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Cis and Trans Isomers of Iodonitrosylbis(vicinal-dioximato)ruthenium(III)

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The mixture of cis and trans isomers of $[RuI(Hdmo)_2(NO)]$ (H_2dmo = 2,3-butanedione dioxime) or $[RuI(Hdpo)_2(NO)]$ (H_2dpo = 1,2-diphenylethanedione dioxime) was prepared, and the isomers were separated with a silica-gel column. The cis isomers together with the trans isomers were identified by the ^1H and ^{13}C NMR, and IR data.

In bis(vicinal-dioximato) complexes, the two ligands strongly tend to coordinate in planar geometry due to the O-H-O hydrogen bondings. Almost all bis(vicinal-dioximato) six-coordinate complexes have the trans form,1) and only a few cis isomers have been reported.2-4) In the reactions of hydrous trichloronitrosylruthenium(III) with dioximes (H_2dmo = 2,3-butanedione dioxime and H_2dpo = 1,2-diphenylethanedione dioxime), we have isolated the cis isomers together with the trans isomers. This letter reports the preparation and identification of the trans and cis isomers of $[RuI(Hdmo)_2(NO)]$ and $[RuI(Hdpo)_2(NO)]$.

The isomer mixture of $[RuI(Hdmo)_2(NO)]$ was prepared by refluxing an ethanol suspension (250 cm^3) containing hydrous trichloronitrosylruthenium(III) (Ru = 30.7%) (3.1 mmol), H_2dmo (6.6 mmol), and sodium iodide (31 mmol) for 14 h. After the solvent had been evaporated off, the residue was dissolved in dichloromethane (50 cm^3), insoluble materials being filtered. The dichloromethane solution was charged on a silica-gel column (Wakogel C-300, φ4 cm x 20 cm), and the complexes were eluted with dichloromethane. The effluents of the first and second adsorption bands were separately evaporated off in a rotary evaporator to obtain two dark red products. The products from the first and second adsorption bands are named hereafter products **1** and **2**, respectively. Yield: 44 and 9% for the products **1** and **2**, respectively, based on the trichloronitrosylruthenium. Found for the product **1**: Ru, 19.7; C, 20.06; H, 2.98; N, 14.26; I, 26.36%. Found for the product **2**: Ru, 20.0; C, 19.52; H, 2.91; N, 14.25; I, 26.08%. Calcd for [RuI(Hdmo)$_2$(NO)] ($RuIC_8H_{14}N_5O_5$): Ru, 20.7; C, 19.68; H, 2.89; N, 14.35; I, 25.99%.

The isomers of [RuI(Hdpo)$_2$(NO)] were prepared similarly to the products **1** and **2**. The product in early effluent was named hereafter product **3** and in later effluent product **4**. The product **3** was deep purple, and the product **4** brownish purple. Yield: 26 and 10% for the products **3** and **4**, respectively, based on the trichloronitrosylruthenium. Found for the product **3**: Ru, 13.1; C, 45.86; H, 3.06; N, 9.19; I, 18.07%. Found for the product **4**: Ru, 13.8; C, 45.93; H, 3.05; N, 9.44; I, 18.31%. Calcd for [RuI(Hdpo)$_2$(NO)] ($RuIC_{28}H_{22}N_5O_5$): Ru, 13.7; C, 45.66; H, 3.01; N, 9.51; I, 17.23%.

The ^1H NMR spectra were measured for the products **1**, **2**, **3**, and **4** in $CDCl_3$, and the ^{13}C NMR spectra in DMSO-d_6. Table 1 shows the chemical shifts and the assignments. The spectral features of the product **1** were explained reasonably as the trans form in which each of the two O-H-O bridges, the four oxime carbons, and the four methyl groups are equivalent. For the product **2**, the ^{13}C NMR spectrum clearly indicated that the four oxime carbons are not equivalent. The signals attributable to the methyl and oxime groups also indicated that the product **2** is the cis form. The signals at δ = 137.1 and 138.1 can be assigned to the deprotonated oxime carbons, and the signals at δ = 151.4 and 162.2 to the protonated

Table 1. ^1H and ^{13}C NMR Data (δ) of Products **1**, **2**, **3**, and **4**, and the Assignments

Product **1**:	^1H	2.21($-CH_3$); 9.31(O-H-O bridge)
	^{13}C	13.3($-CH_3$); 161.7($>C=NOH_{1/2}$)[a]
Product **2**:	^1H	2.11, 2.22, 2.26, 2.52($-CH_3$); 7.19, 7.47(=NOH)
	^{13}C	13.1[b], 14.7, 16.3($-CH_3$); 137.1, 138.1($>C=NO^-$); 151.4, 162.2(>C=NOH)
Product **3**:	^1H	7.26 - 7.35($-C_6H_5$); 9.22(O-H-O bridge)
	^{13}C	127.7 - 130.4($-C_6H_5$); 159.7($>C=NOH_{1/2}$)[a]
Product **4**:	^1H	7.13 - 7.47($-C_6H_5$); 7.77(=NOH)
	^{13}C	126.9 - 130.9($-C_6H_5$); 149.3, 163.0(>C=NOH)

a) >C=NO-H-ON=C<. b) Intensity is about twice as large as the other two signals.

oxime carbons. The NMR pattern of the product **3** is similar to that of the product **1** and consistent with the trans form. For the product **4**, a signal attributable to the oxime hydrogen was observed at δ = 7.77, but one more signal could not be observed; this probably overlapped with those of the aromatic protons. Two signals attributable to the deprotonated oxime carbons were assumed to be also located in the region of the aromatic carbons. Thus the product **4** is the cis form.

The IR spectra for the products **1**, **2**, **3**, and **4** were measured as Nujol mulls. Weak bands characteristic of bending vibration due to the O-H-O bridges were observed at 1619 and 1655 cm^{-1} for the products **1** and **3**, respectively.5) Broad bands observed at 3180 and 3190 cm^{-1} for the products **2** and **4**, respectively, were assigned to the stretching vibrations of the oxime-hydroxyl groups, and the corresponding bands were not observed for the products **1** and **3**. The NO stretching vibrations were observed at 1848, 1862, 1833, and 1871 cm^{-1} for the products **1**, **2**, **3**, and **4**, respectively. All the products can be considered to be Ru^{II}-NO^{+} type complexes.6) The wave number of the NO stretching band of the product **1** was smaller than that of the product **2**, and also that of the product **3** was smaller than that of the product **4**. These relations indicate that the iodo ligand is trans to the NO in the products **1** and **3**, and an oxime nitrogen atom is trans to the NO in the products **2** and **4**, and reflect that the iodo ligand is stronger as a π-donor than the oxime nitrogen atom.7) The IR data support the conclusion that the products **1** and **3** are the trans isomers, and the products **2** and **4** are the cis isomers.

We could also isolate the trans and cis isomers of $[RuBr(Hdpo)_2(NO)]$ and $[RuCl(Hdpo)_2(NO)]$ by a procedure similar to that described above. The cis isomers of $[RuBr(Hdmo)_2(NO)]$ or $[RuCl(Hdmo)_2(NO)]$ were not isolated. In the chromatographic separation of the isomers for these complexes, faint adsorption bands which could be regarded as the cis isomers gradually disappeared during the elution. Even for the iodo complexes whose cis isomers were isolated the amount of cis isomers decreased during the elution, leading to the decrease of the yields for the cis isomers. The decrease of the amount of the cis isomers was found to be due to the cis to trans isomerization. The trans to cis isomerization was not observed for any trans isomers.

The kinetics of the cis to trans isomerization reactions were studied spectrophotometrically in ethanol-dichloromethane (95 : 5 in vol%) solvents at 60 °C. The reactions obeyed the first-order rate law. The rate constants obtained were

2.26×10^{-4} s^{-1} for [RuI(Hdmo)$_2$(NO)] and 3.14×10^{-5} s^{-1} for [RuI(Hdpo)$_2$(NO)]. For nitrosylruthenium(III) complex, the isomerization has been reported only for [RuCl(NH$_3$)$_4$(NO)]$^{2+}$ where cis to trans, but not trans to cis, isomerization was observed.[8)] Therefore, it is supposed that in the preparation of the isomer mixture of [RuI(Hdmo)$_2$(NO)] or [RuI(Hdpo)$_2$(NO)], the cis isomer was first formed, then isomerized to the trans isomer. The isomerization rates of cis-[RuX(vicinal-dioximato)$_2$(NO)] (X = Cl, Br, and I) decreased in the order of Cl > Br > I and Hdmo > Hdpo. Thus, stabilization of the cis isomers against the isomerization is affected by the halogeno ligands and also by the vicinal-dioximato ligands at the cis position.

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