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Synthesis and structural characterization of a triosmium carbonyl cluster containing a 9-anthracenecarbonitrile ligand derived from 9-anthraldehyde oxime

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Abstract

Treatment of $[Os_3(CO)_{11}(MeCN)]$ with 1 equivalent of 9-anthraldehyde oxime in refluxing chloroform afforded a new triosmium cluster $[Os_3(CO)_{11}(C_{14}H_9CN)]$ **1** in moderate yield. Dehydration of oxime and the formation of metal-bound nitrile were observed. Crystal structure analysis revealed that cluster **1** consists of a triangular metal skeleton, with the anthracenecarbonitrile ligand terminally bonded to an osmium atom. Molecular orbital calculations were carried out to gain further insight into the electronic structure of **1**. Cluster **1** was also obtained in a higher yield by the reaction of $[Os_3(CO)_{11}(MeCN)]$ with 9-anthracenecarbonitrile.
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Keywords: Triosmium carbonyl cluster; Oxime ligand; 9-Anthraldehyde oxime; X-ray crystallography

1. Introduction

Aldoximes, $RC(H){=}NOH$, are starting materials for the synthesis of nitriles via dehydration. These reactions are well-documented in the organic chemistry of oximes, but usually require harsh conditions [1a,1b]. In coordination chemistry, the metal-assisted dehydration of oxime species has been studied. However, work in this area is relatively scarce, although several reports describing the dehydration of oximes and the formation of metal-bound nitriles have been reported [2–5]. Schug and coworker [2] have shown that the reaction of the ruthenium(II) complex $[Ru(NH_3)_5(H_2O)]^{2+}$, with the ketoximes $MeRC{=}NOH$, where R is $-C({=}O)Me$, $-C({=}O)Ph$ and $-CH(OH)Ph$, gives the ruthenium(II)-nitrile product $[Ru(NH_3)_5(N{\equiv}CMe)]^{2+}$. The reaction between $RuBr_3 \cdot xH_2O$ and $PhC(H){=}NOH$ in aqueous 6M HBr was reported to result in facile metal-assisted dehydration of the oxime and give $[RuBr(N{\equiv}CPh)_5][RuBr_4(N{\equiv}CPh)_2]$ [3]. Other examples include the conversion of the aldoximes during the reaction between $[(\eta^6\text{-}C_6H_6)OsHI(PMeBu^t_2)]$ and $AgPF_6$ in the presence of $RHC{=}NOH$ ($R = Me$, Ph) to give $[(\eta^6\text{-}C_6H_6)OsH(N{\equiv}CR)(PMeBu^t_2)]$ [4] and dehydration of $RHC{=}NOH$ ($R = Me$, Ph, $p\text{-}C_6H_4OMe$) on treatment with $[W(CO)_5(THF)]$ [5]. However, these examples are limited to mononuclear metal compounds. To our knowledge, the dehydration of oximes resulting in the generation of nitrile complexes in cluster chemistry is quite rare.

In this communication, we present a new triosmium carbonyl cluster containing 9-anthracenecarbonitrile ligand from the reaction of $[Os_3(CO)_{11}(MeCN)]$ with 9-anthraldehyde oxime and $[Os_3(CO)_{11}(MeCN)]$ with 9-anthracenecarbonitrile.

2. Experimental

All reactions were carried out under an inert atmosphere of argon using standard Sclenck techniques. Solvents were freshly purified by standard procedures prior to use [6]. Commercial chemicals such as 9-anthraldehyde

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oxime and 9-anthracenecarbonitrile were used directly as received. The compound $[Os_3(CO)_{11}(MeCN)]$ was prepared by the literature method [7]. Infrared spectra were recorded on a Bio-Rad FTS-135 IR spectrometer, using 0.5 mm calcium fluoride solution cells. ^1H NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer using CD_2Cl_2 with reference to $SiMe_4(\delta\, 0)$. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer by fast atom bombardment techniques, using *m*-nitrobenzyl alcohol as the matrix solvent. Electronic absorption spectra were obtained with a Hewlett-Packard 8453 diode array UV/Vis spectrophotometer, using quartz cells, with 1 cm path length at room temperature. Routine purification of products was carried out in air by thin layer chromatography (TLC) on plates coated with Merck Kiesegel 60 GF_{254}. Elemental analyses were conducted by Butterworth Laboratories, UK.

2.1. Reaction of $[Os_3(CO)_{11}(MeCN)]$ with 9-anthraldehyde oxime

The cluster $[Os_3(CO)_{11}(MeCN)]$ (100 mg, 0.109 mmol) and 9-anthraldehyde oxime (24 mg, 0.109 mmol) were stirred at refluxing chloroform (30 ml) for 5 h. The colour gradually turned dark yellow. The reaction mixture was evaporated to dryness. The residue was finally redissolved in CH_2Cl_2 (ca. $2 cm^3$) and separated by preparative TLC with an eluent of *n*-hexane–CH_2Cl_2 (3:1 v/v) to give yellow complex **1** ($R_f \approx 0.55$, 54 mg, 0.050 mmol, 46%). Anal. found for **1**: C, 28.8; H, 0.8; N, 1.5; calc. for $C_{26}H_9NO_{11}Os_3$: C, 28.9; H, 0.8; N, 1.3%.

2.2. Reaction of $[Os_3(CO)_{11}(MeCN)]$ with 9-anthracenecarbonitrile

To a CH_2Cl_2 solution of $[Os_3(CO)_{11}(MeCN)]$ (100 mg, 0.109 mmol) 9-anthracenecarbonitrile (22 mg, 0.109 mmol) was added at room temperature. Reaction was completed after stirring for 1 h, as monitored by TLC and IR spectroscopy. The reaction solution was concentrated in vacuo and separated by TLC using *n*-hexane–CH_2Cl_2 (3:1, v/v) to give complex **1** ($R_f \approx 0.55$, 85 mg, 0.079 mmol, 72%).

2.3. Carbonylation of cluster **1**

Cluster **1** (50 mg, 0.046 mmol) was dissolved in $CHCl_3$ (30 ml). The bright yellow solution was then carbonylated. The reaction was monitored by spot TLC until complete consumption of **1** (1/2 h). The solvent was removed under reduced pressure and TLC purification (eluent: *n*-hexane–CH_2Cl_2 (3:1, v/v)) afforded $[Os_3(CO)_{12}]$($R_f \approx 0.80$, 13 mg, 0.014 mmol, 30%).

2.4. Photoreaction of cluster **1**

A CH_2Cl_2 solution of **1** (50 mg, 0.046 mmol) was irradiated by means of a 300 W high-pressure mercury lamp for 1/2 h. Evaporation of the solvent and separation of products by TLC, using *n*-hexane–CH_2Cl_2 (3:1, v/v) as eluent, gave $[Os_3(CO)_{12}]$ ($R_f \approx 0.80$, 8 mg, 0.009 mmol, 20%) as the major product accompanied by a small amount of unchanged **1**.

2.5. Hydrogenation of cluster **1**

Cluster **1** (50 mg, 0.046 mmol) was dissolved in $CHCl_3$ (30 ml). Hydrogenation of the bright yellow solution at atmospheric pressure was then attempted at room temperature. The reaction was monitored by spot TLC until complete consumption of **1** (2 h). Chromatography on silica with *n*-hexane–CH_2Cl_2 (4:1, v/v) afforded $[H_2Os_3(CO)_{10}]$ ($R_f \approx 0.75$, 18 mg, 0.021 mmol) with 45% yield.

3. Results and discussion

3.1. Reaction of $[Os_3(CO)_{11}(MeCN)]$ with 9-anthraldehyde oxime

Heating $[Os_3(CO)_{11}(MeCN)]$ with 1 equivalent of 9-anthraldehyde oxime in refluxing chloroform for 5 h afforded $[Os_3(CO)_{11}(C_{14}H_9CN)]$ **1** in moderate yield upon TLC separation. On the other hand, cluster **1** can be prepared in a higher yield (~70%) by stirring $[Os_3(CO)_{11}(MeCN)]$ with 9-anthracenecarbonitrile in CH_2Cl_2 for 1 h (Scheme 1). The acetonitrile group in the parent cluster is shown to be labile and can be easily replaced by the anthracenecarbonitrile. The IR spectrum [1] shows the presence of terminal carbonyl ligands, and the mass spectrum exhibits molecular ion envelopes that agree with the formula of the compound, with ion peaks corresponding to CO loss also being present. The ^1H NMR spectrum of **1** consists of proton signals ranging from δ 7.6 to 8.8, which are due to the aromatic ring system; no metal hydride could be detected. In the UV/Vis spectrum [1] of **1**, six absorption bands are seen, whilst that of free 9-anthracenecarbonitrile exhibits five absorption bands at 259, 348, 365, 383 and 404 nm. To elucidate the molecular structure of cluster **1**, a single crystal X-ray analysis was carried out on a yellow crystal that was obtained by slow evaporation from a *n*-hex-

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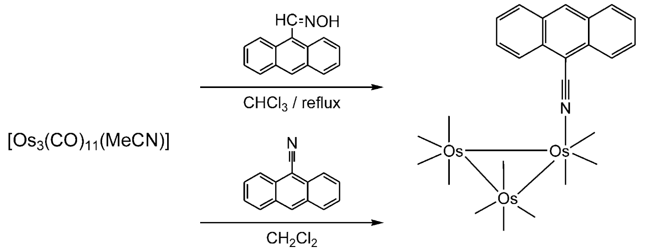
[1] Spectroscopic data of **1**: IR [ν(CO), CH_2Cl_2]: 2105w, 2053vs, 2039vs, 2008vs, 1979m; [$\nu(C{\equiv}N)$, KBr]: 2237w. Positive FAB MS: *m/z* 1082 (calc. 1082). ^1H NMR (CD_2Cl_2) at 298 K: δ 8.79 (s, 1H), 8.15 (m, 4H), 7.80 (m, 2H), 7.68 (m, 2H). λ_{max} (nm) (ε, $dm^3\ mol^{-1}\ cm^{-1}$) in CH_2Cl_2 at 298 K: 259 (140 000), 350 (11 000), 368 (13 000), 392 (13 000), 413 (15 000)and 436 (11 000).



Scheme 1.

ane–CH_2Cl_2 solution at −20 °C. Its molecular structure [2] is depicted in Fig. 1 and selected bond lengths and angles are given in Table 1. Cluster **1** retains the basic metal architecture of the parent cluster $[Os_3(CO)_{11}(MeCN)]$. The metal–metal bond distances of **1** [Os(1)–Os(2) 2.8618(4), Os(2)–Os(3) 2.9011(4), Os(1)–Os(3) 2.8633(4) Å] are comparable to the corresponding values that were observed in $[Os_3(CO)_{11}(MeCN)]$ [8]. The anthracenecarbonitrile ligand is end-on coordinated to Os(1) at the axial position via the nitrogen atom [Os(1)–N(1) 2.113(6) Å] and adopts the same coordination mode to the metal core as that of the acetonitrile group in $[Os_3(CO)_{11}(MeCN)]$. The C≡N bond distance in **1** is 1.133(9) Å, which is comparable to those of other coordinated nitriles [3]. The [Os(1)–N(1)≡C(26)] and [N(1)≡C(26)–C(12)] angles are 176.6(6) and 177.1(8)°, respectively, which indicate that the groups are close to linear. The dihedral angle between the anthracene ring and the triangular metal framework is 94.5°. A crystal-packing diagram of **1** is shown in Fig. 2. The molecules stack with the anthracene rings pointing towards each other along the crystallographic *a* axis so that a layer of organics is sandwiched by two layers of metal cluster core. The separation between two adjacent anthracene rings is ca. 3.5 Å which is similar to those ring systems with π–π interaction.

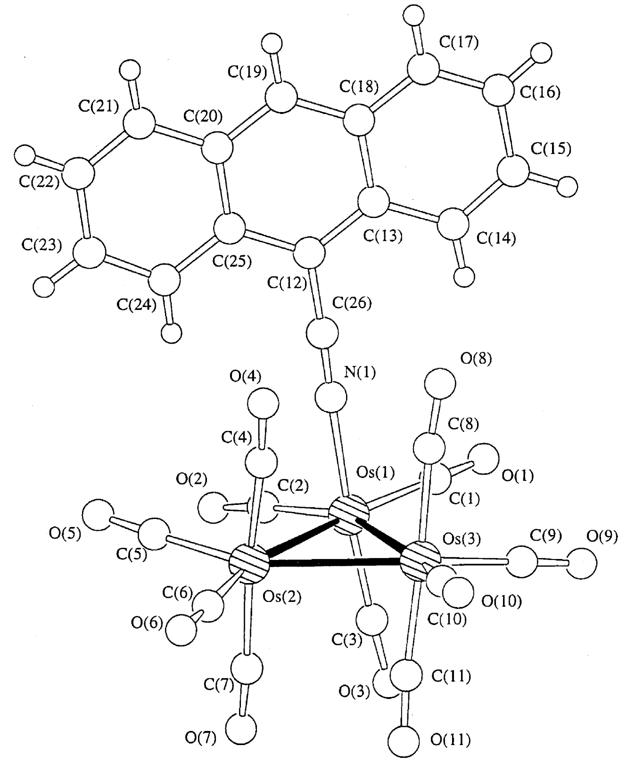


Fig. 1. The molecular structure of $[Os_3(CO)_{11}(C_{14}H_9CN)]$ **1** with the atom numbering scheme.

Table 1
Selected bond lengths (Å) and angles (°) for cluster **1**

Os(1)–Os(2)	2.8618(4)	Os(1)–N(1)	2.113(6)
Os(2)–Os(3)	2.9011(4)	N(1)–C(26)	1.133(9)
Os(1)–Os(3)	2.8633(4)	C(12)–C(26)	1.433(9)
Os(1)–Os(2)–Os(3)	59.58(1)	Os(3)–Os(1)–N(1)	94.9(2)
Os(1)–Os(3)–Os(2)	59.53(1)	Os(1)–N(1)–C(26)	176.6(6)
Os(2)–Os(1)–Os(3)	60.89(1)	N(1)–C(26)–C(12)	177.1(8)
Os(2)–Os(1)–N(1)	89.0(2)		

Upon coordination to the metal complex, the oxime ligand is converted to a coordinated nitrile. It is conceivable that the metal centre facilitates the dehydration of oxime. However, the possibility of dehydration of oxime in the absence of metal cluster at refluxing $CHCl_3$ cannot be ruled out. Therefore, 9-anthraldehyde oxime was heated at refluxing $CHCl_3$. Monitoring of the reaction by both ^1H NMR spectroscopy and spot TLC showed no observable change. Hence, it is believed that dehydration of oxime and the formation of nitrile are promoted in the presence of metal cluster. It is suggested that upon coordination of the oxime nitrogen atom to the metal core, back-bonding from the filled 5d orbitals of osmium metal centre to the empty π* orbitals of nitrogen atom promotes increased electron density on the bound nitrogen, thereby facilitating the rupture of the oxime N–O bond and the conversion of a sp^2-hybridized oxime nitrogen into a sp-hybridized nitrile nitrogen.

To further understand the spectroscopic behaviour, we have carried out molecular orbital calculations on cluster **1** at the B3LYP level of density functional theory based on their experimental geometries. Examining the

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[2] Crystal data: $Os_3C_{26}NO_{11}H_9$ (**1**), $M = 1081.96$, triclinic, space group $P\ \bar{1}$ (No. 2), $a = 7.956(3)$, $b = 13.162(2)$, $c = 13.364(4)$ Å, $\alpha = 78.67(1)$, $\beta = 87.76(2)$, $\gamma = 78.23(1)°$, $U = 1343.3(6)$ Å^3, $Z = 2$, $D_c = 2.675$ g/cm^3, $T = 298$ K, μ(Mo-Kα) = 142.07 cm^{-1}, dimensions 0.23 × 0.18 × 0.30 mm. 4902 observed diffractometer data [$I > 1.50\sigma(I)$] and $R_{int} = 0.021$. Structure solved by direct methods (SHELXS86) and Fourier difference techniques, refined by full-matrix least-squares analysis on F to $R = 0.032$, $R' = 0.038$, $\omega = 1/\sigma^2(F_0)$. All non-hydrogen atoms were included in anisotropic refinement while hydrogen atoms of the ligand moiety were generated in their ideal positions (C–H 0.95 Å) and included in the structure factor calculations but not refined. Calculations were performed on a Silicon Graphics computer using the teXsan [12] crystallographic software package. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 196731.

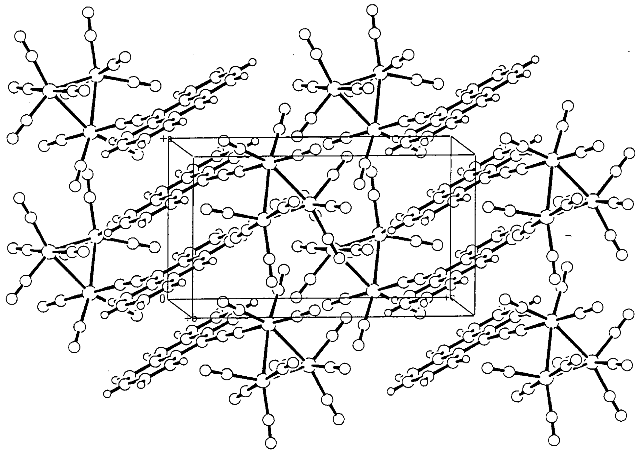

Fig. 2. Crystal packing diagram of **1**.

molecular orbital patterns of the cluster molecule, we found that the highest occupied molecular orbitals (HOMOs) correspond to the Os–Os σ bonds followed by the "t_{2g}" set d orbitals of the three metal centers. The lowest unoccupied orbitals (LUMOs) are π^* of the aromatic organic ligand. This is similar to other trinuclear osmium systems [9,10]. The orbital characteristics that were found in the HOMO–LUMO regions for the cluster allow us to conclude that the UV–visible absorption spectra for the cluster is related to metal-to-ligand charge transfer. The observed high intensity in the absorption peaks is due to the MLCT transition. The spatial plots of the lowest unoccupied (LUMO) and the highest occupied (HOMO) molecular orbitals of **1** are illustrated in Fig. 3.

3.2. Reactivity of cluster **1**

Carbonylation of **1** in chloroform at room temperature results in the formation of $[Os_3(CO)_{12}]$. In a CO saturated environment, the carbonyl group replaces the nitrile ligand. The same triosmium carbonyl cluster, $[Os_3(CO)_{12}]$, was also found in the carbonylation of $[Os_3(CO)_{11}(MeCN)]$ [11]. Apart from carbonylation, the same products were obtained when a CH_2Cl_2 solution of complex **1** was irradiated with a mercury lamp at room temperature. In this case, owing to the absence of any external CO sources, the CO molecules should come from the degradation of other **1** molecules. It is believed that irradiation of **1** by the UV light may trigger cluster degradation. Therefore, significant decomposition of the starting cluster is not unexpected.

Cluster **1** was hydrogenated in chloroform at room temperature. As a result, the unsaturated metal cluster $[H_2Os_3(CO)_{10}]$ was obtained as the major product. Hydrogenation of $[Os_3(CO)_{11}(MeCN)]$ also led to the formation of $[H_2Os_3(CO)_{10}]$ [11]. The behaviour of **1** towards ligand substitution is similar to that of $[Os_3(CO)_{11}(MeCN)]$. The investigation of other chemical and electrochemical properties of **1** is underway.

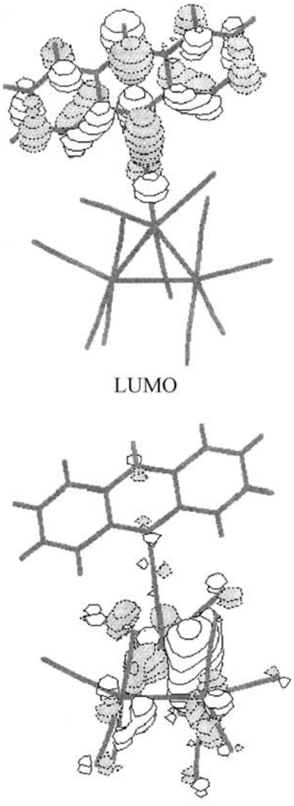

Fig. 3. The spatial plots of the lowest unoccupied (LUMO) and the highest occupied (HOMO) molecular orbitals calculated for $[Os_3(CO)_{11}(C_{14}H_9CN)]$ **1**.

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