Crystal Structure and Electrochemical Behavior of an Unusual Nitrosyl-Ru Complex Obtained by a Reaction of $Ru_2(Me\ COO)_4\ Cl$ with 2-Pyridinecarboxylic Acid

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The crystal structure and the electrochemical behavior of a Ru-complex, which was obtained from a reaction of $[Ru_2(MeCOO)_4Cl]$ with 2-pyridinecarboxylic acid and NO_2^-, were investigated: the complex consists of nitrosyl, 2-pyridinecarboxylato, and acetato ligands. The cyclic voltammogram showed no redox wave in the region of the potential window, unlike common Ru(NO)-complexes.

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] In this work, a ruthenium-acetato complex, $[Ru_2(MeCOO)_4Cl]$, was used as a starting material. One of the aims of this work is to study on the reactivity of $[Ru_2(MeCOO)_4Cl]$, which has a linear chain structure of propeller like $Ru_2(MeCOO)_4$ units linked by a bridging chloro ligand.[5] A reaction of $[Ru_2(MeCOO)_4Cl]$ with 2-pyridinecarboxylic acid and NO_2^- was carried out for introducing NO into a new type of mixed ligand-Ru complex: the investigation was executed in order to explore whether a bidentate ligand with $-COO^-$, such as 2-pyridinecarboxylic acid, can be coordinated to Ru together with acetato ligands and a nitrosyl group can be introduced into the complex or not.

To an aqueous solution of acetic acid (3 mol dm^{-3}, 20 cm^3) $[Ru_2(MeCOO)_4Cl]$ (100 mg), which was prepared according to the method in the previous paper, was added over heating. After filtration (if necessary), an aqueous solution of a two fold excess of 2-pyridinecarboxylic acid (52 mg) in relation to the ruthenium-acetato complex concentration was added. The mixed solution was heated at ca. 90 °C for 1 h, during which time the solution color changed from brown to wine-red, and then changed again to orange when an excess amount of $NaNO_2$ (powder, 200 mg) was added to the solution. After the solution had been dried up to give white solid material, it was dissolved in acetonitrile (5 cm^3). To the solution obtained by filtration was added ether until pale red solid material precipitated (yield ca. 24%).

Figure 1 shows the structure of the product complex (**1**).[6] The structure consists of a ruthenium(II)-centered distorted octahedron coordinated by three oxygen atoms of unidentate acetato ligands, a nitrosyl nitrogen, and oxygen and nitrogen atoms of a chelate 2-pyridinecarboxylato ligand. The coordination arrangements of the three acetato ligands are different.The first acetato ligand is coordinated to a sodium ion by the oxygen atom which is ligated to the ruthenium atom, and the second is bridging the ruthenium and the other sodium ion

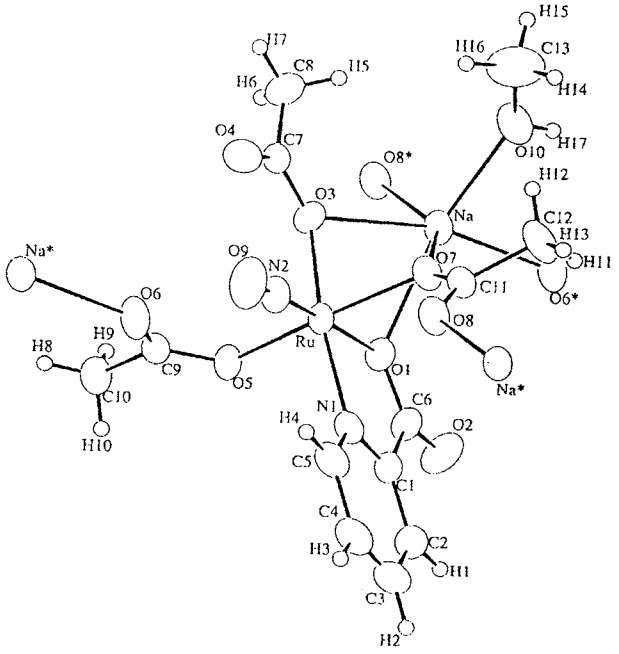

Figure 1. ORTEP drawing of complex 1, Ru-O(1) = 2.032(3), Ru-O(3) = 2.044(3), Ru-O(5) = 2.044(3), Ru-O(7) = 2.047(3), Ru-N(1) = 2.054(4), Ru-N(2) = 1.721(4), N(2)-O(9) = 1.160(6), Na-O(1) = 2.473(4), Na-O(3) = 2.462(4), Na-O(6)' = 2.301(4), Na-O(7) = 2.643(4), Na-O(8)' = 2.383(4), Na-O(10) = 2.359(5), Ru···Na = 3.299(2), Ru···Na*(Ave) = 5.402 Å, Ru-N(2)-O(9) = 174.3(5)°.

by the carboxylate group so as to make a *syn-anti* form.The third is coordinated to two sodium ions and one ruthenium ion: The ligand is bridging Ru and Na by means of the first coordination arrangement and is simultaneously bridging the ruthenium and the third sodium ion by the second arrangement. Moreover the carboxylato oxygen atom of the 2-pyridinecarboxylato is also bridging Ru and Na in the same way as those of the first acetato ligand. A methanol molecule is coordinated to the sodium ion. As the result, the sodium is coordinated by six oxygen atoms. Consequently, the ruthenium complex forms a sheet parallel to the ac plane connected by sodium ions. There is a stacking interaction between the pyridine rings of 2-pyridinecarboxylato in the sheet. By such interaction, the sheets connect with each other and form a three-dimensional structure, as shown in Fig. 2.

The Ru-NO moiety is essentially linear: The ∠Ru-N-O = 174.3(5)°.The Ru-NO and N-O bond lengths are 1.721(4) and 1.160(6) Å respectively. The bond angle and lengths do not deviate much from average values for Ru-NO-$(bpy)_2$[7] and other Ru-NO complexes.[8] In general, the Ru-NO increases as the N-O

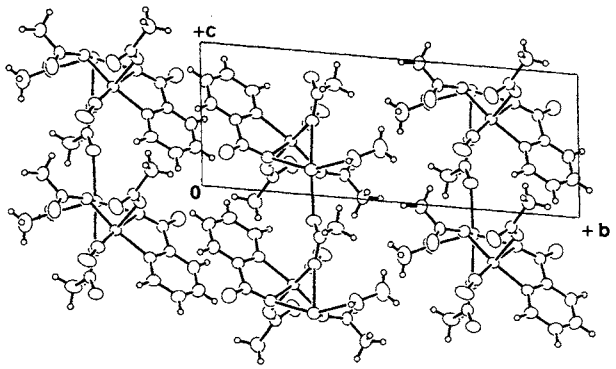

Figure 2. Perspective drawing of Na[Ru(pyca)(ac)$_3$(NO)]-MeOH along the a axis. There is a stacking interaction between the pyridine rings of 2-pyridinecarboxylato in the sheet: the distance between the pyridine rings is 3.443(8) Å.

Table 1. Electrochemical, structural, and infrared data for {RuNO}^{6}-type nitrosyl complexes.

Complex	$E_{1/2}$	∠Ru-N-O/°	Ru-NO/Å	N-O/Å	ν(NO)/cm^{-1}
1[a]	—	174.3(5)	1.721(4)	1.160(5)	1900
2[b]	-0.23	179.4(6)	1.751(3)	1.126(7)	1915
3[c]	-0.19	178.1(9)	1.731(10)	1.13(1)	1928
4[d]	-0.12	172.4(4)	1.754(3)	1.127(4)	1922
5[e]	-0.03	174.8(8)	1.764(8)	1.116(9)	1944
6[f]	0.19	172(1)	1.70(2)	1.15(2)	1954
7[g]	-0.40[i]	172.8(9)	1.770(9)	1.172(14)	1913
8[h]	-0.17	177(1)	1.71(2)	1.17(2)	1936 (1913)

[a]Na[Ru(NO)(pyca)(MeCOO)$_3$]MeOH, [b]*cis*-[Ru(OCHO)(NO)-(2,2'-bpy)$_2$](ClO$_4$)$_2$,[7a] [c]*cis*-[Ru(ONO)(NO)(2,2'-bpy)$_2$](PF$_6$)$_2$,[7b] [d]*cis*-[RuCl(NO)(2,2'-bpy)$_2$](ClO$_4$)$_2$,[7c] [e]*cis*-[Ru(NO$_2$)(NO)(2,2'-bpy)$_2$](PF$_6$)$_2$,[7b] [f]*cis*-[Ru(CH$_3$CN)(NO)(2,2'-bpy)$_2$](ClO$_4$)$_3$,[7d] [g][Ru-(NH$_3$)$_5$(NO)]Cl$_3$·H$_2$O,[8b] [i]reference 8a), [h]*trans*-[Ru(NH$_3$)$_4$nic-(NO)](BF$_4$)$_3$ (nic=nicotinamide), the structural data for **8** are based on *trans*-[Ru(NH$_3$)$_4$nic(NO)](SiF$_6$)$_3$·2H$_2$O.[8b]

decreases. Although Ru-NO is slightly shorter than the corresponding average value in the complex **1**, N-O is somewhat longer.

As is well known, if the pair of electrons forming the Ru-N bond is counted as the ligand electrons, the linear- and bent-nitrosyl groups are regarded as $-N\equiv O^+$ and $-N=O^-$, respectively. Since the redox site of the nitrosyl complex is believed to be the nitrosyl moiety, one is tempted to correlate the redox potential of the nitrosyl group with the N-O length and the Ru-N-O angle. A typical {RuNO}^{6}-type nitrosyl complex exhibits a diffusion-controlled reversible wave at the region of $E_{1/2}$ value between −1.0 and 1.0 V.[9] Some data for {RuNO}^{6}-type nitrosyl complexes are listed in Table 1: structural and infrared data do not exhibit a remarkable difference. However, the cyclic voltammogram of complex **1** in methanol at 25 °C showed no redox wave in the region between −1.0~+1.0 V.[5] This result implies that the redox potential is governed by several other factors, such as electronic effects of other ligands, or nature of the metal. The surroundings of the Ru-NO moiety in methanol are, of course, different from those in crystals. It is reasonable, however, to consider that the Ru-NO moiety in methanol is under the similar conditions to that under the crystals. Three acetato ligands and one 2-pyridinecarboxylato ligand are coordinated to Ru, and these ligands attract sodium ions. The Na^+ will play an important role in the unusual electrochemical behavior of Ru-NO moiety. Further study is required to explicate the unusual behavior.

References and Notes

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6 The crystals decompose after filtering and being irradiated by X-ray within several hours. Therefore, the X-ray reflection intensities of the crystal coated with manicure were collected on a Rigaku RAXIS-IV diffractometer using Mo K_α within several hours. Data for 1: Anal. Calcd for Na[Ru(NO)(pyca)(MeCOO)$_3$]MeOH: N, 5.77; C, 32.17; H, 3.53%. Found: N, 5.26; C, 27.73; H, 3.06%. Crystal data: $RuNaO_{10}N_2C_{13}H_{17}$, *F.W.* = 485.43; triclinic, *P*1 (No. 2), a = 7.942(4), b = 18.005(7), c = 7.028(6) Å, α = 93.17(6), β = 107.58(6), γ = 97.83(5)° ; V = 944(1) Å^3; Z = 2; D_{calc} = 1.707 g cm^{-3}; μ(Mo K_α) = 9.07 cm^{-1}; R = 0.054, R_w = 0.083 (for 3563 reflections).

7 Average of ∠Ru-N-O = 176(3)°, Ru-NO = 1.74(2), and N-O = 1.13(1) Å for Ru-NO-(bpy)$_2$. a) H. Nagao, N. Nagao, D. Ooyama, Y. Sato, T. Oosawa, H. Kuroda, F. S. Howell, and M. Mukaida, *Chem. Lett.*, **1998**, 473. b) D. Ooyama, N. Nagao, H. Nagao, Y. Miura, A. Hasegawa, K. Ando, F. S. Howell, M. Mukaida, and K. Tanaka , *Inorg. Chem.*, **34**, 6024(1995). c) H. Nagao, D. Ooyama, F. S. Howell, M. Mukaida, and K. Mizumachi, *Anal. Sci.*, **14**, 645(1998). d) H. Nagao, K. Ito, N. Tsuboya, D. Ooyama, N. Nagao, F. S. Howell, and M. Mukaida, *Inorg. Chim. Acta*, in press.

8 Average of ∠Ru-N-O = 177(1)°, Ru-NO = 1.71(2), and N-O = 1.17(2) Å for Ru-NO-(NH$_3$)$_4$. a) S. S. S. Borges, C. U. Davanzo, E. E. Castellano, J. Z-Schpector, S. C. Silva, and D. W. Franco, *Inorg. Chem.*, **37**, 2670(1998), and references therein. Average of ∠ Ru-N-O = 172.8(9)°, Ru-NO = 1.770(9), and N-O = 1.172(14) Å for Ru-NO-(NH$_3$)$_4$. b) F. Bottomley, *J. Chem. Soc. Dalton Trans.*, **1974**, 1600.

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10 1 mmol dm^{-3} Na[Ru(NO)(pyca)(MeCOO)$_3$]MeOH in 0.01 mol dm^{-3} tetra-*n*-butylammonium perchlorate-methanol solution at a platinum disk electrode with a silver reference electrode (scan rate = 200 mV s^{-1}).