Synthesis and Electrochemical Behavior of the Complex Having μ_2-Nitrosyl Moiety, as a Two-Electron Reduction Species of a $\{RuNO\}^6$-Type Nitrosyl, $[\{Ru(\mu_2\text{-}NO)\}_2(2,2\text{-}bipy)_4]^{2+}$

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Synthesis of the title complex was accomplished. The structure involving a four-membered cyclic unit with negatively charged NO moieties could be established by ^{13}C NMR measurements. Its electrochemical behavior was compared with that of $[\{Ru(\mu_2\text{-}NO)\}_2(acac)_4]$, which has the same cyclic unit, but with neutral charge on NO· moieties.

Metal nitrosyl complexes are of interest as models for a key material in the biological nitrite-ammonia conversion systems, in which multi-electron transfer systems involving a nitrosyl ligand-based reduction participate.[1] A significant advance has been brought about recently in the redox study of $\{MNO\}^6$-type nitrosyl complexes,[2,3] but little is reported on the synthetic work, which would stimulate the progress of studying the nitrosyl ligand reaction.[4] We describe here the synthesis of $[\{Ru(\mu_2\text{-}NO)\}_2(2,2'\text{-}bipy)_4]^{2+}$, which could be regarded as a two-electron reduction species of a $\{RuNO\}^6$-type complex. Complexes having the $\{M(\mu_2\text{-}NO)_2\}$ moiety, especially ones containing a two-electron reduction nitrosyl, are extremely rare.[1,4] The present result is also important because it differs from those of other related studies on the two-electron reduction of $\{RuNO\}^6$-type nitrosyls reported so far, in which the complex involving a $\{Ru^{II}(NOH)^0\}$ moiety has been believed to form,[3] under the aqueous acidic conditions.

The present reaction was carried out by the following procedures. In addition to the di-μ-nitrosyl complex mentioned above, *cis*-$[Ru(NO)(OCHO)(2,2'\text{-}bipy)_2]^{2+}$ was obtained as a primary product of the reaction.

cis-$[Ru(NO)(OCHO)(2,2'\text{-}bipy)_2](ClO_4)_2$(**1**): To an aqueous solution of *cis*-$[Ru(NO)(H_2O)(2,2'\text{-}bipy)_2](ClO_4)_3\cdot 3H_2O$ (200 mg / 20 cm^3) in a beaker was added sodium formate (250 mg), and then the solution pH was adjusted to 4 by adding several drops of formic acid. The solution was heated on a hot plate at 70 °C for 20 min using a cover glass, during which time the solution color changed from orange-red to orange. After the solution was cooled, **1** was precipitated using $NaClO_4$ as a precipitant. An orange crystalline material was collected by filtration, washed with water, ethanol, and then ether, and dried in vacuo. Yield 55%.[5]

$[\{Ru(\mu_2\text{-}NO)\}_2(2,2'\text{-}bipy)_4](ClO_4)_2$ (**2**): The orange solution containing *cis*-$[Ru(NO)(OCHO)(2,2'\text{-}bipy)_2]^{2+}$ obtained by the above procedure of **1** was heated further (1-2 h), without adding a precipitant; during this time the solution became black-brown. The solution generated was concentrated by gentle heating, without a cover glass, to give black-violet crystalline material. The crude product was collected by filtration, and this was purified by alumina chromatography using a 1:19 (v/v) ethanol/acetonitrile solvent mixture as eluent. The desired product eluted first as a violet band, which was then concentrated by rotary evaporation, and precipitated by addition of diethyl ether. The resulting dark brown precipitate was collected by filtration and washed with diethyl ether. A typical yield for this procedure was 30%.[6]

The data of IR(ν(NO)=1915 cm^{-1}), CV, and ^{13}C-NMR of *cis*-$[Ru(NO)(OCHO)(2,2'\text{-}bipy)_2]^+$ (**1**), including those of X-ray structure determination, support the present formulation as a $\{RuNO\}^6$-type nitrosyl complex. Well-defined ^{13}C NMR spectra show the presence of 21 magnetically inequivalent carbon atoms; this agrees with those of the *cis*-$[Ru(NO)(OCHO)(2,2'\text{-}bipy)_2]^{2+}$, for which 20 resonances are expected from 2,2'-bipyridine and 1 resonance from formato ligand. ORTEP of *cis*-$[Ru(NO)(OCHO)(2,2'\text{-}bipy)_2]^{2+}$ is shown in Figure 1. The cation has the expected octahedral coordination geometry. The oxygen atom of the formato ligand exists at cis position with respect to the nitrosyl nitrogen, and two 2,2'-bpy rings are also situated in a position cis to each other. The Ru-NO unit is essentially linear with the ruthenium atom (179.0(6) °) and the Ru-NO and the N-O bond lengths (1.782(6) and 1.051(9) Å respectively) are similar to the typical values in other linear nitrosylruthenium(II) complexes.[7]

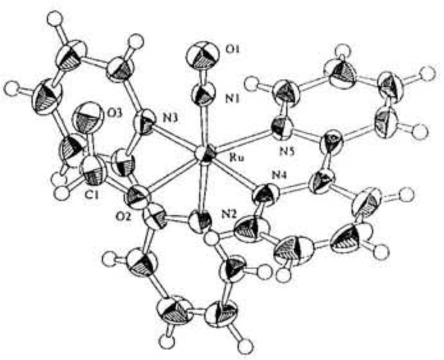

Figure 1. ORTEP drawing of $[Ru(NO)(OCHO)(2,2'\text{-}bipy)_2]^{2+}$.

The second product was formulated as di-μ_2-nitrosyl complex, $[\{Ru(\mu_2\text{-}NO)\}_2(2,2'\text{-}bipy)_4]^{2+}$ (**2**). It showed a characteristic IR absorption band due to the bridging nitrosyl (ν(NO)) at 1363 cm^{-1}, which was shifted to 1340 cm^{-1} on ^{15}N substitution. The frequency region is considerably lower than that observed for **1**, even lower than for a similar dinuclear complex, $[\{Ru(\mu_2\text{-}NO)\}_2(acac)_4]$ (ν(NO)=1543 cm^{-1}), obtained previously as a one-electron reduction product of the $\{RuNO\}^6$-type nitrosyl.[8] Although the molecular structure of **2** can not be determined yet, because single crystals suitable for the X-ray structure work are not available, ^{13}C NMR data preclude the structure depicted in Figure 2(a). The data are only explainable when the complex **2** exists as a di-μ_2-nitrosyl with the Λ-Λ form (Figure 2(b)); 10 resonances observed in **2** showed that the four 2,2'-bpy ligands which coordinate the two ruthenium atoms are all equivalent with a D_2 symmetry.

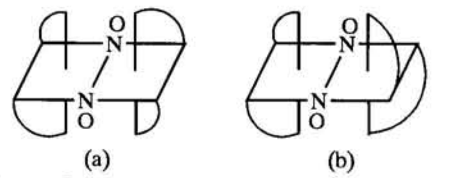

Figure 2. Possible structures of di-μ_2-nitrosyl complex.

The cyclic voltammogram of *cis*-[Ru(NO)(OCHO)(2,2'-bipy)$_2$]$^{2+}$ (**1**) at 25 °C shows a behavior as a typical {RuNO}^{6}-type nitrosyl complex.[9] A single cathodic CV scanning of the CH_3CN solution containing **1** exhibited a diffusion-controlled reversible wave at $E_{1/2}$ = -0.23 V (*vs*. Ag|0.01 mol dm^{-3} $AgNO_3$), together with the coupled anodic wave on the reverse scan. At the more negative potential region, another irreversible wave appeared at $E_{p,c}$ = -0.99 V. A one-electron redox process of the wave at -0.23 V could be confirmed by a controlled-potential electrolysis, which was carried out at -0.30 V (n=0.99).

Cyclic voltammograms of [{Ru(μ_2-NO)}$_2$(2,2'-bipy)$_4$]$^{2+}$ **2** at 25 °C show well-defined reversible two one-electron oxidation waves at $E_{1/2}$ = -0.10 and 0.31 V (Figure 3). The CV feature is different from those of {RuNO}^{n}-type nitrosyls (n = 6, 7). The electron transfer processes of both waves were diffusion-controlled with $ip/v^{1/2}$ constant over the range of scan rate used. One-electron redox systems were indicated by analyses of normal pulse voltammograms. The ratios of cathodic current peak *versus* anodic current peak (Ipc/Ipa) for both waves were nearly unity. The observed electrochemical behavior can be explained if the following electrode reactions proceed on the electrode surface (Eqs. 1 and 2). The controlled-potential electrolysis supports the above CV reduction behavior of **2** (n = 0.94 and 1.02 for the 1st and 2nd oxidation waves respectively). The electrochemical experiment of **2** was carried out at -30 °C, in order to avoid the complexity due to the chemical reaction which occurred along with the oxidation reaction.[10]

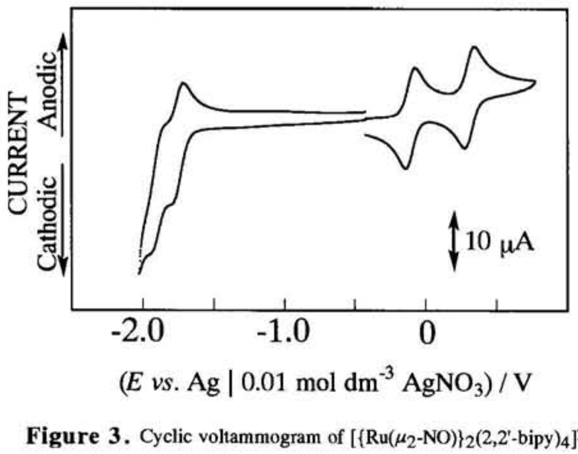

Figure 3. Cyclic voltammogram of [{Ru(μ_2-NO)}$_2$(2,2'-bipy)$_4$]$^{2+}$.

$$[\{Ru(\mu_2\text{-}NO^-)\}_2(2,2'\text{-bipy})_4]^{2+} \rightleftharpoons [\{Ru(\mu_2\text{-}NO\cdot)\}\{Ru(\mu_2\text{-}NO^-)\}(2,2'\text{-bipy})_4]^{3+} + e^- \quad (1)$$

$$[\{Ru(\mu_2\text{-}NO\cdot)\}\{Ru(\mu_2\text{-}NO^-)\}(2,2'\text{-bipy})_4]^{3+} \rightleftharpoons [\{Ru(\mu_2\text{-}NO\cdot)\}_2(2,2'\text{-bipy})_4]^{4+} + e^- \quad (2)$$

We have reported another di-μ_2-nitrosyl complex, [{Ru(μ_2-NO)}$_2$(acac)$_4$], whose molecular structure is essentially the same as that proposed for **2**.[8b] Both complexes differ definitely in the electronic charge of the {Ru(μ_2-NO)}$_2$ fragment; **2** has formally NO^- ligands, while [{Ru(μ_2-NO)}$_2$(acac)$_4$] involves NO^0 ones. Such a difference will result in a different electrochemical behavior of the two complexes. Actually, we have found that either the oxidation (Eq. 3) or the reduction (Eq. 4) occurs in [{Ru(μ_2-NO)}$_2$(acac)$_4$]:

$$[\{Ru(\mu_2\text{-}NO\cdot)\}_2(acac)_4] \longrightarrow [\{Ru(\mu_2\text{-}NO^+)\}_2(acac)_4]^+ + 2e^- \quad (3)$$

$$[\{Ru(\mu_2\text{-}NO\cdot)\}_2(acac)_4] + e^- \rightleftharpoons [\{Ru(\mu_2\text{-}NO^-)\}\{Ru(\mu_2\text{-}NO\cdot)\}(acac)_4]^- \quad (4)$$

No reduction process could be found in [{Ru(μ_2-NO)}$_2$(2,2'-bipy)$_4$]$^{2+}$ (**2**), except the ligand(bpy)-based reduction. In **2**, a large delocalization of π-bonding over the {Ru(μ_2-NO)}$_2$ unit is expected, because the 2,2'-bipyridine stabilizes the four-membered cyclic unit in a lower oxidation state, either in the metal atom or in the nitrosyl ligand. On the other hand, β-diketone anions can form very stable chelate complexes with most metal ions, but the formation of such metal complexes with a lower oxidation state will not be favored.

References and Notes

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5 Data for **1**: Anal. Calcd for [Ru(NO)(OCHO)(2,2'-bipy)$_2$](ClO$_4$)$_2$: N, 10.19; C, 36.70; H, 2.49 %. Found: N, 9.78; C, 36.69; H, 2.46 %. Crystallographic data: $C_{21}H_{17}N_5O_{11}Cl_2Ru$, M = 687.37, triclinic $P\bar{1}$, a = 9.997(1), b = 17.112(2), c = 7.984(3) Å, α = 103.11(2), β = 104.25(2), γ = 80.02(2) °, V = 1279.1(5) Å^3, Z = 2, D_{calcd} = 1.79 g cm^{-3}, μ(MoKα) = 8.92 cm^{-1}, R = 0.034, Rw = 0.051.
6 Data for **2**: Anal. Calcd for [{Ru(NO)}$_2$(2,2'-bipy)$_4$](ClO$_4$)$_2$·2H$_2$O: N, 12.69; C, 43.53; H, 3.10 %. Found: N, 12.61; C, 43.45; H, 2.98 %. ^{13}C NMR (CD$_3$CN): δ 123.98, 124.97, 126.89, 127.71, 138.49, 139.32, 150.42, 150.76, 154.14, 157.79. FAB-MS for [{Ru(NO)}$_2$-(2,2'-bipy)$_4$](CF$_3$SO$_3$)$_2$: m/z 1186(M$^+$), 1037(M$^+$-CF$_3$SO$_3$).
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10 At room temperature, the resultant species ([{Ru(μ_2-NO·)}$_2$(2,2'-bipy)$_4$]$^{4+}$) disintegrated to give *cis*-[Ru(NO·)(CH$_3$CN)(2,2'-bpy)$_2$]$^{2+}$, along with a small amount of *cis*-[Ru(NO$_2$)(CH$_3$CN)(2,2'-bpy)$_2$]$^+$. The formation of the latter nitro species is unexpectable result under the conditions. Mechanistic investigation of the disintegration process of [{Ru(μ_2-NO·)}$_2$(2,2'-bipy)$_4$]$^{4+}$ is now under way.