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Structural and Mechanistic Studies of Coordination Compounds. 14.[1] Preparation and Acid Hydrolysis of Some Trans Isothiocyanato Macrocyclic Quadridentate Amine Complexes of Cobalt (III)

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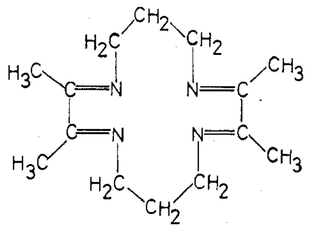
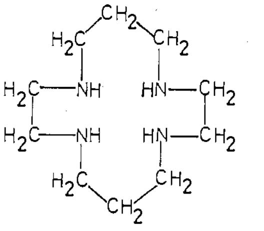
trans-$[Co(TIM)NCSX]^+$ [TIM = 1,4,8,11-tetraaza-2,3,9,10-tetramethylcyclotetradeca-1,3,8,10-tetraene (I); X = Cl, Br] cations have been prepared through a series of intermediate compounds. The specific rates at which an external nucleophile substitutes for X in *trans*-$[CoLNCSX]^+$ have been shown to increase in the following order of L: cyclam < DIM < TIM [cyclam = 1,4,8,11-tetraazacyclotetradecane (II) and DIM = 1,4,8,11-tetraaza-2,3-dimethylcyclotetradeca-1,3-diene (III); at 1:400:1640 for X = Cl and 1:44:170 for X = Br at 25.0 °C]. On the other hand, the kinetic ratio of k_{Br}/k_{Cl} decreases in the above order of L. A linear free energy relationship between these kinetic data and those of the corresponding azido complexes is discussed.

Introduction

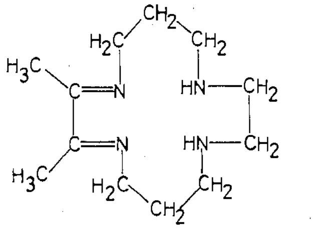
In a previous paper[2] we have shown that the kinetic ratio of k_{Br}/k_{Cl} for the acid hydrolysis of *trans*-$[CoLN_3X]^+$ was about 10 for saturated macrocyclic amines, such as cyclam (1,4,8,11-tetraazacyclotetradecane, II) and teta (*meso*-1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradecane, IV), and that this ratio decreased to about 1.4 for DIM (1,4,8,11-tetraaza-2,3-dimethylcyclotetradeca-1,3-diene, III) and 1.1 for TIM (1,4,8,11-tetraaza-2,3,9,10-tetramethylcyclotetradeca-1,3,8,10-tetraene, I). On the other hand, the kinetic lability of corresponding complexes increased in the order of cyclam < DIM < TIM. It is desirable to see if this trend of kinetic behavior applies also to a different orienting ligand. This paper describes the preparation and kinetic studies of some of these macrocyclic amine complexes containing the isothiocyanate ligand.



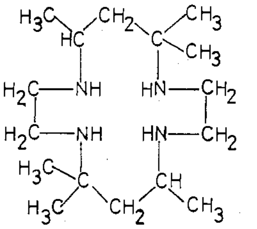
TIM, I



cyclam, II



DIM, III



teta, IV

Experimental Section

Preparation of Complexes. ***trans*-Azidoisothiocyanato(1,4,8,11-tetraaza-2,3,9,10-tetramethylcyclotetradeca-1,3,8,10-tetraene)cobalt(III) perchlorate** (*trans*-$[Co(TIM)N_3NCS]ClO_4$) was prepared by adding an ethanolic solution of NH_4NCS (0.13 g in 10 ml) to *trans*-$[Co(TIM)N_3OH_2](ClO_4)_2{\cdot}H_2O$[2] in a 1:1 mixed ethanol/acetone solvent (1 g in 50 ml). A brown solid came out almost immediately and was then filtered off, washed with ethanol and ether, and air-dried.

***trans*-Aquaisothiocyanato(1,4,8,11-tetraaza-2,3,9,10-tetramethylcyclotetradeca-1,3,8,10-tetraene)cobalt(III) perchlorate monohydrate** (*trans*-$[Co(TIM)NCSOH_2](ClO_4)_2{\cdot}H_2O$) was prepared by boiling for 1 min a suspension of *trans*-$[Co(TIM)N_3NCS]ClO_4$ in ethanol (1 g in 50 ml) which was acidified with $HClO_4$ (70%, 25 ml). The solution was cooled and filtered to remove the undissolved solid. A 1:1 mixed ethanol/acetone solvent (100 ml) was added to the deep purple filtrate. Addition of ether precipitated out an orange solid. This was filtered off, washed with a 1:6 mixed ethanol/ether solvent and then with ether, and dried under vacuum at 65 °C.

Table I. Elemental Analyses and Visible Absorption Spectra of Some *trans*-$[CoLAX]^{n+}$ Complexes

Complexes	Elemental analyses,[a] %	Visible absorption spectra,[b] nm
$[Co(TIM)N_3NCS]$-ClO_4	C, 35.6 (35.6); H, 4.7 (4.7); N, 22.1 (22.1)	λ_{max} 522 (392), λ_{min} 477 (221)
$[Co(TIM)NCSOH_2]$-$(ClO_4)_2{\cdot}H_2O$	C, 29.8 (30.0); H, 4.6 (4.7); N, 11.8 (11.7)	λ_{max} 500 (215), λ_{min} 471 (190)
$[Co(TIM)NCSCl]$-ClO_4	C, 35.8 (36.0); H, 4.7 (4.8); N, 14.0 (14.0); Cl, 13.9 (14.2); S, 6.3 (6.4)	λ_{max} 507 (119), λ_{min} 477 (94)
$[Co(TIM)NCSBr]$-ClO_4	C, 32.9 (33.1); H, 4.3 (4.4); N, 12.7 (12.9); Br, 14.4 (14.7); S, 5.9 (5.9)	λ_{max} 509 (114), λ_{min} 483 (102)
$[Co(TIM)(NCS)_2]$-ClO_4	C, 36.6 (36.8); H, 4.8 (4.6); N, 16.0 (16.1); Cl, 6.5 (6.8); S, 12.2 (12.3)	λ_{max} 503 (165), λ_{min} 475 (146)
$[Co(DIM)(NCS)_2]$-ClO_4	C, 33.9 (33.7); H, 4.8 (4.8); N, 17.1 (16.9); Cl, 7.1 (7.2)	λ_{max} 521 (435), λ_{min} 459 (155)

[a] Calculated values are given in parentheses. [b] Molar absorptivities (cm^{-1} M^{-1}) are given in parentheses.

The preparations of *trans*-$[Co(TIM)NCSX]ClO_4$ (X = Cl, Br) were carried out in a fashion analogous to that of *trans*-$[Co(TIM)N_3NCS]ClO_4$ by adding an ethanolic solution of NH_4X to *trans*-$[Co(TIM)NCSOH_2](ClO_4)_2{\cdot}H_2O$ in a 1:1 mixed ethanol/acetone solvent. Addition of ether precipitated out the desired pale yellow product.

trans-$[CoL(NCS)_2](ClO_4)$ (L = TIM, DIM) compounds were prepared by adding excess NH_4NCS (1 g) to a hot aqueous solution of the corresponding *trans*-$[CoLBr_2]ClO_4$[3] (1 g in 50 ml). Addition of a concentrated solution of $NaClO_4$ to the cooled, filtered solution precipitated out the desired yellowish brown crystalline product.

Yields of the above preparations were all in the range 75 ± 10%. Elemental analyses and visible spectra of the new complexes are collected in Table I.

Table II. First-Order Rate Constants for the Acid Hydrolysis of *trans*-[Co(cyclam)NCSBr]$^+$ in 0.01 M Nitric Acid

Temp, °C	10^5k,[a] s^{-1}	Temp, °C	10^5k,[a] s^{-1}
68.5	2.90	86.6	42.0
74.0	7.20	90.1	70.6
83.5	28.2		

[a] Each entry represents an average of three different runs over a range of complex concentration (6.0–16.2 mM).

Other complexes, *trans*-[$CoLX_2$]ClO_4 (L = DIM, TIM; X = Cl, Br), were prepared by the method of Busch,[3] and *trans*-[Co(cyclam)NCSBr]ClO_4 was kindly supplied by Mak.[4]

Kinetics. The acid hydrolysis of *trans*-[Co(cyclam)NCSBr]$^+$ was followed by sampling the complex solution, made up at room temperature, into different Pyrex tubes which were sealed and placed "simultaneously" into a thermostat. After thermal equilibrium had been attained, tubes were withdrawn at regular intervals and quickly cooled. The solutions were then warmed to room temperature and the visible spectra were recorded using a Unicam SP8000 spectrophotometer. The substitution reactions of *trans*-[$CoLX_2$]$^+$ (L = DIM, TIM) and *trans*-[Co(TIM)NCSX]$^+$ (X = Cl, Br) by thiocyanate were followed spectrophotometrically in situ using a Unicam SP700 or SP8000 spectrophotometer; the latter was equipped with a digital printer, Weyfringe ADCP-2. The reaction was started by dissolving the appropriate complex in a thermostated reagent solution of KNCS in dilute nitric acid. The reaction solution was immediately transferred to a glass cell at the temperature-controlled cell holder of a spectrophotometer and the changing absorbance at a fixed wavelength was recorded as a function of time (at 521 nm for DIM and 503 nm for TIM complexes). Reactions were studied over a range of complex (0.10–0.35 mM for DIM and 0.35–0.80 mM for TIM complexes), acid (0.005-0.01M), and thiocyanate (0.1–1.0M) concentrations. The reaction temperature, accurate to ±0.1 °C, was measured at the end of the reaction.

Physical Measurements. Visible and ultraviolet absorption spectra of complex solutions were measured with a Unicam SP8000 spectrophotometer. Infrared spectra of the complexes in a KBr disk were measured with a Perkin-Elmer 577 spectrophotometer.

Results

(1) Acid Hydrolysis of *trans*-[Co(cyclam)NCSBr]$^+$. In dilute nitric acid (0.01 M) the visible absorption spectrum of *trans*-[Co(cyclam)NCSBr]$^+$ slowly changed to that of *trans*-[Co(cyclam)NCSOH_2]$^{2+}$ [5] with an isosbestic point maintained at 582 nm throughout the entire reaction. Volhard's titration[6] confirmed that the release of bromide was complete at the end of the reaction. This behavior is quite different from that of *trans*-[Co(cyclam)NCSCl]$^+$ which only aquated to ca. 35% completion.[5] The first-order rate constants were obtained from the increasing absorbance at 550 nm using the standard semilogarithmic plots of ln ($D_\infty - D_t$) vs. time, where D_∞ and D_t represent the absorbances after 10 half-lives and at time *t*, respectively. These plots were straight to 2 half-lives. Agreement between runs was generally better than 5%. The kinetic data are collected in Table II.

(2) Substitution Reactions of *trans*-[Co(TIM)NCSX]$^+$ and *trans*-[Co(DIM)X_2]$^+$ (X = Cl, Br) by Thiocyanate. The spectral change in the visible region associated with the acid hydrolysis of *trans*-[Co(TIM)NCSX]$^+$ (X = Cl, Br) was rather complex. Both ionic thiocyanate and halide were detected in the course of the reaction. Samples of reaction solution of the complex in 0.01 M nitric acid at 55 °C were withdrawn at different intervals and passed through a cation-exchange resin column of Amberlite IR-120 in the acid form. The effluent was equally divided into two parts. One part was analyzed for thiocyanate spectrophotometrically at 450 nm[7] using acidified Fe(NO_3)$_3$ and a standard calibration curve. The other part was analyzed for the total concentration of thiocyanate and halide by Volhard's titration.[6] It was found that total ionic thiocyanate and halide increased with time. To follow the rate of chloride release alone, the thiocyanate substitution reaction of these TIM complexes was investigated. Here, the thiocyanate substitution of the coordinated thiocyanate did not lead to any net chemical reaction. When *trans*-[Co(TIM)NCSX]$^+$ was dissolved in 0.01 M nitric acid containing 0.1 M thiocyanate ions, the visible absorption spectrum slowly changed to that of *trans*-[Co(TIM)(NCS)$_2$]$^+$. The semilogarithmic plots of the increasing absorbances, i.e., plots of ln ($D_\infty - D_t$) vs. time, were straight to over 2 half-lives, and the rate constants obtained, which were accurate to better than 5%, were independent of wavelength chosen for kinetic plots and of acid (5–10 mM), complex (0.35–0.80 mM), and thiocyanate (0.1–1.0 M) concentrations. At higher acid concentrations, the reaction was complicated by some side redox reactions involving thiocyanate. When the reaction was started with *trans*-[Co(TIM)X_2]$^+$, the first observable spectrum at a temperature above 45 °C was that of *trans*-[Co(TIM)NCSX]$^+$, confirming that the acid hydrolysis of *trans*-[Co(TIM)X_2]$^+$ was relatively very fast.[8] The subsequent spectral changes and kinetics were identical with those described above starting with the pure *trans*-[Co(TIM)NCSX]$^+$. When *trans*-[Co(DIM)X_2]$^+$ was dissolved in acidified thiocyanate solution at a temperature above 50 °C, the green color of the complexes instantaneously changed through dark green to red. The observable spectral changes maintained an isosbestic point at 570 nm (for both X = Cl and X = Br) throughout the entire reactions. The final spectrum was identical with that of *trans*-[Co(DIM)(NCS)$_2$]$^+$. The first observable spectra were distinctly different from those of *trans*-[Co(DIM)X_2]$^+$ in the presence of a large excess of X. In view of the relatively fast acid hydrolysis of *trans*-[Co(DIM)X_2]$^+$ [8] and the behavior of the corresponding TIM complexes described above, it seemed reasonable to assume that the observed spectral changes corresponded to the second step of the reactions

Table III. First-Order Rate Constants for the Thiocyanate Substitution Reactions of *trans*-[CoLNCSX]$^+$ in Dilute Nitric Acid

L	X	Temp, °C	10^4k,[a] s^{-1}
DIM	Cl	57.7	0.62
DIM	Cl	61.7	1.11
DIM	Cl	64.7	1.48
DIM	Cl	68.1	2.44
DIM	Cl	71.5	3.89
DIM	Br	57.7	1.36
DIM	Br	58.2	1.49
DIM	Br	62.2	2.76
DIM	Br	67.6	6.00
DIM	Br	71.3	10.1
DIM	Br	75.7	18.4
TIM	Cl	49.5	0.76
TIM	Cl	54.8	1.60
TIM	Cl	60.8	3.60
TIM	Cl	64.2	5.53
TIM	Br	50.5	0.98
TIM	Br	56.0	2.14
TIM	Br	60.2	3.60
TIM	Br	64.8	6.48

[a] Each entry represents an average of two to four different runs. The rate constant was independent of acid (5–10 mM), thiocyanate (0.1–1.0 M), and complex (0.10–0.35 mM for DIM and 0.35–0.80 mM for TIM complexes) concentrations.

$$\mathit{trans}\text{-}[\mathrm{Co(DIM)X_2}]^+ + \mathrm{NCS}^- \xrightarrow{\text{fast}} \mathit{trans}\text{-}[\mathrm{Co(DIM)NCSX}]^+ + \mathrm{X}^- \quad (1)$$

$$\mathit{trans}\text{-}[\mathrm{Co(DIM)NCSX}]^+ + \mathrm{NCS}^- \xrightarrow{\text{slow}} \mathit{trans}\text{-}[\mathrm{Co(DIM)(NCS)_2}]^+ + \mathrm{X}^- \quad (2)$$

The kinetics of thiocyanate substitution reactions of *trans*-[Co(DIM)NCSX]$^+$ (i.e., step 2) was found to be similarly independent of wavelength and of acid, complex, and thiocyanate concentrations. The semilogarithmic plots were

Table IV. First-Order Rate Constants at 25.0 °C and Activation Parameters for the Acid Hydrolysis or Thiocyanate Substitution Reactions of Complexes of the Type *trans*-$[CoLNCSX]^+$ [a]

L	k_{Br}, s^{-1}	k_{Cl}, s^{-1}	k_{Br}/k_{Cl}	$\Delta H^{\ddagger}_{Br}$, kcal mol^{-1}	$\Delta H^{\ddagger}_{Cl}$, kcal mol^{-1}	$\Delta S^{\ddagger}_{Br}$, cal K^{-1} mol^{-1}	$\Delta S^{\ddagger}_{Cl}$, cal K^{-1} mol^{-1}
Cyclam	1.3×10^{-8} [b,c]	1.1×10^{-9} [d,e]	11.8	35.5 ± 0.4	34.5 ± 0.3	25 ± 4	17 ± 3
teta	6.1×10^{-6} [f]	7.0×10^{-7} [d,g]	8.7	30.2 ± 0.3	27.5 ± 0.4	19 ± 2	5 ± 2
trans[14]diene	3.0×10^{-6} [f]	1.4×10^{-6} [f]	2.1	30.2 ± 0.3	26.5 ± 0.4	18 ± 2	4 ± 2
DIM	5.7×10^{-7} [b,h]	4.4×10^{-7} [b,h]	1.3	32.4 ± 0.3	29.1 ± 0.6	21 ± 2	10 ± 2
TIM	2.2×10^{-6} [b,h]	1.8×10^{-6} [b,h]	1.2	28.1 ± 0.4	28.7 ± 0.3	10 ± 2	11 ± 2

[a] All acid hydrolysis reactions except those for DIM, TIM, and *trans*-$[Co(cyclam)NCSCl]^+$ complexes. [b] This work. [c] In 0.01 M HNO_3. [d] W. K. Chau, W. K. Lee, and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2419 (1974). [e] Thiocyanate substitution reactions by 0.01–0.05 M KNCS in 0.01 M HNO_3. [f] W. K. Lee and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2423 (1974); in 0.01–0.1 M $HClO_4$ and at $\mu = 0.1$ M with $NaClO_4$. [g] In 0.01–0.1 M HNO_3 and at $\mu = 0.1$ M with $NaNO_3$. [h] Thiocyanate substitution reactions by 0.1–1.0 M KNCS in 0.005–0.01 M HNO_3.

Scheme I. Synthesis of *trans*-$[Co(TIM)NCSX]^+$ (X = Cl, Br)

$$\begin{aligned}
&trans\text{-}[Co(TIM)Br_2]ClO_4 \xrightarrow{NaN_3} trans\text{-}[Co(TIM)(N_3)_2]ClO_4 \\
&\xrightarrow{AgClO_4} trans\text{-}[Co(TIM)N_3OH_2](ClO_4)_2\cdot H_2O \\
&\xrightarrow{NH_4NCS} trans\text{-}[Co(TIM)N_3NCS]ClO_4 \\
&\xrightarrow{HClO_4} trans\text{-}[Co(TIM)OH_2NCS](ClO_4)_2\cdot H_2O \\
&\xrightarrow{NH_4X} trans\text{-}[Co(TIM)NCSX]ClO_4
\end{aligned}$$

straight over 2 half-lives. Agreement between runs was better than 5%. These data are collected in Table III. Activation enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) were obtained by the least-squares plot of ln (k/T) vs. $1/T$, where k represents the average appropriate rate constant, at a temperature T in the absolute scale, of the following absolute theory of rate processes with unit transmission coefficient[9]

$$k = \frac{RT}{Nh} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

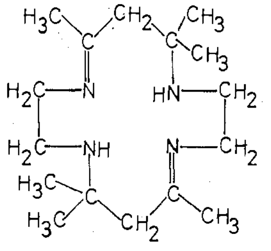
where R represents the universal gas constant, N Avogadro's number, and h Planck's constant.

The activation parameters and rate constants extrapolated to 25.0 °C for the acid hydrolysis or thiocyanate substitution reactions of some of these isothiocyanate–macrocyclic amine complexes are collected in Table IV.

Discussion

The preparation of these *trans*-halogenoisothiocyanato DIM and TIM complexes by the conventional method of treating the appropriate dihalogeno complexes with a stoichiometric amount of thiocyanate was unsuccessful. Analytically pure samples of *trans*-$[Co(TIM)NCSX]ClO_4$ (X = Cl and Br) were prepared from *trans*-$[Co(TIM)Br_2]ClO_4$[3] by an indirect method with an overall yield of ca. 25%, as represented by Scheme I. However, attempts to prepare the corresponding *trans*-$[Co(DIM)NCSX]^+$ complexes have not been successful.

The assignment of a *trans* configuration to the new complexes was made on the basis that these complexes were prepared from *trans*-$[CoLBr_2]^+$ (L = DIM, TIM)[3] and that they could all be converted back to *trans*-$[CoLX_2]^+$ with an excess of X (X = Cl, Br). It is known that ligand substitution reactions of *trans* macrocyclic amine–cobalt(III) complexes proceed with complete retention of configuration.[10] The mode of coordination of the ambidentate thiocyanate ligand in *trans*-$[Co(DIM)(NCS)_2]ClO_4$ was clearly shown to be N bonded by the presence of an infrared band of medium intensity at 857 cm^{-1} assignable to μ(C–S) of an N-bonded thiocyanate,[11] which was absent in the spectra of *trans*-$[Co(DIM)X_2]ClO_4$. However, the mode of coordination is less unambiguous for the TIM complexes. Although bands in the range 690–720 cm^{-1} assignable to μ(C–S) of an S-bonded thiocyanate could not be detected as in the case of *trans*-$[Co(DIM)(NCS)_2]ClO_4$, it was not possible to assign any band in the range 780–860 cm^{-1} to the N-bonded thiocyanate species in these complexes since *trans*-$[Co(TIM)Cl_2]ClO_4$ also showed a number of bands in this region. The absence of any S-bonded μ(C–S) band, however, was taken to indicate that the ligand might probably be N bonded. For all of these TIM complexes, the singlet μ(C–N) bands occurred in the 2100–2110-cm^{-1} region, which was compatible with those in other well-characterized isothiocyanato(macrocyclic amine)cobalt(III) complexes, such as *trans*-$[Co(cyclam)(NCS)_2](PtCl_6)_{1/2}$ at 2110 cm^{-1}, *trans*-$[Co(cyclam)NCSBr]ClO_4$ at 2100 cm^{-1},[4] *trans*-$[Co(teta)(NCS)_2](NCS)\cdot H_2O$ at 2118 and 2107 cm^{-1},[12] *trans*-[Co(trans[14]diene]$NCSCl]ClO_4$ at 2110 cm^{-1},[13] and *trans*-[Co(trans[14]diene)$NCSBr]ClO_4$ at 2115 cm^{-1},[13] where trans[14]diene represents 1,4,8,11-tetraaza-5,5,7,12,12,14-hexamethylcyclotetradeca-1,7-diene, V. This tentative assignment of a N-bonding mode for these TIM complexes was supported by the fitting of the kinetic data of *trans*-$[Co(TIM)NCSX]^+$ into the linear free energy plots to be discussed.



trans[14]diene, V

It has been discussed previously[2,10,13] for macrocyclic amine complexes of the type *trans*-$[CoLAX]^{n+}$ that the polarizability of the central cobalt(III) ion would probably increase with increasing extent of electronic delocalization between the metal ion and the encircling unsaturated macrocycle. This idea is now supported by the observed decreasing ratio of k_{Br}/k_{Cl} from about 10 for saturated macrocyclic amine complexes to about unity for unsaturated DIM and TIM complexes, independent of the nature of the orienting ligand, isothiocyanate or azide,[2] and also by the observation that isothiocyanate is released concurrently with chloride in the unsaturated *trans*-$[Co(TIM)NCSX]^+$ complexes. In saturated macrocyclic cyclam[5] and teta[14] complexes, as well as in other bis(ethylenediamine)-type[15,16] and tetraammine-type complexes,[5] preferential or concurrent release of the coordinated isothiocyanate ligand with halide has never been observed. Since teta and trans[14]diene complexes exhibit serious steric effects,[2,13,14] their aquation rate constants do not directly respond to electronic effects. The following discussion will only be confined to cyclam, DIM, and TIM complexes, where steric and solvation effects are not expected to play an important role in affecting the trend of the kinetic lability of these complexes.[2] The observed increasing lability of corresponding complexes in the order of cyclam < DIM < TIM (1:400:1640

Table V. Some First-Order Rate Constants for the Acid Hydrolysis of Complexes of the Type *trans*-$[CoLAX]^+$ at 25.0 °C[a]

L	X	log k_{NCS}	log k_{N_3}
Cyclam	Cl	−8.96	−5.44[b,c]
teta	Cl	−6.15	−2.19[b,d]
trans[14]diene	Cl	−5.85	−1.68[e]
DIM	Cl	−6.36	−2.80[f]
TIM	Cl	−5.75	−2.06[f]
$(en)_2$	Cl	−7.34[g]	−3.59[h]
cyclam	Br	−7.89	−4.42[f]
teta	Br	−5.21	−1.15[e]
trans[14]diene	Br	−5.52	−1.26[e]
DIM	Br	−6.24	−2.66[f]
TIM	Br	−5.66	−2.00[f]
$(en)_2$	Br	−6.62[g]	−3.07[h]

[a] k_{NCS} and k_{N_3} represent the rate constants in s^{-1} with A = NCS and N_3, respectively. Values of k_{NCS} have been collected in Table IV and those of k_{N_3} were quoted separately. [b] W. K. Chau, W. K. Lee, and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2419 (1974). [c] Thiocyanate substitution reactions by 0.01–0.05 M KNCS in 0.01 M HNO_3. [d] In 0.01–0.1 M HNO_3 and at $\mu = 0.1$ M with $NaNO_3$. [e] W. K. Lee and C. K. Poon, *J. Chem. Soc., Dalton Trans.*, 2423 (1974). [f] C. K. Poon and C. L. Wong, *ibid.*, in press; in 0.01 M HNO_3. [g] $k_{NCS} = 4.6 \times 10^{-8}\ s^{-1}$ for X = Cl and $2.4 \times 10^{-7}\ s^{-1}$ for X = Br; extrapolated from published data: C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956). [h] V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, 9, 1785 (1970); en = ethylenediamine; in 0.01 M $HClO_4$.

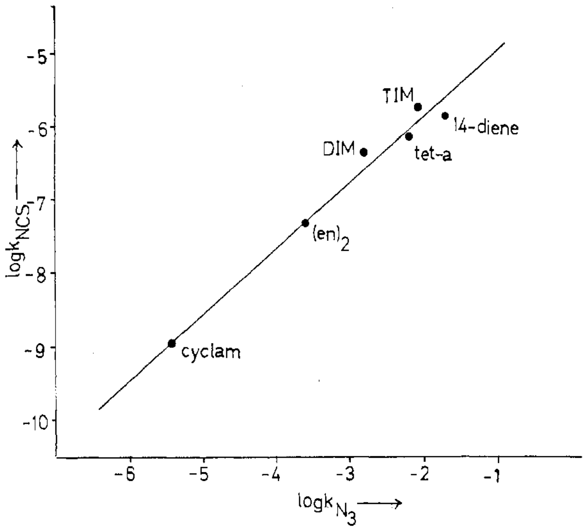


Figure 1. Least-squares plot of log k_{NCS} vs. log k_{N_3} at 25.0 °C for the acid hydrolysis of *trans*-$[CoLACl]^+$ (A = NCS or N_3) over a series of amine ligands L. Reaction conditions are given in Tables IV and V.

for X = Cl and 1:44:170 for X = Br at 25.0 °C) is a direct consequence of the decreasing enthalpies of activation and is, therefore, consistent with the view[10] that increasing degree of electronic delocalization between an amine macrocycle and the central cobalt(III) ion might help stabilize five-coordinate intermediates in the dissociative reactions of these complexes. This observation further indicates that chloride is more susceptible than bromide to this electronic effect.

Some of the first-order rate constants at 25.0 °C for the aquation (or thiocyanate substitution reactions) of complexes of the type *trans*-$[CoLAX]^+$ (A = NCS, N_3; X = Cl, Br), over an extensive series of amines L, are collected in Table V. It has been demonstrated that thiocyanate substitution reactions indeed gave a good measure of aquation rate constants of these macrocyclic cyclam,[14] DIM,[17] and TIM[17] complexes. A plot of log k_{NCS} vs. log k_{N_3} for each series of X was linear with a slope close to unity. Thus, the orienting effects of isothiocyanate and azide appear to respond similarly to changes of these cis $(en)_2$, cyclam, teta, trans[14]diene, TIM, and DIM ligands in the ligand substitution reactions of these cobalt(III) complexes.[18]

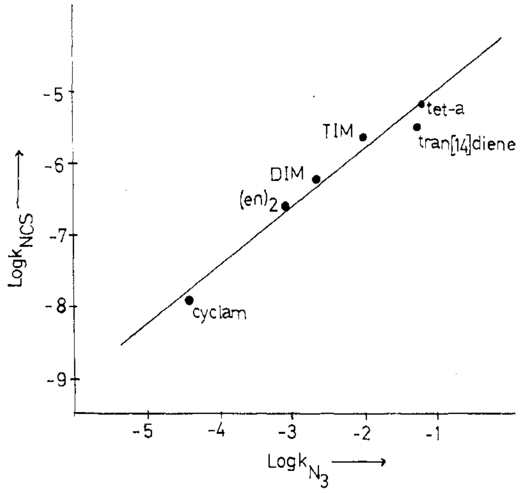


Figure 2. Same as Figure 1 for *trans*-$[CoLABr]^+$.

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Registry No. *trans*-$[Co(TIM)N_3NCS]ClO_4$, 59044-17-6; *trans*-$[Co(TIM)NCSOH_2](ClO_4)_2$, 59033-85-1; *trans*-$[Co(TIM)NCSCl]ClO_4$, 59033-87-3; *trans*-$[Co(TIM)NCSBr]ClO_4$, 59033-89-5; *trans*-$[Co(TIM)(NCS)_2]ClO_4$, 59033-90-8; *trans*-$[Co(DIM)(NCS)_2]ClO_4$, 59033-96-4; *trans*-$[Co(TIM)N_3OH_2](ClO_4)_2$, 59033-92-0; *trans*-$[Co(cyclam)NCSBr]^+$, 59033-98-6; *trans*-$[Co(DIM)NCSCl]^+$, 59033-94-2; *trans*-$[Co(DIM)NCSBr]^+$, 59033-93-1; SCN^-, 302-04-5; chlorine, 7782-50-5; bromine, 7726-95-6.

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