygens. In the present work, we examined the reaction behaviour of 3 towards $[VO(acac)_2]$ (acac = anion of acetylacetone) which is a well-known Lewis acid. Successful synthesis of binuclear complexes of the types $[OsA_3VO(acac)]$ (4) and $[OsA_3VO(B)]ClO_4$ (5) [B = 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen)] and their selected properties are presented below.

Materials and Methods

Arylazo oximes[15] and $Na[OsA_3]$[12,13] were prepared following reported procedures. Published method[16] was used to prepare $[VO(acac)_2]$ from V_2O_5 and acetylacetone. Solvents used for synthetic and spectroscopic works were distilled over appropriate drying and/or purifying agents prior to use. The purification of MeCN and preparation of tetraethylammonium perchlorate (TEAP) respectively used as solvent and supporting electrolyte for electrochemical study were done following an available procedure[17]. All other reagents used for preparative works were of AR grade.
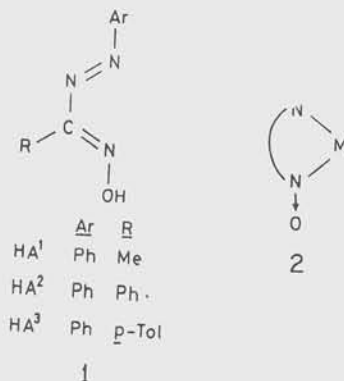
The IR and UV-vis spectra were recorded on a Perkin-Elmer 783 spectrometer and Shimadzu UV 160A spectrophotometer, respectively. Microanalyses (C, H and N) were obtained from a Perkin-Elmer model 240 C elemental analyzer. Molecular weights were determined in chloroform using a Knauer vapour pressure osmometer with benzil as calibrant. Solution electrical conductivity and magnetic susceptibility measurements were done on a Philips PR 9500 (Calcutta) bridge and a PAR 155 vibrating-sample magnetometer, respectively. EPR results were obtained with a Varian 109 C E-line X-band spectrometer fitted with a quartz Dewar for measurements at -196 °C (liquid nitrogen); all the spectra were calibrated using DPPH ($g = 2.0037$). Electrochemical measurements (in MeCN) were carried out under dry nitrogen with a PAR 370-4 electrochemistry system as described elsewhere[18]. In cyclic voltammetry (CV), the following parameters and relation were used : scan rate (v), 50 mVs^{-1}; formal potential, $E^0 = 0.5 (E_{pc} + E_{pa})$, where E_{pc} and E_{pa} are cathodic and anodic peak potentials respectively; ΔE_p, peak-to-peak separation. In differential pulse voltammetry (DPV) : scan rate (v), 10 mVs^{-1}; modulation amplitude (ΔE), 25 mV; $E^\circ = E_p + 0.5(\Delta E)$, where E_p is the DPV peak potential. The agreement between E° data obtained by the two techniques is invariably good (within ± 5 mV). The potentials are referenced to an SCE and are uncorrected for the junction contributions.

Preparation of complexes

Details for each representative member namely [OsA$^1_3$VO(acac)] and [OsA$^1_3$VO(bipy)]ClO$_4$ are given below. Extrusion of binuclear to mononuclear complexes and reaggregation of the latter to the former are also described.

(Acetylacetonato)oxotris (μ-phenylazo acetaldoximato)-osmium(II)vanadium(IV), [OsA$^1_3$VO(acac)] (4a)

To a magnetically stirred solution of 0.1 g (0.13 mmol) of Na[OsA$^1_3$].3H$_2$O in 10 ml acid-free dichloromethane was added 0.035 g (0.13 mmol) [VO(acac)$_2$] dissolved in the same solvent. The green solution immediately changed to greenish brown. After stirring the mixture for 2 h followed by evaporation in air, a residue was obtained. This was washed several times with water and finally with hexane. Recrystallisation from dichloromethane-hexane (:1) ensures analytical purity; yield, 0.1 g (90%). Other acac complexes (4b and 4c) were prepared similarly in good yield

(~ 80-90%) by using the appropriate mononuclear precursors, Na[OsA$^2_3$] and Na[OsA$^3_3$] respectively instead of using Na[OsA$^1_3$]. 3H$_2$O.

(2,2'-Bipyridine)oxotris (μ-phenylazo acetaldoximato)osmium(II) vanadium(IV) perchlorate, [OsA$^1_3$VO(bipy)]ClO$_4$ (5a)

The complex 4a (0.1 g, 0.12 mmol) was dissolved in 15 ml methanol. To this an aqueous solution of 2M HCl (0.6 ml) and bipy (0.02 g, 0.13 mmol) were added while stirring under warming conditions (50°C) for 3 h. An excess NaClO$_4$ was added and the solution allowed to evaporate. The precipitate deposited was filtered through a fine glass-frit, washed with chilled water followed by hexane and dried *in vacuo* over P$_4$O$_{10}$. Pure compound was obtained by recrystallisation from dichloromethane-hexane (1:1) mixture; yield, 0.08 g (65%). Other complexes (5b-5d) were obtained (yield, $\sim$ 60-70%) using the same procedure described above, with the appropriate type 4 complex and diimines.

Extrusion of 4

Aqueous sodium hydroxide (0.5 mmol) was added dropwise to a magnetically stirred solution of 4 (0.1 mmol) in acetone (15 ml). The greenish brown solution immediately turned green. Stirring was continued for 1 h and the mixture evaporated on steam bath. The residue was dried *in vacuo* over P$_4$O$_{10}$ and redissolved in a minimum of acid-free dichloromethane. This was loaded on a neutral alumina column (20 × 1 cm). At first, a small brown solution was eluted with acetonitrile, followed by a slow moving green band eluted with 1:1 acetonitrile-methanol. Slow evaporation of the green eluate afforded sodium salt of 3 in $\sim$ 60% yield. Characterization was made in comparison to physicochemical and spectroscopic properties of the compounds with those of authentic samples[12,13]. Similarly, the complexes of type 5 were extruded as described for 4. The yield is however low ($\sim$ 30-40%) due to some uncharacterized side reactions as is evident from chromatographic behaviour.

The mononuclear complexes obtained as extrusion product of 4 and 5 were again used to prepare the binuclear complexes following the similar procedure as described in case of 4a and 5a.
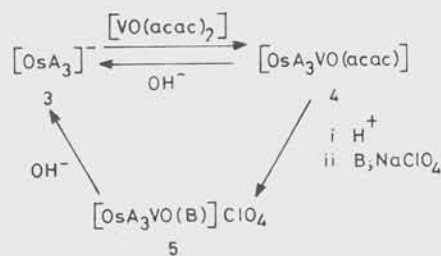
Results and Discussion

For brevity, synthetic routes of the binuclear complexes and their extrusion and reaggregation behaviour are shown in Scheme 1. Treatment of sodium salt of [OsA$_3$]$^-$ (3) with [VO(acac)$_2$] in dichloromethane afforded dark crystals of mixed

Table 1—Analytical and physical data

Compound[a] molec formula	Found (Calcd), %			Λ_M[b] ohm^{-1}cm^{2}mol^{-1}	μ_{eff}[c] BM	EPR data[d]	
	C	H	N			$g_{\parallel}$ $(A_{\parallel}/G)$	$g_{\perp}$ $(A_{\perp}/G)$
[OsA$^1_3$VO(acac)] (4a)	41.57	3.73	15.23	5	1.79	1.951	1.994
C$_{29}$H$_{31}$N$_9$O$_6$VOs	(41.33)	(3.71)	(14.96)			(190)	(65)
[OsA$^2_3$VO(acac)] (4b)	51.22	3.54	12.50	4	1.76	1.947	1.988
C$_{44}$H$_{17}$N$_9$O$_6$VOs	(51.36)	(3.62)	(12.25)			(186)	(68)
[OsA$^3_3$VO(acac)] (4c)	52.66	4.15	11.72	3	1.81	e	
C$_{47}$H$_{43}$N$_9$O$_6$VOs	(52.71)	(4.05)	(11.77)				
[OsA$^1_3$VO(bipy)]ClO$_4$ (5a)	40.76	3.13	15.39	120	1.82	1.942	1.991
C$_{34}$H$_{32}$N$_{11}$O$_8$ClVOs	(40.87)	(3.23)	(15.42)			(179)	(66)
[OsA$^2_3$VO(bipy)]ClO$_4$ (5b)	49.57	3.18	13.17	110	1.83	1.946	1.989
C$_{49}$H$_{38}$N$_{11}$O$_8$ClVOs	(49.64)	(3.23)	(13.00)			(178)	(67)
[OsA$^1_3$VO(phen)]ClO$_4$ (5c)	42.52	3.09	15.37	130	1.84	1.948	1.987
C$_{36}$H$_{32}$N$_{11}$O$_8$ClVOs	(42.25)	(3.15)	(15.06)			(179)	(65)
[OsA$^2_3$VO(phen)]ClO$_4$ (5d)	50.88	3.08	12.84	120	1.81	e	
C$_{51}$H$_{38}$N$_{11}$O$_8$ClVOs	(50.64)	(3.17)	(12.74)				

[a]Molecular weights determined : 4a, 835; 4b, 1015; 4c, 1060. Calcd. for 4a. 842.78; 4b. 1028.99; 4c. 1071.07; [b]In MeCN, solute concentration $\sim 10^{-3}M$; [c]In solid state at 25°C; [d]In 1:1 CH$_2$Cl$_2$-PhMe glass (-196°C); [e]Not studied.

Scheme 1

Table 2—Electrochemical data[a,b] at 25°C

Compound	E°, V(ΔE_p, mV)		
	Os^{III}-Os^{II}	Ligand-based	reductions
4a	0.84(80)	−0.51(70),	−1.16(100)
4b	0.88(80)	−0.47(65),	−1.07(95)
4c	0.87(80)	−0.49(70),	−1.06(95)
5a	1.33(100)	−0.25(60),	−0.81(90)
5b	1.35(100)	−0.22(60),	−0.79(90)
5c	1.34(100)	−0.24(60),	−0.84(90)
5d	1.37(100)	−0.21(60),	−0.78(90)

[a]Meaning and units of symbols are the same as in text; [b]Both CV and DPV results are set; the agreement between data obtained by the two techniques is invariably good (within ± 5 mV).

bimetallic species [OsA$_3$VO(acac)] (4) in high yield. Upon acidification followed by addition of B (B = bipy or phen), 4 yielded [OsA$_3$VO(B)]$^+$ isolated as perchlorate salt 5. Extrusion of 4 with base results in 3 which can again be used to recycle binucleation. Regeneration of 3 from 5 is also achieveable but in a low yield.

All the complexes were characterized by elemental analysis, molecular weight determination (where possible), solution electrical conductivity, magnetic susceptibility, IR, UV-vis and EPR spectroscopy, and electrochemistry (Tables 1 and 2). The results are consistent with the proposed binuclear formulation. The air-stable moisture-insensitive complexes are powders, soluble in common organic solvents such as dichloromethane, chloroform, methanol, ethanol and acetonitrile. Type 5 complexes behave as 1:1 electrolytes whereas 4 are almost non-conductors[19] in acetonitrile (Table 1). Dissociation of the latter to constituent ions [OsA$_3$]$^-$ and [VO(acac)]$^+$ is therefore negligible. In less polar solvent like chloroform, 4

should behave as a perfect non-conductor; osmometric molecular weights were therefore determined in chloroform and the data (Table 1) agree well with the binuclear composition. In IR spectra, 4 and 5 show characteristic V-O stretch at ~ 965 cm^{-1}. Strong absorption at ~ 1230 cm^{-1} assignable to $\nu(N{\rightarrow}O)$ stretch is invariably found in all complexes; a shift towards lower frequency from the corresponding values (~ 1250 cm^{-1}) (refs. 12, 13) in [OsA$_3$]$^-$ is indicative of binding[14] of VO^{2+} core with pendant N$\rightarrow$O arms of A$^-$ in 3. We have not yet succeeded in growing X-ray quality single crystals of any of these complexes and therefore their definitive structures remains unexplored. However, a plausible suggestion can be made on the basis of analogy with iron-vanadium arylazo oximates. A 1:1 correspondence in the IR spectra of [OsA$^2_3$VO(acac)]

and its iron-analogue [FeA²₃VO(acac)] strongly suggests the cognate structure[14]. The oximato oxygens of *facial*-[OsA₃]⁻ (3) occupy three coordination positions around monoacetylacetonatooxovanadium(IV) as shown in 6. Here A⁻ behaves as O,N bridging ligand whereas acac as an end-cap ligand. The metal ions are joined through three oximato bridges.
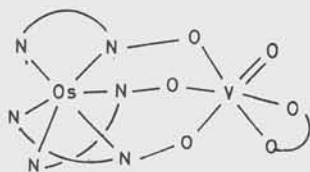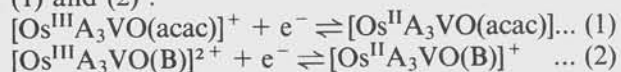

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Room temperature magnetic susceptibility measurements show (Table 1) that the complexes 4 and 5 are one-electron paramagnets corresponding to the VO^{2+} core (S = 1/2) in combination with diamagnetic (S = 0, t_{2g}^6) osmium(II). Characteristic VO^{2+} EPR spectra are therefore expected for these complexes. X-band spectra of all the complexes were recorded in polycrystalline phase as well as in solutions (1:1, dichloromethane-toluene) at 25°C and − 196 °C (liquid nitrogen). Isotropic solution spectra (25 °C) exhibit eight hyperfine lines at − 196 °C due to ^{51}V (I = 7/2); the overall shape of the frozen solution EPR spectra clearly shows axial symmetry with $g_{\parallel} < g_{\perp}$. The unpaired electron is in the d_{xy} oribital (axial compression) as expected for VO^{2+} complexes[20]. The spectral parameters are presented in Table 1. No nitrogen superhyperfine lines are however observed in any of the complexes. This is presumably due to the fact that the unpaired electron of VO^{2+} does not interact to any great extent with the atoms beyond oxygens of oxime and acac.

The complexes display several intense transitions in the region 200-700 nm. The absorptions and corresponding molar extinction coefficients of some of the compounds are : 4a, 605 (6,450), 420 (12,390), 344 (30,000), 250 (45,020); 4b, 610 (7,100), 418 (13,540), 340 (32,000), 255(50,560); 5a, 585 (8,240), 405 (12,040), 350 (26,040), 280(35,170); 5b, 585 (8,290), 405(12,380), 352(26,470), 280(35,780); 5c, 580(8,600), 400(13,020), 350(27,200), 275(38,940). A characteristic feature is transitions near 600 and 400 nm. The bands are blue shifted in going from 4 to 5. These are assignable to metal-ligand charge-transfer (MLCT) transitions, $t_{2g}(Os) \rightarrow \pi^*(A)$ within the pseudooctahedral osmium(II) geometry of the [OsA₃]⁻ moiety; the high intensity vitiates observation of ligand-field transitions of VO^{2+} core. The transitions in the UV region are of ligand origin as described elsewhere[7,10].

Electroactivity of the complexes was studied in some details and the results are given in Table 2. In the potential range 0.8 to 1.4 V, a nearly reversible (ΔE_p, 80-100 mV) one-electron oxidative response is observed at a platinum working electrode. This is presumably due to electrode reactions shown in Eqs (I) and (2) :

$$[Os^{III}A_3VO(acac)]^+ + e^- \rightleftharpoons [Os^{II}A_3VO(acac)]... (1)$$
$$[Os^{III}A_3VO(B)]^{2+} + e^- \rightleftharpoons [Os^{II}A_3VO(B)]^+ ... (2)$$

The one-electron stoichiometry of couples 1 and 2 was confirmed from the comparison of current heights with those of the standard[12,13] osmium(III)-osmium(II) couple, since attempted coulometry at potentials more anodic than E^+ values gives continuous coulomb count due to some unidentified side reactions. The formal potential of couple 1 is ∼ 0.8 V which is shifted to ∼ 1.3 V in couple 2. The anodic shift clearly reflects the better stabilisation of lower oxidation state of osmium in 5. The presence of π-acceptor[21] ligand B may presumably be the prime factor for this observation. It is of note that the corresponding osmium(III)-osmium(II) couple in mononuclear 3 lies near 0.5 V[12,13]. Indeed, a good sequence exists; a shift of ∼ 0.3 V on replacing Na⁺ by [VO(acac)]⁺ and another ∼ 0.5 V by substituting the latter with [VO(B)]²⁺. The $E°$ of such metal-based electrode reactions primarily depends on the energy of t_{2g} level of osmium(II). With the change of counter cation from Na⁺ to [VO(B)]²⁺ via [VO(acac)]⁺, its energy decreases, resulting in a corresponding increase of E^+ value. Two successive reversible/nearly reversible (in CV) azo[7−9,12,13] reductions are observable within the available potential window. The reversibility of these processes increases in going from 4 to 5. The potentials show anodic shift on replacement of acac by B (Table 2). Such a shift is understandable in view of the increased positive charge on the 3d metal ion. The binuclear formulation of 4/5 can be strengthened from comparison of their reductive behaviours with those in mononuclear [OsA₃]⁻ and trinuclear [(OsA₃)₂M]⁰/¹⁺ (M = Mg^{II}, Ni^{II}, Fe^{III} etc.) complexes. Two responses below − 1.0 V with a ptoential difference of ∼ 0.5 V are seen for the mononuclear species. Trinuclears show a pair of overlapping[12,13] responses (separation within ∼ 0.2 V) at much higher potential due to successive electron transfer to two different metal bound [OsA₃]⁻ units. Complexes 4/5 display two reductions with similar separation (∼ 0.5 V) in potentials like that in mononucler species; however, the potentials shift towards higher values as expected. The results strongly suggest the intimate binding of VO^{2+} ions with [OsA₃]⁻ unit.

We conclude that this paper has addressed the potentiality of *facial*-[OsA$_3$]$^-$ as a tridentate O$_3$ lignad to sequester VO^{2+} ion affording hetero-binuclear aggregates of types [OsA$_3$VO(acac)] and [OsA$_3$VO(B)]$^+$. To our knowledge, this is the first example of O,N-bridged OsV complex where an earlier and a late member transition metal ions are present. Further studies on binding of [OsA$_3$]$^-$ with MoO$_2{}^{2+}$ and UO$_2{}^{2+}$ ions are under our current consideration and exciting chemistry emerging therefrom will be reported in due course[22].

Acknowledgement

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