Ruthenium Complexes with Coordinated Hydroxyiminoacetylacetonato or Bridging Nitrosyl Groups Formed by the Reactions of Nitrosylruthenium(III) with Acetylacetone

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Complexes formed by the reactions of nitrosylruthenium(III) with acetylacetone were investigated. The following products: $[Ru(acac)_2(hia)]$, **1**; *cis*-$[RuCl(NO)(acac)_2]$, **2**; and $[\{Ru(NO)(acac)_2\}_4]$, **3**; (acac= $C_5H_7O_2^-$ and hia= $C_5H_6NO_3^-$), were isolated as crystals and were characterized. On the basis of chemical and thermal analyses, and on the basis of observations of the magnetic properties, the conductivities, the molecular weights, the infrared spectra, and the NMR spectra, it was concluded that **1** contains the hydroxyiminoacetyl acetonato ligand, which is formed by the reaction of the coordinated nitrosyl group with acetylacetone, and that **2** contains a terminal nitrosyl group, and **3**, bridging nitrosyl groups.

The reactivity of coordinated nitrosyl has received much attention recently. The reactions of a variety of nitrosylruthenium(III) complexes with nucleophiles, such as ammonia, hydrazins, hydroxylamine, potassium azide, and potassium hydroxide, have recently been investigated.[1-7] The reactions of nitrosylruthenium(III) halides with reducing reagents, such as tin(II) chloride and formaldehyde, have also been reported.[8,9] This paper will describe the preparation and characterization of the ruthenium complexes with the coordinated hydroxyiminoacetylacetonato or bridging nitrosyl groups obtained by the reactions of nitrosylruthenium(III) with acetylacetone.

Experimental

Preparation. *Bis(acetylacetonato)hydroxyiminoacetylacetonatoruthenium(III), [Ru(acac)$_2$(hia)], 1*: To a hydrochloric-acid solution of nitrosylruthenium(III) (100 mg as Ru/10 ml) were added methanol (2 ml) and acetylacetone (2 ml). Then, the pH of the mixed solution was adjusted to 6.5 with an aqueous solution of potassium hydroxide. When the mixed solution was allowed to stand at room temperature for about a week, dark brown crystals appeared. The crystals were recrystallized from ethanol. Yield, 40 mg. Found: Ru, 23.9; C, 42.3; H, 4.75; N, 3.37%. Calcd for $[Ru(C_5H_7O_2)_2(C_5H_6NO_3)]$: Ru, 23.6; C, 42.1; H, 4.68; N, 3.28%.

Bis(acetylacetonato)chloronitrosylruthenium(III), [RuCl(NO)(acac)$_2$], 2: To a hydrochloric-acid solution of nitrosylruthenium(III) (100 mg as Ru/10 ml) were added methanol (2 ml) and acetylacetone (2 ml). Then, the pH of the mixed solution was adjusted to 3.5 with an aqueous solution of potassium hydroxide. The solution was refluxed for 2 hr and was then allowed to stand at room temperature for several days, until dark brown crystals were separated out. The crystals were recrystallized from ethanol. Yield, 35 mg. This complex was also obtained from the filtrate of **3** when the filtrate was allowed to stand at room temperature for a long period. Found Ru, 27.4; C, 32.6; H, 3.80; N, 3.81; Cl, 9.57%. Calcd for $[RuCl(NO)(C_5H_7O_2)_2]$: Ru, 27.7; C, 32.9; H, 3.87; N, 3.84; Cl, 9.73%.

Cyclo-tetra-μ-nitrosyl-tetrakis(diacetylacetonato)ruthenium(II), [{Ru-(NO)(acac)$_2$}$_4$], 3: To a hydrochloric-acid solution of nitrosylruthenium(III) (135 mg as Ru/10 ml) were added acetylacetone (2 ml), and the pH of the solution was adjusted to 3.5 with an aqueous solution of potassium hydroxide. To this mixed solution, an equal volume of ethanol was added. The solution was refluxed for 50 min and was then allowed to stand at room temperature for about ten days, until dark green crystals were separated out. The crystals were recrystallized from a mixed solution of ethanol and benzene three times. Yield, 35 mg. Found: C, 36.2; H, 4.35; N, 4.18%. Calcd for $Ru(NO)(C_5H_7O_2)_2$: C, 36.5; H, 4.25; N, 4.25%.

Materials. Nitrosylruthenium(III) in a hydrochloric acid solution was prepared by a conventional method.[10] The nitrosylruthenium(III) chloride [^{15}N] was prepared by the method reported by Miki *et al.*[11] The palladium complexes, $[Pd(acac)_2]$ and $[Pd(acac)(hia)]$, were prepared according to the method in the literature.[12] $[Pd(hia)_2]$ was obtained by the reaction of Pd(II) chloride with hia, which had been purchased from the Dojin Lab. (Kumamoto, Japan).

Measurements. The infrared spectra of these complexes were recorded on Leitz 221, JASCO DS-301, or Hitachi EPI-L spectrophotometers, using the KBr-pellet or Nujol-mull method. The NMR spectra were taken on a Hitachi R-22 instrument, with tetramethylsilane as the internal standard. The visible absorption spectra were recorded on a Hitachi-Perkin-Elmer 139 spectrophotometer. The conductivity and the molecular weight were measured with a Metrohm Konduktoskop E356 and with a Mecrolab Osmometer 302 respectively. The DTA and TG measurements were carried out by the use of a Rigaku TG-DTA standard-type apparatus. The measurments were made at a heating rate of 10 °C/min in atmosphere. The magnetic susceptibilities were measured by the Gouy method.

Results and Discussion

From the reactions between nitrosylruthenium(III) and acetylacetone, Complexes **1**, **2** and **3** were newly isolated. The chemical formulae of these complexes and some of their properties are shown in Table 1. The molecular weights of **1** and **3**, which were obtained in benzene by a vapor-pressure osmometry, corresponded to those of the monomeric and of the tetrameric species respectively. The molecular weight of **2** could not be measured because of an insufficient solubility in benzene, but the monomeric form of the complex can be expected from the observations of its IR and NMR spectra. All these complexes were non-electrolyte in benzene and DMF. The thermal properties of the complexes were examined by DTA and TG methods. **1**, **2**, and **3** decomposed at about 149 °C, 126 °C and 265 °C respectively, without showing any endothermic

Table 1. Some properties of ruthenium complexes formed by the reactions of RuNO(III) with acetylacetone

Complex	Chemical Formula	χ_g 10^6 c.g.s., e.m.u.	μ_{eff} (B.M.)	Type of[a)] electrolyte	Molecular[b)] weight	Visible[b)] Absorption spectra nm (ε)
1	$[Ru(acac)_2(hia)]$	2.94 (296 K)	1.87	nonelectrolyte	435	460 (4.43×10^3) 395 (3.28×10^3)
2	*cis*-$[RuCl(NO)(acac)_2]$	−0.32 (293 K)	dia	nonelectrolyte		505 (1.84×10^2)
3	$[\{Ru(NO)(acac)_2\}_4]$	−0.28 (293 K)	dia	nonelectrolyte	1324	635 (2.83×10^3) 420sh (7.2×10^3)

a) In MeOH and in DMF. b) in MeOH.

peaks due to the deaquation of crystalline or coordinating water.

The structures of these complexes will now be discussed on the basis of their IR and NMR spectra and their magnetic properties.

$[Ru(acac)_2(hia)]$ (**1**): The composition of **1** is consistent with either of the following two formulae; $[Ru(acac)_2(hia)]$ and $[Ru(NO)(acac)_3]$. However, tris(acetylacetonato)nitrosylruthenium(III) was clearly excluded by the paramagnetism observed, since nitrosylruthenium(III) complexes are essentially diamagnetic. The observed magnetic moment (1.87 B.M.) is fairly close to the value, 1.73 B.M., estimated by the spin-only equation.

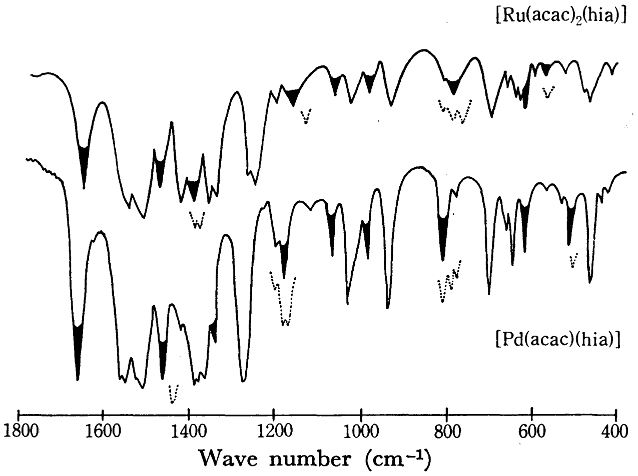


Fig. 1. Infrared spectra of $[Ru(acac)_2(hia)]$ and $[Pd(acac)(hia)]$ (KBr disk). Painted peaks were assigned to the bands which were caused by the hia ligand. Identity of the ligand was established by a comparison of the infrared spectra of $[Ru(acac)_2(hia)]$ (**1**), $[RuCl(NO)(acac)_2]$ (**2**), $[Pd(acac)_2]$, $[Pd(acac)(hia)]$ and $[Pd(hia)_2]$.
^{14}NO-complex, ——; ^{15}NO-complex, ······.

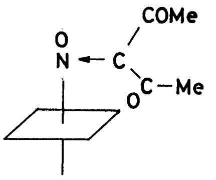


Fig. 2. Proposed structure for Complex **1**.

The infrared spectra of **1** and relevant compounds are shown in Fig. 1. The characteristic vibrations in **1** [^{14}N] and **1** [^{15}N] are summarized in Table 2. Recently, several complexes containing hia and analogous ligands were identified, by Masuda *et al.* and by White on the basis of their infrared spectra.[12,13] The spectral features observed here can be understood on the basis of the idea that one of the acetylacetonato ligands and the coordinated nitrosyl combine through the γ-carbon atom to produce the hia ligand, as is shown in Fig. 2. Evidence for the presence of the hia ligand in **1** may be found in the similarity between the infrared spectrum of **1** and that of $[Pd(acac)(hia)]$, including their ^{15}N isotopic effects. As is shown in

Table 2. Characteristic infeared spectra (cm^{-1}) of complexes **1**, **2**, and **3**

$[Ru(acac)_2(hia)]$		*cis*-$[RuCl(NO)(acac)_2]$		$[\{Ru(NO)(acac)_2\}_4]$		Tentative assignments
1 [^{14}N]	**1** [^{15}N]	**2** [^{14}N]	**2** [^{15}N]	**3** [^{14}N]	**3** [^{15}N]	
		1884 vs	1883 w 1849 vs			νNO(terminal)
1662 vs	1660 vs					νCO (uncoordinated)
1564 vs 1549 s	1565 vs 1553 s	1571 vs	1573 vs	1573 vs	1571 vs	νCO+νCC
					1543 sp	νNO(bridging)
1520 vs	1526 vs	1526 vs	1529 vs	1518 vs	1516 vs	νCO+νCC
1403 s	1400 s					
	1387 sp					νCN(hia)
1162 m	1148 m					νNO(hia)
807 w	796 w			795 m	795 m	
782 s	782 s	787 m	787 m	780 m	780 m	πCH
	771 s			769 m	769 m	
					760 sh	
587 w	582 w	601 w	591 w	553 w	544 w	νRuN
		587 w	575 w			σRuNO

Fig. 1, the bands due to the hia in both complexes were found in almost the same regions and intensities. By comparing the infrared spectrum of **1** with those of analogous complexes,[12–14] the bands at 1387, 1148, and 1660 cm^{-1} in **1** [^{15}N] can be assigned tentatively to the stretching vibrations of the C=N, N–O, and uncoordinated C=O groups of the hia ligand respectively. These bands seem to be most diagnostic for the characterization of this ligand.

cis-[RuCl(NO)(acac)$_2$] (**2**): **2** is diamagnetic. The infrared spectra of **2** [^{14}N] and **2** [^{15}N] are compared in the 200—4000 cm^{-1} region. The characteristic vibrations of both complexes are summarized in Table 2. By comparing these bands with the spectra of pentachloronitrosylruthenium(III) complexes and acetylacetonato metal chelate complexes,[15–19] the presence of the terminal nitrosyl ligand in **2** was easily verified.

TABLE 3. PROTON MAGNETIC RESONANCE DATA (ppm) FOR COMPLEXES **2** AND **3**

Complex	Solvent	Resonance	
		-CH$_3$	-CH
2, *cis*-[RuCl(NO)(acac)$_2$]	CDCl$_3$	2.05 2.14 2.24 2.29	5.47 5.73
3, [{Ru(NO)(acac)$_2$}$_4$]	CDCl$_3$	1.73 2.21	5.31

The NMR spectrum of **2** listed in Table 3 was measured in CDCl$_3$. The assignments are based on those for *cis*- and *trans*-β-diketonato complexes, which have been investigated extensively by Boucher *et al.*[20] The observed chemical shifts for the methyl and the methine protons provide proof that the complex has a *cis* arrangement of the chloride and the nitrosyl.

[{Ru(NO)(acac)$_2$}$_4$] (**3**): The molecular weight of **3** corresponded to that of a tetrameric species. X-Ray single crystal photographs of **3** showed that the cell volume of this complex was about 2598×10^{-24} cm^3 (uncalibrated film). The calculated density for two molecules per cell is 1.68 g/cm^3, and the observed density was 1.70 g/cm^3 (by floatation in CH$_3$Br and CCl$_4$). The possibility of **3** being a tri- or pentanuclear complex may thus be excluded.

The infrared spectrum of **3** is shown in Table 2. The absorption bands of the acetylacetonato moiety in **3** were identical with those of **2**, showing a chelate coordination of the ligand. No absorption band due to the nitrosyl stretching frequency of the linear or near-linear RuNO(III) group was found in the 1700—2000 cm^{-1} region. It has recently been revealed by structural investigations that a marked lowering of the nitrosyl stretching frequency reflects the presence of the NO$^-$ ligand or the bridging nitrosyl ligand.[21–23] One of the present authors (M.M.) has reported that the infrared spectrum of a nitrosyl complex, which is believed to contain bridging nitrosyl, shows frequency shifts for the bands in the 1500, 800 and 550 cm^{-1} regions with the replacement of ^{14}N by ^{15}N.[9] ^{15}N substitution effects for **3** were observed, as is shown in Table 2. The strong band at 1573 cm^{-1} in **3** [^{14}N] was partially split into two bands, at 1571 and 1543 cm^{-1},in **3** [^{15}N]. The weak band at 553 cm^{-1} in **3** [^{14}N] was shifted to the lower-frequency side. As is shown in Fig. 3, a splitting of the bands was observed in the near 800 cm^{-1} region. These findings are quite similar to those found for the complex bridged with nitrosyl mentioned above,[9] suggesting that **3** contains the bridged nitrosyl group.

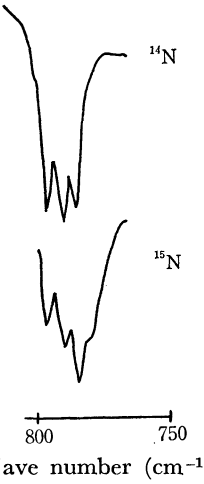


Fig. 3. IR spectra of Complex **3** at 800 cm^{-1} region (KBr).

The NMR spectroscopy provides additional evidence for the bridged structure assumed. As is shown in Table 3, the NMR spectrum of the complex in CDCl$_3$ shows three peaks, with an area ratio of 1: 3: 3. It has been established that two methine protons in monomeric *cis*-bis(acetylacetonato)cobaltate(III), [Co(acac)$_2$X$_2$]$^-$ (X=N$_3^-$ or OH$^-$), are equivalent, while the methyl protons are divided into two sets of methyl groups[20,24] A similar spectrum has also been found for di-μ-hydroxo-bis[bis(acetylacetonato)cobalt(III)],[25] [Co$_2$(acac)$_4$-(OH)$_2$]. In the latter, however, quite a large methyl resonance splitting (0.48 ppm), which is thought to arise because of the hydroxo bridge and the dimeric structure,[25] has been found. The NMR spectrum observed here is identical with that of the dimeric acetylacetonato complex referred to above.

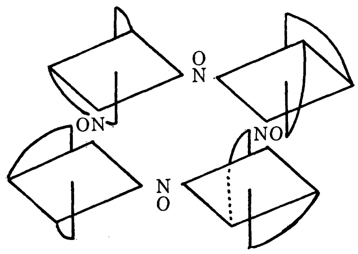
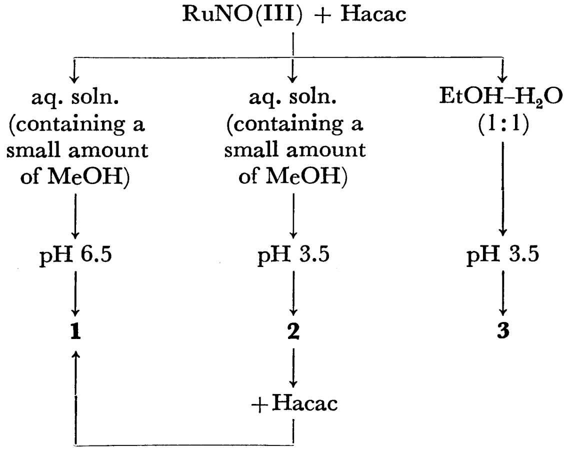


Fig. 4. Probable structure for Complex **3**

On the basis of the spectral observations, the most probable structure of **3** is thought to be the tetrameric structure bridged with nitrosyls, depicted in Fig. 4. This structure consists of four monomeric octahedral unit, Ru(NO)(acac)$_2$, containing both equivalent acetylacetonate anions and the bridged nitrosyl group.

3 is diamagnetic. The majority of nitrosylruthenium(III) complexes which have a linear terminal Ru–N–O group have been considered to contain NO$^+$.[26] The nitrosylruthenium group in **3**, however, may be considered to be Ru(II)NO or Ru(III)NO$^-$. The diamagnetism of **3** may be explained using the bonding scheme applied to a complex bridged with nitrosyls, $(Me_4N)_4[Ru_2(NO)_2(SnCl_3)_2Cl_6]\cdot H_2O$, which has an analogous bridged structure.[9]

Reactions. The reactions of the nitrosylruthenium(III) described above are summarized in the following scheme.



In a neutral solution, the coordinated nitrosyl is converted into the hia ligand under mild reaction conditions. On the other hand, **2** is formed in an acid aqueous or methanolic solution, whereas **3** is produced in an acid ethanolic solution. It should be noted that the isolation of these complexes depends on the pH of the reaction mixture and the kind of alcohol used as a solvent. **1** could also be derived by the reaction of **2** with acetylacetone in a methanolic solution. However, the formation of **1** was not observed in the reaction between RuNO(III) chloride and acetylacetone at pH 8.5—9.0. In an aqueous solution of this pH, dark brown materials were obtained in place of **1**. This is thought to be an acetylacetonato complex containing a terminal nitrosyl group($[Ru(OH)(NO)(acac)_2]$) on the basis of its composition and infrared spectrum.

The reaction of coordinated β-diketonato and analogous ligands with nitric oxide to give an oxime-type bonding has recently been reported.[12,13] However, no reaction between coordinated nitrosyl and β-diketone has yet been reported. The isolation of **1** reported here appears to be the first example of the latter reaction. The mechanism of this reaction is not clear. However, it is thought to differ from the acid-catalyzed mechanism which has been presumed for the formation of [Pd(acac)(hia)] by means of the reaction of NO on $[Pd(acac)_2]$,[12] since it appears unlikely that the cleavage of Ru–NO bonding occurs under the conditions specified above. This discrepancy seems to be responsible for the difference in reactivity between coordinated nitrosyl and free nitric oxide.

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