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Synthesis and structural characterization of a novel diosmium(III) compound: Os₂(*ap*)₄Cl₂

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Abstract

The reaction between $Os_2(OAc)_4Cl_2$ and Hap (Hap is 2-anilinopyridine) under prolonged refluxing conditions resulted in a new $Os_2(III)$ compound, $Os_2(ap)_4Cl_2$ (1). The molecular structure of 1 was determined from a single crystal X-ray diffraction study, which revealed an Os–Os bond length of 2.396[1] Å, and a *cis*-(2,2) arrangement of the *ap* ligands. Also reported are magnetic, electrochemical and spectroscopic properties of 1.

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1. Introduction

The paddlewheel structural motif, $Os_2(LL)_4Cl_2$, is prevalent in diosmium chemistry, where bidentate bridging ligands LL are mostly μ -*O*,*O'*-carboxylates [1,2]. As a convenient starting material, $Os_2(OAc)_4Cl_2$ undergoes either complete ligand metathesis to yield $Os_2(LL)_4Cl_2$ compounds with LL as μ -*O*,*N*-amidates [3] and μ -*N*,*N'*-formamidinates [4,5], or partial metathesis to yield $Os_2(LL)_2(OAc)_2Cl_2$ with LL as μ -*P*,*C*-Ph_2PC₆H₄ [6]. One peculiar exception is $Os_2(ap)_3Cl_3$ (*ap* = 2-anilinopyridinate), which was obtained from brief refluxing (4 h) of $Os_2(OAc)_4Cl_2$ with four equivalents of H*ap* in the presence of Me₃SiCl in toluene [7]. Incomplete metathesis might be attributed to the potential steric conflict between two axial chloro and four *ap* ligands in $Os_2(ap)_4Cl_2$. Indeed, crowding of the ligands in the metathesis reaction involving 6-fluoro-2hydroxypyrinate resulted in the elimination of one of the axial chloro ligands and the concurrent reduction of the Os_2^{6+} core to Os_2^{5+} [8]. Nevertheless, our recent work on $Ru_2(ap)_4(C_2R)_2$ type compounds demonstrated the feasibility of accommodating two axial ligands on a $M_2(ap)_4$ core [9]. In this contribution, we described the successful preparation of $Os_2(ap)_4Cl_2$ and its structural and electrochemical characterizations.

2. Results and discussion

Synthesis of $Os_2(ap)_4Cl_2$ is straightforward using a technique similar to that previously described for $Ru_2(ap)_4Cl$ [10]: refluxing $Os_2(OAc)_4Cl_2$ with eight equivalents of Hap in toluene using a micro Soxhlet extractor. The extractor is fit with a glass thimble containing a 1:1 mixture of K_2CO_3 and sand, which serves as the scavenger for acetic acid to drive the metathesis to completion. Pioneered by the laboratory of Doyle et al.

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Fig. 1. ORTEP plot of molecule A at 30% probability level; hydrogen atoms were omitted for clarity.

[11,12], this technique eliminates potential side reactions caused by the direct contact between the Os-containing species and the base. The previously reported compound $Os_2(ap)_3Cl_3$ was described as dark blue with intense absorptions at 870 and 620 nm [7]. Similarly, $Os_2(ap)_4Cl_2$ has a royal blue color resulted from strong absorptions at 880 and 630 nm. In addition, it has a strong absorption at 450 nm that is absent in $Os_2(ap)_3Cl_3$.

The molecular structure of $Os_2(ap)_4Cl_2$ was elucidated from the single crystal X-ray diffraction studies. Crystallized in the $P\bar{1}$ space group, the asymmetric unit contains the halves of two independent molecules, and each half is related to the other via a crystallographic inversion center that bisects the Os-Os bond. The ORTEP representation of the molecule A is shown in Fig. 1, and selected bond distances and angles for both molecules A and B are listed in Table 1. Since each ap ligand has two distinct N-donor centers, i.e., pyridine N (N_p) and aniline N (N_a) , there are four possible ligand arrangements for a $M_2(ap)_4$ core, as depicted in Scheme 1. The (4,0) arrangement has been dominant in both the $Ru_2(ap)_4L_{ax}$ and $Ru_2(ap)_4(L_{ax})_2$ type compounds, where Lax is an axial ligand [13]. In contrast, $Os_2(ap)_4Cl_2$ adopts the *cis*-(2,2) geometry. A possible

Table 1 Selected bond lengths (Å) and angles (°) for both independent molecules of 1

| Os(1)–Os(1A) | 2.3976(5) | |
|--------------------|------------|--|
| Os(1)-Cl(1) | 2.5215(13) | |
| Os(1)-N(1) | 2.069(5) | |
| Os(1)-N(2) | 2.050(5) | |
| Os(1)–N(3) | 2.074(5) | |
| Os(1)-N(4) | 2.023(5) | |
| Os(2)-Os(2A) | 2.3943(6) | |
| Os(2)-Cl(2) | 2.5503(16) | |
| Os(2)–N(5) | 2.067(5) | |
| Os(2)–N(6) | 2.030(5) | |
| Os(2)–N(7) | 2.068(4) | |
| Os(2)–N(8) | 2.024(4) | |
| N(1)-Os(1)-Os(1A) | 90.24(11) | |
| N(2)-Os(1)-Os(1A) | 87.79(11) | |
| N(3)-Os(1)-Os(1A) | 88.96(11) | |
| N(4)-Os(1)-Os(1A) | 88.79(12) | |
| Os(1A)-Os(1)-Cl(1) | 176.57(4) | |
| N(5)-Os(2)-Os(2A) | 90.16(14) | |
| N(6)-Os(2)-Os(2A) | 88.05(13) | |
| N(7)-Os(2)-Os(2A) | 89.50(13) | |
| N(8)-Os(2)-Os(2A) | 88.62(14) | |
| Os(2A)–Os(2)–Cl(2) | 177.17(4) | |

rationale is that both axial chloro ligands remain Os₂bound during the metathesis process of the bridging ligands, and their presence enforces a symmetric arrangement.

The Os–Os bond lengths determined for molecules A (2.3976(5) Å) and **B** (2.3943(6) Å) are nearly identical within experimental errors, and consistent with the presence of an Os–Os triple bond [1]. In comparison, the Os–Os bond lengths are 2.4672(6) Å in $Os_2(DPhF)_4Cl_2$ (DPhF is diphenylformamidinate) [4] and 2.379(2) Å in Os₂(*hpp*)₄Cl₂ (H*hpp* is 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidine) [5]. Notably, the order of Os–Os bond lengths, DPhF > ap > hpp, is the exact opposite of the donor strength of N,N'-bridging ligands, hpp > ap > DPhF, which was previously determined on the basis of electrode potential data for Ru₂(LL)₄ complexes [14]. The Os-Cl bond length, on the other hand, increases with the increasing donor strength: hpp (2.667(4) Å) > ap (2.522(1) and 2.550(2) Å) > DPhF(2.478(3) Å). Two factors contribute to the observed trend: (1) the Os_2 center with a stronger donor is electron rich, and hence less receptive to the chloro ligand as



Scheme 1. Possible ligand arrangements in a M₂(ap)₄ compound; N_a and N_p denote anilino and pyridino nitrogen centers, respectively.



Fig. 2. Cyclic voltammogram of 1 recorded in 0.20 M THF solution of Bu_4NPF_6 at the scan rate of 0.10 V/s.

a donor and (2) the Os₂ center of higher electron density also has a stronger Os–Os bond, which results in a weaker bond in the *trans*-position, the Os–Cl bond. Among four independent Os–N bond lengths for molecule **A**, the Os–N_a bonds (Os(1)–N(2) and Os(1)–N(4)) are significantly shorter than the Os–N_p bonds (Os(1)– N(1) and Os(1)–N(3)), and the same is true for molecule **B**.

In comparison with Os₂ compounds supported by the *hpp* and *D*Ph*F* ligands, Os₂(*ap*)₄Cl₂ has a fairly large room temperature effective moment of 2.76 μ_B that is consistent with a *S* = 1 ground state. A reasonable ground state configuration for Os₂(*ap*)₄Cl₂ is $\sigma^2 \pi^4 \delta^2 \pi^{*2}$, the same configuration ascribed to Os₂(*D*Ph*F*)₄Cl₂ [4]. It is noteworthy that, despite the structural similarity to the aforementioned compounds, Os₂(*hpp*)₄Cl₂ has a ground state configuration of $\sigma^2 \pi^4 \delta^2 \delta^{*2}$ [5].

 $Os_2(ap)_4Cl_2$ exhibits rich features in the cyclic voltammogram (CV) shown in Fig. 2, which consists of four one-electron waves. In analogy to the redox chemistry of other $Os_2(III)$ species [4,5], the most anodic wave is assigned as the oxidation of the Os₂-core, and the adjacent wave as the first reduction of the Os₂ core (Eq. (1)). The second reduction, ca. 0.90 V more negative than the first, is also attributed to a further reduction of the Os₂ core. Although not noted for $Os_2(hpp)_4Cl_2$ and $Os_2(DPhF)_4Cl_2$, a second reduction of the $Ru_2(ap)_4$ core was observed recently, and the potential difference between two consecutive reductions, i.e., $E(Ru_2^{II,I}/Ru_2^{II,II}) - E(Ru_2^{II,II}/Ru_2^{II,III})$, is about -1 V [15]. The nature of the most cathodic couple at -2.30 V remains uncertain. The $E_{1/2}(+1/0)$ of $Os_2(ap)_4Cl_2$, 0.031 V, is in the middle of those observed for $Os_2(hpp)_4Cl_2$ $(-0.492 \text{ V vs. Fc}^+/\text{Fc})$ [16] and Os₂(*DPhF*)₄Cl₂ (*E*_{pa}, 0.60 V, vs. Fc^{+}/Fc [4], reaffirming the aforementioned order of donor strength

$$[Os_{2}(III, IV)]^{1+\stackrel{+e^{-}}{\rightleftharpoons}}[Os_{2}(III, III)]\stackrel{+e^{-}}{\rightleftharpoons}[Os_{2}(III, II)]^{1-}$$
$$\stackrel{+e^{-}}{\rightleftharpoons}[Os_{2}(II, II)]^{2-\stackrel{+e^{-}}{\rightleftharpoons}}[Os_{2}(I, II)]^{3-''}$$
(1)

3. Conclusion

On the basis of the one-electron oxidation potential, $Os_2(ap)_4Cl_2$ is more electron deficient than $Os_2(hpp)_4$ -Cl₂, and consequently a better candidate for forming stable complexes with more electron-donating alkynyl ligands. With both chloro ligands semi-exposed as a result of the *cis*-(2,2) geometry, $Os_2(ap)_4Cl_2$ should undergo faster axial ligand metathesis reactions than $Os_2(DPhF)_4Cl_2$ and the alkynylation chemistry will be investigated in the near future.

4. Experimental

4.1. General conditions, reagents and instruments

 $Os_2(OAc)_4Cl_2$ [17] and 2-anilinopyridine [18] were prepared as previously described. Anhydrous organic solvents were obtained from Aldrich and used as received. Absorption spectra were obtained with a Perkin–Elmer Lambda-900 UV–Vis–NIR spectrophotometer. The magnetic susceptibility was measured at 294 K with a Johnson Matthey Mark-I Magnetic Susceptibility Balance. Cyclic voltammograms were recorded in 0.2 M (*n*-Bu)₄NPF₆ solution (THF, N₂degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag wire pseudo reference electrode, and the electrode potentials were reported vs. $E(Fc^+/Fc)$. The concentration of $Os_2(ap)_4Cl_2$ was 1.0 mM.

4.2. Synthesis of $Os_2(ap)_4Cl_2$ (1)

A round bottom flask was charged with $Os_2(OAc)_4$ -Cl₂ (0.24 g, 0.35 mmol) and 2-anilinopyridine (0.51 g, 3 mmol), and 40 ml of toluene, and a micro Soxhlet extraction condenser with a glass thimble containing 1:1 K₂CO₃/sand was mounted to the flask. The reaction mixture was heated to reflux in open air for 3 days, during which the initial brown suspension turned to dark purple within the first 2 h, and then to deep blue. Reaction mixture was filtered to remove a small amount brownish residues that are impurities from the $Os_2(OAc)_4Cl_2$ synthesis, and toluene was distilled from the filtrate to yield a deep blue residue. After the removal of excess Hap via vacuum sublimation, the residue was recrystallized from 20 ml of hot CH₃OH to yield 0.22 g (56% based on Os) of blue crystalline material. Data for 1. FAB-MS: 1129, [MH⁺]; molar susceptibility (χ_{mol}), 3.23×10^{-3} emu; $\mu_{eff} = 2.76 \ \mu_B$. Vis–NIR, $\lambda_{max}(nm, \epsilon (M^{-1} cm^{-1}), THF)$: 452 (4540), 632 (7820), 770(sh), 880 (1930). Electrochemical, $E_{1/2}/V$ (vs. Fc⁺/Fc), $\Delta E_p/V$, $i_{backward}/i_{forward}$: +1/0, 0.032, 0.103,

0.93; **0/-1**, -1.068, 0.180, 0.63; -**1/-2**, -1.967, 0.128, 0.67; -**2/-3**, -2.301, 0.108, 0.93.

4.3. X-ray data collection, processing, and structure analysis and refinement

Single crystals of compound 1 were grown via slow evaporation of a saturated CH₃OH/CH₂Cl₂ solution of 1. Data were collected on a Bruker SMART 1K CCD diffractometer using graphite monochromated Mo K α radiation. Crystal was cooled using a Rigaku X-Stream Cryogenic Crystal Cooler. Corrections were applied for Lorentz, polarization, and absorption effects. The structure was solved and refined with the aid of the programs in the SHELXTL-PLUS system of programs [19]. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms except those of the solvent molecule. The solvent molecule is disordered over a special position and was refined with isotropic thermal parameters only. All of the H atoms were included using a riding model.

Crystal data of 1: MW = 1142.11; triclinicic, space group $P\bar{1}$, a = 10.397(2) Å, b = 10.801(2) Å, c = 19.061(3) Å, V = 2024.2(6) Å³, Z = 2, $\rho_{calc} = 1.89$ mg mm⁻³, λ (Mo K α) = 0.71073 Å, $\mu = 6.450$ mm⁻¹, F(000) = 1106, T = 173(2) K, $R_1 = 0.0371$ for 6892 observed ($I > 4\sigma I$) reflections and 0.0645 for the full set of 9510 reflections.

5. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 215552 for $Os_2(ap)_4Cl_2$. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK.

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