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The Formation of the N-bound Hydroxyiminoacetylacetonato Ligand by the Reaction of Nitrosyl in Bis(2,2′-bipyridine)chloronitrosylruthenium(II) with Acetylacetone

Masao Mukaida, Masakazu Yoneda, and Terunosuke Nomura

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioicho, Chiyoda-ku, Tokyo 102

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Synopsis. Nitrosyl in $[RuCl(bpy)_2NO]^{2+}$ reacts with Hacac, giving the N-bound hydroxyiminoacetylacetonato ligand(hia, $CH_3COC(NO)COCH_3^-$) under mild conditions. The reaction product, $[Ru(hia)(bpy)_2(H_2O)]X$ ($X=ClO_4$, PF_6), was characterized on the basis of its IR spectra, including those of the ^{15}N-complex.

Although the reactivities of coordinated nitrosyl in transition metal complexes have been widely studied, little work has been reported on the formation of N–C bonding *via* nitrosyl complexes.[1—4] These reactions are, however, thought to be useful for the nitrosation of some organic compounds.[5] We wish now to report on the complex, $[Ru(hia)(bpy)_2(H_2O)]X$ ($X=ClO_4$, PF_6), which was formed by the reaction of $[RuCl(bpy)_2NO]^{2+}$ with Hacac. The hia ligand in this complex functions as an unidentate ligand coordinating through the nitrogen atom, as is shown in Fig. 1.

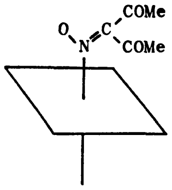

Fig. 1. N-bound hia ligand.

Experimental

Materials. The nitrosyl complex, $[RuCl(bpy)_2NO](ClO_4)_2$, was prepared by the procedure described by Meyer *et al.*, but $[RuCl_2(bpy)_2]Cl$ was used as a starting material instead of $[RuCl_2(bpy)_2]$. $[RuCl_2(bpy)_2]Cl$ was prepared by a new method using a "ruthenium blue" solution which was formed by the reaction of Ru(III) chloride with formic acid.[7]

Formation of Aquabis(2,2′-bipyridine)hydroxyiminoacetylacetonatoruthenium(II), $[Ru(C_5H_6NO_3)(C_{10}H_8N_2)_2(H_2O)]X$ ($X=ClO_4$, PF_6). The nitrosyl complex(200 mg, 0.295 mmol) was dissolved in a mixed solution of $EtOH-H_2O$(20 ml-10 ml), and then Hacac(1 ml) was added. After 10—15 days, a dark brown precipitate was collected, washed with water, and air-dried. The crude product(200 mg) was dissolved in water(300 ml). The resultant solution was charged on the top of a column containing SP sephadex C25 in the Na form (diameter, 12 mm; column height, 150 mm). When an aqueous solution of NH_4OAc(0.06 M) was then poured into the column at the rate of *ca.* 1—2 ml/min, a brown band appeared. Brown crystals were isolated as ClO_4 or PF_6 salt from the eluate of the band. A few further bands can be observed by the addition of an eluent containing KNO_3. The characterization of the products obtained from these bands is now under investigation. The present complex was filtered off, washed with water, and dried *in vacuo* over silica gel. Yield: about 30 mg. Found: N, 10.83; C, 45.76; H, 3.39; ClO_4, 14.70; H_2O, 2.38%. Calcd for $C_{25}H_{24}N_5O_8ClRu$: N, 10.62; C, 45.53; H, 3.64; ClO_4, 15.10; H_2O, 2.73%. Found: N, 10.23; C, 42.83; H, 3.13; PF_6, 21.01%. Calcd for $C_{25}H_{24}N_5O_4PF_6Ru$: N, 9.94; C, 42.59; H, 3.41; PF_6, 20.58%. The complex was soluble in common organic solvents. The crude product was diamagnetic. This suggests that the reaction product is a Ru(II) complex.

Results and Discussion

The complex formed by the reaction of $[RuCl(bpy)_2NO]^{2+}$ with Hacac gave the analytical data corresponding to the formula of $[Ru(hia)(bpy)_2](X\cdot H_2O)$. The complex containing the bidentate hia, $[Ru(acac)_2(hia)]$, has been found in the reaction of $[RuCl(acac)_2NO]$ with Hacac.[3] The IR spectra of the present complex, however, indicate the formula of $[Ru(hia)(bpy)_2(H_2O)]X$ containing the unidentada hia. By a comparison between the spectra of the ^{14}N-complex and the ^{15}N-complex in the 700—4000 cm^{-1} region, the isotopic effects were found two bands at 1350 and 806 cm^{-1}. In contrast, the ^{15}N substitution effects for $[Ru(acac)_2(hia)]$ have been found in three bands—at about 1400, 1160, and 800 cm^{-1}.[3] This finding can be explained by assuming the presence of different types of hia ligand in the two complexes. The bands in the present complex and its related complexes in which the ^{15}N substitution effects were observed are listed in Table 1.

Recently Mayer *et al.* reported that the nitrosyl in $[RuCl(bpy)_2NO]^{2+}$ reacts with aromatic amines to give *N*-bound *p*-nitrosoarene complexes.[2] They identified those products on the basis of the IR spectra. Armor

Table 1. Data of ^{15}N substitution shifts for the hia complexes and relevant complexes

Complex	Tentative assignments		
	ν(N=C)	ν(N-O)	
$[Ru(hia)(bpy)_2(H_2O)]ClO_4$		1342 (1327)	
$[Ru(hia)(bpy)_2(H_2O)]PF_6$		1350 (1340)	806 (793)
$[Ru(hia)(acac)_2]$	(1387)*	1162 (1148)	807 (796) 782 (782) (771)
$[Ru(N(O)C_6H_4RCH_3)(bpy)_2Cl]PF_6$[a]			
R=H		1286 (1261)	875 (860)
$R=CH_3$		1284 (1276)	875 (860)
$[Ru(NH_3)_5\{(NO)CH_2C(CH_3)_2OH\}]B(C_6H_5)_4$[b]		1365 (∼1355)	

* New band. The bands based on ^{15}N complexes are shown in parentheses. a) Ref. 2. b) Ref. 4.

et al. also obtained an alkylnitrosoruthenium(II) complex by the radiolysis of $[Ru(NH_3)_5NO]^{3+}$ in *t*-butyl alcohol.[4] The isotopic shifts observed for the present complex are in almost the same regions and in almost the same magnitude as those of the complexes in Refs. 2 and 4, indicating the presence of the unidentate hia. The bands at 1350 and 806 cm^{-1} in the present complex can be assigned tentatively to the stretching and the rocking vibrations of the N–O and N–C respectively of the unidentate hia, according to the assignments in Ref. 2. The band characteristic of uncoordinated carbonyl in the hia ligand was found in 1660 cm^{-1}. As is shown in Table 1, the band due to the N–O stretching vibration of the unidentate hia was found in a higher region than that of the chelating hia. In addition, the stretching vibration band due to the oxime-type C=N bonding in chelating hia has also been found in a lower region than that expected.[8] No explanation for why the stretching bivrations of both N=C and N–O become lower in $[Ru(acac)_2(hia)]$ can be offered at the present time.

Bottomley *et al.* proposed that coordinated NO^+ with $\nu(NO) > 1886$ cm^{-1} behaves as an electrophile.[9] According to their criterion, $[RuCl(acac)_2NO]$(ν(NO); 1884 cm^{-1}) in Ref. 3 exists on the borderline between complexes reactive and unreactive toward nucleophiles. On the other hand, $[RuCl(bpy)_2NO](ClO_4)_2$(ν(NO); 1927 cm^{-1}) has been known to be very reactive.[2] It was found in the present work that $[RuCl(bpy)_2NO]^{2+}$ reacts with Hacac to give a Ru(II) complex containing the unidentate hia, while $[RuCl(acac)_2NO]$ gives a Ru(III) complex containing the bidentate hia under the same conditions.[3] The formation of the two types of hia seems to be connected with the difference in the reactivities of coordinated nitrosyl between $[RuCl(bpy)_2NO](ClO_4)_2$ and $[RuCl(acac)_2NO]$.

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