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One-electron oxidation behavior of $\{MNO\}^6$ -type nitrosyl complexes having acetylacetonato ligand, $[M(NO)Cl_{5-2n}(acac)_n]^m$ (M=Ru, Os; n=1, 2; acac = acetylacetonato)

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Abstract

The electrochemical behavior of several complexes with the general formula $[M(NO)Cl_{5-2n}(acac)_n]^m$ (M=Ru, Os; n=1, 2; acac=acetylacetonato) was investigated: mer- $[Ru(NO)Cl_3(acac)]^-$ (1, n=1), cis- $[Ru(NO)Cl(acac)_2]$ (2, n=2), mer- $[Os(NO)Cl_3(acac)]^-$ (3, n=1), cis- $[Os(NO)Cl(acac)_2]$ (4, n=2). The study includes the known corresponding n=0 complexes, $[M(NO)Cl_5]^{2-}$ (M=Ru, Os), for comparison. All these complexes undergo a one-electron oxidation, which is rather unusual redox behavior in the {MNO}⁶-type nitrosyl complexes. The behavior of some of these complexes as electrophiles was also described. Molecular structures with a meridional configuration were established for the n=1 complexes ($[Ru(NO)Cl_3(acac)]^-$ (1) and $[Os(NO)Cl_3(acac)]^-$ (3)) by X-ray structure determinations. Crystal data for 1 (Bu₄N salt): $C_{21}H_{43}N_2O_3Cl_3Ru$, a=31.443(9), b=21.86(1), c=19.852(6) Å, $\beta=119.65(2)^\circ$, monoclinic, C2/c, Z=16. Crystal data for 3 (Cs salt): $C_5H_7NO_3Cl_3OsCs$, a=7.942(1), b=12.602(2), c=7.451(2) Å, $\alpha=105.91(2)$, $\beta=98.20(2)$, $\gamma=90.31(1)^\circ$, triclinic, $P\overline{1}$, Z=2.

Keywords: Crystal structures; Nitrosyl complexes; Ruthenium complexes; Osmium complexes; Electrochemistry

1. Introduction

Various {MNO}⁶-type nitrosyl complexes have been reported [1-4]. The complexes showed a characteristic electrochemical behavior due to a ligand (nitrosyl)-based reduction, but no electrode oxidation could be observed in the measurable potential region. This was true for n = 0 nitrosyl complexes $[M(NO)Cl_{5-2n}(acac)_n]^m$, $[M(NO)Cl_5]^{2-1}$ (M=Ru, Os), until recent work by several researchers appeared [5-7]. Tocher and co-workers and Sinitsyn and coworkers have shown that $[M(NO)Cl_5]^{2-}$ exhibits a reversible one-electron oxidation to give $[M(NO)Cl_5]^{-}$, which is believed to contain an $(M^{III}(NO^+))$ moiety [5,6]. We report here that an electrochemical oxidation occurs also in the following complexes of general formula [M(NO)Cl_{5-2n}- $(acac)_n$ ^m (M = Ru, Os; n = 1, 2; acac = acetylacetonato), in addition to the reduction mentioned above: mer-[Ru(NO)- $Cl_3(acac)$]⁻ (1, n=1), cis-[Ru(NO)Cl(acac)₂] (2, n=2), *mer*- $[Os(NO)Cl_3(acac)]^-$ (3, *n*=1), *cis*- $[Os(NO)Cl-(acac)_2]$ (4, *n*=2). This paper describes the syntheses, structures and characteristics of such ruthenium and osmium metal complexes. We paid special attention to the investigation of the electrochemical properties.

2. Experimental

2.1. Materials

The following complexes were prepared by the literature methods. The solutions of nitrosylruthenium (Ru(NO)Cl_n) (used as starting material) and K₂[Ru(NO)Cl₅] were prepared by a conventional method of Fletcher et al. [8]. (Bu₄N)₂[Ru(NO)Cl₅] was obtained using Bu₄NCl, instead of KCl. *Cis*-[Ru(NO)Cl(acac)₂] was prepared by modifying a procedure that was reported previously [9].

2.2. Measurements

Elemental analyses were performed by the Sophia University Analytical Facility. IR spectra were recorded with a Per-

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kin-Elmer FT-1650 spectrophotometer. UV-Vis spectra were obtained with a Hitachi 200-20 spectrophotometer. ¹H and ¹³C NMR spectra were obtained with a JEOL GX-270 spectrophotometer. All NMR spectra were obtained in CD₃COCD₃, CD₂Cl₂ or CDCl₃; Me₄Si was used as an internal reference in the measurements of both ¹H and ¹³C NMR spectra. For the electrochemical measurements, a Huso polarograph model 312 was used; the current potential waves were recorded with a Riken-Denshi Instruments model F-3F recorder. The experiments were performed in CH₃CN, with a supporting electrolyte concentration of 0.1 M (tetraethylammonium perchlorate). Three-electrode, one-compartment bcells were used. They were equipped with a platinum working electrode ($\phi = 1.6 \text{ mm}$), a platinum auxiliary electrode, and a silver reference electrode (Ag|AgNO₃, 0.01 mol dm^{-3}). The coulometric experiments were performed in twocompartment cells, using a platinum-gauze working electrode, with the auxiliary electrode in the second compartment separated by a glass frit. The number of coulombs was measured by a Huso model 343B digital coulometer.

2.3. Syntheses

2.3.1. $Cs[Ru(NO)Cl_3(acac)]$

This complex was prepared as a raw material for $(Ph_4As)[Ru(NO)Cl_3(acac)]$ (1). To a starting solution of $Ru(NO)Cl_n$ (20 cm³, 0.5 g as $RuCl_3$) was added a mixed solution of Hacac–MeOH ($4-4 \text{ cm}^3$). The reaction solution was adjusted to pH = 1.0 with an aqueous solution of NaOH, using a pH meter. The mixture was refluxed for 2 h, and then the reaction solution was transferred to an open beaker. It was concentrated on a hot plate until the solution volume was reduced to 10 cm³. Then the solution was allowed to stand at room temperature for 3 days. After the solution had been filtered, using a piece of filter paper, CsCl (500 mg) was added to the filtrate. From this a pale reddish brown crystalline material deposited. The product was collected by filtration, and washed with cold water, EtOH, and ether, then air dried. Yield 40% (350 mg). The product was used as a raw material for the preparation of $(Ph_4As)[Ru(NO)Cl_3(acac)]$ (see the next procedure).

2.3.2. $(Ph_4As)[Ru(NO)Cl_3(acac)](1)$

To a hydrochloric acid solution of Cs [Ru(NO)Cl₃(acac)] (100 mg, H₂O–HCl 10 cm³ (4:1)), Ph₄AsCl (100 mg) was added. A pale brown precipitate was formed immediately. It was collected by filtration, washed with cold water, and then air dried. Yield 70% (170 mg). *Anal*. Found: C, 48.24; N, 2.33; H, 3.66. Calc. for (Ph₄As) [Ru(NO)Cl₃(C₅H₇O₂)]:C, 48.38; N, 1.95; N, 3.79%.

2.3.3. $Cis-[Ru(NO)Cl(acac)_2](2)$

To a starting solution of $Ru(NO)Cl_n$ (20 cm³, 0.5 g as $RuCl_3$) was added a mixed solution of Hacac–MeOH (4–4 cm³). The reaction solution was adjusted to pH = 3.7 with an aqueous solution of NaOH, using a pH meter. The mixture

was refluxed for 2 h; during this time the pH of the solution was adjusted repeatedly. The reaction solution was transferred to an open beaker, and then was concentrated on a hot plate until crystalline material deposited. The product was collected by filtration, and washed with cold water. The product was recrystallized from ethanol containing a small amount of water. The purified black–brown product was collected by filtration and washed with ether, and then air dried. Yield 30% (140 mg). *Anal*. Found: C, 32.6; N, 3.81; H, 3.80. Calc. for [Ru(NO)Cl(C₅H₇O₂)₂]H₂O: C, 32.9; N, 3.84; H, 3.87%.

2.3.4. $Cs[Os(NO)Cl_3(acac)](3)$

The complex was obtained from the reaction solution, from which *cis*- $[Os(NO)Cl(acac)_2]$ (4) was separated by the procedure described below. The volume of the solution was reduced by spontaneous evaporation at room temperature, until just before the solution had dried up. The solid material which deposited was collected by filtration, and then recrystallized from acetone–MeOH solution. The reddish brown product was collected by filtration, washed using cold water, EtOH and ether, and then air dried. Yield 15% (50 mg). *Anal.* Found: C, 10.74; N, 2.50; H, 1.16. Calc. for Cs[Os(NO)Cl₃(C₅H₇O₂)]: C, 10.75; N, 2.51; H, 1.27%.

2.3.5. $Cis-[Os(NO)Cl(acac)_2](4)$

To a solution of $Cs_2[Os(NO)Cl_5]$ (0.4 g) in water (15 cm³) was added a mixed solution of Hacac–MeOH (4–6 cm³). The mixed solution was adjusted to pH=3.5 with an aqueous solution of NaOH, using a pH meter. The mixture was refluxed for 6 days, during which time the pH of the solution was adjusted repeatedly. The reaction solution was transferred to an open beaker and was concentrated on a hot plate until red–purple crystalline material deposited. The product was collected by filtration, then washed with water. The product was recrystallized from the mixed solution of CH₂Cl₂–EtOH–H₂O (7–4–1 cm³). The purified reddish purple product was collected by filtration and washed with water, and then air dried. Yield 50% (140 mg). *Anal*. Found: C, 26.57; N, 3.04; H, 3.17. Calc. for [Os(NO)Cl(acac)₂]: C, 26.46; N, 3.09; H, 3.12%.

2.4. X-ray crystallographic study

The reflections of an X-ray analysis with Mo K α radiation $(\lambda = 0.71069 \text{ Å})$ were collected by the ω -2 θ technique for **1** $(2\theta < 45.0^{\circ})$ and for **3** $(2\theta < 50.0)$ on a Rigaku AFC5S diffractometer at room temperature (20°C) ; the resulting crystal data and details concerning data collection and refinement are given in Table 1. All calculations were carried out on a Silicon Graphics Indy Computer, using the program TEXSAN.

Compound	$(Bu_4N)[Ru(NO)Cl_3(acac)]$ (1)	$Cs[Os(NO)Cl_3(acac)]$ (3)
Chemical formula	$C_{21}H_{43}N_2O_3Cl_3Ru$	C ₅ H ₇ NO ₃ Cl ₃ CsOs
Formula weight	579.01	558.58
a (Å)	31.443(9)	7.942(1)
<i>b</i> (Å)	21.86(1)	12.602(2)
c (Å)	19.852(6)	7.451(2)
α (°)	90	105.91(2)
β (°)	119.65(2)	98.20(2)
γ (°)	90	90.31(1)
Volume (Å ³)	11856(8)	709.1(2)
Space group	C2/c	$P\overline{1}$
Ζ	16	2
Density (calc.) $(g cm^{-3})$	1.297	2.616
μ (cm ⁻¹)	8.20	120.64
$T(\mathbf{K})$	293	293
R	0.048	0.035
$R_{ m w}$	0.031	0.049

3. Results and discussion

3.1. Syntheses, characterization and structures

Both $[Ru(NO)Cl_5]^{2-}$ and $[Os(NO)Cl_5]^{2-}$ (n=0 complexes for $[M(NO)Cl_{5-2n}(acac)_n]^m$ have been reported [1–4], but a detailed electrochemical investigation was not completed until recently [5-7]. These authors showed that $[M(NO)Cl_5]^{2-}$ (M=Ru, Os) could be oxidized to give a one-electron oxidation species, $[M(NO)Cl_5]^-$, which was believed to contain the $(M^{III}(NO^+))^{4+}$ moiety. The isolation of the one-electron oxidation product has succeeded in the osmium case, as $R[Os(NO)Cl_5]$ (R = Et₄N, Ph₄As, Ph_4P) [6,7]. The corresponding ruthenium species, however, did not give such a solid material, due to chemical instability. Our recent attempt to isolate $[Ru(NO)Cl_5]^-$ also failed; but, instead, we were able to characterize the self-decomposition reaction of [Ru(NO)Cl₅]⁻, which occurred along with the one-electron oxidation of $[Ru(NO)Cl_5]^{2-}$ [10]: $[Ru(NO)Cl_5]^-$ gave *cis*- $[Ru(NO)Cl_4(solvent)]^-$ (at 25°C in the dark), instead of the expected trans- $[Ru(NO)Cl_4(solvent)]^-$, and then the *cis*-form product changed further to *trans*- $[RuCl_4(solvent)_2]^-$ (at 25°C under room light). Two more unidentified species were detected as taking part in this reaction.

Several ruthenium complexes with the acetylacetonato ligand have been investigated recently [11]. However, the ruthenium complexes with the general formula $[M(NO)Cl_{5-2n}(acac)_n]^m$ (n=1 and 2) have not been synthesized, except for *cis*- $[Ru(NO)Cl(acac)_2]$ (2). Detailed electrochemical investigations of the latter have not yet been carried out. In addition, the corresponding osmium complexes, either *mer*- $[Os(NO)Cl_3(acac)]^-$ (3) or *cis*- $[Os(NO)Cl(acac)_2]$ (4), have not been prepared. In the course of our work on the isolation of the complexes, we observed some differences between the ruthenium and osmium complexes. As described in Section 2, both *mer*-

 $[Ru(NO)Cl_3(acac)]^-$ (1) and *cis*- $[Ru(NO)Cl(acac)_2]$ (2) are obtainable in different pH conditions: pH=1.0 for *mer*- $[Ru(NO)Cl_3(acac)]^-$ (1) and 3.7 for *cis*- $[Ru(NO)-Cl(acac)_2]$ (2). The conditions for the synthesis of 1 must be strictly adhered to, and the complex could be obtained only when the solution was kept near pH=1, otherwise the species was contaminated by 2.

The preparative conditions of the osmium analogues are different from those of the ruthenium complexes: either *mer*- $[Os(NO)Cl_3(acac)]^-(3)$ or *cis*- $[Os(NO)Cl(acac)_2](4)$ was formed under the same acidic conditions, pH = 3.5. Complex **3** could be isolated only when a counter-ion was added to the reaction solution, but **4** was precipitated as crystalline material during the process of concentration of the reaction solution. All these complexes were characterized according to satisfactory elemental analyses, cyclic voltammetric parameters, visible and UV spectra, and ¹H and ¹³C NMR spectra. The data used for the characterization are summarized in Table 2.

The {MNO}⁶-type nitrosyl complexes show well-defined NMR spectra, which aid greatly in the identification of their steric configurations: the *cis*-type of coordination mode of the acetylacetonato ligand was established in both **2** and **4**, *cis*-[Ru(NO)Cl(acac)₂] and *cis*-[Os(NO)Cl(acac)₂] (Table 2). Although two other different steric forms, *mer*-and *fac*-configuration, are possible for the mono-acetyl-acetonato complexes, $[Ru(NO)Cl_3(acac)]^-$ (**1**) and $[Os(NO)Cl_3(acac)]^-$ (**3**), as precursor species of **2** and **4**, respectively, the NMR data suggested that **1** and **3** have the meridional configuration.

The meridional assignments in both $[Ru(NO)-Cl_3(acac)]^-(1)$ and $[Os(NO)Cl_3(acac)]^-(3)$ could also be confirmed by X-ray structure determination. ORTEPs drawings of the complex anions are shown in Fig. 1 and their atomic coordinates are listed in Tables 3 and 4. Some of the selected bond lengths and angles are listed in Tables 5 and 6. The NO moiety is essentially linear with the Ru atom and the

Table 2	
Data used for	the characterization

	$[Ru(NO)Cl_5]^{2-}$	$[Ru(NO)Cl_3(acac)]^-$	[Ru(NO)Cl(acac) ₂]
ν(NO) ^a	1850	1862	1873
$\lambda_{\max}^{b}(nm) (\epsilon (mol^{-1} dm^{3} cm^{-1}))$	520 (52)	486 (55)	505 (184) °
¹ H NMR (δ)		2.02, 2.07 (-CH ₃); 5.59 (-CH) (CD ₃ COCD ₃)	2.05, 2.14, 2.24, 2.29 (-CH ₃); 5.47, 5.73 (-CH) (CDCl ₃)
¹³ C NMR (δ)		26.49, 27.51 (-CH ₃); 100.4 (-CH); 206.0 ^d (-C=O) (CD ₃ COCD ₃)	
	$[Os(NO)Cl_5]^{2-}$	$[Os(NO)Cl_3(acac)]^-$	[Os(NO)Cl(acac) ₂]
$\nu(\mathrm{NO})^{\mathrm{a}}$	1803	1814	1819, 1841
$\lambda_{\max}^{b}(nm) (\epsilon (mol^{-1} dm^{3} cm^{-1}))$	575 (40), 440 (57)	545 (96)	512 (14)
¹ H NMR (δ)		2.03, 2.06 (-CH ₃); 5.77 (-CH) (CD ₃ COCD ₃)	2.10, 2.22, 2.31, 2.58 (-CH ₃); 5.68, 5.90 (-CH) (CD ₂ Cl ₂)
13 C NMR (δ)			25.88, 26.70, 26.99, 27.60 (-CH ₃); 101 6, 102 7 (-CH): 187 2, 193 3

^a In CH₃CN.

^b In CH₃CN.

° In CH₃OH.

^d Overlapped with the spectral line due to the solvent.



Fig. 1. ORTEP drawings of the *mer*- $[Ru(NO)Cl_3(acac)]^-$ ion (1) and *mer*- $[Os(NO)Cl_3(acac)]^-$ ion (3).

Ru–NO and N–O bond lengths are similar to typical values in other $\{RuNO\}^{6}$ -type nitrosyl complexes [12,13].

In octahedral geometry, one of the oxygen atoms of the acetylacetonato ligand in both complexes exists in the *trans* position to the nitrosyl group, and another oxygen atom lies in the *cis* position. Reports by other researchers have shown that either the *fac*-form or the *mer*-form was available in $[Ru(NO)X_3(L-L)]$ -type complexes (X = halogeno, L-L = bidentate ligand), when ethylendiamine or 2,2'-bipyridine was employed as the bidentate ligand [14–16].

3.2. Reactivity as an electrophile

Some differences in the nitrosyl reactivity between *mer*- $[Ru(NO)Cl_3(acac)]^-(1)$ and *mer*- $[Os(NO)Cl_3(acac)]^-(3)$ could be observed in their formation reactions. As mentioned earlier, *mer*- $[Ru(NO)Cl_3(acac)]^-(1)$ or *cis*-

 $[Ru(NO)Cl(acac)_2]$ (2) were produced under different pH conditions: *mer*- $[Ru(NO)Cl_3(acac)]^-$ (1) was obtained from the solution of pH = 1.0 and *cis*- $[Ru(NO)Cl(acac)_2]$ (2) from that of pH = 3.7. Further increasing the pH value of the solution to give neutral conditions results in a nitrosyl ligand reaction, in which a hydroxyiminoacetylacetonato ligand (hia) is formed [17]:

 $[Ru(NO)Cl(acac)_2] + Hacac = [Ru(hia)(acac)_2]$

$$+2H^{+}+Cl^{-} \quad (hia=CH_{3}COC(NO)COCH_{3}^{-}) \quad (1)$$

Although the hydroxyiminoacetylacetonato (hia) ligand formation occurred relatively easily for *cis*-[Ru(NO)Cl-(acac)₂] (**2**), *cis*-[Os(NO)Cl(acac)₂] (**4**) did not undergo the reaction, even in neutral solution. We assume that this difficulty in producing the hia ligand stems mainly from the inertness of the chloro ligand in osmium complex **4**. The assumption is supported by a result of our previous work [17]: the ligand formation occurred immediately at room temperature in the reaction between *cis*-[Ru(NO)(H₂O)-(bpy)₂]³⁺ and Hacac, in which *cis*-[Ru(hia)(bpy)₂]⁺ was isolated as the PF₆ salt. However, a similar experiment using *cis*-[Ru(NO)Cl(bpy)₂]²⁺, instead of *cis*-[Ru(NO)(H₂O)-(bpy)₂]³⁺, required at least 1 week for the completion of the hia ligand formation under the same conditions [17].

b An acid-base interconversion reaction which occurs between the nitrosyl and the nitro species (Eq. (2)) can be regarded as one of the criteria for the electrophilic behavior of the coordinated nitrosyl [1-4]:

$$(\operatorname{RuNO})^{3+} + 2\operatorname{OH}^{-} \rightleftharpoons (\operatorname{Ru}(\operatorname{NO}_{2}))^{+} + \operatorname{H}_{2}\operatorname{O}$$
(2)

Table 3 Positional parameters for the non-hydrogen atoms in (Bu_4N) - $[Ru(NO)Cl_3(acac)]$ (1)

Atom	x	у	Z.	$B_{\rm eq}$
Ru(1)	0.01410(4)	0.70717(6)	0.50979(6)	5.27(3)
Ru(2)	0.21127(4)	-0.00445(6)	0.48893(6)	5.14(3)
Cl(1)	0.0215(1)	0.7115(2)	0.3974(2)	8.1(1)
Cl(2)	0.0091(1)	0.7162(2)	0.6238(2)	9.2(1)
Cl(3)	-0.0675(1)	0.6731(2)	0.4397(2)	5.96(9)
Cl(4)	0.2015(1)	-0.1098(2)	0.5055(2)	6.8(1)
Cl(5)	0.2155(1)	0.1027(2)	0.4783(2)	7.2(1)
Cl(6)	0.2956(1)	-0.0074(2)	0.5750(2)	6.78(10)
O(1)	0.0442(4)	0.5821(5)	0.5386(8)	13.4(5)
O(2)	-0.0130(3)	0.7911(4)	0.4837(5)	7.1(2)
O(3)	0.0834(3)	0.7416(4)	0.5697(5)	6.8(3)
O(4)	0.2246(4)	-0.0285(5)	0.3611(5)	10.1(4)
O(5)	0.2046(3)	0.0101(4)	0.5826(4)	6.1(2)
O(6)	0.1381(3)	0.0024(5)	0.4213(4)	7.1(3)
N(1)	0.0335(4)	0.6347(6)	0.5280(7)	8.1(4)
N(2)	0.2186(3)	-0.0175(5)	0.4129(5)	6.0(3)
N(3)	0.3651(3)	0.2085(5)	0.6146(5)	4.8(3)
N(4)	0.3668(3)	0.1744(6)	0.1824(6)	6.3(3)
C(1)	0.0122(6)	0.8404(7)	0.4996(9)	7.8(5)
C(2)	0.0627(6)	0.8456(8)	0.5383(10)	9.0(6)
C(3)	0.0944(5)	0.7973(8)	0.5727(8)	7.1(5)
C(4)	-0.0186(5)	0.8976(6)	0.468(1)	12.8(6)
C(5)	0.1487(4)	0.8098(8)	0.6193(8)	10.3(6)
C(6)	0.1642(5)	0.0097(6)	0.5851(7)	6.6(4)
C(7)	0.1182(4)	0.0083(7)	0.5203(8)	6.8(4)
C(8)	0.1078(5)	0.0041(8)	0.4440(7)	6.8(4)
C(9)	0.1722(5)	0.0143(7)	0.6656(7)	8.3(5)
C(10)	0.0532(5)	0.004(1)	0.3823(8)	11.7(6)
C(11)	0.4014(4)	0.2529(6)	0.6/2/(6)	5.5(3)
C(12)	0.3816(4)	0.3079(6)	0.6942(7)	7.4(4)
C(13)	0.4231(5)	0.3525(6)	0.7376(8)	10.1(4)
C(14)	0.4043(5) 0.2206(4)	0.4089(7)	0.7571(7)	5.6(4)
C(15)	0.3290(4) 0.2512(4)	0.1830(6)	0.0390(0)	3.0(4)
C(10)	0.3312(4) 0.2006(5)	0.1440(0) 0.1257(7)	0.7100(7) 0.7257(7)	7.0(4)
C(17)	0.3090(5)	0.1237(7)	0.7237(7) 0.7904(8)	10.2(4)
C(10)	0.3200(3) 0.3937(3)	0.0828(0) 0.1569(6)	0.7904(8) 0.6033(6)	53(3)
C(20)	0.3557(3)	0.1305(0) 0.1126(5)	0.0033(0) 0.5384(7)	5.5(3)
C(20)	0.3050(4) 0.3968(4)	0.0576(6)	0.5364(7) 0.5470(7)	7.2(4)
C(21)	0.3753(5)	0.0370(0) 0.0145(7)	0.3470(7) 0.4790(8)	120(5)
C(22)	0.3735(3)	0.0143(7) 0.2393(5)	0.4790(0) 0.5365(6)	48(3)
C(23)	0.3520(3) 0.3600(4)	0.2393(3) 0.2712(6)	0.5005(0) 0.5016(6)	6.3(4)
C(25)	0.3230(4)	0.2851(7)	0.4162(7)	8.5(4)
C(26)	0.3467(5)	0.3178(7)	0.3774(8)	10.6(5)
C(27)	0.3716(6)	0.2399(8)	0.2022(8)	10.7(5)
C(28)	0.4106(5)	0.2744(9)	0.1948(8)	12.7(6)
C(29)	0.4281(6)	0.340(1)	0.243(1)	22.6(8)
C(30)	0.3963(7)	0.369(1)	0.220(1)	24.6(9)
C(31)	0.3211(5)	0.1489(7)	0.1833(7)	8.3(4)
C(32)	0.3185(5)	0.1477(7)	0.2565(7)	8.7(4)
C(33)	0.2737(4)	0.1194(8)	0.2448(8)	10.1(5)
C(34)	0.2628(5)	0.1200(9)	0.3038(8)	13.3(6)
C(35)	0.4122(4)	0.1394(7)	0.2418(7)	7.6(4)
C(36)	0.4119(5)	0.0739(7)	0.2343(9)	9.8(5)
C(37)	0.4589(7)	0.0466(7)	0.305(1)	14.0(7)
C(38)	0.4601(6)	-0.010(1)	0.307(1)	19.9(8)
C(39)	0.3601(4)	0.1608(6)	0.1037(7)	7.4(4)
C(40)	0.3192(4)	0.1915(6)	0.0361(7)	7.3(4)
C(41)	0.3132(5)	0.1705(7)	-0.0395(7)	9.2(5)
C(42)	0.2679(4)	0.1913(7)	-0.1073(7)	11.0(5)

Table 4 Positional parameters for the non-hydrogen atoms in $Cs[Os(NO)-Cl_3(acac)]$ (3)

Atom	x	у	z	$B_{\rm eq}$
Os	0.21771(5)	0.29359(3)	0.12907(6)	2.714(9)
Cs	0.7142(1)	0.49163(7)	0.2711(1)	4.81(2)
Cl(1)	0.4225(4)	0.2804(3)	-0.0783(4)	457(8)
Cl(2)	0.0413(4)	0.0006(3)	0.3635(5)	4.74(8)
Cl(3)	0.2620(4)	0.4883(2)	0.2319(4)	4.18(7)
O(1)	-0.069(1)	0.3022(9)	-0.152(2)	8.3(3)
O(2)	0.4171(9)	0.2899(6)	0.326(1)	3.2(2)
O(3)	0.1968(9)	0.1260(6)	0.055(1)	3.4(2)
N(1)	0.048(1)	0.3007(7)	-0.040(1)	4.0(2)
C(1)	0.484(1)	0.2031(9)	0.358(1)	2.8(2)
C(2)	0.428(1)	0.0955(9)	0.266(2)	3.5(3)
C(3)	0.291(1)	0.0615(9)	0.124(2)	3.2(2)
C(4)	0.634(1)	0.224(1)	0.508(2)	3.7(3)
C(5)	0.240(2)	-0.0576(10)	0.041(2)	4.6(3)

Table 5			
Selected bond lengths	(Å)	for 1	and 3

(Bu ₄ N)[Ru(NO)C	$l_3(acac)](1)$		
Ru1–N1	1.67(1)	Ru2–N2	1.661(9)
N101	1.19(1)	N2-O4	1.16(1)
Ru1–Cl1	2.357(3)	Ru2–Cl4	2.367(4)
Ru1–Cl2	2.354(4)	Ru2–Cl5	2.360(4)
Ru1–Cl3	2.354(3)	Ru2–Cl6	2.339(3)
Ru1–O2	1.980(8)	Ru2–O5	1.997(7)
Ru1–O3	2.041(7)	Ru2–O6	2.016(7)
O2C1	1.28(1)	O5–O6	1.30(1)
C1-C2	1.38(2)	C6–C7	1.38(1)
C2–C3	1.38(2)	C7–C8	1.38(1)
O3–C3	1.26(1)	O6–C8	1.24(1)
C1C4	1.51(2)	C6–C9	1.49(1)
C3–C5	1.51(1)	C8-C10	1.54(1)
Cs[Os(NO)Cl ₃ (aca	ac)](3)		
Os-N1	1.729(9)	Os–O3	2.031(7)
N101	1.16(1)	O2C1	1.28(1)
Os-Cl1	2.375(3)	C1–C2	1.38(1)
Os-Cl2	2.374(3)	C2–C3	1.38(1)
Os-Cl3	2.370(3)	C1C4	1.48(1)
Os–O2	2.010(7)	C3-C5	1.49(2)

Published data on the equilibria for several ruthenium and osmium complexes show that the p*K* value is strongly dependent upon both metal ion and co-existing ligands [18]. The effect on the steric factor of the complexes used for measuring the p*K* value is estimated to be quite small: almost the same p*K* values have been estimated for both *cis*-[Ru(NO)Cl(bpy)₂]²⁺ and the corresponding *trans*-form complex [19]. We attempted to measure the p*K* value of the acid–base reaction in both *cis*-[Ru(NO)Cl(acac)₂] (**2**) and *cis*-[Os(NO)Cl(acac)₂] (**4**) photometrically, but the results were not useful, because partial decomposition of both complexes occurred in basic media. The acetylacetonato complexes seem to be insensitive to the nitrosyl–nitro conversion reaction (Eq. (2)). This is in accord with the judgement of

Table 6		
Selected bond angles (°)	for 1	and 3

$(Bu_4N)[Ru(NO)Cl_3($	(acac)] (1)		
Ru1-N1-O1	175(1)	Ru2-N2-O4	177(1)
Cl1-Ru1-Cl2	172.7(2)	Cl4-Ru2-Cl5	173.8(1)
N1-Ru1-O2	176.4(4)	N2-Ru2-O5	178.1(4)
Cl3-Ru1-O2	176.8(3)	Cl6-Ru2-O6	175.2(3)
Ru1-O2-Cl	125.5(8)	Ru2-O5-C6	126.2(7)
O2-C1-C2	127(1)	O5-C6-C7	123(1)
C1C2C3	124(1)	C6-C7-C8	126(1)
C2-C3-O3	127(1)	C7-C8-O6	126(1)
Ru1-O3-C3	124.9(9)	Ru2-O6-C8	126.1(8)
Cs[Os(NO)Cl ₃ (acac))](3)		
Os-N1-O1	177(1)	O2C1C2	125.8(9)
Cl1-Os-Cl2	172.6(1)	C1C2C3	126(1)
N1-Os-O2	178.3(4)	C2-C3-O3	124(1)
Cl3-Os-O3	175.4(2)	Os-O3-C3	127.4(7)
OsO2C1	126.3(6)		

Bottomley et al. based on IR (ν (NO)) data [20]: the IR (ν (NO)) data of *cis*-[Ru(NO)Cl(acac)₂] (2) (1890 cm⁻¹) and of *cis*-[Os(NO)Cl(acac)₂] (4) (1860 cm⁻¹) suggest that these are rather inactive nitrosyl complexes.

3.3. Electrochemical behavior of $[Ru(NO)Cl_{5-2n}(acac)_n]^m$ (n=0, 1, 2) complexes

3.3.1. The n = 0 complex, $[M(NO)Cl_5]^{2-1}$

In line with previous reports [5–7], a well-defined reversible one-electron oxidation wave was found in both $[Ru(NO)Cl_5]^{2-}$ and $[Os(NO)Cl_5]^{2-}$. $[Ru(NO)Cl_5]^{2-}$ showed also an irreversible one-electron reduction wave at

Table 7 Electrochemical data of $[M(NO)Cl_{5-2n}(acac)_n]^m$ -type complexes

-1.44 V. Multiple scanning showed that the reduction of $[Ru(NO)Cl_5]^{2-}$ at this potential results in the gradual appearance of a new wave at 0.8 V. No experiments attempting the identification of the species responsible were undertaken. A reduction wave was also found in $[Os(NO)Cl_5]^{2-}$, but the wave was detected at the limited negative end of the potential window, discouraging further investigation.

The CV pattern of $[M(NO)Cl_{5-2n}(acac)_n]^m$, including that of $[M(NO)Cl_5]^{2-}$, is quite different from those of other $\{MNO\}^6$ -type nitrosyl complexes, such as *cis*- $[Ru(NO)Cl-(bpy)_2]^{2+}$ which has been well-investigated electrochemically [21]. In the latter nitrosyl complexes, we found usually two one-electron reduction waves, without any electrode oxidation reaction. The site of the reduction is regarded to be a nitrosyl ligand [21].

3.3.2. The n = 1 complexes, $[M(NO)Cl_3(acac)]^-$ (1 and 3)

All electrochemical data are listed in Table 7. A typical cyclic voltammogram of *mer*- $[Os(NO)Cl_3(acac)]^-$ (3) is shown in Fig. 2.

Either the reversible oxidation wave or the irreversible reduction wave was found at 1.12 V ($E_{1/2}$) and -1.60 V (E_{pc}), respectively. The reversible nature of the one-electron oxidation wave was confirmed based on the data of ln plots (26 mV), peak current ratio ($i_{pc}/i_{pa}=1$), and peak potential separation ($\Delta E_p = 70$ mV). Plots of peak current versus the square root of the scan rate are linear, indicating that diffusion-controlled redox processes are occurring at the electrode surface. The reversibility indicates that the following

	$[\mathbf{R}_{\mathbf{u}}(\mathbf{NO})\mathbf{C}\mathbf{L}_{\mathbf{u}}]^{2-}$	$[\mathbf{R}_{\mathbf{u}}(\mathbf{NO})\mathbf{C}_{\mathbf{u}}(\mathbf{acac})]^{-}$	$[\mathbf{R}\mathbf{u}(\mathbf{NO})\mathbf{C}](\mathbf{acac})_{\mathbf{c}}]$
Oxid. $E_{1/2}^{a,b}$ (V)	1.19	1.46 °	1.67 °
Reduc. $E_{\rm pc}^{\rm a}$ (V)	-1.44	-1.08	-0.84, -1.34
RT/nF (mV)			
(30 ms)	26.7	25.1	33.2
(50 ms)	26.6	25.0	32.9
(70 ms)	26.2	25.1	32.0
Q/nF	0.85 ^d	(1.5) ^e	(3.1) ^e
	$[Os(NO)Cl_5]^{2-}$	$[Os(NO)Cl_3(acac)]^-$	[Os(NO)Cl(acac) ₂]
Oxid. $E_{1/2}^{a,b}$ (V)	0.75	1.12	1.43
Reduc. $E_{\rm pc}^{\rm a}$ (V)	-2.0?	-1.60	-1.56, -1.72
RT/nF (mV)			
(30 ms)	32.2	32.0	26.5
(50 ms)	32.4	32.1	27.1
(70 ms)	30.7	32.8	26.7
Q/nF	0.82	(1.5) ^e	(3.3) ^e

 $^{\rm a}$ vs. Ag | AgNO_3 (0.1 mol dm $^{-3}$ TEAP–CH_3CN) at 298 K.

^b $E_{1/2} = (E_{\rm pa} + E_{\rm pc})/2.$

^e Decomposition occurred during the exhaust electrolysis.

^c E_{pa}. ^d At 298 K.

Al 298 K.



Fig. 2. Typical cyclic voltammogram of the *mer*- $[Os(NO)Cl_3(acac)]^-$ (**3**) ion. [Complex] (1.0 mmol dm⁻³) in 0.1 mol dm⁻³ TEAP–CH₃CN on a stationary Pt electrode at 25°C (200 mV s⁻¹).

electrode reaction is operating, probably in the $(OsNO)^{3+}$ moiety (Eq. (3)):

$$[Os(NO)Cl_3(acac)]^{-} \rightleftharpoons [Os(NO)Cl_3(acac)] + e^{-} \quad (3)$$

Oxidative controlled-potential electrolysis carried out on the wave at 1.12 V did not give useful data. The one-electron oxidation species, *mer*-[Os(NO)Cl₃(acac)] (**3**), underwent a facile decomposition (see Table 7), even in the experiment at -40° C (Eq. (4)).

$$mer$$
-[Os(NO)Cl₃(acac)] \rightarrow unidentified species (4)

Clearly, the one-electron oxidation species of osmium having the acetylacetonato ligand, *mer*- $[Os(NO)Cl_3(acac)]$ (**3**), is more chemically unstable than $[Os(NO)Cl_5]^-$, which could be isolated, as mentioned earlier. In addition, the CV experiment on *mer*- $[Os(NO)Cl_3(acac)]^-$ (**3**) suggested that a one-electron reduction occurred, but it was not carried further, because the reduction wave appeared too near the potential window of this solvent.

Almost the same CV pattern was found in *mer*- $[Ru(NO)Cl_3(acac)]^-(1)$, but, in this case, an irreversible oxidation was found. The complex also underwent an irreversible reduction at -1.12 V. Multiple-scanning shows that the reduction of *mer*- $[Ru(NO)Cl_3(acac)]^-(1)$ causes formation of an unidentified species, whose oxidation wave is found at around 0.9 V (Eq. (5)).

$$[\operatorname{Ru}(\operatorname{NO})\operatorname{Cl}_{3}(\operatorname{acac})]^{-} + e^{-} \rightarrow [\operatorname{Ru}(\operatorname{NO})\operatorname{Cl}_{3}(\operatorname{acac})]^{2-}$$
(5)

 $[Ru(NO)Cl_3(acac)]^{2-} \rightarrow$ unidentified species

As in the case of *mer*- $[Os(NO)Cl_3(acac)]^-$ (3), the species generated in the reduction could not be identified.

3.3.3. The n = 2 complexes, $cis - [M(NO)Cl(acac)_2]$ (2 and 4)

CV experiments show that both *cis*-[Ru(NO)Cl(acac)₂] (2) and *cis*-[Os(NO)Cl(acac)₂] (4) undergo a one-electron oxidation, in addition to the expected reduction. The oxidation wave of *cis*-[Os(NO)Cl(acac)₂] (4) was reversible in the cyclic voltammogram $(E_{1/2}=1.43 \text{ V}, \Delta E_p=70 \text{ V})$ mV, $i_{pc}/i_{pa}=1$, ln plots=26–27 mV), but that of *cis*-[Ru(NO)Cl(acac)₂] (2) showed an irreversible one-electron oxidation wave. Again, exhaustive oxidative electrolysis of *cis*-[Os(NO)Cl(acac)₂] (4) did not give useful data.

3.4. Summary

We can summarize the electrochemical features in osmium and ruthenium complexes of $[M(NO)Cl_{5-2n}(acac)_n]^m$ (n=0, 1, 2) as follows.

(i) The CV pattern of the oxidation process differs depending on the central metal atom. Under the same conditions, $[Ru(NO)Cl_{5-2n}(acac)_n]^m (n=1,2)$ showed an irreversible behavior, while that of the osmium complexes proved to be reversible. This suggests that the species resulting from oneelectron oxidation of the nitrosylosmium complexes are chemically more stable than those of nitrosylruthenium. A similar result was found in previous work on the n=0 complex; $[Os(NO)Cl_5]^-$ is so stable that it could be isolated as $R[Os(NO)Cl_5]$ ($R=Et_4N$, Ph_4As , Ph_4P) [6,7], but isolation of the corresponding salts of $[Ru(NO)Cl_5]^-$ was unsuccessful [10].

(ii) In agreement with (i), redox potentials move to the negative direction when the central metal atom is altered from Ru to Os (Table 1). The oxidation potentials (E_{pa}) of $[\operatorname{Ru}(\operatorname{NO})\operatorname{Cl}_{5-2n}(\operatorname{acac})_n]^m$ (n=1,2) were in the more positive potential region than those of the corresponding $[Os(NO)Cl_{5-2n}(acac)_n]^m$ (n=1, 2). Despite a ligand (NO)-based electrode reaction, the reduction potentials (E_{pc}) of $[M(NO)Cl_{5-2n}(acac)_n]^m$ (n=0, 1, 2) show a similar trend. However, these irreversible potentials are affected by the kinetic behavior of the reactions which are accompanied by the one-electron oxidation-reduction of the complexes. Although the same trend has also been found in some ruthenium- and osmiumnitrosyl complexes with polypyridyl ligands, the reductions of these complexes proceed reversibly [18], which is the typical behavior of $\{MNO\}^6$ -type nitrosyl complexes.

(iii) In the comparative study on the polypyridyl nitrosyl complexes mentioned above, a linear correlation between IR data ($\nu(NO)$) and the potentials for a ligand-based reduction $(E_{1/2}(1))$ was found, although there is a significant scattering of the experimental points from the least-squares line [18]. We obtained a similar relation for a series of $[M(NO)Cl_{5-2n}(acac)_n]^m$ complexes, using the data of the reduction (Fig. 3(a)). Such a relation, however, was not the case in the oxidation. Plots of IR (ν (NO)) versus $E_{1/2}$ (ox) gave clearly two straight lines (Fig. 3(b)), depending on the metal atoms of $[M(NO)Cl_{5-2n}(acac)_n]^m$. This may reflect mainly the different redox sites between the reduction and the oxidation in $[M(NO)Cl_{5-2n}(acac)_n]^m$: a ligand (nitrosyl)-based electron transfer takes place in the reduction of the $\{RuNO\}^{6}$ -type nitrosyl complexes [21], while the site of the oxidation is believed to be mainly a central metal atom [5-7].



Fig. 3. (a) Plots of reduction potentials for ruthenium complexes (\checkmark) and osmium complexes (\blacktriangle). (b) Plots of oxidation potentials for ruthenium complexes (\blacktriangle) and for osmium complexes (\blacklozenge). The individual values are tabulated in Table 7.

(iv) Additionally, the values of the potential differences between the oxidation and the reduction waves $(|E_{pc}(ox) - E_{pc}(red)|)$ are different depending on the complex, whether it has a nitrosyl ligand or not. The values fall in the range 2.5-2.6 V for the ruthenium complexes, and in the range 2.7-2.9 V for the osmium complexes. The extent of the potential ranges is larger than that observed in trisacetylacetonato complexes of ruthenium(III) which lack a nitrosyl ligand: ~1.8 V for [Ru(acac)₃] (-0.93 V ($E_{1/2}$) versus Ag|AgNO₃ for $[Ru(acac)_3]^{0/1-}$ and +0.84 V $(E_{1/2})$ for $[Ru(acac)_3]^{+/0}$. The difference in the potential range between cis-[M(NO)Cl(acac)₂] (or mer-[M(NO)- $Cl_3(acac)$]⁻) (M=Ru,Os) and [M(acac)₃] (M=Ru) can be attributed to their different redox sites: an electrode reaction of the $[M(acac)_3]$ complexes occurs in the metal atom, either in the reduction or in the oxidation.

4. Supplementary material

Observed and calculated structure factors, all calculated atomic coordinates, all anisotropic thermal parameters, complete lists of bond lengths and angles, torsion angles, and structure factor tables are available from the authors on request.

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