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Preparation and Characterization of *trans*- and *cis*-Halogenobis-(vicinal-dioximato)nitrosylruthenium(III) Complexes

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The complexes of nitrosylruthenium(III) with vicinal-dioximato ligands, [Ru(vic-dioximato)$_2$X(NO)] (vic-dioximato=2,3-butanedione dioximato (Hdmo), 1,2-diphenylethanedione dioximato (Hdpo), or 1,2-cyclohexanedione dioximato (Hcho); X=Cl, Br, or I), and the complexes of carbonylruthenium(II) with Hdpo, [Ru(Hdpo)$_2$(CO)L] (L=H_2O or pyridine), were synthesized. The results of the ^{1}H, ^{13}C NMR, and IR spectra showed that the trans and cis isomers were present in some of the nitrosylruthenium(III) complexes.

Ruthenium forms many nitrosyl complexes that are more stable than nitrosyl complexes of other transition metals,[1] and the {RuNO}^{6} [2] group generally forms six-coordinate octahedral complexes.

Vicinal-dioxime (vic-dioxime) is a bidentate ligand containing two nitrogen donor atoms. In many six-coordinate octahedral complexes, [M(vic-dioximato)$_2$L$_2$] forms trans complexes in which two vic-dioximato ligands take a plane configuration due to hydrogen bonds between the oxime groups.[3] Wilkinson et al. synthesized the complexes of ruthenium with various oximes including *trans*-[Ru(vic-dioximato)$_2$(PPh$_3$)$_2$].[4] A cis form has been reported for cobalt(II) complex, *cis*-[Co(CF$_3$CO$_2$)$_2$(H$_2$dmo)$_2$], in which hydrogen bonds between the oxime group and CF$_3$COO$^-$ stabilize the cis form.[5] Although the preparation of a rhodium(III) complex, *cis*-H[RhCl$_2$(Hdmo)$_2$],[6] was reported, no detailed descriptions have been reported yet.

In our continuous effort to synthesize geometrical isomers of nitrosylruthenium(III) complexes including bidentate ligands, we synthesized cis and trans isomers of [RuIL$_2$(NO)] (L=Hdmo or Hdpo) and characterized by the ^{1}H, ^{13}C NMR, and IR spectra.[7] During the further investigation, Muller and Takeuchi synthesized *trans*-[RuClL$_2$(NO)] (L=Hdmo, Hdpo, Hcho, or α-furil dioximato).[8]

In this research, we wish to report the syntheses the complexes of nitrosylruthenium(III) with vic-dioxime ligands, [Ru(vic-dioximato)$_2$X(NO)] (vic-dioximato =Hdmo, Hdpo, or Hcho; X=Cl, Br, or I), and carbonylruthenium(II) with Hdpo, [Ru(Hdpo)$_2$L(CO)] (L=H_2O or pyridine). On the basis of ^{1}H, ^{13}C NMR, and IR spectra, structures of the respective complexes were investigated. Both the trans and cis isomers were isolated for some of the nitrosyl complexes, and their properties were elucidated.

Experimental

Reagents. Hydrous RuCl$_3$NO (Ru=30.7%) was prepared by the reaction of commercial RuCl$_3$·3H$_2$O with NO in dilute hydrochloric acid.[9] *trans*-Cs$_2$[RuCl$_4$(H$_2$O)CO] was prepared according to Ref.10. The other reagents used were of reagent grade, and used without further purification.

Separation of the trans and cis Isomers by Column Chromatography. A crude product containing the isomer mixture prepared according to the procedures mentioned later was dissolved in CH_2Cl_2 (50 cm^3). The CH_2Cl_2 solution was charged on a silica-gel column (Wakogel C-300; ϕ 4×20 cm), and the complexes were eluted with CH_2Cl_2. The trans and cis isomers were separated as the first and second adsorption bands, respectively, and other by-products were left behind. The effluents of the first and second adsorption bands were separately evaporated in vacuo to obtain the trans and cis isomers.

Preparation. [RuX(Hdmo)$_2$NO]: (i) Chloro-Complex. The hydrous RuCl$_3$NO (1.0 g, 3.1 mmol) was added to a suspension of H$_2$dmo (0.77 g, 6.6 mmol) in ethanol (200 cm^3) and the suspension was refluxed for 14 h. After the solvent had been removed from the resulting red solution by a rotary vacuum evaporator, the residue was dissolved in CH_2Cl_2 (50 cm^3) and insoluble materials were filtered off. The solution was treated by the column chromatography. Two adsorption bands were observed at first, but the second band faded away gradually, and only the trans isomer was obtained. It was dried at 60 °C for 1 h and was stored in a $CaCl_2$ desiccator. Color: Orange. Yield: 62% (based on hydrous RuCl$_3$NO). Found: C, 24.68; H, 3.52; N, 18.09; Cl, 9.10%. Calcd for RuC$_8$H$_{14}$N$_5$O$_5$Cl: C, 24.22; H, 3.56; N, 17.65; Cl, 8.94%.

(ii) Bromo-Complex. The same procedure as for the chloro-complex was used but NaBr (3.2 g, 31 mmol) was added to a suspension of H$_2$dmo in ethanol. The refluxed solution was treated by the column chromatography, but only the trans isomer was obtained similar to the chloro-complex. It was dried at 60 °C for 1 h and was stored in a $CaCl_2$ desiccator. Color: Dark orange. Yield: 54%. Found: C, 22.06; H, 3.22; N, 15.86; Br, 18.16%. Calcd for RuC$_8$H$_{14}$N$_5$O$_5$Br: C, 21.78; H, 3.20; N, 15.87; Br, 18.11%.

(iii) Iodo-Complexes. The preparation scale was the same as that of the bromo-complex, except for the use of NaI (4.6 g, 31 mmol) instead of NaBr in the reaction mixture. The column chromatography gave the both trans and cis isomers. Color: Dark red for the trans and cis isomers. Yield: 44% for the trans isomer, and 9% for the cis isomer. Found for the trans isomer: Ru, 19.7; C, 20.06; H, 2.98; N, 14.26; I, 26.36%. Found for the cis isomer: Ru, 20.0; C, 19.52; H, 2.91; N, 14.25; I, 26.08%. Calcd for RuC$_8$H$_{14}$N$_5$O$_5$I: Ru, 20.7; C, 19.68; H, 2.89; N, 14.35; I, 25.99%.

[RuX(Hdpo)$_2$NO]: (i) Chloro-Complexes. The hydrous RuCl$_3$NO (1.0 g, 3.1 mmol) was added to a suspension of H$_2$dpo (1.6 g, 6.6 mmol) in ethanol (200 cm^3) and the suspension was

refluxed for 18 h. After the solvent had been removed from the resulting purple solution by a rotary vacuum evaporator, the residue was dissolved in CH_2Cl_2 (50 cm^3) and insoluble materials were filtered off. The solution was treated by the column chromatography to obtain the trans and cis isomers. The isomers were dried at 60 °C for 1 h and stored in a $CaCl_2$ desiccator. Color: Reddish purple for the trans isomer, and purple for the cis isomer. Yield: 41% for the trans isomer, and 6% for the cis isomer. Found for the trans isomer: Ru, 15.7; C, 52.49; H, 3.41; N, 10.86; Cl, 5.66%. Found for the cis isomer: Ru, 15.3; C, 51.65; H, 3.39; N, 10.82; Cl, 5.39%. Calcd for $RuC_{28}H_{22}N_5O_5Cl$: Ru, 15.7; C, 52.14; H, 3.44; N, 10.86; Cl, 5.49%.

(ii) Bromo-Complexes. The same procedure as for the chloro-complexes was used but NaBr (3.2 g, 31 mmol) was added to a suspension of H_2dpo in ethanol. After the reflux, the trans and cis isomers were isolated similarly to the chloro isomers. Color: Purple for the trans isomer, and brownish purple for the cis isomer. Yield: 33% for the trans isomer, and 10% for the cis isomer. Found for the trans isomer: Ru, 15.2; C, 49.11; H, 3.23; N, 10.69; Br, 11.31%. Found for the cis isomer: Ru, 14.4; C, 48.09; H, 3.23; N, 10.78; Br, 11.64%. Calcd for $RuC_{28}H_{22}N_5O_5Br$: Ru, 14.7; C, 48.78; H, 3.22; N, 10.16; Br, 11.59%.

(iii) Iodo-Complexes. The preparation scale was the same as that of the bromo-complexes, except for the use of NaI (4.6 g, 31 mmol) instead of NaBr in the reaction mixture. Color: Deep purple for the trans isomer, and brownish purple for the cis isomer. Yield: 26% for the trans isomer, and 10% for the cis isomer. Found for the trans isomer: Ru, 13.1; C, 45.86; H, 3.06; N, 9.19; I, 18.07%. Found for the cis isomer: Ru, 13.8; C, 45.93; H, 3.05; N, 9.44; I, 18.31%. Calcd for $RuC_{28}H_{22}N_5O_5I$: Ru, 13.7; C, 45.66; H, 3.01; N, 9.51; I, 17.23%.

[RuX(Hcho)$_2$NO]: (i) Chloro-Complex. The hydrous $RuCl_3NO$ (1.0 g, 3.1 mmol) was added to a suspension of H_2cho (1.1 g, 6.6 mmol) in ethanol (200 cm^3) and the suspension was refluxed for 20 h. After the solvent had been removed from the resulting dark purple solution by a rotary vacuum evaporator, the residue was dissolved in CH_2Cl_2 (50 cm^3) and the insoluble materials were filtered off. Separation of the geometrical isomers was attempted by the column chromatography, but only the trans isomer was obtained. It was dried at 60 °C for 1 h and was stored in a $CaCl_2$ desiccator. Color: Brownish yellow. Yield: 43%. Found: Ru, 21.5; C, 29.96; H, 4.00; N, 14.88; Cl, 8.31%. Calcd for $RuC_{12}H_{18}N_5O_5Cl$: Ru, 22.5; C, 32.11; H, 4.04; N, 15.60; Cl, 7.89%.

(ii) Bromo-Complex. The same procedure as for the chloro-complex was used but NaBr (3.2 g, 31 mmol) was added to a suspension of H_2cho in ethanol. After the solvent had been removed from the resulting dark red solution by a rotary vacuum evaporator, the residue was dissolved in CH_2Cl_2 (50 cm^3) and insoluble materials were filtered off. Separation of the geometrical isomers was attempted by the column chromatography, but only the trans isomer was obtained. It was dried at 60 °C for 1 h and was stored in a $CaCl_2$ desiccator. Color: Dark yellow. Yield: 28%. Found: C, 28.80; H, 3.79; N, 14.63; Br, 16.09%. Calcd for $RuC_{12}H_{18}N_5O_5Br$: C, 29.22; H, 3.68; N, 14.19; Br, 16.19%.

(iii) Iodo-Complex. The preparation was the same as that of the bromo-complex, except for the use of NaI (4.6 g, 31 mmol) instead of NaBr in the reaction mixture. The column chromatography gave only the trans isomer. It was dried at 60 °C for 1 h and was stored in a $CaCl_2$ desiccator. Color: Purple. Yield: 30%. Found: C, 26.21; H, 3.21; N, 12.07; I, 23.21%. Calcd for $RuC_{12}H_{18}N_5O_5I$: C, 26.68; H, 3.36; N, 12.96; I, 23.49%.

[Ru(Hdpo)$_2$(H$_2$O)CO]: *trans*-$Cs_2[RuCl_4(H_2O)CO]$ (0.50 g, 0.90 mmol) was added to a solution of H_2dpo (0.50 g, 2.0 mmol) in *N,N*-dimethylformamide (300 cm^3) and the solution was refluxed for 20 h. On the addition of the resulting brown solution to water (2 dm^3), a brownish yellow precipitate was formed. The precipitate was collected by filtration. Although the separation of the geometrical isomers was attempted by column chromatography using activated alumina, only the trans isomer was obtained. It was dried at 60 °C for 3 h, and was stored in a $CaCl_2$ desiccator. Color: Brownish yellow. Yield: 69% based on $Cs_2[RuCl_4(H_2O)CO]$. Found: Ru, 15.8; C, 55.43; H, 3.81; N, 8.99%. Calcd for $RuC_{29}H_{24}N_4O_6$: Ru, 16.2; C, 55.68; H, 3.87; N, 8.96%.

[Ru(Hdpo)$_2$(CO)py]: *trans*-[Ru(Hdpo)$_2$(H$_2$O)CO] (1.0 g, 1.6 mmol) was added to a solution of pyridine (1.6 mmol) in ethanol (100 cm^3) and the solution was refluxed for 5 h. After the solvent had been removed from the resulting dark brown solution by a rotary vacuum evaporator, the residue was dissolved in CH_2Cl_2 (50 cm^3). Although the separation of the geometrical isomers was attempted by the column chromatography using activated alumina, only the trans isomer was obtained. It was dried at 60 °C for 3 h and was stored in a $CaCl_2$ desiccator. Color: Dark brown. Yield: 90% based on *trans*-[Ru(Hdpo)$_2$(H$_2$O)CO]. Found: C, 58.79; H, 3.91; N, 10.81%. Calcd for $RuC_{34}H_{27}N_5O_5$: C, 59.47; H, 3.96; N, 10.20%.

Measurements. Electric conductivities in CH_2Cl_2 solutions of the complexes were measured with a YHP model universal bridge. The ^1H and ^{13}C NMR spectra in $CDCl_3$ and DMSO-d_6 solutions were measured with a JEOL model GX-270FT spectrometer. The IR spectra in the 4000—400 cm^{-1} region were recorded as Nujol mulls, using a JASCO model A-202 spectrophotometer. All the complexes were analyzed for C, H, N, and halogen at The Organic Microanalysis Center, The Institute of Physical and Chemical Research. Ruthenium was determined colorimetrically by the ruthenate method.[11]

Results and Discussion

Preparation of Complexes. In the preparation of the bromo and iodobis(vic-dioximato) complexes, sodium bromide and sodium iodide were added to the ethanol solution of the hydrous $RuCl_3NO$ and vic-dioxime, respectively, and the reaction mixtures were refluxed. When the amount in moles of NaBr was equal to that of ruthenium, the yield of the bromo complex was extremely poor, and the chloro complex was recovered. As the amount of NaX was increased, yields increased, and when the molar ratio of NaX to ruthenium was more than 10, the bromo or iodo complexes was obtained with good yield and the chloro complex was scarcely recovered.

When the two adsorption bands were observed during the chromatographical separation, it was clearly observed that the width of the second band decreased during the elution. For [RuX(Hdmo)$_2$NO] (X=Cl or Br), the second adsorption band was observed at first as a very

narrow band. When the elution was further continued, the band faded away gradually and the cis isomer could not be obtained. This phenomenon can be presumed to be due to isomerization from the cis complex to the trans complex.[7] When the two components were obtained for [RuI(Hdmo)$_2$NO] and [RuX(Hdpo)$_2$NO] (X=Cl, Br, or I), the yield of the component eluted first (trans isomer) was always greater than that of the component eluted second (cis isomer). The isomerization of nitrosylruthenium(III) complexes induced by thermal reaction has been reported only for $[RuX(NH_3)_4NO]^{2+}$ (X=Cl or OH) where cis to trans, but not trans to cis, isomerization was observed.[12]

The elementary analysis data were closely coincident with the calculated values. Molar conductivities of *trans*- and *cis*-[RuI(Hdpo)$_2$NO] in CH_2Cl_2 were 1.98×10^{-4} and 3.08×10^{-4} S m^2 mol^{-1} at 19.5°C, respectively. It has been known that the molar conductivities of neutral complexes in CH_2Cl_2 are less than about 2×10^{-3} S m^2 mol^{-1}.[13] Therefore, the nitrosyl complexes are regarded as non electrolyte.

^{1}H and ^{13}C NMR Spectra. Table 1 shows the chemical shifts and their assignments for all pairs of the trans and cis isomers of [RuI(Hdmo)$_2$NO] and [RuX(Hdpo)$_2$NO] (X=Cl, Br, or I). The ^{1}H and ^{13}C NMR spectra of *trans*- and *cis*-[RuI(Hdmo)$_2$NO] and *trans*- and *cis*-[RuI(Hdpo)$_2$NO] in $CDCl_3$, DMSO-d_6. The spectra for the trans isomers were easily assigned on the basis of the data of the free ligands and the signal due to the proton in hydrogen bond. The spectra were similar to those of *trans*-[RuCl(Hcho)$_2$NO] and *trans*-[RuCl(Hdpo)$_2$NO].[8] The spectra consisted with two equivalent O···H···O bridges (^{1}H NMR) and four equivalent oxime-carbons (^{13}C NMR) in the trans isomers. These observations verified the trans form for these complexes, in which two Hdmo or Hdpo ligands form a plane. The carbons of the phenyl group in free H_2dpo gave four signals, while seven signals were observed in the phenyl carbon region for *trans*-[RuX(Hdpo)$_2$NO] (X=Cl, Br, or I). The reason why seven signals were observed, and the assignments of the signals, are not clear.

The ^{1}H NMR spectra for cis isomers were more intricate than those for trans isomers. The two signals δ=7.19 and 7.47 of *cis*-[RuI(Hdmo)$_2$NO] were assigned to protons of the oxime-hydroxyls. The plural signals for each of the oxime-hydroxyl protons, methyl protons, oxime carbons, and methyl carbons indicated non-equivalency among each of these functional groups. Thus, the configuration of the complex is concluded to be the cis form, in that two Hdmo ligands do not form a plane. The ^{13}C NMR signals of oxime carbons were observed in the region of δ=137.1—162.2. When a drop of concentrated hydrochloric acid was added to the DMSO-d_6 solution of *cis*-[RuI(Hdmo)$_2$NO] ([HCl]=0.7 mol dm^{-3}), the NMR spectra were changed. The electronic spectrum of the acidified solution was not changed for 10 h that corresponded to the duration of measurement of the ^{13}C NMR spectra. All the four oxime groups in the complex should be protonated in acidified DMSO-d_6. Since nitrosyl group is a weak σ-donor and a strong π-acceptor,[1,2] and since iodo ligand is a strong σ- and π-donor,[14] it seems reasonable that the signals δ=152.6 and 168.4 of the acidified Hdmo complex are assigned to carbons in the oximes situated at trans to the iodo ligand and to the nitrosyl group, respectively. The strong signal δ=164.4, whose intensity is about as

Table 1. The ^{1}H and ^{13}C NMR Data (δ)[a] of All Pairs of the trans and cis Isomers Prepared and the Assignments

trans-[RuI(Hdmo)$_2$NO]	^{1}H 2.21 (12H, s): $-CH_3$; 9.31 (2H, s): O···H···O bridge
	^{13}C 13.3: $-CH_3$; 161.7: >C=NOH$_{1/2}$
cis-[RuI(Hdmo)$_2$NO]	^{1}H 2.11 (3H, s), 2.22 (3H, s), 2.26 (3H, s), 2.52 (3H, s): $-CH_3$; 7.19 (1H, s), 7.47 (1H, s): >C=NOH
	^{13}C 13.1,[c] 14.7, 16.3: $-CH_3$; 137.1, 138.1: >C=NO$^-$; 151.4, 162.2: >C=NOH
cis-[RuI(Hdmo)$_2$NO]+HCl[b]	^{13}C 12.3, 13.6, 15.3:[c] $-CH_3$; 152.6, 164.4,[c] 168.4: >C=NOH
H_2dmo (free ligand)	^{13}C 13.8: $-CH_3$; 153.3: >C=NOH
trans-[RuI(Hdpo)$_2$NO]	^{1}H 7.26—7.35 (20H, s): $-C_6H_5$; 9.22 (2H, s): O···H···O bridge
	^{13}C 127.7—130.4: $-C_6H_5$; 159.7: >C=NOH$_{1/2}$
cis-[RuI(Hdpo)$_2$NO]	^{1}H 7.13—7.47 (21H, s): $-C_6H_5$ and >C=NOH; 7.77: >C=NOH
	^{13}C 126.9—130.9: $-C_6H_5$ and >C=NO$^-$; 149.3, 160.3: >C=NOH
cis-[RuI(Hdpo)$_2$NO]+HCl[b]	^{13}C 128.1—133.5: $-C_6H_5$; 148.8, 155.3, 156.4, 162.9: >C=NOH
trans-[RuBr(Hdpo)$_2$NO]	^{1}H 7.38—7.46 (20H, s): $-C_6H_5$; 9.35 (2H, s): O···H···O bridge
	^{13}C 129.0—132.8: $-C_6H_5$; 159.6: >C=NOH$_{1/2}$
cis-[RuBr(Hdpo)$_2$NO]	^{1}H 6.98—7.48 (21H, s): $-C_6H_5$ and >C=NOH; 7.90 (1H, s): >C=NOH
	^{13}C 127.4—131.5: $-C_6H_5$ and >C=NO$^-$; 147.9, 163.9: >C=NOH
trans-[RuCl(Hdpo)$_2$NO]	^{1}H 7.13—7.41 (20H, s): $-C_6H_5$; 9.12 (2H, s): O···H···O bridge
	^{13}C 127.6—130.4: $-C_6H_5$; 160.4: >C=NOH$_{1/2}$
cis-[RuCl(Hdpo)$_2$NO]	^{1}H 7.27—7.50 (21H, s): $-C_6H_5$ and >C=NOH; 7.77 (1H, s): >C=NOH
	^{13}C 127.4—133.0: $-C_6H_5$ and >C=NO$^-$; 140.8, 163.1: >C=NOH
H_2dpo (free ligand)	^{13}C 127.5, 128.4, 129.5, 132.9; $-C_6H_5$; 155.1: >C=NOH

a) In δ relative to TMS as internal reference. b) A drop of concd HCl was added to the sample solution ([HCl]=0.7 mol dm^{-3}). c) Intensity of this signal is about twice that of the other signals.

twice as the other two is assigned to carbons of the oximes situated at trans position with each other.

In *cis*-[RuI(Hdmo)$_2$NO], two of the four oxime groups should be protonated and the other two should be dissociated. The two signals δ=137.1 and 138.1 were assigned to the carbons of the dissociated oximes, because these two signals were observed in a higher magnetic field than the other two signals δ=151.4 and 162.2. It seems reasonable that the signals δ=151.4 and 162.2 are assigned to carbons in the protonated oximes situated at trans to the iodo ligand and to the nitrosyl group, respectively considering electronic nature of iodide and nitrosyl group.

For *cis*-[RuI(Hdpo)$_2$NO], the ^{1}H NMR signal δ=7.77 was assigned to one of the protons of the oxime-hydroxyls. Another one might be present in the higher field region δ=7.13 to 7.47 of the aromatic protons, which prevent the assignment. The signals due to the dissociated oxime carbons were also assumed to be in the region of the aromatic carbons, δ=126.9 to 130.9. For *cis*-[RuI(Hdpo)$_2$NO], the effect on the acidification of the solvent was almost the same as the case of *cis*-[RuI(Hdmo)$_2$NO]. In the acidified DMSO-d_6 solution of *cis*-[RuI(Hdpo)$_2$NO]([HCl]=0.7 mol dm^{-3}), new two signals, δ=155.3 and 156.4 due to the oxime carbons, appeared. It is considered that these signals are shifted from the region of signals due to the aromatic carbons. The spectra for *cis*-[RuBr(Hdpo)$_2$NO] and *cis*-[RuCl(Hdpo)$_2$NO] were similar to those for *cis*-[RuI(Hdpo)$_2$NO]. These spectra indicate that the complexes have the cis-type configuration, where two Hdpo ligands do not form a plane.

IR Spectra. Table 2 shows IR spectral data on the complexes prepared. In all the thirteen nitrosylruthenium complexes, strong bands were found between 1833 to 1902 cm^{-1}. The stretching vibration due to the nitrosyl group in linear Ru–NO groups, ν(NO), has been observed in the range of ca. 1845 to 1930 cm^{-1}.[1,2,15] It is concluded that all the thirteen complexes are Ru(II)–NO$^+$ type complexes. NO$^+$ is a strong π-electron acceptor and has a great influence on a ligand trans to it. In all pairs of the cis and trans isomers, wave numbers of the ν(NO) of the trans isomer was smaller than that of the cis isomer. In the trans complexes, the trans position of the nitrosyl group is occupied by Cl, Br, or I, which are good σ- and π-electron donating ligands.[16] Thus, the withdrawal of π-electron density from Ru(II) to the π-anitibonding orbital of the nitrosyl group takes place easily. On the other hand, in the cis complexes, the trans position of the nitrosyl group is occupied by a nitrogen atom of an oxime group of the vic-dioximato ligand. This nitrogen atom is a σ-electron donor, but it is deficient in a π-electron donating ability. Therefore, it is reasonable that the electron density in the π-antibonding orbital of the nitrosyl group should be greater in a trans isomer than in the corresponding cis isomer and that the ν(NO) frequency of the trans isomer is smaller than that for the cis isomer.

For each of *trans*-[RuX(Hdmo)$_2$NO], *trans*-[RuX(Hdpo)$_2$NO], and *trans*-[RuX(Hcho)$_2$NO](X=Cl, Br, or I), the ν(NO) values decreased in the order of Cl>Br>I. This reflects the inverse order of π-electron donating ability of the halide ions.[16] On the contrary, the ν(NO) values of the *cis*-Hdpo complexes were substantially constant, irrespective of the kind of the halogeno ligands at the cis position to the NO. This fact reflects that the coordinating atoms at the trans positions of the nitrosyl groups are the same in the cis complexes.

The bands due to the deformation vibration of H···O···H hydrogen bonds, δ(O···H···O), were observed in the region of 1608 to 1655 cm^{-1} for all the trans complexes, but the bands due to the stretching vibration,

Table 2. IR Data[a] of All the Complexes Prepared and the Assignments (ν/cm^{-1})

trans-[RuI(Hdmo)$_2$NO]	1619w δ(O···H···O);[b] 1848s ν(NO)[d]
cis-[RuI(Hdmo)$_2$NO]	1862s ν(NO);[d] 3180m ν(O–H)[c]
trans-[RuBr(Hdmo)$_2$NO]	1621w δ(O···H···O);[b] 1871s ν(NO)[d]
trans-[RuCl(Hdmo)$_2$NO]	1617w δ(O···H···O);[b] 1897s ν(NO)[d]
H$_2$dmo (free ligand)	3210m ν(O–H)[c]
trans-[RuI(Hdpo)$_2$NO]	1655w δ(O···H···O);[b] 1833s ν(NO)[d]
cis-[RuI(Hdpo)$_2$NO]	1871s ν(NO);[d] 3190m ν(O–H)[c]
trans-[RuBr(Hdpo)$_2$NO]	1650w δ(O···H···O);[b] 1845s ν(NO)[d]
cis-[RuBr(Hdpo)$_2$NO]	1886s ν(NO);[d] 3180m ν(O–H)[c]
trans-[RuCl(Hdpo)$_2$NO]	1653w δ(O···H···O);[b] 1881s ν(NO)[d]
cis-[RuCl(Hdpo)$_2$NO]	1884s ν(NO);[d] 3300m ν(O–H)[c]
H$_2$dpo (free ligand)	3290m ν(O–H)[c]
trans-[RuI(Hcho)$_2$NO]	1610w δ(O···H···O);[b] 1871s ν(NO)[d]
trans-[RuBr(Hcho)$_2$NO]	1617w δ(O···H···O);[b] 1887s ν(NO)[d]
trans-[RuCl(Hcho)$_2$NO]	1608w δ(O···H···O);[b] 1902s ν(NO)[d]
H$_2$cho (free ligand)	3200m ν(O-H)[c]
trans-[Ru(Hdpo)$_2$(H$_2$O)CO]	1648w δ(O···H···O);[b] 1970s ν(CO)[e]
trans-[Ru(Hdpo)$_2$CO(py)]	1645w δ(O···H···O);[b] 1968s ν(CO)[e]

a) In Nujol mull. b) Deformation vibration of the hydrogen bond between two vic-dioximato ligands. c) Stretching vibration of the oxime-hydroxyls. d) Stretching vibration of the nitrosyl group. e) Stretching vibration of the carbonyl group.

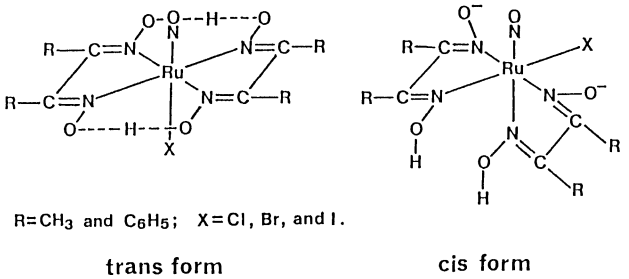

Fig. 1. Probable structure of trans and cis isomers of [Ru(vic-dioximato)$_2$X(NO)].

ν(O···H···O), and those due to the stretching vibration of oxime-hydroxyls, ν(O–H), could not be observed. The absorption bands due to ν(O–H) were observed in the region of 3180 to 3300 cm^{-1} for all the cis isomers and also for the free ligands, H_2dmo, H_2dpo, and H_2cho. The bands due to δ(O···H···O) were not observed for the cis isomers. For trans type of bis(vic-dioximato) complexes such as [Ni(Hdmo)$_2$], it has been known that the O···H···O hydrogen bond provides an absorption band due to ν(O···H···O) in the range of 2200 to 2400 cm^{-1}, and an absorption band due to δ(O···H···O) in the range of 1600 to 1800 cm^{-1}.[17] The absorptions due to the ν(O···H···O) in the complexes were indefinite in many cases. Therefore, the absorption bands for the δ(O···H···O) are possibly utilized for the identification of the trans isomers. It has been also reported that the O–H stretching vibration of oxime groups generally gives a broad band due to the stretching vibration in the region between 3000 to 3500 cm^{-1}.[18] This band is also utilized for the identification of the cis isomer. These facts indicate that the vic-dioximato ligands in each cis isomer do not form the O···H···O bridges and the oxime-hydroxyls are present. Thus, all the IR data are consistent with the NMR data in the identification of trans and cis configurations. The probable structures of the trans and cis isomers are shown in Fig. 1.

For [Ru(Hdpo)$_2$(CO)L] (L=H_2O or py), only one kind of component was obtained by column chromatography. It is likely that [Ru(Hdpo)$_2$(H_2O)CO] is prepared by the reaction of *trans*-Cs_2[$RuCl_4$(H_2O)CO] with H_2dpo with stereo-retention of the Ru(H_2O)CO moiety followed by displacement of H_2O by pyridine to obtain [Ru(Hdpo)$_2$-(CO)py], because carbonyl group is a strong π-acceptor just as nitrosyl group. The IR spectra (see Table 2) indicate that the carbonyl complexes are trans form.

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