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Contribution from the U.E.R. de Chimie and Ecole Nationale Superieure de Chimie de Lille,
Université de Lille I, 59650 Villeneuve d'Ascq, France

Kinetics and Stereochemistry of the Reversible Nitrosylation of the *fac*-Tris(violurato)ruthenate(II) Anion. Evidence for a Unidentate Violurato Intermediate

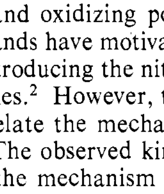
CLAUDE BREMARD,*[1a] GUY NOWOGROCKI,[1b] and STEPHANE SUEUR[1b]

Received October 4, 1977

The tris(violurato)ruthenate(II) anion *fac*-Ru$(H_2vi)_3^-$ reacts with acidic solutions of nitrite salts to form a new series of mononitrosylruthenium complexes *cis*-Ru$(H_2vi)_2$NOX (X is monodentate ligand Cl, Br, OH, or NO_2 or monodentate H_2vi). A nitrosylation mechanism of *fac*-Ru$(H_2vi)_3^-$ is proposed on the basis of kinetic and stereochemical criteria. The introduction of the nitrosonium ion NO^+ into the coordination sphere of ruthenium occurs according to a second-order rate law; however, the mechanism is thought to be dissociative. The rate-determining step is the breaking of the ring chelate, but a strongly coordinating ligand such as NO^+ must be present to prevent the ring chelate reformation. The substitution of the dangling ligand H_2vi by a Cl, Br, OH, or NO_2 anion occurs by an acid-catalyzed process. The proposed mechanism of the overall nitrosylation reaction is checked by the solvolysis of *cis*-Ru$(H_2vi)_3$NO.

The synthesis,[2] structure,[3] and reactivity[4] of nitrosyl complexes have long been of great interest, but the thermodynamic instability and oxidizing power of NO and NO^+ against metal and ligands have motivated the development of new approaches to introducing the nitrosyl functionality into coordination complexes.[2] However, there are relatively few publications which relate the mechanistic data of the substitution reactions. The observed kinetics of a substitution reaction rarely give the mechanism unambiguously[5] and a further criterion of the mechanism that has been widely used is that of stereochemistry. The role of solvents[6,7] and added components such as ionic species[6] is very important and has been extensively investigated.

The synthesis and stereochemistry of the tris chelates of the Ru$(AB)_3^-$ type, where AB represents an unsymmetrical bidentate ligand, have been achieved in previous works.[9,10]



1,3-dihydrogenoviolurate, H_2vi^-; R = R′ = H

1,3-dimethylviolurate, $dmvi^-$; R = R′ = CH_3

These complexes are inert to substitution and do not react with nucleophiles such as Cl^- or H_2O. However, they are very sensitive to acidic nitrite solutions forming nitrosyl complexes of the Ru$(AB)_2$NOX[10] type, where X represents a monodentate ligand. The kinetics and stereochemistry of nitrosylation of *fac*-Ru$(H_2vi)_3^-$ have determined specific pieces of information about the reaction mechanism.

Experimental Section

Starting Materials. Na[Ru$(H_2vi)_3$]·$4H_2O$ and H_3O[Ru$(H_2vi)_3$]·$3H_2O$ were obtained as described in ref 9 and 10. The compounds gave satisfactory elemental analyses.

Preparation of Ruthenium–Nitrosyl Complexes. All syntheses were performed in darkness under an argon atmosphere.

Ru$(H_2vi)_3$NO, Ru$(H_2vi)_2$NOCl, and Ru$(H_2vi)_2$NOBr were obtained as described in ref 10. The compounds gave satisfactory elemental analyses.

Ru$(H_2vi)_2$(NO)(OH) was prepared by adding of 0.14 g of sodium nitrite (2 mmol) to a stirred solution of 0.5 g of Na[Ru$(H_2vi)_3$]·$4H_2O$ (0.75 mmol) with perchloric acid (5 mmol) in 25 mL of twice-distilled water. After filtration, the yellow solution was held at 5 °C a few days, during which time small yellow crystals appeared. The product was collected and washed rapidly with 5 mL of ethanol and 5 mL of ether. The yellow crystals were dried in vacuo over P_4O_{10} and then at 100 °C for 3 h under argon yielding 0.29 g (85%) of end product. Anal. Calcd for $RuC_8H_5N_7O_{10}$: Ru, 21.95; C, 20.86; H, 1.08; N, 21.30. Found: Ru, 21.64; C, 20.55; H, 1.2; N, 20.94.

Ru$(H_2vi)_2$(NO)(NO_2) was prepared using a modification of the former procedure. Na[Ru$(H_2vi)_3$]·$4H_2O$, 0.5 g (0.75 mmol), and $NaNO_2$, 1.4 g (20 mmol), were added to 25 mL of twice-distilled water. The solution was stirred and perchloric acid added (10 mmol). After filtration, the yellow solution was held at 5 °C a few days, during

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which time small yellow crystals appeared. The product was collected and washed rapidly with 5 mL of ethanol and 50 mL of ether. The product was dried in vacuo over P_4O_{10} and then at 100 °C for 3 h under argon; yield 0.2 g (55%). Anal. Calcd for $RuC_8H_4N_8O_{11}$: Ru, 20.65; C, 19.63; H, 0.82; N, 22.90. Found: Ru, 20.50; C, 19.61; H, 1.1; N, 22.98.

The elemental analyses were performed by the microanalytical laboratory of CNRS, Thiais, France. Ruthenium analysis was performed by a method described in a previous work.[11]

Physical Measurements. UV–visible spectra were run on a Jobin and Yvon DF 170 instrument, using jacketed quartz cells. Infrared spectra were obtained on a Beckman IR 20 AX spectrophotometer using KBr plates and Nujol mulls. ^1H NMR spectra were taken on a Brücker WH 90 or on a Perkin-Elmer R 24 B spectrometer. Magnetic susceptibilities in the solid state were measured at room temperature according to the Faraday technique. The potentiometric data were obtained on a Radiometer PM 52 instrument using a glass electrode/solution/KCl (saturated solution)/calomel electrode system.

Rate Measurements. Nitrosylation of *fac*-$Ru(H_2vi)_3^-$. The rate of nitrosylation for the reaction

$$fac\text{-}Ru(H_2vi)_3^- + HNO_2 + HX \rightarrow cis\text{-}Ru(H_2vi)_2NOX + H_2vi^- + H_2O$$

(where X is Cl, Br, NO_2, or OH) was studied by spectrophotometry. Acidity was controlled with buffer for the pH 1.00–2.50 range. The concentrations of $Ru(H_2vi)_3^-$ and HCl were fixed by measuring the requisite volumes of the respective stock solutions. Ionic strength was maintained at 0.5 mol L^{-1} with sodium chloride. A 200-mL aqueous solution containing HCl and $Na[Ru(H_2vi)_3]\cdot 4H_2O$ was degassed with argon and thermostated at 25.0 ± 0.1 °C. The circulation from the thermostated flask to the spectrophotometer cells was performed by a micropump. To initiate the reaction a small volume of $NaNO_2$ solution was syringed quickly into the flask. The reaction was followed at 495 nm to more than 95% completion in all cases. The pH was controlled during the reaction, with variations less than 0.02 for the runs at higher acidity.

Hydrolysis of *cis*-$Ru(H_2vi)_3NO$. The rate of acid hydrolysis for the reaction

$$cis\text{-}Ru(H_2vi)_3NO + \alpha H_2O + (1-\alpha)HX \rightarrow \alpha Ru(H_2vi)_3^- + \alpha HNO_2 + H^+ + (1-\alpha)cis\text{-}Ru(H_2vi)_2NOX + (1-\alpha)H_3vi$$

was studied by spectrophotometry. A 200-mL aqueous solution containing supporting electrolyte, 0.5 mol L^{-1} NaCl, and the requisite concentration of HCl was degassed with argon and thermostated at 25.0 ± 0.1 °C. The solution was stirred and a known amount of solid $Ru(H_2vi)_3NO$ was rapidly added and mixed. The kinetics were studied as above.

Calculations. In the rate measurements of the nitrosylation reaction the nitrite concentration $[NO_2^-]_T$ exceeded that of Ru(II) by at least a factor of 100. If the reaction is a consecutive kinetic process (reversible or nonreversible) of pseudo first order, the average molar absorptivity coefficient $\bar{\epsilon}(t)$ can be represented by

$$\bar{\epsilon}(t) = \epsilon_\infty + \sum_{i=1}^{n} I_i \exp(-\gamma_i t)$$

in which $\bar{\epsilon} = A(t)/C_TL$ is the average molar absorptivity coefficient at 495 nm ($A(t)$ is the absorbance at 495 nm at time t, C_T is the concentration of Ru(II), and L is the spectrophotometer cell length in centimeters), $\epsilon_\infty = A_\infty/C_TL$ (A_∞ is the final absorbance), γ_i is the pseudo-first-order rate constant, I_i is a constant, a function of the molar extinction coefficients, and ϵ_i is the molar extinction coefficient of species C_i.

A first approximation of γ_i was obtained graphically from plots of log $(\epsilon_\infty - \bar{\epsilon}(t))$ against time, linear for at least 2 half-lives (log $(\epsilon_\infty - \bar{\epsilon}(t)) = -\gamma_n t + \log(-I_n)$), then log $(\epsilon_\infty - \bar{\epsilon}(t) + I_n \exp(-\gamma_n t))$ vs. time (log $(\epsilon_\infty - \bar{\epsilon}(t) + I_n \exp(-\gamma_n t)) = \gamma_{n-1} + \log(-I_{n-1})$), and so on until all the experimental data were used. The best values of γ_i and I_i were obtained using a least-squares computer program that minimized the $\sum_1^N(\bar{\epsilon}_{obsd} - \bar{\epsilon}_{calcd})^2$ function in which N is the number of data points. In the fitting procedure, the γ_i, I_i, t_0, and ϵ_∞ parameters were considered, in which t_0 was the unknown zero time. The fitting procedure computed also the standard errors of the best-fit values of γ_i, I_i, t_0, and ϵ_∞. The values of the final residuals of $(\bar{\epsilon}_{obsd} - \bar{\epsilon}_{calcd})$ proved that no systematic error has been made.

Table I. Stretching Vibrations ν(NO) and UV-Visible Characteristics of the Nitrosyl Compounds

compd	$\bar{\nu}$(NO), cm^{-1}	$\pi \rightarrow \pi^*$ ligand H_2vi, nm	d(Ru(II)) → $\pi^*(H_2vi)$, nm
$Ru(H_2vi)_3NO$	1924	328	365 sh
$Ru(H_2vi)_2NOCl$	1950	325	360 sh
$Ru(H_2vi)_2NOBr$	1949	325	360 sh
$Ru(H_2vi)_2NO(OH)$	1905	325	360 sh
$Ru(H_2vi)_2NO(NO_2)$	1956	325	360 sh

Results

Nitrosylation Products. Stoichiometry. The products of the nitrosylation reaction of the sodium nitrite in an acid aqueous solution on *fac*-tris(dihydrogenoviolurato)ruthenate(1−), *fac*-$Ru(H_2vi)_3^-$, are dependent on the acid used. The reaction of NO_2^-/H^+ on *fac*-$Ru(H_2vi)_3^-$ yields a yellow solid, having the $Ru(H_2vi)_3NO$ composition with all the acids employed ($HClO_4$, H_2SO_4, HCl, HBr). But if the nitrosylation was performed with a large excess of Cl^-, Br^-, or NO_2^-, the isolated products were respectively $Ru(H_2vi)_2NOCl$, $Ru(H_2vi)_2NOBr$, and $Ru(H_2vi)_2(NO)(NO_2)$. However, when $Ru(H_2vi)_3NO$ was dissolved in the noncomplexing media ClO_4^- at pH ≃2, the final compound formed was the hydroxo complex $Ru(H_2vi)_2NO(OH)$. At this pH the dissociation of coordinated H_2O was very important. At pH <1 the formation of the aquo complex $Ru(H_2vi)_2NO(H_2O)^+$ is probable, but $[Ru(H_2vi)_2NO(H_2O)]ClO_4$ was not isolated. It is reasonable to assume that dissociation of coordinated H_2O occurs in the pH range under consideration, but that is difficult to prove, because of the higher solubility of the aquo complex compared to that of the hydroxo complex.

The $Ru(H_2vi)_3NO$ and $Ru(H_2vi)_2NOX$ (X = Cl, Br, NO_2, OH) products were characterized by their elemental analysis, infrared spectra, far-infrared spectra, ^1H NMR spectra, electronic spectra, and magnetic properties. The values of the characteristic stretching vibrations ν(NO) of the nitrosyl compounds are given in Table I with UV–visible characteristics.

In the solid state, X-ray studies[9] have demonstrated that $H_3O[Ru(H_2vi)_3]\cdot 3H_2O$ has a *fac*-$Ru(H_2vi)_3^-$ anion with three different Ru–O(6) bonds and three different Ru–N(7) bonds: the heterocyclic violurato ligand is planar. However, in solution the complex is expected to realize a tris-chelate structure with three equivalent violurato ligands as in the corresponding 1,3-dimethylviolurato compound.[10] Although attempts to obtain suitable crystals of $Ru(H_2vi)_2(NO)Cl\cdot xH_2O$ and $Ru(H_2vi)_2(NO)Br\cdot yH_2O$ have been successful, X-ray studies have not been undertaken yet. We have, therefore, used IR, far-IR, and ^1H NMR measurements and $^{14}NO \rightarrow {}^{15}NO$ isotopic exchange to make preliminary structure assignments[10] for $Ru(AB)_3NO$ and $Ru(AB)_2(NO)X$, where AB is H_2vi or dmvi and X is Cl or Br. All of the complexes possess a six-coordinate structure with cis X and NO; in $Ru(H_2vi)_3NO$ one H_2vi^- ligand is monodentate through the O(6) atom and it is cis to the NO ligand.[10] The unequivocal assignment of nitrosyl group on the basis of any method other than X-ray crystallography is difficult. Using Haymore and Ibers' suggestion[12] that ν(NO) can be used to assign the geometry of the nitrosyl ligand, we believe that these nitrosyl complexes contain linear nitrosyl groups. All violurato and mononitrosylviolurato complexes exhibit diamagnetic properties at 25 °C. These complexes are d^6 low spin just as 1,3-dimethylviolurato complexes are and contain ruthenium in the formal oxidation state of 2.

The $Ru(H_2vi)_3NO$ and $Ru(H_2vi)_2NOX$ complexes were characterized also by electronic spectra in aqueous solutions at pH <2. The spectra are analogous and consistent with d^6

Table II. Observed Rates of Nitrosylation Reaction on *fac*-$Ru(H_2vi)_3^-$ [a]

$10^2[H^+]$, mol L^{-1}	$10^3[NO_2^-]$, mol L^{-1}	$10^4\gamma_2$, s^{-1}	$I_2/(I_1+I_2)$	$10^3\gamma_1$, s^{-1}	$I_1/(I_1+I_2)$	$k_1^{obsd}/[NO_2^-]_T$, s^{-1} mol^{-1} L	$10^4 \times k_{-1}^{obsd}$, s^{-1}	$10^4 \times k_2^{obsd}$, s^{-1}
3.2 (2)	2.93	4.03 (2)	0.587 (8)	3.00 (8)	0.413 (6)	0.50 (2)	12 (2)	8.2 (8)
3.0 (1)	2.93	4.34 (2)	0.621 (9)	2.78 (8)	0.379 (7)	0.45 (2)	9 (2)	9.1 (8)
2.9 (1)	2.93	3.57 (2)	0.59 (1)	3.33 (8)	0.40 (1)	0.52 (2)	13 (2)	7.7 (6)
2.6 (1)	2.93	3.10 (3)	0.52 (2)	2.6 (2)	0.47 (2)	0.49 (3)	9 (3)	6 (1)
2.4 (1)	2.93	3.31 (2)	0.62 (1)	3.1 (1)	0.380 (7)	0.47 (2)	13 (2)	7.4 (8)
2.2 (1)	2.93	2.94 (1)	0.646 (8)	2.74 (7)	0.354 (5)	0.39 (1)	11 (1)	6.9 (8)
2.1 (1)	2.93	2.67 (1)	0.665 (7)	2.64 (5)	0.335 (4)	0.36 (1)	11 (1)	6.6 (7)
1.64 (7)	2.93	2.15 (1)	0.707 (8)	2.18 (4)	0.293 (3)	0.27 (1)	10 (1)	5.9 (6)
1.17 (5)	2.93	1.62 (1)	0.74 (1)	1.67 (5)	0.256 (6)	0.18 (1)	8 (2)	4.9 (5)
0.77 (3)	2.93	1.10 (1)	0.86 (3)	1.8 (2)	0.14 (2)	0.13 (1)	10 (3)	4.8 (9)
1.44 (6)	1.46	1.30 (1)	0.81 (2)	1.1 (1)	0.19 (2)	0.22 (1)	5 (3)	4.6 (9)
1.46 (6)	1.99	1.57 (1)	0.77 (2)	1.48 (4)	0.22 (2)	0.22 (1)	7 (1)	4.6 (9)
1.62 (7)	2.34	2.03 (1)	0.74 (1)	2.07 (3)	0.25 (1)	0.28 (1)	10 (1)	6.3 (8)

[a] At 25 °C and ionic strength 0.50 mol L^{-1} with added NaCl; $C_T = 2.45\ (5) \times 10^{-5}$ mol L^{-1}. The estimated standard deviations of the last digit are in parentheses.

low-spin complexes; they exhibit a broad absorption at 320 nm and a shoulder at 360 nm (Table I). The first absorption was attributed to a $\pi \rightarrow \pi^*$ transition[13,14] in the violurato ligand and the shoulder to a $d\pi(Ru(II)) \rightarrow \pi^*$ transition. The weak absorption generally attributed[15,16] to the $d(Ru(II)) \rightarrow \pi^*(NO)$ transition in the near-UV region is masked by the broad absorption of the charge-transfer transition but can explain the sunlight photolysis of the nitrosyl complexes.[10,16,17]

Contrary to the related 1,3-dimethylviolurato compounds, the tris(dihydrogenoviolurato)nitrosylruthenium and bis(dihydrogenoviolurato)chloronitrosylruthenium complexes are only slightly soluble in water. When the ruthenium concentration was sufficiently low, the medium was homogeneous and the stoichiometry of the nitrosylation reaction was studied by spectrophotometry. The absorbance at 495 nm vs. $[NO_2^-]_T/C_T$ demonstrates the reaction of 1 mol of $NaNO_2$ for 1 mol of $Ru(H_2vi)_3^-$ in 0.1 mol L^{-1} $HClO_4$ and in 0.1–0.5 mol L^{-1} HCl (Figure 1).

The nitrosylation reaction has the stoichiometry

$$Ru(H_2vi)_3^- + HNO_2 + H^+ \rightleftarrows Ru(H_2vi)_3NO + H_2O$$

The nitrosylation reaction was incomplete in 0.1 mol L^{-1} $HClO_4$ and 0.1–0.2 mol L^{-1} HCl media, and the reverse reaction could be studied in the hydrolysis reaction of $Ru(H_2vi)_3NO$. Moreover, complete nitrosylation could be followed by a substitution reaction of the dangling ligand H_2vi^- with X^-:

$$Ru(H_2vi)_3NO + HX \rightarrow Ru(H_2vi)_2NOX + H_3vi$$

Nitrosylation Kinetics. The experimental I_i and γ_i values derived by a least-squares evaluation of the spectrophotometric data at 495 nm in the nitrosylation kinetics of *fac*-$Ru(H_2vi)_3^-$ by NO_2^-/H^+ are given in Table II with appropriate standard deviations. At that wavelength the nitrosyl complexes have no absorption and the $A(495)$ absorbance is a direct measurement of the $Ru(H_2vi)_3^-$ concentration. The $[H^+]$ values are measured by means of a glass electrode after its standardization in the experimental media: 0.5 mol L^{-1} NaCl with standard HCl concentrations. For all experiments, the spectrophotometrically observable $\bar{\epsilon}(t)$ is consistent and is in good agreement with eq 1.

$$\bar{\epsilon}(t) = I_1 \exp(-\gamma_1 t) + I_2 \exp(-\gamma_2 t) \tag{1}$$

Using the best values of I_1, I_2, γ_1, and γ_2, we find $\sum_1^N(\bar{\epsilon}_{obsd} - \bar{\epsilon}_{calcd})/\bar{\epsilon}_{calcd} < 0.5\%$ for at least 90% of the reaction. N is the number of data points $\bar{\epsilon}(t)$ of the experiment.

The two steps observed in the nitrosylation rate are consistent with the assumption of two consecutive kinetic processes observed with a reversible first process, because at 495 nm, $Ru(H_2vi)_3^-$ is the only stable species which has a significant absorption. The most probable hypothesis can be represented by (2) with $C_1 = Ru(H_2vi)_3^-$ ($\epsilon_1 = 25\,000$ mol^{-1} L cm^{-1}), C_2

$$\boxed{C_1} \underset{k_{-1}^{obsd}}{\overset{k_1^{obsd}}{\rightleftarrows}} C_2 \xrightarrow{k_2^{obsd}} C_3 \tag{2}$$

$= Ru(H_2vi)_3NO$ ($\epsilon_2 = 0$), and $C_3 = Ru(H_2vi)_2NOCl$ ($\epsilon_3 = 0$). The starting material is boxed. ϵ_1, ϵ_2, and ϵ_3 are the molar extinction coefficients of the C_1, C_2, and C_3 species, respectively, and k_1^{obsd}, k_{-1}^{obsd}, and k_2^{obsd} are the rate constants observed. The resolution of the differential equations with the above assumption gives the concentration of the $C_1(t)$, $C_2(t)$, and $C_3(t)$[18] species. The initial conditions are $[C_1(0)] = C_T$, $[C_2(0)] = 0$, and $[C_3(0)] = 0$. The concentration $[C_1(t)]$ is only necessary because C_2 and C_3 have no absorption at 495 nm. Thus

$$[C_1(t)]/C_T = \frac{k_1^{obsd} - \gamma_2}{\gamma_1 - \gamma_2}\exp(-\gamma_1 t) + \frac{\gamma_1 - k_1^{obsd}}{\gamma_1 - \gamma_2}\exp(-\gamma_2 t) \tag{3}$$

where $\gamma_1 = {}^1/_2(k_1^{obsd} + k_{-1}^{obsd} + k_2^{obsd} + \sqrt{\Delta})$ and $\gamma_2 = {}^1/_2(k_1^{obsd} + k_{-1}^{obsd} + k_2^{obsd} - \sqrt{\Delta})$ and $\Delta = (k_1^{obsd} + k_{-1}^{obsd} + k_2^{obsd})^2 - 4k_2^{obsd}k_1^{obsd}$.

Among the several possible mechanisms for two steps, only the proposed equation (2) is consistent with the experimental data which fit the relations $I_1 = \epsilon_1(k_1^{obsd} - \gamma_2)/(\gamma_1 - \gamma_2)$, $I_2 = \epsilon_1(\gamma_1 - k_1^{obsd})/(\gamma_1 - \gamma_2)$, $k_1^{obsd} = (I_1\gamma_1 + I_2\gamma_2)/(I_1 + I_2)$,

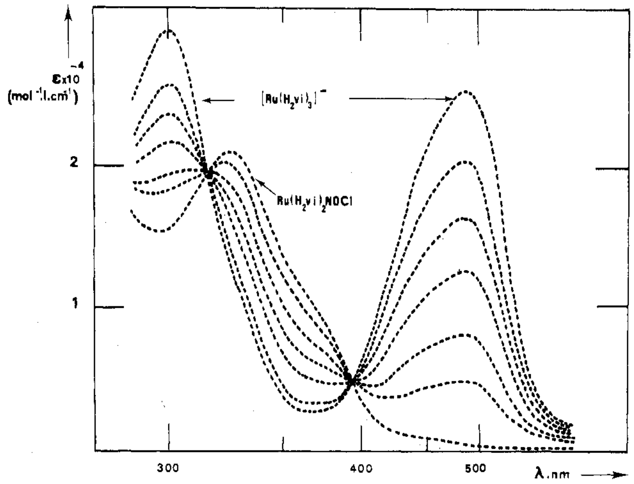


Figure 1. Spectral changes accompanying addition of $NaNO_2$ in an aqueous solution of *fac*-$Ru(H_2vi)_3^-$ (3×10^{-4} mol L^{-1}). Conditions: 25 °C, pH 1, ionic strength 0.5 mol L^{-1} (NaCl).

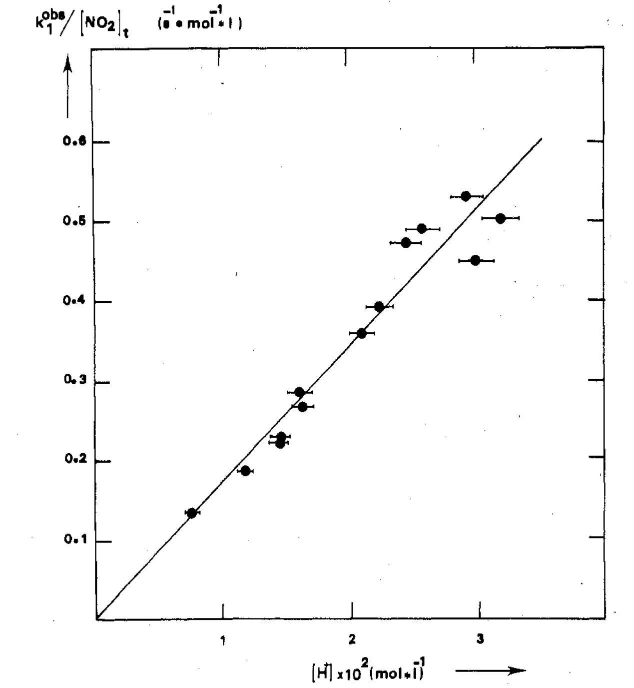


Figure 2. Dependence of the pseudo-first-order rate constants $k_1^{obsd}/[NO_2^-]_T$ on $[H^+]$ in the nitrosylation reaction of *fac*-$Ru(H_2vi)_3^-$. Conditions: 25 °C, ionic strehgth 0.5 mol L^{-1} (NaCl).

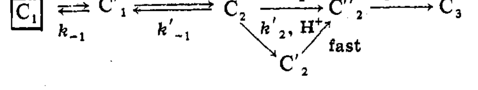
$k_2^{obsd} = (I_1 + I_2)\gamma_1\gamma_2/(I_1\gamma_1 + I_2\gamma_2)$, and $k_{-1}^{obsd} = I_1I_2(\gamma_1 - \gamma_2)^2/(I_1 + I_2)(I_1\gamma_1 + I_2\gamma_2)$. Figures 2 and 3 and Table II show the dependence of k_1^{obsd}, k_2^{obsd}, and k_{-1}^{obsd} on $[H^+]$ and $[NO_2^-]_T$, respectively. The plots of k_1^{obsd} against $[H^+]$ or $[NO_2^-]_T$ are linear over the experimental $[H^+]$ or $[NO_2^-]_T$ range. The rate constant observed, $k_1^{obsd}/[NO_2^-]_T$, varies with $[H^+]$ (Figure 2) and fits eq 4.

$$k_1^{obsd}/[NO_2^-]_T = a_1[H^+] \qquad (4)$$

At $[H^+] > 3 \times 10^{-2}$ mol L^{-1} deviation of $k_1^{obsd}/[NO_2^-]_T$ against $[H^+]$ from eq 4 was attributed to the pH measurement. k_2^{obsd} is independent of $[NO_2^-]_T$, but the plot of k_2^{obsd} vs. $[H^+]$ (Figure 3) shows the variation with $[H^+]$ and that k_2^{obsd} fits eq 5.

$$k_2^{obsd} = a_2[H^+] + b_2 \qquad (5)$$

k_1^{obsd} seems independent of the two $[H^+]$ and $[NO_2^-]_T$ parameters; the deviations of k_2^{obsd} and k_{-1}^{obsd} vs. $[H^+]$ from straight lines were attributed not only to the pH measurement but also to a number of mathematical operations. It is necessary to give and discuss the significance of a_1, a_2, b_2, and k_{-1}^{obsd} in order to establish a mechanism taking into consideration all species present in nitrosylation reaction 6.



$$\begin{tikzcd}
\boxed{C_1} \arrow[r, shift left, "k_1"] & C'_1 \arrow[l, shift left, "k_{-1}"] \arrow[rr, shift left, "{k'_1,\ NO^+}"] & & C_2 \arrow[ll, shift left, "k'_{-1}"] \arrow[rr, "k_2"] \arrow[dr] & & C''_2 \arrow[r, "{k_3,\ Cl^-}"] & C_3 \\
 & & & & C'_2 \arrow[ur, "{k'_2,\ H^+}", "fast"'] & &
\end{tikzcd} \qquad (6)$$

In a dissociation mechanism[5] it is necessary to introduce three intermediates C'_1, C'_2, and C''_2. A steady-state treatment using the assumption used previously gives differential equations as for eq 1 with

$$k_1^{obsd} = k_1k'_1[NO^+]/(k_{-1} + k'_1[NO^+]) \qquad (7)$$

$$k_{-1}^{obsd} = k_1k'_{-1}/(k_{-1} + k'_1[NO^+]) \qquad (8)$$

$$k_2^{obsd} = k_2 + k'_2[H^+] \qquad (9)$$

At 495 nm C_2 and C_3 have no absorption, and the k_3 rate constant does not appear in $\bar{\varepsilon}(t)$ (eq 1). The electronic spectra of the C_2 and C_3 species are quite analogous (Table I) and the rate measurement of the anation step by spectrophotometry is not very easy.

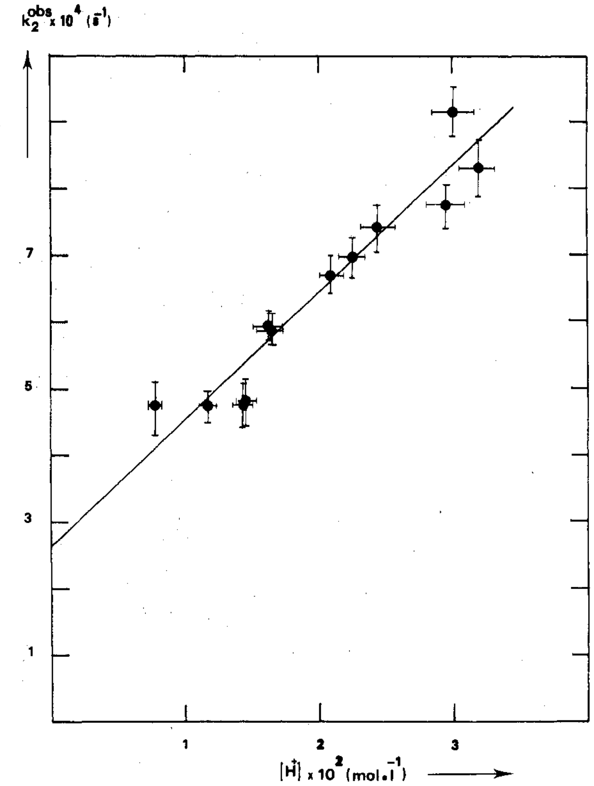


Figure 3. Dependence of the pseudo-first-order rate constants k_2^{obsd} on $[H^+]$ in the nitrosylation reaction of *fac*-$Ru(H_2vi)_3^-$. Conditions: 25 °C, ionic strength 0.5 mol L^{-1} (NaCl).

Of the species generated in aqueous solutions by the sodium nitrite, NO^+ is the active one.[19,20]

$$H^+ + NO_2^- \underset{}{\overset{k_{N1}}{\rightleftarrows}} HNO_2 \text{ (fast)}$$

$$H^+ + HNO_2 \overset{k_{N2}}{\rightleftarrows} H_2NO_2^+ \text{ (fast)}$$

$$H_2NO_2^+ \underset{k_y}{\overset{k_x}{\rightleftarrows}} NO^+ + H_2O$$

$$C'_1 + NO^+ \underset{k'_{-1}}{\overset{k'_1}{\rightleftarrows}} C_2$$

The derived rate law for NO^+ is

$$d[NO^+]/dt = k_x[H_2NO_2^+] + k'_{-1}[C_2] - (k_y + k'_1[C'_1])[NO^+]$$

Assuming a steady-state concentration of NO^+

$$[NO^+] = \frac{k_x[NO_2^-]_T}{\left(1 + \frac{k_{N_2}}{[H^+]} + \frac{k_{N_1}k_{N_2}}{[H^+]^2}\right)(k_y + k'_1[C'_1])} + \frac{k'_{-1}[C_2]}{k_y + k'_1[C'_1]}$$

with $k_y >> k'_1[C'_1]$,[20] $k_x[NO_2]_T/(1 + k_{N2}/[H^+] + k_{N1}k_{N2}/[H^+]^2 >> k'_{-1}[C_2]$, and $1 + k_{N2}/[H^+] + k_{N1}k_{N2}/[H^+]^2 \approx k_{N2}/[H^+]$ for the $[H^+]$ range, the equation reduces to

$$[NO^+] \approx \frac{k_x}{k_yk_{N_2}}[NO_2]_T[H^+] \qquad (10)$$

Table III. Nitrosylation Rate Constants of *fac*-$Ru(H_2vi)_3^-$ [a]

$k_1k'_1/k_{-1}$	$(5.0 \pm 0.2) \times 10^8$ mol L s^{-1}
k'_{-1}	$(10 \pm 2) \times 10^{-4}$ s^{-1}
k_2	$(2 \pm 0.5) \times 10^{-4}$ s^{-1}
k'_2	$(10 \pm 3) \times 10^{-3}$ mol^{-1} L s^{-1}

[a] At 25 °C and ionic strength 0.50 mol L^{-1} with added NaCl.

If $k'_1[NO^+]/k_{-1} << 1$, eq 7–9 give respectively $k_1^{obsd}/[NO_2]_T = k_1k'_1k_x[H^+]/k_{-1}k_{N2}k_y$, $k_{-1}^{obsd} = k'_{-1}$, and $k_2^{obsd} = k_2 + k'_2[H^+]$. It is possible to give the significance of $a_1 = k_1k'_1k_x/k_{-1}k_{N2}k_y$, $a_2 = k_2$, and $b_2 = k'_2$. The value for k_x/k_yk_{N2}[19-21] of 3×10^{-7} mol^{-1} L gives the values of $k_1k'_1/k_{-1}$, k'_{-1}, k_2, and k'_2.

The equations are consistent with the experimental data and the proposed mechanism of eq 6. A value of 2.2×10^3 mol L^{-1} s^{-1} for k_x/k_{N2} was obtained by Anbar and Taube,[22] which allows a value of 7×10^9 s^{-1} for k_y. It can now be shown that $k_y >> k'_1[C'_1]$ and $k'_{-1}[C_2] << (k_x/k_{N2})[NO_2]_T[H^+]$.

Hydrolysis Kinetics. Some minutes after the dissolution of $Ru(H_2vi)_3NO$ in water, the color changes from pale yellow to deep red, even without photolysis. The visible spectrum of the red solution was identical with that of $Ru(H_2vi)_3^-$; a broad absorption was detected at 495 nm. The rate of appearance of the red color increases with $[H^+]$. This observation is consistent with the removal of the nitrosyl group from the coordination sphere which does not occur by a photolytic process, with electronic transfer d(Ru(II)) → π*(NO), but by spontaneous decomposition. In protic solvents such as water or ethanol,[23] the NO^+ nitrosyl ion combines with the associate base. If the hydrolysis of $Ru(H_2vi)_3NO$ or $Ru(dmvi)_3NO$ is carried out under argon and darkness, it is possible to establish the presence of the NO group by the study of its Brønsted acid properties. The hydrolysis of $Ru(H_2vi)_3NO$ or $Ru(dmvi)_3NO$ appears while pH decreases. That result is consistent only with NO^+ loss from $Ru(H_2vi)_3NO$ or $Ru(dmvi)_3NO$. The nitrosonium ion brings about the equilibria $NO^+ + H_2O \rightarrow H_2NO_2^+ \rightleftarrows H^+ + HNO_2 \rightleftarrows H^+ + NO_2^-$. Only in the case of $Ru(dmvi)_3NO$ is it easy to separate after several days the hydrolysis products by filtration.[24] The tris-chelate $Ru(dmvi)_3^-$ concentration is determined from the spectrophotometric data at 495 nm, and then $Ru(dmvi)_3^-$ is quantitatively isolated by introducing the precipitating cation Ba^{2+}. The spectrophotometric determination of nitrite concentration in the filtrate by the sulfanilic acid method agrees with the $[Ru(dmvi)_3^-]/[NO_2^-]_T = 1/1$ stoichiometry. The solvolysis of *cis*-$Ru(H_2vi)_3NO$ or $Ru(dmvi)_3NO$ in aprotic media gives interesting information about the mechanism and is the subject of ongoing research. The solvolysis of *cis*-$Ru(H_2vi)_3NO$ or $Ru(dmvi)_3NO$ can be studied qualitatively by ^1H NMR in dimethyl-d_6 sulfoxide at different temperatures.[10] The recorded spectra vs. time show the course of the reaction. The final spectrum is consistent with a mixture of *fac*-$Ru(H_2vi)_3^-$, *cis*-$Ru(H_2vi)_2NO(Me_2SO)$,$^+$ and H_2vi^-.[10,25]

The hydrolysis of *cis*-$Ru(H_2vi)_3NO$ is studied quantitatively by spectrophotometry. The absorbance vs. time data at 495 nm of the hydrolysis reaction was analyzed in the same way as for nitrosylation data.

Compared with that of the nitrosylation mechanism (eq 2) the rate constant k_1^{obsd} was negligible, and the *cis*-$Ru(H_2vi)_3NO$ hydrolysis reaction can be reduced to eq 11.

$$C_1 \xleftarrow{k_{-1}^{obsd}} \boxed{C_2} \xrightarrow{k_2^{obsd}} C_3 \qquad (11)$$

Assuming the mechanism of eq 11, the hydrolysis reaction of *cis*-$Ru(H_2vi)_3NO$ requires a rate law of the form

$$[C_1]/C_T = \epsilon_\infty - I'_1 \exp(-\gamma'_1 t) \qquad (12)$$

with $\gamma'_1 = k_{-1}^{obsd} + k_2^{obsd}$, $I'_1 = \epsilon_1 k_{-1}^{obsd}/(k_{-1}^{obsd} + k_2^{obsd})$, and $\epsilon_\infty = \epsilon_1 k_{-1}^{obsd}/(k_{-1}^{obsd} + k_2^{obsd})$. The product ratio $R_1 = [C_1]/C_T$ for $t \rightarrow \infty$ is given by

$$\bar{\epsilon}^\infty_{495}/\epsilon^1_{495} = k_{-1}^{obsd}/(k_{-1}^{obsd} + k_2^{obsd})$$

Table IV. Observed Rate Constants for the Acid Hydrolysis of *cis*-$Ru(H_2vi)_3NO$[a]

$[H^+]$, mol L^{-1}	$10^3\gamma'_1$, s^{-1}	R_1
0.0054	1.7 (1)	0.50 (2)
0.1	2.4 (1)	0.37 (2)
0.11	2.5 (1)	0.36 (2)
0.22	3.2 (2)	0.28 (1)
0.34	3.8 (3)	0.26 (2)

[a] At 25 °C and ionic strength 0.50 mol L^{-1} with added NaCl.

The results of the rate measurements are given in Table IV.

For all experiments, the observable $\bar{\epsilon}(t)$ is consistent with the equation

$$\bar{\epsilon}(t) = \bar{\epsilon}_\infty - I'_1 \exp(-\gamma'_1 t)$$

which is identical with eq 12. It appears from the agreement of the experimental points with the calculated curve using the best values of $I'_1\gamma'_1$ and $\bar{\epsilon}_\infty$ that results are fully accounted for by the assumption made for at least 80% of the reaction. Table IV shows the dependence of γ'_1 and R_1 on $[H^+]$. The plot of observed rate constants γ'_1 vs. $[H^+]$ gives a straight line over the experimental $[H^+]$ range. The R_1 product ratio varies inversely with $[H^+]$; the plots of $1/R_1$ vs. $[H^+]$ also give a straight line.

The approximations $k_1^{obsd} = 0$ and $k'_1[NO^+] = 0$ lead to the hydrolysis mechanisms in eq 13. In protic media such as

$$\begin{tikzcd}
C_1 \arrow[r, shift left, "k_1"] & C'_1 \arrow[l, shift left, "k_{-1}"] & \boxed{C_2} \arrow[l, "k'_{-1}"'] \arrow[rr, "k_2"] \arrow[dr, "{k'_2, H^+}"] & & C''_2 \arrow[r, "k_3"] & C_3 \\
& & & C'_2 \arrow[ur, "fast"'] & &
\end{tikzcd} \qquad (13)$$

H_2O

$$NO^+ + H_2O \underset{k_x}{\overset{k_y}{\rightleftarrows}} H_2NO_2^+$$

$$H_2NO_2^+ \overset{k_{N2}}{\rightleftarrows} H^+ + HNO_2 \quad \text{(fast)}$$

$$HNO_2 \overset{k_{N1}}{\rightleftarrows} H^+ + NO_2^- \quad \text{(fast)}$$

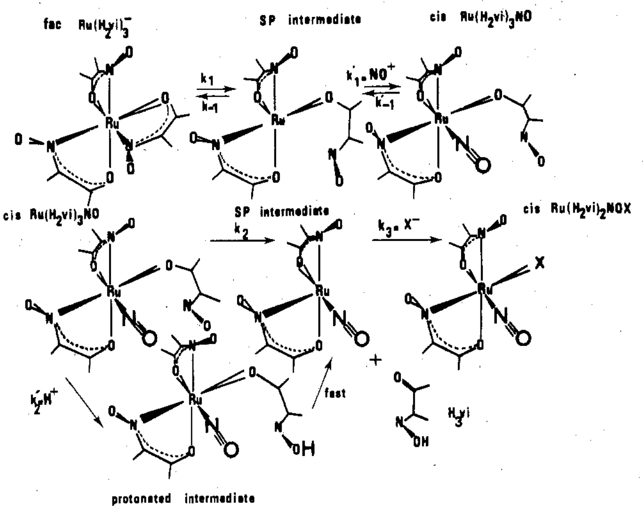
A steady-state treatment using the assumption used previously gives differential equations where $k_{-1}^{obsd} = k'_{-1}$, $k_2^{obsd} = k_2 + k'_2[H^+]$, and $R_1 = k'_{-1}/(k'_{-1} + k_2 + k'_2[H^+])$.

The equations are consistent with experimental data, and graphical determination of $k'_{-1} + k_2$ and k'_2 gives values of $(16 \pm 3) \times 10^{-4}$ s^{-1} and $(10 \pm 4) \times 10^{-3}$ mol^{-1} L s^{-1}, respectively, which are consistent with the nitrosylation experiments.

Discussion

The low-spin d^6 complexes are the most inert to substitution.[5] Moreover, for $Ru(H_2vi)_3^-$ the chelate ring increases this inertness. However, while *fac*-$Ru(H_2vi)_3^-$ does not react with nucleophiles such as Cl^-, H_2O, etc., it is very sensitive to acidic $NaNO_2$ and goes through a fast and quantitative reaction. In attempting to categorize reported nitrosylation reactions there is some difficulty in distinguishing reactions of the types[2] involving (a) attack of NO^+ generated by acidic solutions of nitrite salts on metal complexes and involving (b) coordination of NO_2^- followed by oxide O^{2-} abstraction. Godwin and Meyer[26] have successfully distinguished between the latter in the preparation of $Ru(bpy)_2NOCl^{2+}$ and $Ru(phen)_2NOCl_2^+$. In this case no association by nitrite in the absence of added H^+ is observed. The nitrosylation reaction, on the other hand, is instantaneous. In the reaction of *fac*-$Ru(H_2vi)_3^-$ with nitrite our observations are the same. The nitrosylation of *fac*-

Scheme I. Nitrosylation Reaction Scheme



$Ru(H_2vi)_3^-$ occurs by direct attack of NO^+ generated by acidic solutions of nitrite salts.[10,26-28]

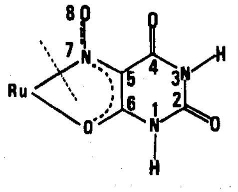
Pathway for Ruthenium(II) Chelate Ring Opening and Closing and Reversible Nitrosylation. The introduction of the nitrosonium ion NO^+ into the coordination sphere of Ru(II) occurs by a second-order rate law; it is not possible from the kinetic data only to attribute a S_N1 dissociation or S_N2 displacement process to the reaction.[29]

Stereochemical study gives more information about the mechanism. The starting material racemic *fac*-$Ru(H_2vi)_3^-$ possesses in the solid state a pseudo-tris-chelate molecular structure,[9] but in solution it is expected to have a tris-chelate structure with three equivalent ligands[10] with no diastereotopic substituents. No coalescence is observed in the temperature range allowed by the solubility of the compounds in Me_2SO. A very rapid isomerization *mer* ⇄ *fac* with bond rupture cannot explain the ^1H NMR spectra.

The $\Delta \rightleftarrows \Lambda$ enantiomerization cannot be checked from a racemic starting material but is still possible. $\Delta \rightleftarrows \Lambda$ inversion without metal–ligand bond rupture is possible by means of various twist motions of the chelate rings.[30]

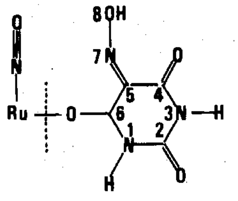
The structures of $Ru(AB)_2NOX$, in which AB is dmvi or H_2vi and X is Cl, Br, or unidentate AB, were described in a previous work[10] and this paper demonstrates the stereospecificity of the nitrosylation reaction of *fac*-$Ru(H_2vi)_3^-$ by nitrite in acidic media (Scheme I). One geometrical isomer was also obtained for $Ru(H_2vi)_2NOX$ with X = OH and NO_2 in the present work. All of the complexes possess a six-coordinate structure with a cis position for X and NO; for X = unidentate H_2vi the bond is through the O(6) atom of the heterocycle.[10] The ^1H NMR spectra of $Ru(AB)_2NOX$ are not consistent with fast rearrangement.[31] No coalescence is observed in the temperature range allowed by the solubility and thermal stability of the compounds. The formation of an intermediate with seven-coordination as in $Mo(S_2CNMe_2)_3NO$[32] is not detected, while the structure of $Ru(S_2CNMe_2)_3NO$[33] which is analogous to that of $Ru(H_2vi)_3NO$ and $Ru(dmvi)_3NO$[10] is known to contain a monodentate dithiocarbamate ligand cis to NO. The enantiomerization $\Delta \rightleftarrows \Lambda$ by twist motions[31] cannot be checked as for *fac*-$Ru(H_2vi)_3^-$.

In the nitrosylation of the racemic *fac*-tris(1,3-dihydrogenoviolurato)ruthenate(1−) anion in acidic media, the rate-determining step is the breaking of the ring chelate by the Ru–N(7) bond.[10] In the bond-rupture mechanism, the geometry of the intermediate may have either an idealized square-pyramidal (SP) or trigonal-bipyramidal (TBP) geometry with the dangling ligand in an axial or equatorial position. The lower coordinated polyhedron has a very short lifetime and cannot be isolated, as an octahedral complex is re-formed by bond formation at Ru–N(7) to give tris-chelate *fac*-$Ru(H_2vi)_3^-$ or by NO^+ addition to give *cis*-$Ru(H_2vi)_3NO$ with a dangling H_2vi^-. Unidentate bpy is evident in the substitution kinetics of $Fe(bpy)_3^{2+}$[34] whereas with $Fe(phen)_3^{2+}$ this complication does not occur as each ligand is constrained by the steric rigidity of the ring system which requires that both nitrogen atoms must be coordinated at the same time.[6] The stereochemistry of $Ru(H_2vi)_3NO$ and the stereospecificity of the nitrosylation reaction are consistent with a five-coordinate complex with square-pyramidal geometry; this intermediate is extremely short-lived and is likely to escape detection. The acid dependence on k_1^{obsd} is attributed only to the $H_2NO_2^+$ protolysis and $k_1k'_1/k_{-1}$ is independent of H^+ concentration.



secondary pathway for ruthenium(II)–oxygen bond breaking

Acid-catalyzed bond rupture by protonation at an O(8) site in the tris chelate is unlikely because the absorption spectrum of a molar acid solution of $Ru(H_2vi)_3^-$ is the same as that of a neutral solution so that there cannot be any appreciable quantity of protonated species present. The hydrolysis of $Ru(H_2vi)_3NO$ demonstrates the reversibility of the nitrosylation reaction, the transformation *cis*-$Ru(H_2vi)_3NO \rightarrow$ *fac*-$Ru(H_2vi)_3^- + NO^+$, is essentially due to the strong "chelate effect" of the H_2vi ligands which leads to the closure of the chelate ring with the concomitant displacement of the NO^+ nitrosyl. However, that can be prevented by an electrophilic reagent (H^+) reacting with the released end of the chelate group. The overall dissociation would then be accelerated by acid catalysis of the bond rupture[35,36] with protonation of the O(8) site.



All of the complexes are "low spin" and stereochemically rigid or "slow" complexes.[37] The decomposition of *cis*-$Ru(H_2vi)_3NO$ by loss of unidentate H_2vi leads to a pentacoordinated intermediate $Ru(H_2vi)_2NO$ which is extremely short-lived and reacts rapidly with nucleophiles X such as Cl^-, Br^-, or NO_2^- and the solvent to give the *cis*-$Ru(H_2vi)_2NOX$ hexacoordinated complexes. The stereochemistry of $Ru(AB)_2NOX$ and the stereospecificity of the substitution reaction are consistent with a square-pyramidal intermediate (SP).

The preceding discussion was limited to stereochanges of geometrical isomers. However, it is probable that nitrosylation occurs with retention of configuration with two square-pyramidal intermediates in the experimental media and at 25 °C. The effect of solvent on the dissociation rate appears to be due to the solvation of the ligands in the transition state and the solvent ability to act as a replacing ligand. However, a strongly coordinating ligand as NO^+ must be present to replace irreversibly the dissociated ligand violurato.

Registry No. $Ru(H_2vi)_3NO$, 67529-72-0; $Ru(H_2vi)_2NOCl$, 67529-73-1; $Ru(H_2vi)_2NOBr$, 67529-74-2; $Ru(H_2vi)_2NO(OH)$, 67505-82-2; $Ru(H_2vi)_2NO(NO_2)$, 67505-83-3; $Na[Ru(H_2vi)_3]$, 66538-16-7; $NaNO_2$, 7632-00-0.

Supplementary Material Available: A listing of the calculated and observed average molar absorptivity coefficients at 495 nm and an appendix on the $\epsilon(t)$ calculation (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, W. R. Kenan Laboratory 045A,
University of North Carolina, Chapel Hill, North Carolina 27514

Unusual Magnetic Properties in Two Copper(II) Chelates of Schiff Bases Derived from α-Amino Acids: A Dimeric Interaction in a Structural Linear Chain

WILLIAM E. ESTES and WILLIAM E. HATFIELD*

Received May 3, 1978

The magnetic properties of two unusual Schiff base copper(II) chelates, (*N*-salicylideneglycinato)aquocopper(II) hemihydrate and (*N*-salicylidene-α-aminoisobutyrato)aquocopper(II), have been measured as a function of temperature (1.6–160 K) and applied field strength (10–50 kOe). The data reveal that the exchange interaction in $[\mathrm{Cu}(N\text{-sal}{=}\mathrm{gly})\mathrm{H_2O}]\cdot0.5\mathrm{H_2O}$ is predominantly between pairs of copper(II) ions in different structural chains rather than between an infinite linear array of copper(II) ions along the obvious crystallographic chain, in moderate magnetic fields. The dimer model yields an exchange energy, J, of $-2.19\ \mathrm{cm^{-1}}$ with the intercluster exchange being only about $-0.09\ \mathrm{cm^{-1}}$. High-field isothermal magnetization data with the applied field stronger than the exchange energy, $H > 2J/g\beta$, indicate that the intercluster terms become significant as longer range interactions occur when the ground-state multiplicity changes. The data for the structurally similar $[\mathrm{Cu}(N\text{-sal}{=}\mathrm{aiba})\mathrm{H_2O}]$ complex reveal interactions which are about an order of magnitude smaller ($J = -0.8\ \mathrm{cm^{-1}}$) than the glycinato analogue; in addition, the choice between the pair model and the linear-chain model is much less certain. The similarities and differences in the interactions present in both compounds are compared to their known crystallographic structures. The possibilities of long-range magnetic ordering in strong applied magnetic fields and of unusual adiabatic cooling are postulated for $[\mathrm{Cu}(N\text{-sal}{=}\mathrm{gly})\mathrm{H_2O}]\cdot0.5\mathrm{H_2O}$.

Introduction

Ordinarily one expects the structural and magnetic properties of a given substance to be intimately related[1-6] with the dimensionality of the magnetic or electrical interactions that are present reflecting the lattice dimensionality.[3] For example, a cluster of two interacting magnetic ions should obey a theoretical model whose statistics treat only the pair of interacting spins. Systems in which there are interactions between a small number of spins in a definable cluster within a macroscopic crystal are considered to be zero-dimensional (0-D) from a lattice viewpoint.[3] Each cluster is assumed to be isolated from neighboring clusters in the crystal structure, and interactions of spins of the individual clusters with the spins on neighboring clusters are assumed to be absent. This basic idea may be generalized to include one-dimensional chains (1-D) and two-dimensional layers (2-D). Eventually such a process leads to the ultimate reality of a three-dimensional (3-D) crystal structure in which there are more or less equally interacting near neighbors.[3]

The above simplified description of the effects of lattice dimensionality on the isotropic Heisenberg exchange interaction rarely applies to real chemical systems.[3,6-8] Crystal packing requirements and weak *interunit* bonding or hydrogen bonding often occur and these features can give rise to ad-

0020-1669/78/1317-3226$01.00/0