Reactions of *mer*(*exo*)- and *mer*(*endo*)-[Co(dien)(dapo)X]²⁺ Isomers (X = OH, Cl, ONO₂, N₃)[1])

by **Rebecca J. Browne**[a]), **David A. Buckingham**[*a]), **Charles R. Clark**[a]), **Josephine A. McKeon**[b]),
and **W. Gregory Jackson**[b])

[a]) Chemistry Department, University of Otago, P. O. Box 56, Dunedin, New Zealand
[b]) The School of Chemistry, University College, University of New South Wales, Australian Defence Force
Academy, Canberra, ACT 2600, Australia

Properties indirectly determined, or alluded to, in previous publications on the titled isomers have been measured, and the results generally support the earlier conclusions. Thus, the common five-coordinate intermediate generated in the OH^--catalyzed hydrolysis of *exo*- and *endo*-[Co(dien)(dapo)X]²⁺ (X = Cl, ONO₂) has the same properties as that generated in the rapid spontaneous loss of OH^- from *exo*- and *endo*-[Co(dien)(dapo)OH]²⁺ ($40 \pm 2\%$ *endo*-OH, $60 \pm 2\%$ *exo*-OH) and an unusually large capacity for capturing N_3^- ($R = [CoN_3]/[CoOH][N_3^-] = 1.3$; *exo*-$[CoN_3]$/*endo*-$[CoN_3] = 2.1 \pm 0.1$). Solvent exchange for spontaneous loss of OH^- from *exo*-[Co(dien)(dapo)OH]²⁺ has been measured at 0.04 s⁻¹ (k_1, 0.50M NaClO₄, 25°) from which similar loss from the *endo*-OH isomer may be calculated as 0.24 s⁻¹ (k_2). The OH^--catalyzed reactions of *exo*- and *endo*-[Co(dien)(dapo)N₃]²⁺ result in both hydrolysis of coordinated N_3^- *via* an OH^--limiting process ($k_{OH}^{N3}(exo) = 153$ M⁻¹ s⁻¹; $k_{OH}^{N3}(endo) = 295$ M⁻¹ s⁻¹; $K_H = 1.3 \pm 0.1$ M⁻¹; 0.50M NaClO₄, 25.0°) and direct epimerization between the two reactants ($k_E^{N3}(exo) = 33$ M⁻¹ s⁻¹; $k_E^{N3}(endo) = 110$ M⁻¹ s⁻¹; 1.0M NaClO₄, 25.0°). Comparisons are made with other rapidly reacting Co^III-acido systems.

Introduction. – For many years, we have been interested in both the base hydrolysis of Co^III-acido complexes and the inversion rates of Co^III-coordinated *sec*-NH centers. From 1992 on, we have carried out detailed studies of the [Co(cyclen)(Y)X]²⁺ system; these showed promise in allowing problems associated with both areas to be unravelled. As the [Co(dien)(dapo)X]²⁺ complexes have similar properties like [Co(cyclen)(NH₃)X]²⁺ species (they have similar isomeric possibilities, and are also unusually reactive), we were interested in the early report of the optical stability in the [Co(dien)(dapo)OH]²⁺ system [1].

We report here results that largely support the observations and conclusions reached by *Comba et al.* in their extensive studies of the title complexes, which were published in this journal in 1992 [2] (we have retained the *exo,endo* designation used in these reports (*cf. Fig. 1*) rather than the alternate *anti, syn* classification [3]). The experimental work has been extended to include direct measurement of some of the properties alluded to in previous accounts [2], and additional data have also been obtained. The results allow more certain conclusions to be drawn, which leads to a better general understanding of these very reactive Co^III systems.

Experimental. – 1. *Reagents and Instrumentation*. Reagents, including buffers, were of *AR* or similar grade. Once-distilled H₂O was used in all cases. Normalized H₂¹⁷O (*ca.* 6 atom-% ¹⁷O) was purchased from *Yeda*

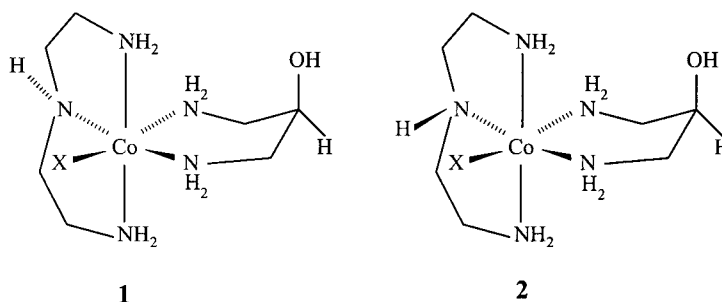[1])   Abstracted in part from the B.Sc. (Hons) project report of *R. J. B.*, University of Otago, 1992.

Fig. 1. *Representations of the* mer*(exo)- and* mer*(endo)-[Co(dien)(dapo)X]$^{n+}$ isomers* (**1** and **2**, resp.)

Research and Development Co. Ltd., Rehovot, Israel. Ion exchange resins used were: cation: *Dowex 50W × 2* (200 – 400 mesh); anion: *Dowex AG 1 × 4* (200 mesh). The latter was used in its ClO_4^- form, which was prepared from the Cl$^-$ form by washing with a dil. NaOH soln. (0.1 M) until free from Cl$^-$, and then neutralizing with $HClO_4$ (to pH *ca.* 3.5). Reversed-phase ion-pair HPLC was carried out on a *Varian 5000* instrument coupled to a *Hewlett Packard 3390A* integrator and a *Varian 9050* UV/VIS detector. Separations were achieved with *Waters C-18* cartridges in a radial compression *Z*-module and 25 mM solns. of toluene-4-dihydrogenphosphate ion-pairing reagent containing MeOH (in the range 0 – 35%, isocratic) and adjusted to pH 3.5 (NaOH). pH Measurements were conducted with a *Radiometer PHM 62* pH-meter fitted with *G2040B* glass and *K4040* calomel electrodes together with a salt bridge (1.60 M NH_4NO_3, 0.20 M $NaNO_3$). NMR Measurements (^1H, ^{13}C, ^{17}O) including NOE and COSY experiments were performed with a *Varian VXRS 300* spectrometer and 5-mm (^1H, ^{13}C) or 10-mm (^{17}O) probes. In the latter, an external CD_3OD reference (5 mm, 0.7 ml, $\delta = -35$ ppm) and lock were used. VIS/UV Spectra and some rate measurements were recorded on a *Cary 219* spectrophotometer, and other rates on a *Durrum D-110* instrument connected to a *Northstar Horizon* computer with an OLIS data storage and manipulation system. Azide anation kinetics of the *exo*- and *endo*-OH complexes was studied in ethanolamine or triethanolamine buffers, as previously described ($I = 1.0$ M NaN_3, 25°) [2b]. A *HP8453* diode-array VIS/UV spectrophotometer was employed with thermally equilibrated 1-cm pathlength bifurcated cells, which facilitated rapid mixing and data collection. The *Specfit*® package was used to analyze the rate data. Optically resolved azido complexes were original samples [4], which had been stored appropriately.

2. *Stopped-Flow/Quench Apparatus*. A hand-operated stopped-flow device was adapted so as to rapidly mix two solns. (each 8.5 ml; thermostated) and tangentially deliver the resultant soln. through *Tygon*® tubing (2.5 mm i.d., thick walled) to a beaker containing rapidly stirred (magnetic stirrer) quenching soln. The length of tubing dictated the time between mixing of reactant solns. and quenching. With practice, reactant solns. could be mixed in 1.1 ± 0.1 s, and, for the experiments reported here, a 40-cm length of tubing was used, which represented a residence time of 125 ms. Prior to each run, the tubing was filled with H_2O (2.0 ml) so that 15.0 ml of mixed reactants was delivered to the quenching soln. (18.0 ml, 0.060 M $HClO_4$, 15.0 ml, 0.50 M $HClO_4$). Solns. of complex (25.0 ml, 8.5×10^{-3} M; $I = 1.0$ M $NaClO_4$; 5.0 mM $HClO_4$) and buffer (25.0 ml) were prepared immediately before experiments were initiated.

3. *Complexes*. The *mer(exo)*- and *mer(endo)*-[Co(dien)(dapo)X](ClO$_4$)$_2$ complexes (X = Cl, N$_3$) were prepared essentially as described by *Comba et al.* [4]. The complexes were purified by ion-exchange (IE) chromatography (1 – 3 M HCl (X = Cl); 1 – 2 M NH$_4$Cl (X = N$_3$)), and/or analyzed by reversed-phase (RP) ion-pair HPLC. Most complexes were first isolated as $ZnCl_4^{2-}$ salts and converted to ClO_4^- salts by repeated crystallization with $NaClO_4$ or $LiClO_4$. *mer(exo)*- and *mer(endo)*-[Co(dien)(dapo)OH$_2$]Cl$_3$ were likewise prepared as required from the corresponding [Co(dien)(dapo)N$_3$]ZnCl$_4$ complexes [2a], and were stored below 0° (gradual anation occurs at r.t.). *mer(exo)*-[Co(dien)(dapo)ONO$_2$](NO$_3$)$_2$ was prepared by adding the corresponding Cl complex (ClO_4^- salt, 1.00 g) to a soln. of Hg(NO$_3$)$_2$ (prepared by addition of 0.45 g HgO to 10 ml of conc. HNO$_3$). Precipitated HgCl$_2$ was removed by filtration, and the filtrate was added slowly with stirring to 100 ml of ice-cold EtOH/Et$_2$O 1 : 1 (*Caution:* explosion hazard). The pink-orange solid was recovered, washed with EtOH/Et$_2$O, and dried under vacuum. It was quickly recrystallized from the minimum volume of H$_2$O by addition of LiNO$_3$. Anal. calc. for CoN$_8$C$_7$H$_{23}$O$_{10}$: N 25.57, C 19.18, H 5.29; found: N 25.76, C 19.35, H 5.22. ^{1}H-NMR Spectrum (DCl): NH peaks at 7.0 ppm (most downfield), 3.80 ppm (characteristic of *exo*-isomers).

For comparison, the ^{1}H-NMR spectra of these complexes proved useful, with characteristic NH resonances ((D_6)DMSO; ppm, 1 H) occurring at 6.6 – 6.7, 3.9 (*exo*-Cl); 7.1 – 7.2, 3.6 (*endo*-Cl); 6.4 – 6.5, 3.95 (*exo*-N_3); 6.7 – 6.8, 3.65 (*endo*-N_3); 7.0, 3.8 (*exo*-ONO_2); 7.3 – 7.4, 4.0 (*exo*-OH_2); 7.4, 3.6 (*endo*-OH_2). The upfield resonance at 3.8 – 3.9 (*exo*), 3.6 ppm (*endo*) was integrated for semi-quant. analysis.

^{17}*O-Labelled* mer*(*exo*)-[Co(dien)(dapo)OH₂](ClO₄)₃*. To mer*(exo)*-[Co(dien)(dapo)N₃] (ClO₄)₂ (0.37 g) suspended in 5 ml of $H_2{}^{17}O$ (*ca.* 6 atom-%) containing 130 µl 6.0M $HClO_4$ (50 ml flask fitted with *B19* male joint) was added $NaNO_2$ (60 mg) over 5 min. The deep red soln. was then frozen (dry-ice/i-PrOH), evacuated, degassed, and then freeze-dried (10^{-3} mm Hg, $H_2{}^{17}O$ recovered). The red-orange residue was then powdered, dried (10^{-3} mm Hg), and stored below 0°.

Stability of mer*(*exo*)- and* mer*(*endo*)-Isomers*. Although complexes with X = Cl or N_3 appear to be reasonably stable both as solids and in soln., the complex with X = H_2O (chloride salt) undergoes slow anation under both sets of conditions. The isomers with X = OH are, however, much less stable, and their solns. readily (within minutes) produce mixtures that contain *unsym*-isomers [4]; but once formed, the *mer*-isomers can be stabilized as the aqua complexes by quenching with acid.

4. *Competition Experiments*. To each of mer*(exo)*- and mer*(endo)*-[Co(dien)(dapo)OH₂]Cl₃ (*ca.* 100 mg) in 0.010M $HClO_4$ (5 ml) was added rapidly with vigorous stirring an aliquot of 2.0M NaN_3 soln. adjusted to pH 8.0 (0.20M triethanolamine buffer). After 4 s (*endo*) and 2.0 min (*exo*), the reaction (final pH 7.8) was quenched with 0.50M $HClO_4$ (5 ml, fumehood). The (*exo,endo*)-N_3 products were separated by IE chromatography and analyzed spectrophotometrically.

For the stopped-flow/quenching experiments, the following stock solns. were prepared: *A*) an accurately weighed quantity of either mer*(exo)*- or mer*(endo)*-[Co(dien)(dapo)Cl](ClO₄)₂, or mer*(exo)*-[Co(dien)(dapo)ONO₂](NO₃)₂ (*ca.* 100 mg) was dissolved in 0.010M $HClO_4$ (12.5 ml), and an equal volume of 2.0M $NaClO_4$ was added; *B*) 0.10M *Caps* buffer (25 ml, 0.95M in $NaClO_4$) was adjusted so that, when mixed with an equal volume of 5.0 mM $HClO_4$ (1.0M $NaClO_4$), the final soln. pH was 10.0; *C*) 0.10M *Caps* buffer (25 ml, 1.0M in NaN_3) was adjusted as for soln. *B*. For quenching experiments in the absence of N_3^-, equal volumes (8.5 ml) of solutions *A* and *B* were mixed with the stopped-flow mixer and quenched with 18.0 ml of 0.060M $HClO_4$. The quenched soln. was diluted and the (*exo,endo*)-H_2O products sorbed onto, and then eluted from (1 – 3M HCl) *Dowex 50Wx2* IE resin. The product eluate was then evaporated to near dryness, warmed to 80°, and taken to dryness. The (*exo,endo*)-Cl product was then analyzed by ion-pair HPLC. For experiments in the presence of NaN_3, the mixture (*A* plus *C*, 0.50M NaN_3, 0.50M $NaClO_4$) was quenched with 15 ml 0.50M $HClO_4$ (final pH 3.25, fume hood), immediately cooled (ice-bath), and samples (1.0 ml) were removed for analysis of the (*exo,endo*)-N_3 products by ion-pair HPLC. The remaining soln. was diluted, sorbed onto IE resin, and eluted with 1M $NaClO_4$ (pH *ca.* 2) to recover the (*exo,endo*)-N_3 products (not analyzed) and then with 1 – 3M HCl to recover the (*exo,endo*)-H_2O products, which were treated and analyzed as described previously.

The *exo*- and *endo*-OH_2 ions were not separated by RP ion-pair HPLC (although they are on *Dowex* [4]), and so were anated to the Cl^- ions, which are separable. Control experiments on the pure *exo*- or *endo*-OH_2 complexes established complete retention of configuration for the dapo and closely related tn species, although *fac* isomers do appear if solns. are overheated.

5. *Equilibration Experiments*. 5.1. mer*(*exo*,*endo*)-N₃ *Isomers*. The separate *exo*-N_3, *endo*-N_3 isomers (*ca.* 15 mg) or a mixture (*ca.* 8 mg each) were left to stand at pH 8.0 (0.10M *Tris* buffer, 500 µl) for 60 and 120 min, and the mixture was analyzed by ion-pair HPLC (500 nm, 5 runs).

5.2. mer*(*exo*,*endo*)-OH *Isomers*. Quenched (HCl) product solns. from the isomerization rate studies (X = OH_2/OH) were sorbed onto IE resin and eluted with 1 – 3M HCl. The eluate was reduced to near dryness, warmed to *ca.* 80° (5 min) and then reduced to dryness. This material was analyzed by ion-pair HPLC.

5.3. *Products of Base Hydrolysis:* mer*(*exo*,*endo*)-Cl,* mer*(*exo*)-ONO₂ *Isomers*. Two methods of analysis were carried out: *a*) acid-quenched (HCl) product solns. from the rate studies were collected and treated as described above; *b*) samples of the complexes (50 – 100 mg) were base-hydrolyzed for *ca.* $10 \times t_{1/2}$ in 2.0 ml of 0.10M *Mes* buffer (*exo*-Cl, 23 min, pH 6.01; *endo*-Cl, 13 min, pH 6.60; *exo*-NO_3, 7 min, pH 5.50) and the HCl-quenched aqua products were crystallized by adding acetone (40 ml). These were examined by ^{1}H-NMR (D_2O/DCl), and the NH peaks at *ca.* 4.0 ppm (*exo*-OH_2) and 3.6 ppm (*endo*-OH_2) were integrated.

6. *Isomerism During Base Hydrolysis*. 6.1. Samples of mer*(exo)*- and mer*(endo)*-[Co(dien)(dapo)Cl] (ClO₄)₂ (90 and 30 mg, resp.) and mer*(exo)*-[Co(dien)(dapo)ONO₂](NO₃)₂ (30 mg) were hydrolyzed in 0.10M *Pipes* buffer (15 ml, 1.0M $NaClO_4$) for $1 \times t_{1/2}$ (32 s, pH 6.65; 70 s, pH 6.65; 6 s, pH 6.34, resp.) before quenched with 2M HCl. Following filtration of precipitated *Pipes*, the solns. were diluted, sorbed onto IE resin, and remaining 2+ reactants were removed (1 – 3M HCl), reduced to dryness, and examined by ^{1}H-NMR (D_2O/DCl, peaks at 3.9 (*exo*-Cl), 3.6 (*endo*-Cl), and 3.8 ppm (*exo*-ONO_2)). These experiments

were subsequently repeated (*exo*-Cl and *endo*-Cl), and the reactant was recovered after $1 \times t_{1/2}$ and examined by ion-pair HPLC.

6.2. Experiments were also carried out with both *mer(exo)*- or *mer(endo)*-[Co(dien)(dapo)N$_3$](ClO$_4$)$_2$ (*ca.* 0.4 mg) in *Hepes* buffer (2.0 ml, 0.10M, $I = 0.50$ M NaClO$_4$, pH 7.63), with aliquots (20.0 μl) being withdrawn at known times (interval *ca.* 20 min) and immediately subjected to HPLC analysis (309 nm, 25 mM sodium hexanesulfonate, pH 3.25, 30% MeOH, 2.0 ml min^{-1}). Under the conditions, the *mer(endo)*- and *mer(exo)*-[Co(dien)(dapo)N$_3$]$^{2+}$ isomers had retention times of 14 and 18 min, resp., and concentrations (from peak areas) were obtained by comparison with standard mixtures.

Results. – 1. *Isomerization, Solvent Exchange, and N$_3^-$ Competition in the* mer*(exo,endo)-[Co(dien)(dapo)OH]$^{2+}$ System*. There was a sufficiently large absorbance change at 330 nm to allow the isomerization reaction to be followed spectrophotometrically. Rate data obtained from stopped-flow studies using the *mer(endo)* isomer for various [OH$^-$] are given in *Fig. 2*. These show that the rate is pH independent below pH 11, with a first-order dependence on OH$^-$ concentration from 0.10 to 0.40M. The rate law

$$k_{obs} = k_I + k_I' [OH^-] \tag{1}$$

holds, with $k_I = (0.20 \pm 0.01)$ s^{-1}, $k_I' = (3.6 \pm 0.1)$ M^{-1} s^{-1} ($I = 1.0$M NaClO$_4$, 25.0°). Reanation of the equilibrated products (aq. 4M HCl, 80°, 5 min), followed by HPLC analysis of the resulting Cl complexes, gave $K_{eq}^{OH}(endo/exo) = 0.11 \pm 0.01$ (4 experiments; 10% *endo*-OH at equilibrium) in agreement with the reported value [2a]. Thus, we have for the equilibrium:

$$exo - OH \xrightleftharpoons[k_I^{OH}(endo)]{k_I^{OH}(exo)} endo - OH \tag{2}$$

$k_I^{OH}(exo) = 0.020$ s^{-1}, $k_I^{OH}(endo) = 0.18$ s^{-1}. One ^{17}O-NMR experiment (such experiments require both care and significant amounts of complex [5]) with ^{17}O-labelled *mer(exo)*-[Co(dien)(dapo)OH$_2$](ClO$_4$)$_3$ in 0.50M NaClO$_4$, pH 4.0 (25°) gave less than ideal data (due to a large residual solvent signal), but the increase in the solvent signal with time accorded with $t_{1/2} \approx 30$ min for exchange. This corresponds to k_{ex} for the hydroxo complex of 0.013 s^{-1} based on the reported pK_a of ~ 5.5 [2b]. However, we believe the pK_a for *exo*-OH$_2$ may well be closer to 6.0 in this medium [6], which would correspond to $k_{ex} = 0.04$ s^{-1}. Clearly, however, the ^{17}O experiment shows that isomerization results from the loss of a coordinated ligand, and that the reaction is rather fast around neutral pH.

To determine the immediate azido competition products of isomerization, freshly prepared *mer(endo)*-[Co(dien)(dapo)OH$_2$]Cl$_3$ was reacted in 1.0M NaN$_3$ (pH 7.8) for 4 s before acid-quenching. Ion-exchange separation and analysis of the resulting azido products gave a distribution of 33% *endo*-N$_3$ and 67% *exo*-N$_3$. Two similar experiments with the *exo*-OH$_2$ isomer and longer times (2.0 min) gave essentially quantitative yields of azido products (32, 30% *endo*-N$_3$; 68, 70% *exo*-N$_3$). If neutralized solutions of the aqua complexes are left for longer times prior to anation, then *unsym-fac* isomers are produced. *Fig. 3* shows that these are readily distinguished from their meridional counterparts by HPLC.
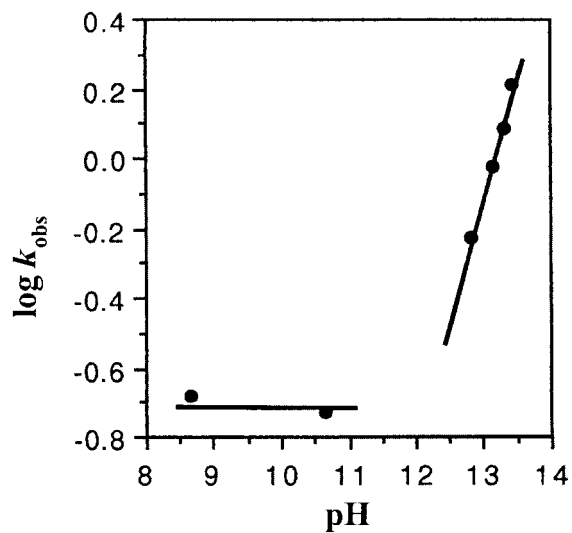
Fig. 2. *log* k*$_{obs}$* vs. *pH for the reaction of* mer*(*endo*)-[Co(dien)(dapo)OH]$^{2+}$ in alkali* ($I = 1.0$M, NaClO$_4$; 25.0°). The points represent experimental data, the fitted lines correspond to the rate law of *Eqn. 1*, and the values of the constants are given in the text.
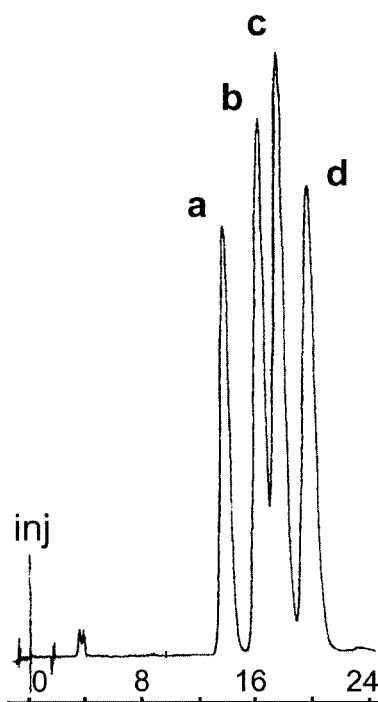

Fig. 3. *HPLC Separation of [Co(dien)(dapo)N$_3$]$^{2+}$ isomers obtained following equilibration* (1 h pH 7.85, 1 h pH 9.3) *of [Co(dien)(dapo)OH]$^{2+}$ in the presence of* N$_3^-$ (*ca.* 2.0M); *a*) *mer*(*endo*)-, *b*) *unsym-fac*(*endo*-OH)-, *c*) *mer*(*exo*)-, *d*) *unsym-fac*(*exo*-OH)-isomer (25 mM sodium hexanesulfonate, 30% MeOH, 2 ml min^{-1}, 309 nm).

2. *Base Hydrolysis and N_3^- Competition for* mer(exo,endo)-[Co(dien)(dapo)X]$^{2+}$ *(X = Cl, ONO$_2$)*. Earlier kinetic data for X = Cl gave almost identical rate constants for the two isomers [2a], and this could have been interpreted in terms of prior epimerization [2a][6]. However, our stopped-flow data consistently gave somewhat faster rates for the *exo*-Cl isomer. One such set of data is given in *Table 1*, with $k_{OH}^{Cl}(exo) = 2.85 \times 10^5$ M^{-1} s^{-1}, $k_{OH}^{Cl}(endo) = 1.29 \times 10^5$ M^{-1} s^{-1} (1.0M NaClO$_4$; 25.0°). Furthermore, HPLC analysis after *ca.* $1 \times t_{1/2}$ for hydrolysis showed that no epimerization had taken place in either starting material. It is to be noted here that $k_{OH}^{Cl}(endo)$ approaches $k_{H/D}$ for proton exchange at the meridional *sec*-NH center ($k_{H/D} = (6.6 \pm 0.5) \times 10^5$ M^{-1} s^{-1}) [2a]. Thus, if the two processes are related, the deprotonated reactant is very reactive towards loss of Cl$^-$. A separate set of six quenching experiments were also carried out on solid samples of both optically active and racemic *exo*- and *endo*-Cl. Two solvents were used, 0.1M NaOH/0.9M NaClO$_4$ and 0.01M NaOH/0.99M NaClO$_4$. The immediately acid-quenched product solutions were diluted, and sorbed on and eluted from *Dowex* with 2M NaClO$_4$ (pH 1) as eluant. The chloro isomer (trace), which had survived the short time in alkaline solution, was collected first, followed by the *endo*- and then the *exo*-aqua ions. The three eluates were examined spectrophotometrically and polarimetrically. Traces of recovered reactants remained unepimerized and fully active, but the OH products, $59 \pm 3\%$ *exo*, $41 \pm 3\%$ *endo* (values in agreement with those better defined in HPLC experiments), were now optically inactive.

Table 1. *Base Hydrolysis Rate Data for the* mer-(exo,endo)-[Co(dien)(dapo)X](ClO$_4$)$_2$ *Complexes* (25.0°, $I = 1.0$M, NaClO$_4$).

	pH	10^8 [OH$^-$]/M^a)	k_{obs}/s^{-1}	10^{-5} k_{Cl}/M^{-1} s^{-1}
exo-Cl	6.68	8.12	0.0217	2.67
	7.32	35.4	0.107	3.12
	7.62	70.7	0.2111	2.98
	7.71	86.9	0.272	3.13
	7.91	138	0.394	2.86
	8.48	512	1.35	2.64
	8.84	1170	3.10	2.65
endo-Cl	7.88	129	0.175	1.36
	7.88	129	0.176	1.37
	8.64	741	0.930	1.26
	8.64	741	0.930	1.26
	9.07	1980	2.45	1.23
	9.07	1980	2.54	1.28
exo-ONO$_2$	6.34	3.71	0.117	31.5
	6.34	3.71	0.118	31.8
	6.74	9.32	0.274	29.4
	6.74	9.32	0.286	30.7
	7.10	21.4	0.681	31.9
	7.10	21.4	0.708	33.1
	7.64	69.0	2.04	29.6
	7.64	69.0	2.15	31.2

^{a}) Based on pK_w = 13.77 ($I = 1.0$M, NaClO$_4$).

Kinetic data for *mer(exo)*-ONO$_2$ are also given in *Table 1*, and it can be seen that this complex is *ca.* 10 fold more reactive than the *mer(exo)*-Cl complex, $k_{OH}^{NO_3}(exo) = 3.16 \times 10^6$ M^{-1} s^{-1} (1.0M NaClO$_4$, 25.0°). No H-exchange data was collected for this complex, and the very real possibility of general base catalysis in the hydrolysis reaction was not tested.

Re-anation of the hydrolysis products (aq. HCl, 80°) gave the same equilibrium distribution as previously ($K_{eq}^{OH}(endo/exo) = 0.11 \pm 0.01$). However, we recognized that, by choosing an appropriate pH (in the vicinity of 10) and by rapid acid-quenching, the true (kinetic) distribution of OH products could be found. This was accomplished with our home-made rapid mixing-quenching device, used previously [6], but described here for the first time (*cf. Experimental*). Such experiments, carried out at pH 9.98 ± 0.05 (*Caps* buffer; 1.0M NaClO$_4$, room temp. (*ca.* 16°)) with acid quenching, after a residence time of 125 ± 10 ms and after conversion of products to the chloro complexes, led to the results listed in *Table 2*. Clearly, the immediate OH product distribution is the same for all complexes: 60 ± 2% *exo*-OH, 40 ± 2% (*endo*)-OH.

Table 2. *Immediate Products*[a]) *Formed on Hydrolysis of* mer*(exo)-* (X = Cl, ONO$_2$) *and* mer*(endo)-* (X = Cl) *[Co(dien)(dapo)X]²⁺ Isomers at pH 9.98 ± 0.05 (25.0°, I = 1.0M, NaClO$_4$)*

Reactant	% *endo*-OH (B)	% *exo*-OH (A)
exo-Cl	40	60
exo-Cl	41	59
endo-Cl	42	58
endo-Cl	42	58
exo-ONO$_2$	41	59
exo-ONO$_2$	40	60

[a]) Quenched after 125 ± 25 ms with 0.060M HClO$_4$.

Likewise, the immediately formed Co−OH and Co−N$_3$ products in the presence of N$_3^-$ were found, and these data are listed in *Table 3* (pH 9.98, *Caps* buffer; 0.50M NaN$_3$, 0.50M NaClO$_4$, *ca.* 16°). The 32 ± 1% *endo*-N$_3$, 68 ± 1% *exo*-N$_3$ distribution agrees with that obtained previously (*vide infra*), while the similar distribution for the Co−OH isomers (32 ± 2% *endo*-OH, 68 ± 2% *exo*-OH) shows that somewhat less *endo*-OH is produced in this medium. Why the distribution of Co−N$_3$ and Co−OH isomers is the same (*endo/exo* 1:2) is not known, but is probably coincidental.

The overall competition ratio $R = [CoN_3]/[CoOH] \cdot [N_3^-] = 1.3$ obtained from this data (*Table 3*) agrees with that reported earlier [2a] and clearly establishes substantial N$_3^-$ entry into the five-coordinate intermediate (*i.e.*, *ca.* 56% in 1.0M N$_3^-$). This is an important result (*cf. Discussion*).

3. *Base Hydrolysis and Epimerization of* mer*(exo,endo)-[Co(dien)(dapo)N$_3$]²⁺*. We considered that OH$^-$-catalyzed epimerization in the six-coordinate Co−N$_3$ system would be a real possibility once we found that it occurred with [Co(cyclen)(NH$_3$)N$_3$]²⁺ [6]. This view was reinforced when preparative samples of *exo*- or *endo*-N$_3$ were allowed to stand in buffered solutions at pH *ca.* 8; ion-exchange separations always gave mixtures, with little or no hydrolysis product, and, when left long enough (*ca.* 60 min), full equilibration occurred (79.6 ± 0.4% *exo*-N$_3$; 20.4 ± 0.4% *endo*-N$_3$; five experiments), $K_{eq}^{N_3}(endo/exo) = 0.25$. However, once the N$_3^-$ anation data for this

Table 3. *Immediate Products* (X = OH, N$_3$) *Formed on Hydrolysis of* mer*(exo)-* (X = Cl, ONO$_2$) *and* mer-*(endo)-* (X = Cl) *[Co(dien)(dapo)X]²⁺ Isomers in 0.5*M *NaN$_3$/0.50*M *NaClO$_4$ at pH 9.98* (25.0°)

Reactant	X = N$_3$ Products[a]					X = OH Products	
	% *endo*	% *exo*	Total %	Ratio % *endo*	R[b]	Ratio % *endo*	% *exo*
exo-Cl	12.8	27.2	40.0	32	1.3	32	68
	12.1	26.3	38.4	31.5	1.2		
exo-Cl[c]	9.7	20.8	30.5	32		30	70
	9.9	21.0	30.9	32			
endo-Cl	12.3	26.4	38.7	32	1.3	35	65
	12.7	26.3	39.0	33	1.3		
exo-ONO$_2$	12.9	27.3	40.2	32	1.3	32	68
	12.5	25.8	38.3	33	1.2		

[a]) Expressed as % reactant (mmol) used. [b]) R = (total % X = N$_3$ product)/(total % X = OH product) × 0.50. [c]) Some reactant solution was lost in this experiment so that the total % X = N$_3$ product is low.

system was published [2b], we realized that re-anation by released N$_3^-$ would occur subsequent to hydrolysis, even at 10^{-3} M concentration.

But our spectrophotometric hydrolysis data, obtained with *ca.* 10^{-4} M complex, continued to cause problems (*cf. Fig. 4*). The stopped-flow trace for *exo*-N$_3$ (*Fig. 4,A*) gave a good fit for all the data, $k_{obs} = 18.9$ s^{-1}, but that for the *endo*-N$_3$ isomer (*Fig. 4,B*) did not. It clearly shows that another process is occurring at early times, and only the final 10% of the trace gives a good first-order fit, $k_{obs} = 18.4$ s^{-1} (*Fig. 4,C*). These data suggest that epimerization in the starting complex is occurring, at least to some extent, and that the k_{obs} values refer to the epimerized mixture.

To quantify this problem exactly, we decided to carry out a hydrolysis experiment at very low concentration and to analyze the mixture by HPLC as the reaction proceeded. This result, with both the *exo*-N$_3$ and *endo*-N$_3$ isomers is shown in *Fig. 5* ([Co]$_T$ ∼ 4 × 10^{-4} M (slightly different for the two isomers); pH 7.63 (0.10M *Hepes* buffer, 0.50M NaClO$_4$). Clearly, hydrolysis is occurring, but the *endo*-N$_3$ isomer produces some *exo*-N$_3$ at the same time, and the *exo*-N$_3$ isomer produces smaller amounts of *endo*-N$_3$. A complete analysis is given by the full curves, and values of pseudo first-order rate constants (k_{ij}) are given in *Scheme 1*.

Scheme 1
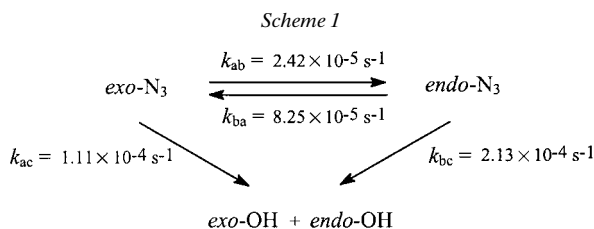
Both the hydrolysis and isomerization reactions are known to be OH$^-$-catalyzed, and second-order rate constants are listed in *Table 4*. These show that hydrolysis is favored over epimerization for both isomers ($k_{OH}/k_E = 4.6$ (*exo*), 2.7 (*endo*)), and that the *endo*-isomer is more reactive than *exo*-N$_3$ (twofold for hydrolysis; threefold for
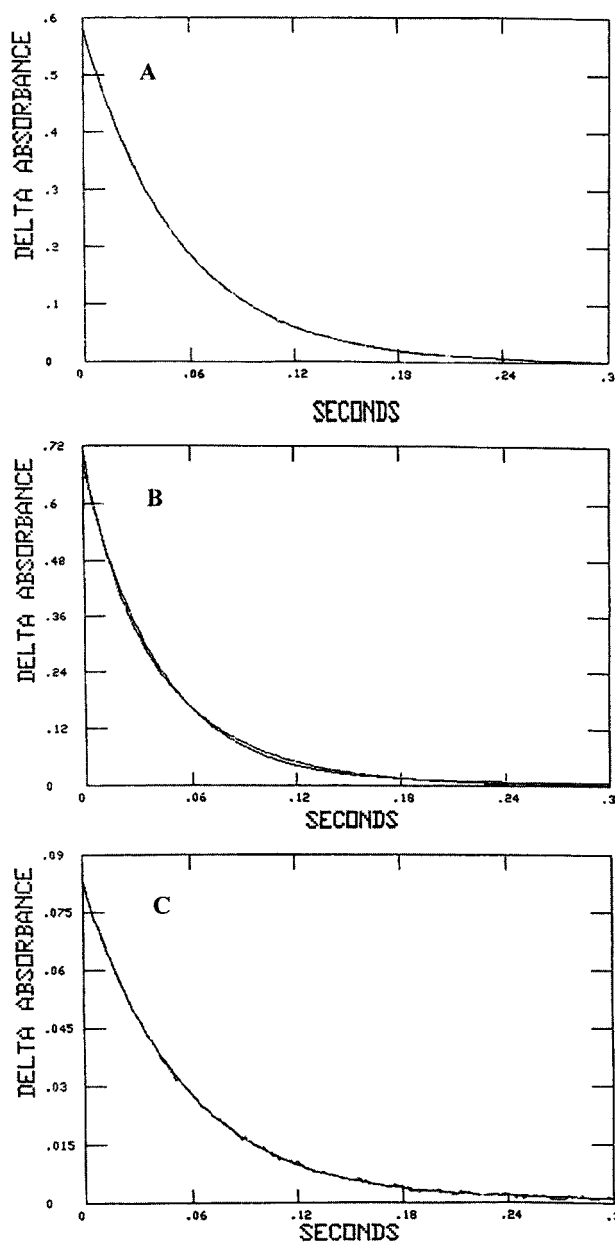
Fig. 4. *Stopped-flow traces for reaction of [Co(dien)(dapo)N₃]²⁺ isomers (ca.* 10^{-4} M*) in 0.10*M *NaOH. A*) *mer*(*exo*)-Isomer (510 nm) with the fitted curve corresponding to $k_{obs} = 18.9$ s^{-1} superimposed exactly over the observed data. *B*) *mer*(*endo*)-Isomer (370 nm) showing the deviation of observed data from pure (pseudo) first-order kinetics. *C*) The final 10% of the absorbance time-trace from *B* (*i.e.*, data collection delay 0.10 s) with the fitted curve corresponding to $k_{obs} = 18.4$ s^{-1} now superimposed exactly over the observed data.
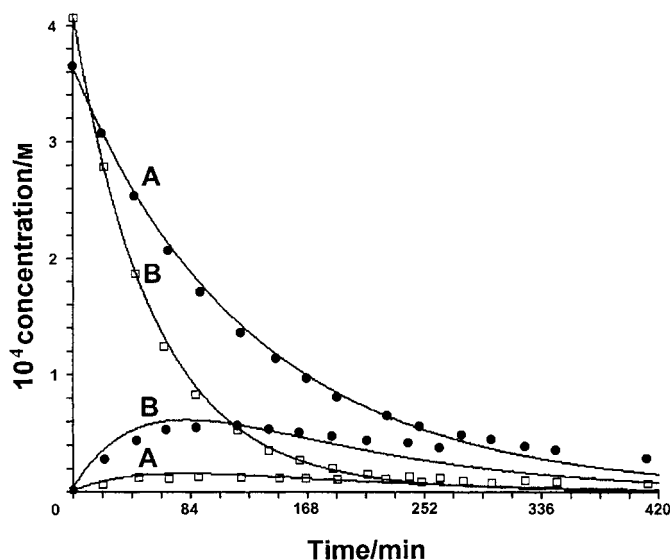
Fig. 5. *Experimentally determined concentrations of* mer*(exo)-isomer* (●) *and* mer*(endo)-isomer* (□) *of [Co(dien)(dapo)N₃]²⁺ as a function of time for reaction of the separate complexes. A) mer(exo)-[Co(dien)(da-po)N₃]ZnCl₄, 3.65×10^{-4} M. B) mer(endo)-[Co(dien)(dapo)N₃]ZnCl₄, 4.14×10^{-4} M in pH 7.63 Hepes buffer (0.10M, $I = 0.50$M NaClO₄) at 25.0°. The curves were obtained from a global fit of all these data in accord with the rate constants given in Scheme 1.*

epimerization). While the observed rate-constant ratio $k_E^{N_3}(exo)/k_E^{N_3}(endo)$ does not now give the true equilibrium constant of $K_{eq}^{N_3} = 0.25$ (differential hydrolysis now interferes), the rate constant calculated for the equilibrium mixture ($0.80\ k_{OH}^{N_3}(exo) + 0.20\ k_{OH}^{N_3}(endo) = 1.81 \times 10^2\ \text{m}^{-1}\ \text{s}^{-1}$) agrees well with the observed spectrophotometric value.

Table 4. *Comparisons of Rate Constants for Proton Exchange ($k_{H/D}$), Hydrolysis (k_{OH}), and Epimerization (k_E) in the Six-Coordinate* mer*(exo,endo)-[Co(dien)(dapo)X]²⁺ Ions*

Complex	$k_{H/D}$/M⁻¹ s⁻¹ [a])	k_{OH}/M⁻¹ s⁻¹	k_E/M⁻¹ s⁻¹	k_{OH}/k_E	$k_{OH}/k_{H/D}$	$k_{H/D}/k_E$
exo-N₃	7.8×10^6	1.53×10^2	3.3×10^1	4.6	2×10^{-5}	2×10^5
endo-N₃	1.3×10^6	2.95×10^2	1.1×10^2	2.7	2.5×10^{-4}	1×10^4
exo-Cl	6.0×10^6	2.9×10^5			5×10^{-2}	
endo-Cl	6.6×10^5	1.3×10^5			2×10^{-1}	
exo-ONO₂	*ca.* 10^6 [b])	3.2×10^6			*ca.* 1	
exo-OH		0.013 (s⁻¹)[c])				
endo-OH			3.6[d])			

[a]) From [2a]. [b]) Estimated value. [c]) This solvent-exchange value equates to 0.04 s⁻¹ for a revised pK_a of 6.0. [d]) OH⁻-catalyzed pathway for epimerization.

We also examined polarimetrically the base hydrolysis of resolved *endo*-N₃ [4]. The expectation was that one would find two rates, the formation of active *exo*-N₃, followed by its subsequent racemization. The two rate constants obtained from the fit for a pH

8.35 buffer ($[Co] = 1.0 \times 10^{-3}$ M) were 1.52×10^{-3} and 5.75×10^{-4} s^{-1}. Further, with reference to *Scheme 1*, k_{ba}/k_{bc} was defined by the pre-exponential factors, yielding $k_{ba} = 3.6 \times 10^{-4}$ and $k_{bc} = 1.16 \times 10^{-3}$ s^{-1} for the pH 8.35 condition (the quantities $[M]_{436} = 1166$ for *exo*-N$_3$, and $[M]_{436} = 873$ for *endo*-N$_3$ were required to determine this). These numbers correspond to k_{OH} values of 97 and 310 M^{-1} s^{-1}, respectively, for the two isomers and are in reasonable agreement with those in *Table 4* (the analysis used neglects contributions from the reverse reaction, k_{ab}). The ratio k_{bc}/k_{ba} from this experiment gives $76 \pm 4\%$ hydrolysis, $24 \pm 4\%$ epimerization for the *endo*-isomer. The reactivity ratio for the *endo*- and *exo*-N$_3$ ions is $11.6/5.75 = 2.0$. Such values agree with those obtained from the HPLC experiment given above, but, more importantly, the polarimetric experiment requires that the 24% *exo*-N$_3$ product is fully optically active and that the OH products are optically inactive.

Additional spectrophotometric hydrolysis rate data were collected over the [OH$^-$] range 0.10 to 1.0M and are shown in *Fig. 6*. ($I = 1.0$M NaClO$_4$; 25.0°). The observed curvature fits the rate expression:

$$k_{obs} = k_{OH}^{N_3}[OH^-]/(1 + K_H[OH^-])$$

with $k_{OH}^{N_3} = 190 \pm 15$ M^{-1} s^{-1}, $K_H = 1.3 \pm 0.1$ M^{-1}. Clearly $k_{OH}^{N_3}$ refers to the equilibrium mixture, while K_H is attributed to ionization of an acidic NH proton, corresponding to a pK_a of 13.7. This proton need not be that responsible for base hydrolysis (S_N1CB mechanism), although, for this complex, proton exchange data [2a] indicate that the *sec*-NH center may well be the most acidic.

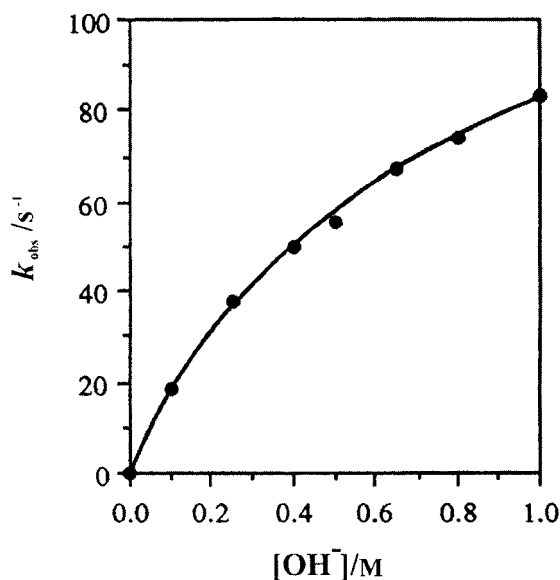Fig. 6. *Plot of* k$_{obs}$ vs. [OH$^-$] (0.10–1.0M; $I = 1.0$M, NaClO$_4$) *for hydrolysis of* mer*(exo)-[Co(dien)(dapo)N$_3$]$^{2+}$ (ca.* 10^{-4} M). The points represent experimental data, and the curve is calculated according to *Eqn. 3*, and values of constants are given in the text.

Discussion. – Our immediate goal was to measure the critical properties alluded to, or indirectly determined, in the previous ingeniously designed study [2]. In that work, the aim was to establish the geometry of the five-coordinate intermediate generated in the base hydrolysis reaction. If it were the symmetric trigonal bipyramid **3a**, then all products would be racemic; if it were an asymmetric species, or a pair of rapidly interconverting enantiomeric intermediates, such as **3b**, then at least some of the product would be expected to be optically active. It is known that deprotonated *sec*-N centers joining five-membered chelate rings in the same plane (so-called 'planar' N-centres) invert rapidly ($k_I = 10^6 - 10^8$ s^{-1} [7]; *cf.* other Co^{III} $-$ N centers, $k_I = 10^2 - 10^4$ s^{-1} [8–10]), but it is also known that most deprotonated five-coordinate Co^{III} intermediates are very unstable, scavenging immediately available species Y$^-$ or H$_2$O ($k > 10^{10}$ s^{-1}) [11]. The observation of a racemic product, especially for Y$^- = $ N$_3^-$, therefore, implied the symmetric intermediate **1a**. However, earlier studies with complexes designed to investigate similar properties, *viz.*, *sym*-[Co(trenen)X]$^{2+}$ (**4**; X $=$ Cl [12], MeSO$_3$ [13]); [Co(bamp)(dapo)Cl]$^{2+}$ (**5**) [14]; [Co(dienim)(en)Cl]$^{2+}$ (**6**) [15], all gave at least partial optical retention in the hydrolysis product (Y $=$ OH, N$_3$). Such studies placed certain restrictions on both the site of deprotonation and the life-time of the five-coordinate intermediate.


3a

3b
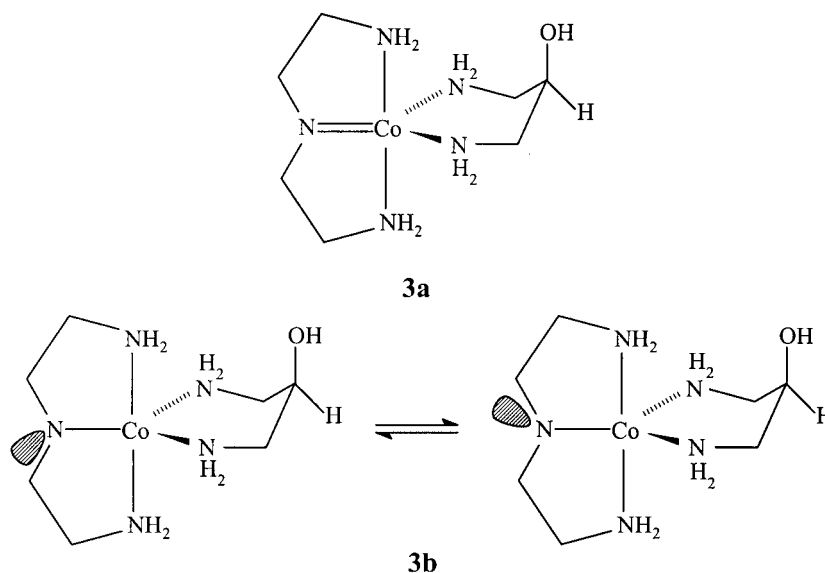
Our concerns with the published work [2] were twofold. First, the competition value for N$_3^-$ in the base hydrolysis reaction (X $=$ Cl; $R = $ [CoN$_3$]/[CoOH] $\cdot$ [N$_3$]) of 1.4 ± 0.2 was unusually large, although indirectly determined by allowing for subsequent slower anation by N$_3^-$ of the equilibrated *exo,endo*-OH product. It did not, however, allow for anation of the kinetically produced *endo*-OH product, and we knew from studies on [Co(cyclen)(NH$_3$)Cl]$^{2+}$ [6] that the first formed hydrolysis product was (in that case) largely the *endo*-OH isomer, and that this underwent subsequent anation at a

4

$k_{OH} = 5.2 \times 10^2$ M⁻¹ s⁻¹

5

$k_{OH} = 3 \times 10^3$ M⁻¹ s⁻¹

6

$k_{OH} = 6.0 \times 10^2$ M⁻¹ s⁻¹
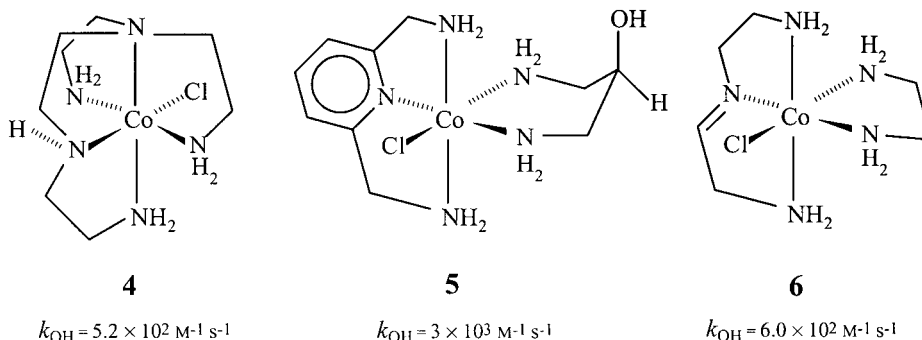
considerably faster rate than did the *exo*-OH isomer or equilibrium mixture. It was, therefore, conceivable that the competition ratio R was considerably overstated, and, more importantly, that the observed racemic *exo,endo*-N$_3$ product could have arisen, in large part, from repeated cycles through the five-coordinate intermediate. This could have allowed equilibration between ground-state enantiomeric intermediates **3b**, rather than involving symmetric **3a**. We, therefore, set out to determine both the immediate competition numbers and the amount of kinetically produced *endo*-OH product. Second, we needed to know precisely the epimerization rate for the *endo*-OH isomer, as well as to ensure that this reaction proceeds *via* the same intermediate (or set of intermediates) as the base hydrolysis reaction.

Our result of $R = 1.3$ confirms the earlier value [2a] and means that large amounts of Co−N$_3$ are formed directly from the five-coordinate intermediate (56% in 1.0M, 72% in 2.0M N$_3^-$). Furthermore, the immediately formed 70% *exo*-OH, 30% *endo*-OH distribution (in the presence of N$_3^-$) means that only small amounts of Co−N$_3$ (*ca.* 7 – 8%) arise from the subsequent fast anation of first-formed *endo*-OH product before it reaches equilibrium. Thus, the observation of racemic *exo,endo*-N$_3$ in 0.50 – 2.0M N$_3^-$ [2a] must result, in large part, from the first-formed five-coordinate intermediate, which must, therefore, be symmetric, *i.e.*, of type **3a**. Our only reservation is that the larger than usual competition value suggests a rather more stable intermediate, with greater discrimination amongst entering groups (N$_3^-$ is now markedly preferred over H$_2$O). This suggestion receives support from exploratory experiments with *endo*-[Co(dien)(dapo)OH$_2$]Cl$_3$ in 1.0M NaCl, (30 s, pH 6.0), which suggest that Cl$^-$ is a considerably poorer competitor than N$_3^-$. Thus, intermediates of type **3b** (either trigonal bipyramidal or square pyramidal) may well have time to equilibrate before reacting. The possibility of pπ-dπ stabilization involving a truly planar N-atom as an intermediate or transition state is, therefore, left open to question.

Let us now look at some of the other data. That the *exo,endo*-OH isomerization reaction proceeds *via* the same intermediate (or set of intermediates) as base hydrolysis is required by the observation of the same *exo,endo*-N$_3$ distribution (68 ± 2% (*exo*), 32 ± 2% (*endo*)) following *ca.* 1 × $t_{1/2}$ for epimerization of the *endo*-OH isomer, pH 7.8. This is an important result, since it means that the same proton is involved in assisting the departure of OH as is involved in the base hydrolysis of X (Cl, ONO$_2$, N$_3$).
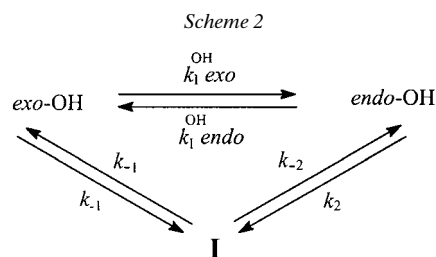
Scheme 2

According to *Scheme 2*, we have:

$$k_I^{OH}(endo) \cdot k_1 \cdot k_{-2} = k_I^{OH}(exo) \cdot k_2 \cdot k_{-1} \qquad (4)$$

which gives

$$k_1/k_2 = \left(k_I^{OH}(exo)/k_I^{OH}(endo)\right) \cdot (k_{-1}/k_{-2}) \qquad (5)$$

i.e.,

$$k_1/k_2 = k_{eq}^{OH}(exo) \cdot (k_{-1}/k_{-2}) \qquad (6)$$

Both values on the right hand side are now known experimentally: 0.11 and 60/40, respectively. This leads to the conclusion that the *exo*-OH isomer is less reactive than the *endo*-OH species by a factor of 6.0 (25°). Using the experimental value of 0.04 s^{-1} for k_1 gives $k_2 = 0.24 \text{ s}^{-1}$ for the loss of OH from the *endo*-OH isomer.

Limiting N_3 anation rate constants are proportional to the specific dissociation rates k_2 and k_1, as discussed elsewhere [2], and measurements on the N_3 anation rates for the *endo*- and *exo*-OH species in 1M NaN_3 under conditions where the base-catalyzed pathway does not contribute provided an estimate of k_2/k_1. Data for *endo*-reactant at 25° were resolved into two exponentials: $k_{fast} = (1.57 \pm 0.10) \times 10^{-1} \text{ s}^{-1}$, $k_{slow} = (2.44 \pm 0.08) \times 10^{-2} \text{ s}^{-1}$, whereas the data for the *exo*-reactant followed a single exponential: $k = (2.40 \pm 0.06) \times 10^{-3} \text{ s}^{-1}$. This is in excellent agreement with k_{slow} and the value previously reported [2]. Thus, the ratio $k_{fast}/k_{slow} (= k_2/k_1)$ is 6.4, in good agreement with the above value of 6.0.

These values are in agreement with our previous suggestion [5][6] that, in the six-coordinate system, the concerted transfer of an *endo*-NH proton provides a low-energy pathway for the loss of OH^- (as H_2O). Several other *cis*-NH protons appear to be geometrically available for such a transfer, but the concordance with the base hydrolysis result locates this proton precisely. However an *exo(sec)*-NH proton must be involved with the *exo*-OH isomer, and, clearly, transfer of this proton is competitive, probably *via* the solvent. For the reverse process, entry of H_2O into the five-coordinate deprotonated intermediate now favors *exo* protonation, but this could be because the lone pair is not as accessible to the incoming H_2O molecule in this geometry (trigonal bipyramid), with reprotonation coming late in the reaction profile. Clearly, however, energy differences between *endo/exo* loss of H_2O from the six-coordinate system and addition to the five-coordinate intermediate are not large. Likewise, the $k_{OH}/k_{H/D}$ ratios given in *Table 4* suggest that deprotonated *endo*-X (X = Cl, N_3) is more reactive than

the corresponding *exo*-species, and this supports our earlier suggestion [6][16] that repulsive overlap between the *endo*-lone pair and filled bonding and π-nonbonding lobes of X assists its departure.

The above value of the rate constant for the loss of OH from the *exo*-OH isomer ($k_1 = 0.04 \text{ s}^{-1}$) agrees well with the limiting rate constant for N_3^- anation of the equilibrium *exo,endo*-OH mixture, $k_{N_3}(\lim) \sim 0.03 \text{ s}^{-1}$ found previously [2b]. Clearly, anation is controlled by k_1 with rapid subsequent entry of N_3^- into the five-coordinate intermediate. In 0.50M N_3^-, the intermediate forms 38–40% (*exo* + *endo*)-N_3, together with some 20% *endo*-OH (*Table 3*). The latter will react rapidly to form an additional *ca.* 8% *exo,endo*-N_3 giving $k_{N_3}(0.5\text{M } N_3^-) = 0.04 \times 0.48 = 0.019 \text{ s}^{-1}$, a value in reasonable agreement with that observed under this condition ($k_{obs} = 0.022 \text{ s}^{-1}$) [2b].

Likewise, for epimerization and hydrolysis of Co–N_3 (*Scheme 3*), we have

$$k_{OH}^{N_3}(endo) \cdot k_{-4} \cdot k_E^{N_3}(exo) = k_{OH}^{N_3}(exo) \cdot k_{-3} \cdot k_E^{N_3}(endo) \tag{7}$$

i.e.,

$$k_{-3}/k_{-4} = k_{OH}^{N_3}(endo) \cdot k_E^{N_3}(exo)/k_{OH}^{N_3}(exo) \cdot k_E^{N_3}(endo) \tag{8}$$

or

$$k_{-3}/k_{-4} = k_{OH}^{N_3}(endo)/k_{OH}^{N_3}(exo) \cdot k_{eq}^{N_3}(endo/exo) \tag{9}$$

Using the observed rate constants for hydrolysis (*Table 4*) and the known equilibrium constant we have $k_{-3}/k_{-4} = (295/153) \times 0.25 = 0.48$; or 68% *exo*-$N_3$, 32% *endo*-$N_3$ from the five-coordinate intermediate. This distribution is in excellent agreement with that observed (*Table 3*), so, once again, the kinetic, equilibrium, and product data are in accord.

Scheme 3
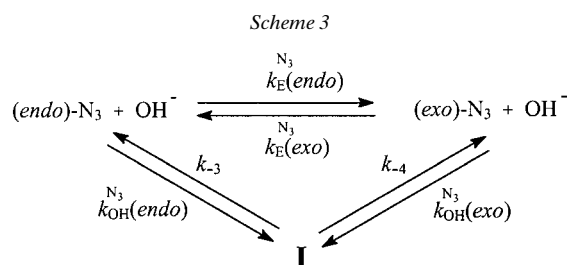
Epimerization in this six-coordinate *exo,endo*-N_3 system gave us a clue as to possible epimerization in the other six-coordinate systems (X = Cl, ONO_2, OH) prior to hydrolysis of X or loss of OH. Both reactions are OH^--catalyzed and are competitive for X = N_3 (k_{OH}/k_E values (*Table 4*)). For X = OH, the somewhat slower OH^--catalyzed isomerization reaction, $k_E = 3.6 \text{ M}^{-1} \text{ s}^{-1}$, is also, in our opinion, likely to result from epimerization in the six-coordinate complex; it could, however, represent OH^--catalyzed loss of coordinated OH. For X = ONO_2 or Cl, the epimerization rate is unlikely to differ much from $10–10^2 \text{ M}^{-1} \text{ s}^{-1}$ found for X = N_3 (acidity constants are

similar) so that the much faster hydrolysis rates for these complexes $(k_{OH}^X = 10^5 - 10^6 \text{ M}^{-1} \text{ s}^{-1})$, as well as the rapid loss of $X = OH$ around neutral pH, means that N-inversion (epimerization) in the six-coordinate complex will not compete with hydrolysis of X or loss or coordinated OH^-. Indeed, no epimerization was found for the *exo,endo*-Cl reactants after *ca.* $1 \times t_{1/2}$ for hydrolysis.

Finally, the k_E values for *exo,endo*-N$_3$ (*Table 4*) are not large compared to those found for many other Co^{III} systems (*cf.* $10^2 - 10^5 \text{ M}^{-1} \text{ s}^{-1}$, [7]; *cf.* $1.5 \times 10^5 \text{ M}^{-1}$ for $[Co(cyclen)(NH_3)N_3]^{2+}$ [6]), and the $k_{H/D}/k_E$ ratios (*Table 4*) are not particularly small ($10^3 - 10^6$ mostly [7]). It may, therefore, be concluded that the deprotonated *sec*-NH center undergoing inversion is not particularly strained in the six-coordinate system, as it clearly prefers to re-protonate rather then invert. This agrees with previous arguments concerning this system [2].

REFERENCES

[1] P. Comba, W. Marty, *Helv. Chim. Acta* **1980**, *63*, 683.
[2] a) P. Comba, W. G. Jackson, W. Marty, L. Zipper, *Helv. Chim. Acta* **1992**, *75*, 1147; b) P. Combo, W. G. Jackson, W. Marty, L. Zipper, *Helv. Chim. Acta* **1992**, *75*, 1172.
[3] D. A. Buckingham, C. R. Clark, A. J. Rogers, J. Simpson, *Inorg. Chem.* **1995**, *34*, 3646; D. A. Buckingham, C. R. Clark, A. J. Rogers, *Inorg. Chim. Acta* **1995**, *240*, 125.
[4] P. Comba, D. A. House, W. G. Jackson, W. Marty, H. Stoeckli-Evans, L. Zipper, *Helv. Chim. Acta* **1992**, *75*, 1130.
[5] N. E. Brasch, D. A. Buckingham, C. R. Clark, A. J. Rogers, J. Simpson, *Inorg. Chem.* **1998**, *37*, 4865.
[6] D. A. Buckingham, C. R. Clark, A. J. Rogers, J. Simpson, *Inorg. Chem.* **1998**, *37*, 3497.
[7] D. A. Buckingham, C. R. Clark, A. J. Rogers, J. Simpson, *J. Am. Chem. Soc.* **1997**, *119*, 4050.
[8] B. Halpern, A. M. Sargeson, K. R. Turnbull, *J. Am. Chem. Soc.* **1966**, *88*, 4630.
[9] D. A. Buckingham, L. G. Marzilli, A. M. Sargeson, *J. Am. Chem. Soc.* **1967**, *89*, 825.
[10] D. A. Buckingham, L. G. Marzilli, A. M. Sargeson, *J. Am. Chem. Soc.* **1969**, *91*, 5227.
[11] N. E. Brasch, D. A. Buckingham, C. R. Clark, K. S. Finnie, *Inorg. Chem.* **1989**, *28*, 4567.
[12] D. A. Buckingham, L. G. Marzilli, A. M. Sargeson, *Inorg. Chem.* **1969**, *8*, 1595.
[13] P. J. Cresswell, Ph.D. Thesis, Australian National University, 1974.
[14] W. Tinner, W. Marty, *Inorg. Chem.* **1981**, *20*, 3750.
[15] W. G. Jackson, R. J. Walsh, *Inorg. Chem.* **1991**, *30*, 4813.
[16] A. J. Clarkson, D. A. Buckingham, A. J. Rogers, A. G. Blackman, C. R. Clark, *Inorg. Chem.* **2000**, *39*, 4796.