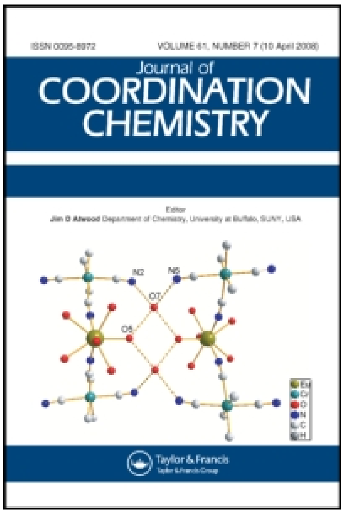

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KINETICS OF SUBSTITUTION AND ISOMERIZATION OF NITRITE ION ON AQUA(7-METHYL-4,10-DITHIA-1,7,13-TRIAZATRIDECANE)COBALT(III) AND THE STRUCTURE OF THE PRODUCT

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The influence of placing a CH_3N- linkage *trans* to a site of nitro substitution and spontaneous nitrito-to-nitro isomerization is reported for the $Co(NSNSN)H_2O^{3+}$ cation where NSNSN is 7-methyl-4,10-dithia-1,7,13-triazatridecane, $NH_2CH_2CH_2–S–CH_2CH_2–N(CH_3)–CH_2CH_2–S–CH_2CH_2NH_2$. Preparation and characterization is described for the aqua and nitrito complexes. $Co(NSNSN)H_2O^{3+}$ is 435 times more reactive than $Co(NH_3)_5H_2O^{3+}$ under identical conditions. Nitrito-to-nitro isomerization is much slower than the conversion of $Co(NSNSN)H_2O^{3+}$ to $Co(NSNSN)ONO^{2+}$. The isomerization was studied at a number of wavelengths, temperatures and at various concentrations of acid and nitrite ion at ionic strengths of 0.11–0.60 M. Isomerization rate constants are $1.10 \pm 0.11 \times 10^{-5}\,sec^{-1}$ at 20.0°C, $5.24 \pm 0.83 \times 10^{-5}\,sec^{-1}$ at 30.0°C, and $18.1 \pm 1.1 \times 10^{-5}\,sec^{-1}$ at 39.0°C. Thermodynamic activation parameters are $\Delta H^{\ddagger} = 109.3\,kJ\,mol^{-1}$, $\Delta S^{\ddagger} = +33\,J\,mol^{-1}\,K^{-1}$ and $\Delta G^{\ddagger} = 99.4\,kJ\,mol^{-1}$. Single-crystal X-ray diffraction data refined to an R of 0.032 are presented for the product, $[Co(NSNSN)NO_2](ClO_4)_2$. The complex has the symmetrical $\alpha\alpha$ geometric configuration. Nitrite ion causes a structural *trans* influence of 0.042 Å on the *trans* nitrogen-Co(III) bond in the $Co(NSNSN)NO_2^{2+}$ ion. These results are discussed in the context of present knowledge and experience with other cobalt(III) ligand systems.

Keywords[8]: Cobalt(III), pentadentate, X-ray, structure, nitrito ligand, kinetics, isomerization

INTRODUCTION

A report by Yoneda and coworkers[1] on rate effects due to the chemical nature of various ligands positioned both adjacent to and remote from the site of nitrito-to-nitro isomerization persuaded us to examine what rate effects would result if thioether linkages were positioned *trans* to the site of isomerization.[2] Heretofore, $Co(NSSSN)H_2O^{3+}$ was used to study the effect of thioether donors on the nature of nitrite ion substitution and the rate of *nitrito* to *nitro* isomerization.[2,3] We have extended this previous study to a complex in which the isomerization site is *trans* to a $(CH_3)N$- group. Earlier we observed that replacement of chloride in $[Co(NSNSN)Cl](ClO_4)_2$ by nitrite was very rapid.[4,5] In a matter of minutes the nitrogen bound nitro complex, $[Co(NSNSN)NO_2](ClO_4)_2$, forms.[6] This prompted us to examine the properties and kinetic reactivity of the family of complexes $Co(NSNSN)H_2O^{3+}$ (reactant),

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$Co(NSNSN)ONO^{2+}$ (intermediate) and $Co(NSNSN)NO_2^{2+}$ (product). The structures of the parent chloro complex and the product nitro complex which had been inferred from chemical interconversion information[4,5,6] are now confirmed by single crystal X-ray diffraction studies.[7] The results of the kinetic and structural study are reported below.

EXPERIMENTAL SECTION

$[Co(NSNSN)Cl](ClO_4)_2$ and $[Co(NSNSN)NO_2](ClO_4)_2$ were prepared according to reported methods.[6] Each complex was purified by recrystallization and its composition confirmed by equivalent weight determination using ion exchange techniques and electronic spectroscopy. The electronic spectra of the eluted species were in exact agreement at all wavelengths with those found earlier (*i.e.*, $\varepsilon = 207\ M^{-1}\,cm^{-1}$ and $313\ M^{-1}\,cm^{-1}$ at λ_{max} 565 nm and 490 nm, respectively.[6]

All chemicals were of reagent grade. Solutions for spectroscopic and kinetic studies were prepared and standardized using appropriate analytical procedures and volumetric glassware. Stock solutions of $\sim 5 \times 10^{-3}$ M $Co(NSNSN)H_2O^{3+}$ were prepared by treating aqueous $Co(NSNSN)Cl^{2+}$ with Hg^{2+}. When the solution colour changed form purple to red, excess chloride ion was added to complex the mercuric ion as $HgCl_4^{2-}$. The mixture was separated by ion exchange chromatography on Dowex 50-X8 (100–200 mesh) in the acid form. The column was eluted first with 200 cm³ of 1.0 M $HClO_4$ to remove any mercuric ion and then the $Co(NSNSN)H_2O^{3+}$ complex was eluted using standardized $HClO_4$. Preweighed, solid, anhydrous Na_2CO_3 was carefully added to the stock solution to neutralize the excess $HClO_4$. The neutralization was monitored using a Dow Corning pH meter and stopped at pH 2.5. The solution was transferred to a volumetric flask and diluted to the mark. From the mass of added Na_2CO_3, pH, volume, and the concentration of complex, one can calculate the needed concentration parameters for kinetic experiments. The spectrum (absorption coefficients as a function of wavelength) of $Co(NSNSN)H_2O^{3+}$ was established using ion exchange methodology in conjunction with stoichiometric conversion of $Co(NSNSN)Cl^{2+}$ to $Co(NSNSN)H_2O^{3+}$ in the presence of mercuric ion.

Solution spectra and kinetic data were collected using a Cary 14 recording spectrophotometer equipped with a doubly thermostatted cell compartment and matched quartz cells of appropriate path length. $NaNO_2$ (as a standard solution or solid) was added directly to the cell of known volume containing predetermined quantities of complex, acid, $NaClO_4$ and distilled water at the desired temperature. The cell was quickly inverted, shaken and placed in the cell holder. Optical density measurements were started at a fixed wavelength within 15 seconds of mixing.

Kinetic and spectroscopic data were manually encoded and stored, displayed, plotted and analyzed using a Macintosh IIcx computer equipped with Cricket Graph, Microsoft Basic, and Fortran software.

A number of computer programs were specifically written to calculate the rate constants, extinction coefficients, and to fit the data to a series of consecutive first-order reactions. The computer programs were installed on an IBM 370 main-frame computer equipped with VM/HPO release 5.1 system software, a VS FORTRAN 66 and a VS FORTRAN 77 compiler running on an IBM 3381D processor.

Single crystal X-ray structure

A Syntex $P2_1$ four-circle diffractometer module on-line with a Data General NOVA-4S minicomputer, equipped with an equivalent Nicolet R3 program package, was used for intensity data collection and crystal structure determination.

Intensity Data Collection: A golden yellow crystal of $[Co(NSNSN)NO_2](ClO_4)_2$ was selected, measuring $0.308 \times 0.231 \times 0.116$ mm. It was mounted on a glass fibre and positioned on the Syntex $P2_1$ diffractometer. The preliminary lattice constants were obtained by a least-squares fit to 25 centred reflections, obtained from a preliminary rotation photograph. They indicated the triclinic crystal system. Further, more accurate cell parameters were determined by the same method using 25 centred reflections with $2\theta \geqslant 20^\circ$. Intensity data were recorded using MoK_α radiation. A Wyckoff scan mode was employed by holding the detector arm (2θ) and scanning the ω angle. A normal 13-step scan was used to measured the peak profile and six extra steps were used for weak reflections. A total of 2822 reflections, of which 2515 were unique, were measured for $3^\circ \leqslant 2\theta \leqslant 45^\circ$. Four quadrants of the reflection data were collected within the reflection sphere. Of the unique reflections, 2359 were treated as observed $I \geqslant 1.5\sigma(I)$ and none of the reflections was rejected. Two standards, (115) and (221), were measured every 48 reflections to monitor crystal deterioration and to obtain re-scaling factors. Lorentz and polarization corrections were applied to the intensity data. An additional 252 azimuthal psi scan data on seven reflections, (010), (021), $(1\bar{3}0)$, $(\bar{2}42)$, (050), $(0\bar{6}0)$, and $(0\bar{6}3)$, were measured for absorption correction. The maximum and minimum transmission factors were 0.890 and 0.722, respectively. The space group $P\bar{1}$ was assigned, first since there are two molecules in the unit cell. This proved to be correct during further structure refinement.

Structure Determination and Refinement: The position of the cobalt atom was located in a Patterson map. A subsequent Fourier map indicated the positions of the coordinated sulfur and nitrogen atoms. Next, the positions of the carbon atoms and one of the perchlorate ions were identified. The structure was refined for three cycles using isotropic thermal parameters and unit weights to give $R = 0.12$. The positions of the oxygen atoms for one of the perchlorate ions could not be fixed at this stage. There were six peaks surrounding the chloride atom with reasonable Cl-O bond length (1.39–1.52 Å). Arbitrary assignment for any four oxygens followed least-squares refinement did not further reduce the R factor. The temperature parameters of the perchlorate oxygen atoms indicated some disorder and large vibrational motion of the ion. At this point, two sets of oxygen atoms were assigned with variable site occupation factors (s.o.f.), and restrained such that the sum of s.o.f. for any two equivalent oxygen atoms was 1.0. After further refinement using anisotropic temperature factors, the R factor dropped to 0.066 and R_w to 0.080. Hydrogen atoms were added at positions found in a difference map and ten refinement cycles involving 293 parameters, including hydrogen atom positions and an overall

TABLE I

Crystal data for [Co(NSNSN)NO$_2$](ClO$_4$)$_2$ collected from two different crystals.

Molecular formula		[Co(N$_3$S$_2$C$_9$H$_{23}$)(NO$_2$)]-(ClO$_4$)$_2$	
Molecular weight		541.27 g mol^{-1}	
Space group	P$\bar{1}$		P$\bar{1}$
Cell constants	a=9.136(2)Å		a=9.132(2)Å
	b=9.588(2)Å		b=9.582(2)Å
	c=11.771(3)Å		c=11.767(3)
	α=69.22(2)°		α=69.22(2)
	β=84.94(2)°		β=84.93(2)
	γ=88.46(2)°		γ=88.48(2)
	V=960.3(4)Å^3		V=958.8(4)Å^3
Crystal size	0.31 × 0.23 × 0.12 mm		0.54 × 0.54 × 0.19 mm
Molecules/unit cell		2	
Density (calc.)		1.87 g cm^{-3}	
Abs. coeff.		14.37 cm^{-1}	
Transmission factor	0.722–0.890		
Radiation (MoK$_\alpha$)		0.71073 Å	
Temperature		25°C	
Data collection mode	Wyckoff scan		ω scan
Collection range		3°$\leqslant 2\theta \leqslant$45°	
Scan speed range		4–29.3°/min	
Total data collected	2708		2692
Independent data	2359[I>1.5$\sigma(I)$]		2389[I>1.5$\sigma(i)$]
Total variables		293	
Primary extinction	1.65 × 10^{-3}		3 × 10^{-5}
R	0.034		0.032
R_w	0.038		0.037
R_g	0.046		0.047

$R=\Sigma[|F_o|-|F_c|)^2/\Sigma|F_o|^2$; $R_w=\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2$.

hydrogen atom isotropic temperature factor, led to a converged R value of 0.034, R_w of 0.038, and R_g of 0.046 using unit weights. A difference map at this stage indicated maximum and minimum residual electron densities of 0.33 and −0.39 e/Å^3, respectively. The (Δ/σ_{max} is 0.42 and the primary extinction parameter is 0.00165.

A second single crystal of the title compound from another preparation was selected and a different data collection scanning mode (ω scan) was used. Two independent structure analyses showed similar results and they are listed in Table I.

RESULTS AND DISCUSSION

Complex ion spectra

The visible electronic spectra for Co(NSNSN)H$_2$O^{3+}, Co(NSNSN)ONO^{2+}, and Co(NSNSN(NO$_2^{2+}$ are presented in Figure 1 as a plot of wavelength *vs* absorption coefficient. The visible spectrum of [Co(NSNSN)H$_2$O]$^{3+}$ exhibits a single symmetrical absorption band at 520 nm (ε = 186 M^{-1} cm^{-1}) followed by a minimum at 440 nm (ε = 54 M^{-1} cm^{-1}).

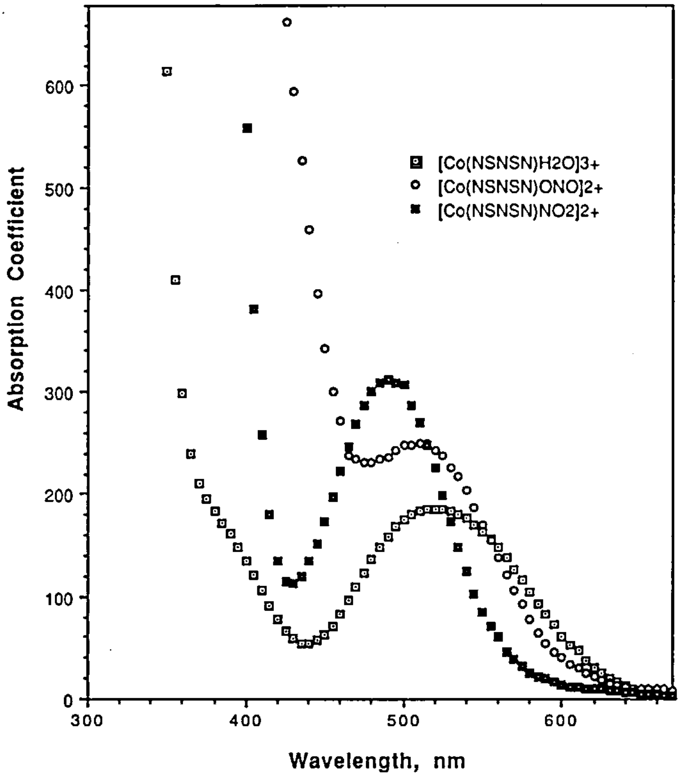


FIGURE 1 Visible spectra for Co(NSNSN)(aqua)$^{n+}$, -nitro, and -nitro complexes.

Because the Co(NSNSN)ONO^{2+} intermediate cannot be isolated as a pure solid, its spectrum was determined *via* two independent methods. At pH 4.1 and at high nitrite ion concentrations, the replacement of water in Co(NSNSN)H_2O^{3+} is very rapid, being complete within the time of mixing. The spectrum of the nitrito intermediate was recorded immediately after mixing. Isomerization of the nitrito complex to the nitro isomer in this time is negligible. Four determinations at different complex and nitrite ion concentrations gave identical results. The absorption coefficients for the nitrito complex were calculated from a knowledge of the initial reactant complex concentration and by assuming 100% reaction. From D_t *vs* time plots and an accurate knowledge of the absorption coefficients at two wavelengths for both the reactant and product and the rate constants for substitution (k_{obs}) and isomerization (k_{isom}), one can calculate the concentration of all species present at any time as well as the expected spectrum of the intermediate.[8] Typical computer calculated results were consistently within 5% of the absorptivity value obtained directly using the first method above. From the calculated visible spectrum, the intermediate [Co(NSNSN)ONO]$^{2+}$ ion has one band maximum at 510 nm ($\varepsilon = 246\,M^{-1}\,cm^{-1}$), a band minimum at 475 nm ($\varepsilon = 224\,M^{-1}\,cm^{-1}$) and a shoulder (infection) at

410 nm which tails off strongly into the UV range. The product nitro complex, $[Co(NSNSN)NO_2]^{2+}$, has a band maximum at 490 nm ($\varepsilon = 313\,M^{-1}cm^{-1}$) and a minimum at 430 nm ($\varepsilon = 112\,M^{-1}cm^{-1}$). These three cobalt(III) complexes do not share a common isosbestic point in the visible range.

pKa determination

The acid dissociation constants for both $[Co(NSNSN)H_2O]^{3+}$ and $[Co(NSSSN)H_2O]^{3+}$ were determined as a result of a study to investigate whether spontaneous base hydrolysis or base-catalyzed rate behaviour would hold. Unlike the robust $[Co(NH_3)_5Cl]^{2+}$ ion (pKa = 6.55), which can endure quite basic conditions (0.1 M OH^-), experiments with both $[Co(NSSSN)H_2O]^{3+}$ and $[Co(NSNSN)H_2O]^{3+}$ demonstrated that both complexes decompose at pH 10.0 and pH 11.0 within minutes. The $[Co(NSSSN)H_2O]^{3+}$ ion can survive longer than $[Co(NSNSN)H_2O]^{3+}$ in pH 8.0 buffer solution; however, both complexes totally decompose over several days. The results suggest that these complexes are unsuitable for base hydrolysis kinetic studies. The acid dissociation constants (pKa) for $[Co(NSSSN)H_2O]^{3+}$ and $[Co(NSNSN)H_2O]^{3+}$ were established by standard derivative titration methods to be 6.03 ± 0.30 and 6.85 ± 0.21, respectively.

Kinetic data for the replacement of coordinated H_2O by ONO^-

Specific rate data for the reaction of $[Co(NSNSN)H_2O]^{3+}$ with NO_2^- are presented in Table II. The ratio of $[HNO_2]$ to $[NO_2^-]$ was adjusted to a fixed value of 1/7.92 (pH 4.1). The initial concentration of $[Co(NSNSN)H_2O]^{3+}$ was 2.44×10^{-4} M. Optical density traces (a typical display in presented in Figure 2) as a function of time were analyzed by plotting time *vs* $\ln(D_t - D_i)$ as is usual for pseudo-first-order reaction kinetics (a typical plot is presented in Figure 3). Nitrite ion was always in excess. A 250 fold excess of nitrite ion produced a reactin too fast to follow with the available instrumentation. This limited the range over which the nitrite ion concentration could be varied and prevented us from exploring the region where k_{obs} should become independent of nitrite ion concentrations.

A series of calculations were performed to compute and compare the substitution rate constants using the equation below where $k_1 = k_{obs}$ and $k_2 = k_{isom}$.

$$\varepsilon_{obs} = \varepsilon_A \exp(-k_1 t) + \varepsilon_B \frac{k_1}{(k_2 - k_1)}[\exp(-k_1 t) - \exp(-k_2 t)] + \varepsilon_C \left\{ 1 - \frac{k_2 \exp(-k_1 t)}{(k_2 - k_1)} + \frac{k_1 \exp(-k_2 t)}{(k_2 - k_1)} \right\}$$

The calculated best fit for k_{obs} was based on the average deviation of all the recorded optical density *versus* time values in order to minimize the difference between the experimental and the calculated absorbance values. From Table II, it is seen that the calculated rate constants are very close to the experimental values.

TABLE II

ate constants and concentration data for nitrite ion substitution at $[Co(NSNSN)H_2O]^{3+}$.

mp., °C	$[HNO_2] \times 10^4$/M	$[NO_2^-] \times 10^3$/M	$k_{obs}{}^a \times 10^3/s^{-1}$	$k_{calc}{}^b \times 10^3/s^{-1}$
.0	5.00	3.96	2.38±0.06	2.38
	10.0	7.92	4.09±0.12	3.70
	15.0	11.9	5.20±0.19	5.47
	20.0	15.8	7.08±0.14	8.81
	30.0	23.8	9.77±0.31	11.8
.0	5.00	3.96	1.01±0.02	0.85
	10.0	7.92	1.74±0.04	1.73
	15.0	11.9	2.43±0.05	2.50
	20.0	15.8	3.13±0.06	3.19
	30.0	23.8	5.28±0.70	5.39
.0	5.00	3.96	0.266±0.015	0.222
	10.0	7.92	0.453±0.016	0.409
	15.0	11.9	0.738±0.019	0.674
	20.0	15.8	1.05±0.048	1.09
	30.0	23.8	1.84±0.051	1.84

[a] Average k_{obs} determined by graphical methods. The ± value is the std. dev.

[b] Calculated best fit k using the absorption coefficients and concentrations of the reactant, intermediate d product and the experimental value for $k_{isomerization}$.

Figure 2 displays a typical reaction trace obtained at 39°C at 430 nm. A very rapid crease in absorbance occurs as the nitrito complex is formed, followed by a much ɔwer decrease in absorbance as the $Co(NSNSN)ONO^{2+}$ ion slowly isomerizes to e nitro form. Representative first-order plots of $\ln(D_t - D_i)$ *vs* time, for data recorded 20°C and 430 nm, are given in Figures 3 and 4 for the substitution and isomerization, spectively. Individual plots of k_{obs} *vs* $[HNO_2][NO_2^-]$ are presented in Figure 5 r rate data at three different temperature. At moderate $[NO_2^-]$, an intermediate ıear region is evident. At higher $[NO_2^-]$, the plot begins to bend, as k_{obs} comes independent of $[NO_2^-]$. This is similar to what was found for the reaction nitrite ion with the aquapentamminecabolt(III) and nitroaquabis(ethylenediamine)-balt(III) ions.[9] These facts are consistent with a rate law having the general rm rate $= k''[Co(NSNSN)H_2O^{3+}][HNO_2][NO_2^-]$. If one considers the acid-se equilibrium between the aqua and hydroxo complex ions in solution, $\text{'o}(NSNSN)H_2O]^{3+} + OH^- = [Co(NSNSN)OH]^{2+} + H_2O$, a kinetically indistin-ishable rate law exists, having the form rate $= k''[Co(NSNSN)OH^{2+}][HNO_2]^2$. ıis expression is analogous to the rate expression often found for the nitrosation ammonia and ammines where it is believed that the nitrosation agent is N_2O_3, nerated from nitrous acid.[10] The nature of the rate law derived from data in ıble II contributes further support for the general mechanism advanced by Basolo d Pearson several decades ago[9,11,12,13] in which a pre-equilibrium step first oduces the nitrosation agent prior to the rate determining reaction with the balt(III) complex.

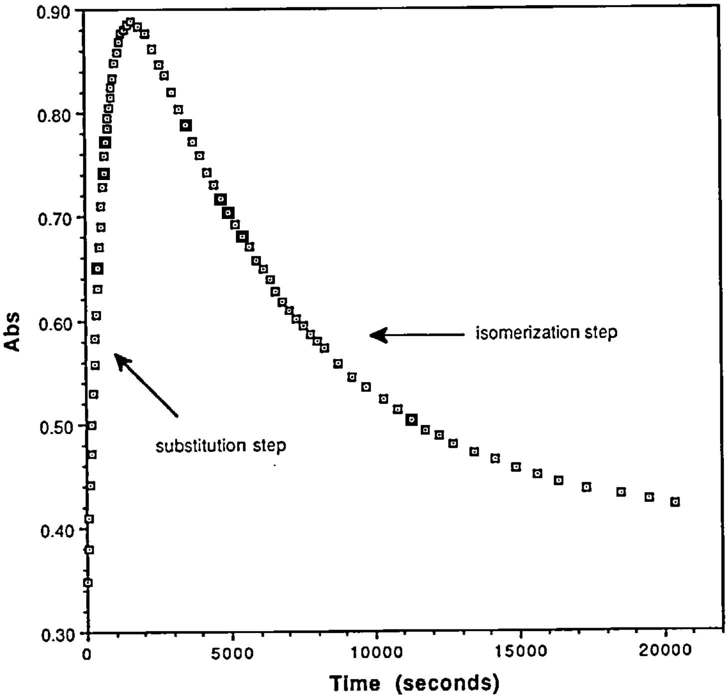


FIGURE 2 A 430 nm trace of D_t *vs* time for the reaction at 30°C between NO_2^- and $[Co(NSNSN)H_2O]^{3+}$, followed by the nitrito-to-nitro isomerization.

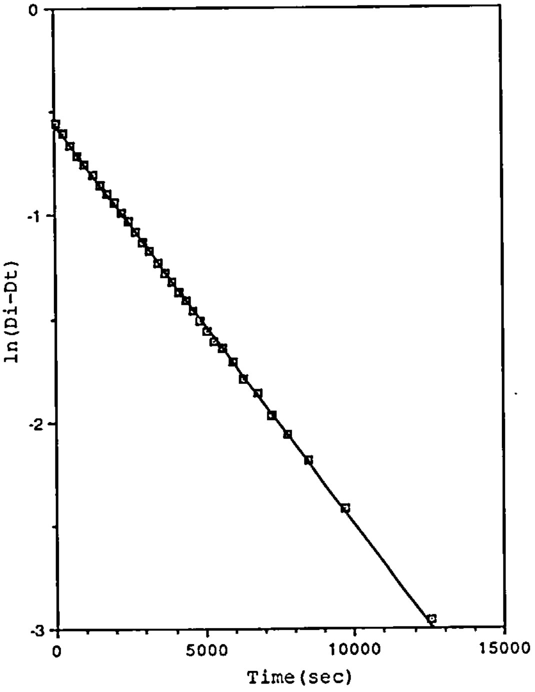


FIGURE 3 A (typical plot of $\ln(D_\infty - D_t)$ *vs* time for the reaction of $[Co(NSNSN)H_2O]^{3+}$ with nitrite ion.

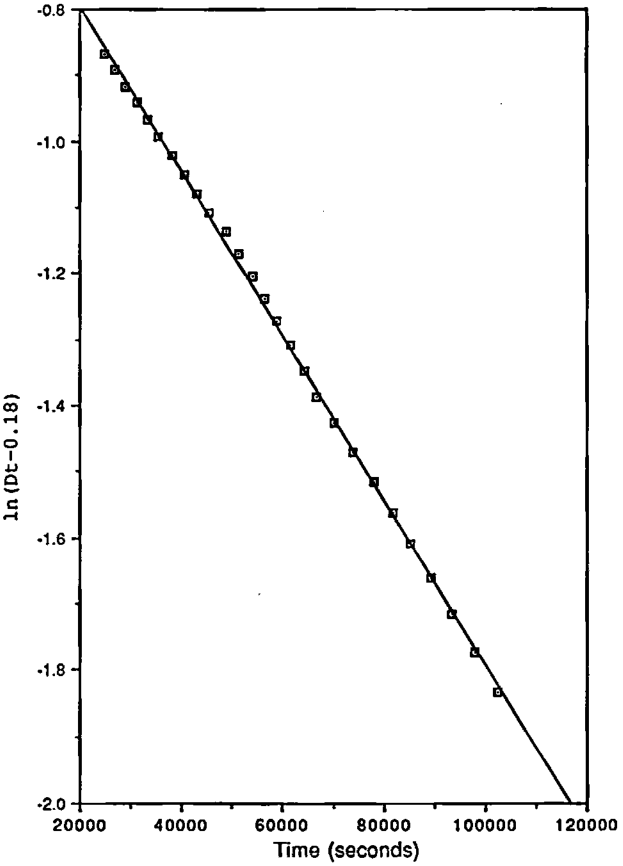
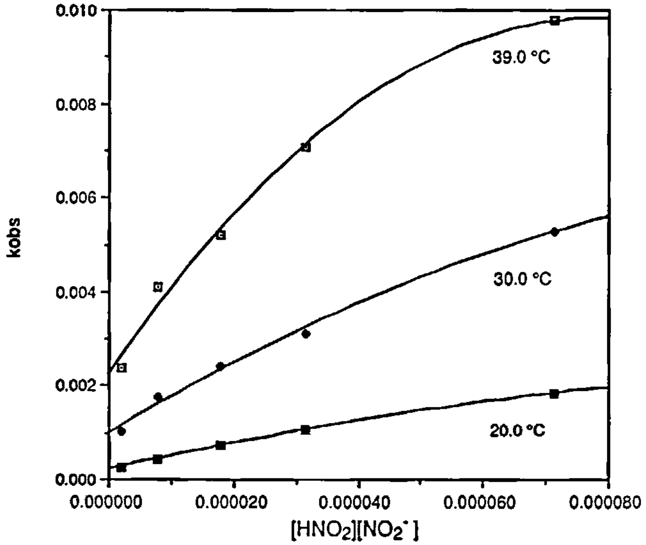


FIGURE 4 A typical plot of $\ln(D_t - D_\infty)$ *vs* time for the isomerization of $[Co(NSNSN)ONO]^{2+}$.



GURE 5 A plot of k_{obs} *vs* $[HNO_2][NO_2^-]$ at three temperatures for the reaction of $[Co(NSNSN)H_2O]^{3+}$ h nitrite ion.

The slopes of the linear plots in Figure 5 represent a composite rate constant that may suggest the steady state generation of N_2O_3 followed by its reaction with $[Co(NSNSN)H_2O]^{3+}$. Interestingly, the value for this slope at 25°C for $[Co(NH_3)_5H_2O]^{3+}$ is $0.0847\ sec^{-1}\ M^{-2}$ whereas $[Co(NSNSN)H_2O]^{3+}$ gives a value of $36.75\ sec^{-1}\ M^{-2}$ under identical conditions, clearly quantifying the latter's 435-fold greater reactivity.

Preliminary implications from the above data suggests that three reactions have a significant role in the replacement of coordinated water by nitrite ion. These are

$$NO_2^- + H_2O \leftrightharpoons HNO_2 + OH^-$$

$$2HNO_2 \leftrightharpoons N_2O_3 + H_2O$$

$$[Co(NSNSN)H_2O]^{3+} + OH^- \leftrightharpoons [Co(NSNSN)OH]^{2+} + H_2O$$

Mechanistically, these reactions imply that in weakly acidic aqueous media the nitrosation agent may be N_2O_3 and that attack would most likely occur at the oxygen atom of the coordinated hydroxy group. Assuming that N_2O_3 is the nitrosating agent under these conditions, and further that its order is one with respect to reaction with $[Co(NSSSN)OH]^{2+}$, allows the interpretation that $k_{obs} = k'[N_2O_3]$.

Isomerization study

The isomeric conversion of $[Co(NSNSN)ONO]^{2+}$ to $[Co(NSNSN)NO_2]^{2+}$ is fairly slow, requiring about 16 hours for complete reaction at 20°C. Table III presents conditions and values for the isomerization rate constant, k_{isom}. The rate constants determined at each temperature are remarkably consistent and independent of the quantity of the nitrite ion added. The calculated average values for k_{isom} at 20.0°C, 30.0°C, and 39.0°C are $1.81 \pm 0.11 \times 10^{-4}$, $0.52 \pm 0.08 \times 10^{-4}$ and $0.11 \pm 0.01 \times 10^{-4}\ s^{-1}$ respectively. Table III presents the calculated activation parameters from an Erying plot of $\ln(k_{isom}/T)$ *vs* $1/T$, giving $\Delta H^{\ddagger} = 109.3 \pm 1.0\ kJ\ mol^{-1}$, $\Delta S^{\ddagger} = +33.3 \pm 3.2\ J\ mol^{-1}\ K^{-1}$ and $\Delta G^{\ddagger} = 99.4 \pm 1.4\ kJ\ mol^{-1}$.

Crystal structure of $[Co(NSNSN)NO_2](ClO_4)_2$

One can draw four distinct geometric isomers for an octahedrally coordinated pentadentate ligand.[2] Figure 6 shows the geometrical structure and chelate ring conformation for $[Co(NSNSN)NO_2](ClO_4)_2$. The ligand exists in the $\alpha\alpha$ configuration, coordinated in a pseudo-octahedral environment through three nitrogen and two sulfur atoms. The *N*-alkyl group is *trans* to the site occupied by the replaceable monodentate group. The cation crystallized in a centrosymmetric space group but is not resolvable into optical isomers.[6] If one considers the number of individual chelate ring conformations that are theoretically possible for the pentadentate ligand, there are 16 different combinations, $\lambda\lambda\lambda\lambda$(one), $\lambda\delta\delta\delta$(four), $\lambda\lambda\delta\delta$(six), $\lambda\delta\delta\delta$(four), and

TABLE III
Isomerization rate constants for $[Co(NSNSN)ONO]^{2+}$.

Temp., °C	$[HNO_2] \times 10^4$/M	$[NO_2^-] \times 10^3$/M	$k_{isom} \times 10^4/s^{-1}$
39.0	5.00	3.96	1.92
	10.0	7.93	1.92
	15.0	11.9	1.75
	20.0	15.8	1.73
	30.0	23.8	1.72
30.0	5.00	3.96	0.652
	10.0	7.92	0.504
	15.0	11.9	0.476
	20.0	15.8	0.502
	30.0	23.8	0.486
20.0[a]	5.00	3.96	0.123
	10.0	7.92	0.102
	15.0	11.9	0.114
	20.0	15.8	0.100
	30.0	23.8	0.113

[a] k_{isom} at 25.0°C is $2.79 \times 10^{-5} s^{-1}$.

TABLE IV
Comparison of thermodynamic parameters and isomerization studies for $[Co(NSSSN)ONO]^{2+}$ and $[Co(NSNSN)ONO]^{24}$ complexes.[a]

Temp., °C	$Co(NSSSN)ONO^{2+}$ $k_{isom} \times 10^5/s^{-1}$	*Temp.*, °C	$Co(NSNSN)ONO^{2+}$ $k_{isom} \times 10^5/s^{-1}$
17.7	3.84±0.65	20.0	1.10±0.11
25.0	12.1±1.2	25.0	2.79[b]
35.0	53.9±1.3	30.0	5.24±0.83
		39.0	18.1±1.1
$\Delta H^‡$ kJ mol^{-1}	111.3±0.2	$\Delta H^‡$	109±1.1
$\Delta S^‡$ J $mol^{-1} K^{-1}$	53.3±0.7	$\Delta S^‡$	33.3±3.2
$\Delta G^‡$ kJ mol^{-1}	95.3±0.3	$\Delta G^‡$	99.4±1.4

a Reaction studied at: 430, 440, 469, 550 and 590 nm; pH range: 4.1 to 5.2; nitrite ion conc.: 0.03 to 0.20 M; ionic strength range: 0.11 to 0.60 M.

[b] Calculated from thermodynamic data.

δδδ(one). A λλδλ orientation is found to be present in $[Co(NSNSN)NO_2](ClO_4)_2$ starting from N3).

Bond lengths, bond angles and torsion angles for $[Co(NSNSN)NO_2]$-$(ClO_4)_2$ are presented in Tables V, VI, and VII, respectively. Calculated bond length averages nclude: Co-S = 2.231(2)Å, Co-N = 2.017(3)Å, S-C = 1.812(4)Å, N-C = 1.475(5)Å, and C-C = 1.504(5)Å. Among the S-C bonds, S1-C3 and S2-C6 (1.804 Å) are slightly horter than the other S-C bonds.

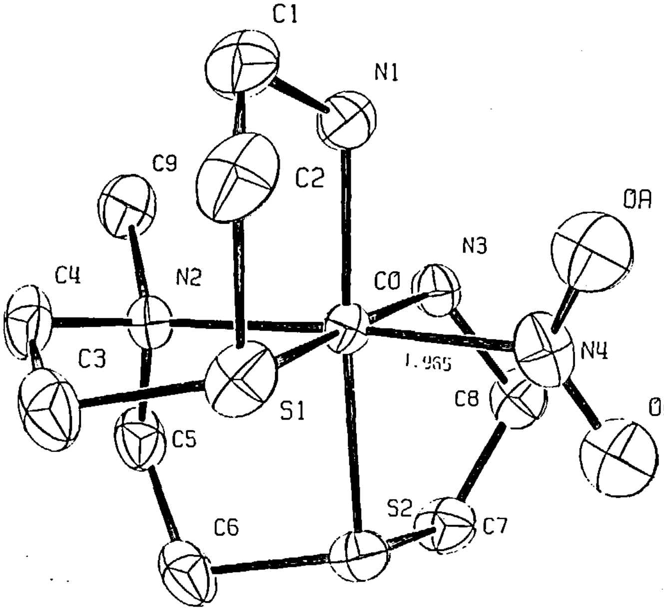


FIGURE 6 Perspective view of the $[Co(NSNSN)NO_2]^{2+}$ cation.

TABLE V

Bond lengths (Å) for $[Co(NSNSN)NO_2](ClO_4)_2$.

Co-N(1)	1.979(3)	Co-S(1)	2.225(2)
Co-N(2)	2.081(3)	Co-S(2)	2.237(1)
Co-N(3)	1.990(3)	Co-N(4)	1.954(3)
N(1)-C(1)	1.493(6)	C(1)-C(2)	1.507(7)
S(1)-C(2)	1.816(4)	S(1)-C(3)	1.804(4)
C(3)-C(4)	1.498(6)	N(2)-C(4)	1.507(4)
N(2)-C(5)	1.502(5)	N(2)-C(9)	1.497(4)
C(5)-C(6)	1.505(4)	S(2)-C(6)	1.804(4)
S(2)-C(7)	1.826(4)	C(7)-C(8)	1.508(5)
N(3)-C(8)	1.487(4)	N(4)-OA	1.234(4)
N(4)-OB	1.233(3)	Cl(1)-O(1)	1.430(3)
Cl(1)-O(2)	1.425(3)	Cl(1)-O(3)	1.429(3)
Cl(1)-O(4)	1.431(3)	Cl(2)-O(5)	1.414(9)
Cl(2)-O(6)	1.494(4)	Cl(2)-O(7)	1.354(7)
Cl(2)-O(8)	1.420(6)	Cl(2)-O(5′)	1.347(9)
Cl(2)-O(6′)	1.403(10)	Cl(2)-O(7′)	1.454(6)
Cl(2)-O(8′)	1.486(6)		

TABLE VI
Bond angles in degrees for [Co(NSNSN)NO$_2$](ClO$_4$)$_2$.

N(1)-Co-S(1)	88.5(1)	N(1)-Co-N(2)	94.1(1)
S(1)-Co-N(2)	88.8(1)	N(1)-Co-S(2)	177.1(1)
S(1)-Co-S(2)	93.0(1)	N(2)-Co-S(2)	88.4(1)
N(1)-Co-N(3)	91.1(1)	S(1)-Co-N(3)	176.5(1)
N(2)-Co-N(3)	94.8(1)	S(2)-Co-N(3)	87.3(1)
N(1)-Co-N(4)	89.0(1)	S(1)-Co-N(4)	86.2(1)
S(2)-Co-N(4)	88.5(1)	N(3)-Co-N(4)	90.3(1)
N(2)-Co-N(4)	174.0(1)	Co-N(1)-C(1)	115.8(3)
N(1)-C(1)-C(2)	109.9(6)	C(1)-C(2)-S(1)	112.8(3)
Co-S(1)-C(2)	98.7(1)	Co-S(1)-C(3)	100.1(1)
C(2)-S(1)-C(3)	104.5(2)	S(1)-C(3)-C(4)	111.4(3)
C(3)-C(4)-N(2)	114.9(2)	Co-N(2)-C(4)	111.5(3)
Co-N(2)-C(5)	109.1(2)	C(4)-N(2)-C(5)	110.5(2)
Co-N(2)-C(9)	115.0(2)	C(4)-N(2)-C(9)	105.0(2)
C(5)-N(2)-C(9)	105.5(3)	N(2)-C(5)-C(6)	113.3(3)
C(5)-C(6)-S(2)	109.1(2)	Co-S(2)-C(6)	99.7(1)
Co-S(2)-C(7)	99.6(1)	C(6)-S(2)-C(7)	100.9(2)
S(2)-C(7)-C(8)	110.(3)	C(7)-C(8)-N(3)	110.1(2)
Co-N(3)-C(8)	113.9(2)	Co-N(4)-OA	119.7(2)
Co-N(4)-OB	121.0(3)	OA-N(4)-OB	119.3(3)
O(1)-Cl(1)-O(2)	109.1(2)	O(1)-Cl(1)-O(3)	114.4(7)
O(2)-Cl(1)-O(3)	108.6(2)	O(1)-Cl(1)-O(4)	109.5(4)
O(2)-Cl(1)-O(4)	110-8(2)	O(3)-Cl(1)-O(4)	101.6(4)
O(5)-Cl(2)-O(6)	104.1(4)	O(5)-Cl(2)-O(7)	109.3(2)
O(6)-Cl(2)-O(7)	107.6(4)	O(5)-Cl(2)-O(8)	108.2(2)
O(6)-Cl(2)-O(8)	104.9(4)	O(7)-Cl(2)-O(8)	110.8(2)
O(5')-Cl(2)-O(6')	116.5(6)	O(5')-Cl(2)-O(7')	113.8(6)
O(6')-Cl(2)-O(7')	107.5(5)	O(5')-Cl(2)-O(8')	110.2(5)
O(6').Cl(2)-O(8')	106.0(5)	O(7')-Cl(2)-O(8')	115.2(5)

TABLE VII
Torsion angles in degrees for [Co(NSNSN)NO$_2$](ClO$_4$)$_2$.[a]

N2-Co-N3-C8	−114.4(0.2)	C6-C5-N2-C4	−78.4(0.3)
Co-N3-C8-C7	47.0(0.4)	C5-N2-C4-C3	88.2(0.4)
N3-C8-C7-S2	−43.7(0.4)	N2-C4-C3-S1	42.2(0.4)
C8-C7-S2-Co	21.8(0.2)	C4-C3-S1-Co	−28.7(0.3)
N3-Co-S2-C6	−101.1(0.1)	N2-Co-S1-C2	−97.5(0.1)
C8-C7-S2-C6	123.7(0.2)	C4-C3-S1-C2	73.1(0.3)
C7-S2-C6-C5	−71.3(0.3)	C3-S1-C2-C1	−77.9(0.3)
S2-C6-C5-N2	−51.0(0.3)	S1-C2-C1-N1	−41.3(0.5)
C6-C5-N2-Co	44.6(0.3)	C2-C1-N1-Co	39.0(0.5)
S2-Co-N2-C4	104.0(0.2)		

[a] The atomic sequence was renumbered here in order to allow a direct comparison between the chloro and nitro complexes.

Replacing the chloride ion with nitrite in [Co(NSNSN)Cl]$^{2+}$ causes the Co-S bonds Co-S1 and Co-S2 on the N1-S1-S2-N3 coordinated axial plane to become significantly longer, increasing from 2.209 Å(av) to 2.231 Å(av).[7,14] The Co-N2 bond length in[Co(NSNSN)NO$_2$]$^{2+}$, positioned *trans* to the coordinated NO_2^- group, is longer than the corresponding bond in the chloro complex. The Co-N2 bond length increases from 2.038 Å to 2.018 Å. For [Co(NSSSN)Cl]$^{2+}$ the Co-S2 bond length increases from 2.236 Å to 2.278 Å on replacement of Cl$^-$ by NO_2^-, respectively.[7] The Co-N2 and Co-S2 elongation in these two different complexes is almost identical, being around 0.042 Å. On the whole, the bond distance averages within the chelate ring moiety for C-C, C-N, and C-S are normal.

The hydrogen bonding network found in [Co(NSNSN)NO$_2$](ClO$_4$)$_2$ is tabulated in Table VIII. For [Co(NSNSN)NO$_2$](ClO$_4$)$_2$, an extensive hydrogen bonding network is evident. Three of the oxygen atoms (except for one O1) of the perchlorate group are bound to different carbon hydrogen atoms in different cations. The oxygen atoms of the NO_2^- ligand are also associated to nitrogen(N1) and carbon(C8)'s hydrogen atoms through intramolecular hydrogen bonding.

No close contact of sulfur donor atoms with the perchlorate anions is evident. It seems that the preference of the $\lambda\lambda\delta\lambda$ conformation is not dependent on the degree of hydrogen bonding, cell packing or unit cell dimensions, or the variation of the monodentate ligand. The same conformation is found in other compounds derived from the NSSSN and NSNSN ligands.[7]

Atomic positional parameters and estimated standard deviations are given in Table IX.

Mechanistic considerations for nitrite ion substitution

Oxygen labelling experiments have shown that addition of sodium nitrite to an aqueous solution (pH = 4) of CoLH$_2$O^{3+} results in the formation of CoLONO^{2+} without cleavage of the original Co-O bond.[15] L represents any combination of ligands or donor atoms that occupy five of the six coordination sites on an octahedral ion (*i.e.*, NSNSN and NSSSN).

TABLE VIII
Hydrogen bonding distances in [Co(NSNSN)NO$_2$](ClO$_4$)$_2$ (Å).

X-H...Y	X...Y	H...Y	X-H...Y	X...Y	H...Y
C1-H1C...O2^{b}	3.314	2.444	C3-H3A...O6^{h}	3.408	2.537
C4-H4A...O4^{f}	3.328	2.410	C5-H5B...O4^{f}	3.365	2.518
C6-H6B...O7'^{g}	3.319	2.446	C6-H6A...O3^{f}	3.256	2.700
C7-H7B...O5^{g}	3.328	2.825	C7-H7B...O5^{g}	3.109	2.643
C8-H8B...OB^{a}	2.985	2.361	C8-H8B...O8^{c}	3.311	1.587
C9-H9B...O2^{e}	3.417	2.530	C9-H9B...Cl1^{e}	3.528	2.894
N1-H1B...OA^{a}	2.737	2.165	N1-H1A...O2^{e}	3.160	2.404
N1-H1A...O3^{e}	3.351	2.448	N3-H3C...OA^{d}	2.992	2.192

Symmetry transformation is as follows: (a) x, y, z; (b) $x, 1+y, z$; (c) $x, -1+y, z$; (d) $1-x, -y, 1-z$; (e) $1-x, -y, -z$; (f) $-x, -y, -z$; (g) $-x, -y, 1-z$; (h) $-x, 1-y, 1-z$.

TABLE IX

Fractional atomic coordinates ($\times 10^4$) and temperature factors ($\times 10^3$) for $[Co(NSNSN)NO_2](ClO_4)_2$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Co	2704(1)	880(1)	3170(1)	23(1)
N(1)	4459(3)	2191(3)	2722(2)	33(1)
C(1)	4162(6)	3820(5)	2383(5)	44(2)
C(2)	2894(4)	4066(4)	3201(3)	47(1)
S(1)	1411(1)	2730(1)	3483(1)	38(1)
C(3)	455(4)	3387(4)	2113(3)	47(1)
C(4)	1324(4)	3109(4)	1075(3)	38(1)
N(2)	2053(3)	1605(3)	1404(2)	28(1)
C(5)	1030(4)	469(4)	1291(3)	36(1)
C(6)	−113(4)	−93(4)	2353(3)	39(1)
C(9)	3273(4)	1791(4)	425(3)	42(1)
S(2)	780(1)	−684(1)	3754(1)	32(1)
C(7)	1687(4)	−2382(4)	3699(3)	36(1)
C(8)	3318(4)	−2303(3)	3786(3)	35(1)
N(3)	3899(3)	−809(3)	2994(2)	28(1)
N(4)	3114(3)	270(3)	4879(2)	33(1)
OA	3902(3)	1061(3)	5204(2)	47(1)
OB	2577(3)	−883(3)	5645(2)	50(1)
Cl(1)	2900(1)	−2434(1)	76(1)	36(1)
O(1)	3672(3)	−2320(3)	1044(2)	50(1)
O(2)	3514(3)	−3616(3)	−277(2)	58(1)
O(3)	3070(5)	−1073(4)	−948(3)	72(2)
O4	1384(3)	−2721(4)	505(3)	77(2)
Cl(2)	2369(1)	3966(1)	6826(1)	49(1)
O(5)	1675(8)	3838(12)	5840(6)	103(5)
O(6)	1242(5)	3404(5)	7886(4)	68(2)
O(7)	3578(7)	3104(10)	7105(9)	138(6)
O(8)	2569(8)	5493(6)	6657(6)	98(3)
O(5′)	1147(8)	4148(13)	6227(9)	107(6)
O(6′)	2339(9)	4563(10)	7757(7)	104(5)
O(7′)	2862(10)	2431(6)	7325(8)	85(4)
O(8′)	3637(7)	4687(8)	5950(6)	83(3)
H(1a)	4997(3)	2053(3)	2032(2)	42(2)
H(1b)	5051(3)	1883(3)	3402(2)	42(2)
H(1c)	3931(6)	4234(5)	1549(5)	42(2)
H(1d)	5019(6)	4308(5)	2485(5)	42(2)
H(2a)	3239(4)	3985(4)	3968(3)	42(2)
H(2b)	2519(4)	5051(4)	2815(3)	42(2)
H3a)	279(4)	4438(4)	1898(3)	42(2)
H(3b)	−466(4)	2867(4)	2270(3)	42(2)
H(3c)	4878(3)	−711(3)	3194(2)	42(2)
H(3d)	3925(3)	−746(3)	2160(2)	42(2)
H(4a)	673(4)	3195(3)	457(3)	42(2)
H(4b)	2074(4)	3863(3)	757(3)	42(2)
H(5a)	1597(4)	−366(4)	1237(3)	42(2)
H(5b)	540(4)	917(4)	560(3)	42(2)
H(6a)	−791(3)	695(4)	2339(3)	42(2)
H(6b)	−635(3)	−919(4)	2298(3)	42(2)
H(7a)	1527(4)	−2495(3)	2941(3)	42(2)
H(7b)	1278(4)	−3226(3)	4364(3)	42(2)
H(8a)	3804(3)	−3054(3)	3528(3)	42(2)
H(8b)	3498(3)	−2477(3)	4616(3)	42(2)
H(9a)	3786(4)	863(4)	584(3)	42(2)
H(9b)	3946(4)	2553(4)	404(3)	42(2)
H(9c)	2859(4)	2064(4)	−346(3)	42(2)

* U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensors.

In the presence of acid, nitrite ion is protonated, forming nitrous acid, which in turn partially decomposes to produce NO and HNO_3 by the reaction $3\,HNO_2 \rightleftharpoons HNO_3 + 2\,NO + H_2O$. The active nitrosation reagent present in acidic solutions of nitrite ion, is postulated to be either NO^+ ot N_2O_3. It is thought that N_2O_3 exists in solution as a loosely bound aggregate[16] formulated as $NO^+NO_2^-$. The formation of NO^+ also can be envisaged as being formed from the protonation of nitrous acid.[17–20]

$$2\,HNO_2 \overset{K_1}{\rightleftharpoons} N_2O_3(NO^+NO_2^-) + H_2O$$

$$H^+ + HNO_2 \overset{K_2}{\rightleftharpoons} H_2NO_2^+ \overset{k_3}{\rightarrow} H_2O + NO^+$$

The best explanation, mechanistically consistent with the individual chemistries of all the participant species, is summarized in the reactions below.[17]

$$\begin{array}{ll}
2\,NO_2^- + 2\,H^+ \rightleftharpoons 2\,HNO_2 & K_a \\
2\,HNO_2 \rightleftharpoons N_2O_3 + H_2O & K_d \\
CoLH_2O^{3+} \rightleftharpoons CoLOH^{2+} + H^+ & K_{Co} \\
CoLOH^{2+} + N_2O_3 \rightarrow CoLONO^{2+} + HNO_2 & k_1
\end{array}$$

One can use the principles of steady state kinetics to derive a relationship between k_{obs} and the equilibrium constants for the above reactions.

$$k_{obs} = \left\{\frac{k_1 K_{Co}}{K_{Co} + [H^+]}\right\}\{N_2O_3\}$$

$$k_{obs} = \left\{\frac{k_1 K_{Co} K_d}{K_{Co} + [H^+]}\right\}\left\{\frac{[H^+][\text{total } NO_2^-]}{K_a + [H^+]}\right\}^2$$

Knowing k_{obs} and the other parameters in the equation, one would predict that k_1 should be constant over a range of HNO_2 and NO_2^- concentrations. Literature values[7,17] for the other constants are $k_a = 10^{-2.8}$, $K_d = 0.2\,M^{-1}$, $k_{Co} = 10^{-6.85}$ for $[Co(NSNSN)H_2O]^{3+}$. Using these values, the data in Table I, and the above equation, did not give a constant value for k_1 as shown in Table X. A definite trend to smaller k_1 values occurs as the $[NO_2^-]$ and $[HNO_2]$ increase. This may occur because a finite amount of N_2O_3 escapes from solution and thus is unavailable for reaction.

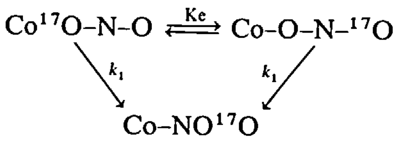
Mechanism of isomerization

The fate of $CoLONO^{2+}$ is determined by the acidity of the aqueous solution. In acidic media, it can rapidly undergo acid-catalyzed aquation, giving $CoLH_2O^{3+}$ and an as yet unidentified acidic form of NO^+, or it can isomerize to the more stable

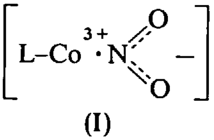
TABLE X
Calculated k_1 values for the reaction of $[Co(NSNSN)H_2O]^{3+}$ with nitrite ion.

$[NO_2^-] \times 10^3$ M	$k_1 \times 10^{-7}/M^{-1}s^{-1}$ at 20.0°C	$k_1 \times 10^{-7}/M^{-1}s^{-1}$ at 30.0°C	$k_1 \times 10^{-7} M^{-1}s^{-1}$ at 39.0°C
3.96	0.186	1.37	2.26
7.92	0.107	0.569	1.15
11.9	0.072	0.228	0.652
15.8	0.953	0.136	0.500
23.8	0.032	0.118	0.276

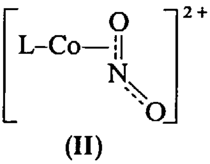
nitro form, $CoLNO_2^{2+}$. One must ask, how this occurs. Studies using oxygen-18 and oxygen-17 atoms (NMR) demonstrate that[21,22] on substitution, the oxygen atom of the OH or H_2O originally bound to cobalt ends up in the Co-O-N-O moiety.[15] Oxygen scrambling ($Co\text{-}^{17}O\text{-}N\text{-}O \rightleftharpoons Co\text{-}O\text{-}N\text{-}^{17}O$) does occur at a slow rate during the spontaneous isomerization process and a rapid scrambling of oxygen atoms occurs in the acid-catalyzed aquation



of $CoLONO^{2+}$. It is apparent that the mechanism by which the nitrito complex is formed initially, is different from the mechanism by which acid-catalyzed aquation takes place. At least three intermediates can be envisionedto accommodate the intramolecular quintessence of oxygen-to-nitrogen isomerization. The most obvious but least likely arrangement is the formulation of an ion-pair between the nitrite ion and the cobalt-complex, (I). The reasons for this include the fact that ion-apris dissociate in water, added labelled nitrite ion does not exchange with the cobalt complex,[15] and the experimentally determined negative activation volume for the reaction is inconsistent with an expanded transition state.[24] A second grouping such as in (II) can satisfy the oxygen-to-nitrogen isomerization but cannot provide an unequivocal interpretation for the spontaneous oxygen-to-oxygen scrambling. A π-bonded structure such as in (III) would

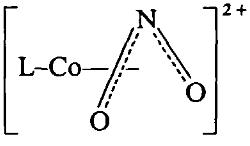


(I)



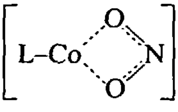
(II)

allow effective competition by both oxygen atoms and the nitrogen atom for the cobalt(III) centre; this is also consistent with a negative activation volume and retention

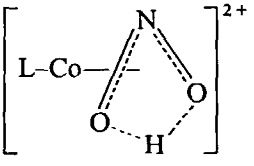


(III)

of the Co-nitrite bond. Unfortunately, this intermediate cannot explain the rapid acid-catalyzed aquation of $CoLONO^{2+}$. The rapid oxygen exchange during aquation of the nitrito complex may be promoted by an unstable, protonated version of (III). Structures such as (IV) and (V) could ameliorate the 50% retention of oxygen label in the $CoLH_2O^{3+}$ product.[24] Obviously, additional study, focussed on the nature of the intermediates is needed.



(IV)



(V)

Structure and reactivity patterns

According to Jackson *et al.*,[21,22,25] the activated isomerization intermediate for $[Co(NH_3)_5ONO]^{2+}$ favours a six-coordinated π-bonded arrangement rather than the formation of a hepta-coordinated complex ion. Based on the extreme inertness of both $[Co(NSNSN)Cl]^{2+}$ and $[Co(NSSSN)Cl]^{2+}$ toward spontaneous acid hydrolysis, we considered the possibility that an increase in both σ and π bonding in the Co-Cl bond may be operative. The Co-Cl bond length[7,14] of 2.268(1)Å in $[Co(NSSSN)Cl]^{2+}$, and 2.263(1)Å in $[Co(NSNSN)Cl]^{2+}$ *vs* 2.286 Å in $[Co(NH_3)_5Cl]^{2+}$ suggests that a significant π interaction is available for the Cl or ONO group. The electron donating property of the tertiary amine in $[Co(NSNSN)ONO]^{2+}$ may somewhat reduce the π bonding interaction and thus result in the decrease of its isomerization rate constant. We do observe a four-fold decrease in the rate of nitrito-to-nitro isomerization when the central thioether donor is replaced with a tertiary amine.

One interesting feature in these structures is that the nitro ligand does influence the *trans* Co-N or the *trans* Co-S bond lengths in $[Co(NSSSN)NO_2]^{2+}$ and $[Co(NSNSN)NO_2]^{2+}$. The *trans* Co-S or Co-N bond distances in these complexes are 2.278(1)Å and 2.081(3)Å, respectively. In the parent chloro complexes the corresponding bond lengths are 2.236(1)Å and 2.038(8)Å, respectively. Typically a Co-N bond distance is about 1.960 Å for cobalt(III) metal ions coordinated to various polydentate ammine ligands.[26,27] In our case, it is clearly demonstrated that the NO_2^- ligand exerts a structural *trans* bond elongation of ~0.042 Å on both the *trans* Co-S and the *trans* Co-N bonds of the coordinated NSSSN and NSNSN ligands.

The rates of ONO-to-NO_2 isomerization reported in the literature for cobalt(III) complexes were recently summarized.[1,2] Surprisingly, there have been very few compounds studied. One would like ideally to correlate specific rate differences with structural factors such as charge on the complex, degree and type of chelation, geometrical isomer factors, bonding nature and/or the basicity of the group positioned *cis*- or *trans*- to the site of isomerization. It appears that the degree of chelation (number of connected chelate rings that make up the ligand) does not uniformly affect the rate constant for isomerization. Likewise, the size of the chelate ring (2, 3 or more connected carbon atoms) and the charge carried by the complex ion has little affect on the rate constant. Such non-specific chelation effects suggests that any geometrical distortion of the complex ion during isomerization remains localized within the axial plane of the complex.[1] The above general observations suggest that we need to know more about the role of the reorganization of the solvation sheath around the complex in order to understand differences in isomerization rates.

A single divergent feature stands out in any comparison of nitro-to-nitro isomerization rate data, the thermodynamic parameters. $\Delta H^\ddagger$ for eleven compounds[2] averages $+90\,\mathrm{kJ\,mol^{-1}}$ whereas cyclam, NSNSN and NSSSN complexes are +115, +109 and $+111\,\mathrm{kJ\,mol^{-1}}$, respectively. Likewise, $\Delta S^\ddagger$ for the same group averages −20 e.u. but the cyclam, NSNSN and NSSSN complexes exhibit values of +40, +53, and +33 e.u., respectively. Molecular models show that the extended ligand framework in $[\mathrm{Co(cyclam)ONO}]^{2+}$, $[\mathrm{Co(NSNSN)ONO}]^{2+}$ and $[\mathrm{Co(NSSSN)ONO}]^{2+}$ creates a larger, more disrupted solvent sheath around the complex. The unique differences in $\Delta S^\ddagger$ may reflect the degree of solvent "tightness" which the isomerization intermediate expeiences.

It is reported that α-$[\mathrm{Co(tetran)(ONO)}]^{2+}$ isomerizes with a geometric change to form the β-$[\mathrm{Co(tetran)NO_2}]^{2+}$ isomer.[28] Also, Rindermann and Eldik[29] reported that *cis*-$[\mathrm{Co(en)_2(NO_2)_2}]^+$, with heating at 86°C, is transformed into *trans*-$[\mathrm{Co(en)_2(NO_2)_2}]^+$ with a half life *ca* 20 hours. In the present study, we did not observe any abnormal spectral changes or see any evidence for geometrical change occurring during substitution or isomerization.

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