Inorg. Chem. **1991**, *30*, 4813–4820 **4813**

a FORTRAN 77 program specifically designed for the nonlinear, least-squares refinement of unknown equilibrium constants from spectrophotometric data.

The spectrophotometric pK_a for the succinimide-*O* complex was determined as 3.0 by fitting the data of Table IX (supplementary material) as described.[41]

Oxygen-18 Analysis. $[(NH_3)_5Co\overline{NCO(CH_2)_2C}O](ClO_4)_2$ was dissolved in 0.5 M NaOH in H_2O which was nominally 5 atom % in ^{18}O. The reaction was quenched with 6 M $HClO_4$ after 1 half-life (115 s), diluted with ice water, and chromatographed on a Sephadex column jacketed at 2 °C with water from a circulating Lauda bath. The temperature was maintained at 2 °C during recovery to minimize isotopic exchange. The unreacted succinimido-*N* complex was eluted with 0.25 M NaCl (pH 5) and crystallized as the tetraphenylborate salt, which was dried in vacuo over silica gel for 24 h. The dried salt showed no detectable H_2O (^1H NMR, dry Me_2SO-d_6). The complex was analyzed for ^{18}O using the method of Anbar and Guttmann.[42] A sample (0.1 g) with an equimolar mixture of $HgCl_2$ and $Hg(CN)_2$ (May & Baker) was sealed under vacuum in a breakseal tube and pyrolyzed at 400 °C for 4 h to convert the oxygen in the complex to carbon dioxide. The tube was then broken open on a vacuum line; the carbon dioxide was separated from other products by gas chromatography and then analyzed by mass spectrometry.

Acknowledgment. The oxygen-18 analysis was performed by P.M.A. as a School Visitor at the Research School of Chemistry of the ANU, and we thank Professor A. M. Sargeson for his assistance and for the loan of the equipment. We thank Dr. A. P. Arnold for his assistance and advice in measuring the acidity constants and Dr. F. Bergeson and G. Turner of CSIRO Canberra for mass spectrometric analyses. Financial support from the Australian Research Council is gratefully acknowledged.

Registry No. **2**, 28627-67-0; **6**, 136545-43-2; **7**, 136545-45-4; **12**, 136545-47-6; **13**, 16632-75-0; **14**, 136545-49-8; **17**, 136545-51-2; **19**, 136545-53-4; $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$, 75522-50-8; $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3$, 51667-94-8; $[(NH_3)_5CoOH_2](ClO_4)_3$, 13820-81-0; succinamic acid, 638-32-4; succinic anhydride, 108-30-5; ammonium succinamate, 136545-54-5.

Supplementary Material Available: Rate data (Tables VIII, X, and XI) and spectral pK_a data (Table IX) (2 pages). Ordering information is given on any current masthead page.

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(41) Fairlie, D. P.; Jackson, W. G.; Thompson, K. H. *Inorg. Chem.* **1990**, *29*, 3146.

(42) Anbar, M.; Guttmann, S. *J. Appl. Radiat. Isot.* **1959**, *5*, 233–235.

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Kinetics and Stereochemistry of Base Hydrolysis of (+)-$[Co(dienim)(en)Cl]^{2+}$ and the Racemization of (+)-$[Co(dienim)(en)OH]^{2+}$

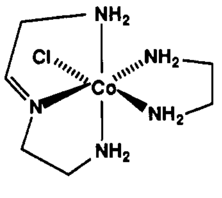
W. Gregory Jackson* and Rachelle J. Walsh

Received May 8, 1991

The complex *mer*-$[Co(dienim)(en)Cl]ZnCl_4$ (dienim = $NH_2(CH_2)_2N{=}CHCH_2NH_2$) has been synthesized from NH_2CH_2CHO, $NH_2(CH_2)_2NH_2$, and $Co^{II}Cl_2$ by H_2O_2 oxidation; it is identical to the material isolated by House et al.[1,2] as a side product in the synthesis of *trans*-$[Co(en)_2Cl_2]Cl$. It has been characterized by spectroscopy (^{13}C, ^1H NMR, vis/UV), and the *mer* configuration is confirmed by BH_4^- reduction to the known *mer*-$[Co(dien)(en)Cl]^{2+}$. The aqua complex *mer*-$[Co(dienim)(en)OH_2]Cl_3$ has been prepared by several routes, including reaction of the chloro complex in aqueous Hg^{2+} and OH^- or in neat CF_3SO_3H followed by hydrolysis. The chloro complex has been optically resolved using hydrogen L-dibenzoyltartrate and the active aqua ion crystallized after reaction of the resolved chloro complex with Hg(II). Base hydrolysis of (+)-*mer*-$[Co(dienim)(en)OH]^{2+}$ follows the rate law $k_r(\text{obsd}) = k^s{}_r + k^{OH}{}_r[OH^-]$, where $k^s{}_r = (4.8 \pm 0.1) \times 10^{-4}\ s^{-1}$ and $k^{OH}{}_r = 69 \pm 2\ M^{-1}\ s^{-1}$, at 25 °C and $I = 0.1$ M ($NaClO_4$). It is argued that the unusually rapid spontaneous racemization of the hydroxo ion proceeds via its internal conjugate base $[Co(dienimH)(en)OH_2]^{2+}$. Base hydrolysis of the (+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$ ion follows the rate law $k(\text{obsd}) = k^s + k_{OH}[OH^-]$, where $k^s = (8.5 \pm 2.5) \times 10^{-5}\ s^{-1}$ and $k_{OH} = 603 \pm 36\ M^{-1}\ s^{-1}$ at 25 °C and $I = 0.1$ M ($NaClO_4$). The first formed product is 75% (+)- and 25% (−)-*mer*-$[Co(dienim)(en)OH]^{2+}$ and not racemate as previously reported.[2] The mechanistic implications are discussed.

Introduction

House et al. have reported an interesting side product in the synthesis of *trans*-$[Co(diamine)_2Cl_2]^+$ complexes by direct oxidation of $Co^{II}Cl_2$ plus amine (amine = en, tn, ibn, 2,2-Me_2tn).[1-5] Two diamines are condensed to give a triamine with loss of a nitrogen and the production of an imine linkage. With ethylenediamine, for example, the tridentate dienim related to the saturated dien ligand is obtained,[1,2] as the complex *mer*-$[Co(dienim)(en)Cl]ZnCl_4$; crystal structures for the tn and ibn analogues have been reported. These syntheses, however, are not very efficient; for example, the yield is reported to be 7–8% in the cases of en.[1] This cation was required for the reinvestigation[2] of the stereochemistry of base hydrolysis (vide infra) and therefore an improved, direct synthesis was devised. Herein we report the complex prepared via Co(II)-mediated Schiff base formation from aminoacetaldehyde and ethylenediamine, as well as the synthesis of a new and a related imine complex using the same strategy.



(+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$

The meridional form of the $[Co(dienim)(en)Cl]^{2+}$ complex is chiral. House et al.[2] obtained a molar rotation of +62 deg mol^{-1} dm^2 at 589 nm for one enantiomer using the arsenyl-(+)-tartrate dianion as the resolving agent. The low value suggested incomplete resolution, and we report an improved resolution using hydrogen L-dibenzoyltartrate (DBHT⁻).

The base hydrolysis of (+)-$[Co(dienim)(en)Cl]^{2+}$ has been investigated[2] using two different methods in order to evaluate the kinetics: polarimetry and spectrophotometry. The value for the rate constant obtained using the polarimetric method was found

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(1) House, D. A. *Helv. Chim. Acta* **1985**, *68*, 1872.

(2) Watson, A. A.; Prinsep, M. R.; House, D. A. *Inorg. Chim. Acta* **1986**, *115*, 95.

(3) Riesen, A.; Zehnder, M.; House, D. A. *Inorg. Chim. Acta* **1986**, *113*, 163.

(4) McKee, V.; Harnett, M.; House, D. A. *Inorg. Chim. Acta* **1985**, *102*, 83.

(5) House, D. A. *Inorg. Chem.* **1986**, *25*, 1671.

0020-1669/91/1330-4813$02.50/0

Table I. Polarimetric Rate Data for the Racemization of (+)-*mer*-$[Co(dienim)(en)OH]^{2+}$ at 25 °C and I = 0.1 M ($NaClO_4$)

pH	k_r(obsd),[a] s^{-1}	pH	k_r(obsd),[a] s^{-1}
7.61	$(5.18 \pm 0.02) \times 10^{-4}$	8.72	$(1.17 \pm 0.06) \times 10^{-3}$
8.10	$(7.41 \pm 0.18) \times 10^{-4}$	8.88	$(1.39 \pm 0.07) \times 10^{-3}$
8.58	$(9.40 \pm 0.27) \times 10^{-4}$		

[a] Mean of at least duplicate determinations.

to be about half the value determined spectrophotometrically.[2] Consecutive reactions can often appear to be simple one-stage first-order processes,[6] and we supposed that there were actually two consecutive reactions, hydrolysis followed by racemization, the first detected spectrophotometrically but both detected polarimetrically.

We have therefore reexamined the kinetics and stereochemistry of base hydrolysis of the (+)-$[Co(dienim)(en)Cl]^{2+}$ ion: first to resolve the anomaly[2] in the kinetics for the two methods of determination and second to establish the stereochemistry of the first formed hydroxo product $[Co(dienim)(en)OH]^{2+}$ reported previously[2] as racemic. This work required the synthesis of the resolved aqua complex, and the rates of racemization of the active hydroxo complex generated from this salt in base have been determined to properly interpret the kinetics of the base hydrolysis and racemization of (+)-$[Co(dienim)(en)Cl]^{2+}$.

Results

Kinetics of Racemization of (+)-*mer*-$[Co(dienim)(en)OH]^{2+}$. This reaction was followed polarometrically at 578 nm in five Tris/$HClO_4$ buffers over the pH range 7.6–8.9 at 25 °C. Simple first-order kinetics were observed, and final rotations were zero. The rate data (Table I) followed the equation $k_r(\mathrm{obsd}) = k^s_r + k^{OH}_r[OH^-]$; Figure 1 (supplementary material) shows k_r(obsd) plotted against $[OH]^-$. Weighted linear regression yielded the values $k^s_r = (4.8 \pm 0.1) \times 10^{-4}\ s^{-1}$ and $k^{OH}_r = (69 \pm 2)\ M^{-1}\ s^{-1}$. Independent measurements showed that the aqua ion racemizes much more slowly than the hydroxo ion, which is unusual Co(III) chemistry,[7-9] and we note that the lowest pH for the racemization study (above) is well above the pK_a for the aqua ion; i.e., we are dealing with the spontaneous and base-catalyzed reactions of the hydroxo species.

Kinetics and Stereochemistry of Base Hydrolysis of *mer*-$[Co(dienim)(en)Cl]^{2+}$. For the base hydrolysis of *mer*-$[Co(dienim)(en)Cl]^{2+}$ sharp isosbestic points were found at 323, 351, 388, and 498 nm, at each pH studied in the range 7.6–8.9, consistent with a simple reaction (or a set of parallel reactions), as Watson et al. claimed.[2] Also, the final spectra (in acid and base) were identical to those of the isolated *mer*-$[Co(dienim)(en)OH_2]^{3+}$ in the same media ($\epsilon_{459}(\max) = 126$ and $\epsilon_{472.5}(\max) = 134$, respectively), showing that in the pH range 7.6–8.9 and with [Co] $\leq 10^{-2}$ M, the hydrolysis reaction

$$mer\text{-}[Co(dienim)(en)Cl]^{2+} + OH^- \rightarrow mer\text{-}[Co(dienim)(en)OH]^{2+} + Cl^-$$

is not reversible and a single isomeric product results.

Rate data for this reaction were determined spectrophotometrically and polarimetrically at five pH values in the range 7.6–8.9. The kinetics were accurately first order and the same (spectrophotometric) value was obtained at each of several wavelengths. The polarimetric values are a little different from the spectrophotometric numbers (Table II) and are wavelength dependent, despite adequately fitting a first-order relation. Figure 2 (supplementary material) shows the spectrophotometric data plotted to indicate compliance with the expected linear relationship $k(\mathrm{obsd}) = k^s + k_{OH}[OH^-]$, where $k^s = (8.5 \pm 2.9) \times 10^{-5}\ s^{-1}$ and $k_{OH} = 603 \pm 36\ M^{-1}\ s^{-1}$, at I = 0.1 M ($NaClO_4$, 25 °C) (weighted linear regression).

Table II. Spectrophotometric and Polarimetric Rate Data for the Base Hydrolysis of (+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$ at 25 °C and I = 0.1 M ($NaClO_4$)

	k(obsd), s^{-1}	
pH	polarimetric[a]	spectrophotometric[d]
7.61	$(4.10 \pm 0.02) \times 10^{-4}$ (4.5, 4.1)[b]	$(5.46 \pm 0.08) \times 10^{-4}$
8.10	$(1.32 \pm 0.005) \times 10^{-3}$ (1.46, 1.17)[b]	$(1.61 \pm 0.006) \times 10^{-3}$
8.58	$(3.53 \pm 0.03) \times 10^{-3}$ (3.23, 4.13)[b]	$(4.21 \pm 0.01) \times 10^{-3}$
8.72	$(6.15 \pm 0.08) \times 10^{-3}$[c]	$(5.39 \pm 0.03) \times 10^{-3}$
8.88	$(7.29 \pm 0.09) \times 10^{-3}$[c] (6.87, 7.43)[b]	$(8.20 \pm 0.004) \times 10^{-3}$

[a] Mean of at least triplicate determinations; weighted averages of 578- and 546-nm results. [b] 578- and 546-nm results, respectively. [c] 546-nm results only. [d] 520-nm data.

Activity of First-Formed Base Hydrolysis Product. Although the rates for the first and second steps of the base hydrolysis reaction are each first order in $[OH^-]$, the racemization of the hydroxo complex has a significant $[OH^-]$-independent term in the pH range 7.6–8.9, which of course becomes more significant at lower pH. The ratio $k(\mathrm{obsd})/k_r(\mathrm{obsd})$ ratio is hence pH dependent, changing from about 1:1 to about 5:1 at the highest pH studied (Tables I and II). Thus the experiment that tested the optical activity of the first-formed product directly was more easily performed at pH 8.9. A sample of the active chloro complex was reacted for the optimal period at pH 8.9 and acid quenched. An ion-exchange separation was used to recover the aqua complex (in 3 M HCl), which was separated from residual reactant, and the activity was compared directly with a sample similarly recovered but derived from the same active chloro sample treated with excess Hg^{2+}. The first-formed product was found to be 49.5% active (i.e. 75% (+) and 25% (−)) thus establishing a reaction sequence involving partial racemization during hydrolysis. [The first-formed hydroxo sample was actually observed to be 45.9% active but a small correction[10] was applied for the subsequent racemization using the following relationship: $(\%\ \mathrm{activity})_{t=0} = (\%\ \mathrm{activity})_{\mathrm{obsd}}(k_r(\mathrm{obsd}) - k(\mathrm{obsd}))(1 - e^{-k(\mathrm{obsd})t})/k(\mathrm{obsd})(e^{-k(\mathrm{obsd})t} - e^{-k_r(\mathrm{obsd})t})$.]

Polarimetric Rate Data for the Base Hydrolysis of (+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$. The α, t data obtained from the polarimeter were refitted to a double exponential for the consecutive reaction scheme A → B → C where k(obsd) is the specific rate of hydrolysis rate for the first step (Table II) and k_r(obsd) is the specific rate of racemization for the second step (Table I). Attempts at fitting of two exponentials using both k(obsd) and k_r(obsd) as parameters often did not converge or converged at false minima. Indeed, and perhaps not surprisingly, better fits (lower $\sum[\alpha(\mathrm{calcd}) - \alpha(\mathrm{obsd})]^2$) could be obtained in the more parametrized data analyses, but these results proved to be unrealistic. Since we knew that the data already provided a reasonable fit to a single exponential, in the final analysis k_r(obsd) was confined to its independently measured value, and the final optical rotation was fixed at zero. The result was that the computed k(obsd) was closer to and now in reasonable agreement with the spectrophotometric value for the hydrolysis step.

Discussion

Syntheses. Aminoacetaldehyde diethyl acetal was deprotected by reaction with aqueous HCl:

$$NH_2CH_2CH(OC_2H_5)_2 + HCl + H_2O \rightarrow [NH_3CH_2CHO]^+Cl^- + 2C_2H_5OH$$

The amino aldehyde, stable as its protonated form, was then mixed with $CoCl_2{\cdot}6H_2O$, and sufficient ethylenediamine was added to

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(6) Jackson, W. G.; Harrowfield, J. MacB.; Vowles, P. D. *Int. J. Chem. Kinet.* **1977**, *9*, 535.

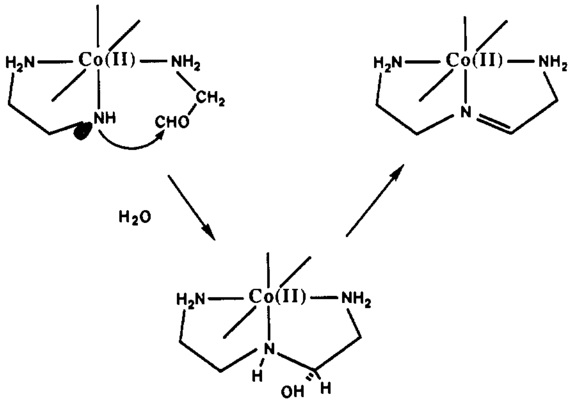
(7) Tobe, M. L. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 1.

(8) Jackson, W. G.; Sargeson, A. M. *Org. Chem.* **1980**, *42*, 273.

(9) Jackson, W. G. The Stereochemistry of the Bailar Inversion and Related Substitution Processes. In *The Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. 1; pp 255–357.

(10) Jackson, W. G.; Hookey, C. N. *Inorg. Chem.* **1984**, *23*, 668.

consume excess acid, to deprotonate the aminoaldehyde thus allowing it to bond to the cobalt and to permit coordination of one en. The formation of the dienim ligand is completed by a metal ion directed condensation between the coordinated en and the amino aldehyde, with the usual elimination of water from the carbinolamine to generate the imine:



Finally, oxidation to kinetically inert Co(III) locks in the ligand system.

If the ethylenediamine was added before the cobalt(II), very little $[Co(dienim)(en)Cl]^{2+}$ and large amounts of $[Co(en)_3]Cl_3$ are formed. In the absence of the cobalt(II), the dienim ligand has difficulty forming because after the aminoaldehyde is deprotonated by the ethylenediamine it can self-condense. The early presence of the cobalt(II) minimizes the opportunity for this reaction and also functions as a template in bringing the amine and aldehyde functions in close proximity, thus enhancing the rate of reaction.

The total product from a small-scale synthesis as above was chromatographed and the 2+ red band analyzed by ^{13}C NMR spectroscopy. It was a single isomer, showing just six lines (Figure 3). A sample of $[Co(dienim)(en)Cl]ZnCl_4$ was synthesized by the published method,[1,2] and its ^{13}C and ^1H NMR and vis/UV spectra were compared with those of the product from the new synthesis. They were identical and additionally, isomeric purity was established (see Experimental Section). Furthermore, the 300-MHz NMR spectra for the $ZnCl_4^{2-}$ and ClO_4^- salts (Figure 4) illustrate the difficulty of using this technique in fingerprinting if the counteranion is varied—the shifts in Me_2SO are significantly different. Much the same is true of the ^{13}C NMR spectra (not shown), and the effect is obviously due to ion-pairing.

Although single-crystal X-ray structures of the ibn and tn analogues[3,4] establish the common *mer* configuration, there is no certainty that the en analogue is also *mer*. In fact facial isomers are known for tridentate ligands of this kind (two five-membered ring),[11] although there is a clear thermodynamic preference for the planar *mer* arrangement because of the presence of the imine double bond.

In the absence of a crystal structure, an unambiguous structural assignment can be made by BH_4^- reduction of the imine to generate $[Co(dien)(en)Cl]^{2+}$, all three topological isomers of which are known[12,13] and crystal structures of which are determined.[14,15] Since imine reduction does not involve substitution at the metal ion, the topological configuration should be retained and thus a direct comparison of product with authentic $[Co(dien)(en)Cl]^{2+}$ isomers should establish structure. In addition, there was the prospect of observing and even isolating the missing[16] *mer-endo*-$[Co(dien)(en)Cl]^{2+}$ isomer in this series, especially as imine hydrogenations in complexes of this kind do not normally show a marked specificity;[18] exo and endo refer to the NH proton orientation relative to the coordinated Cl^-, and these isomers arise by "H_2" addition above or below the –NH=CH– plane:

mer-$[Co(dienim)(en)Cl]^{2+}$ + "H_2" →
mer-exo- + *mer-endo*-$[Co(dien)(en)Cl]^{2+}$

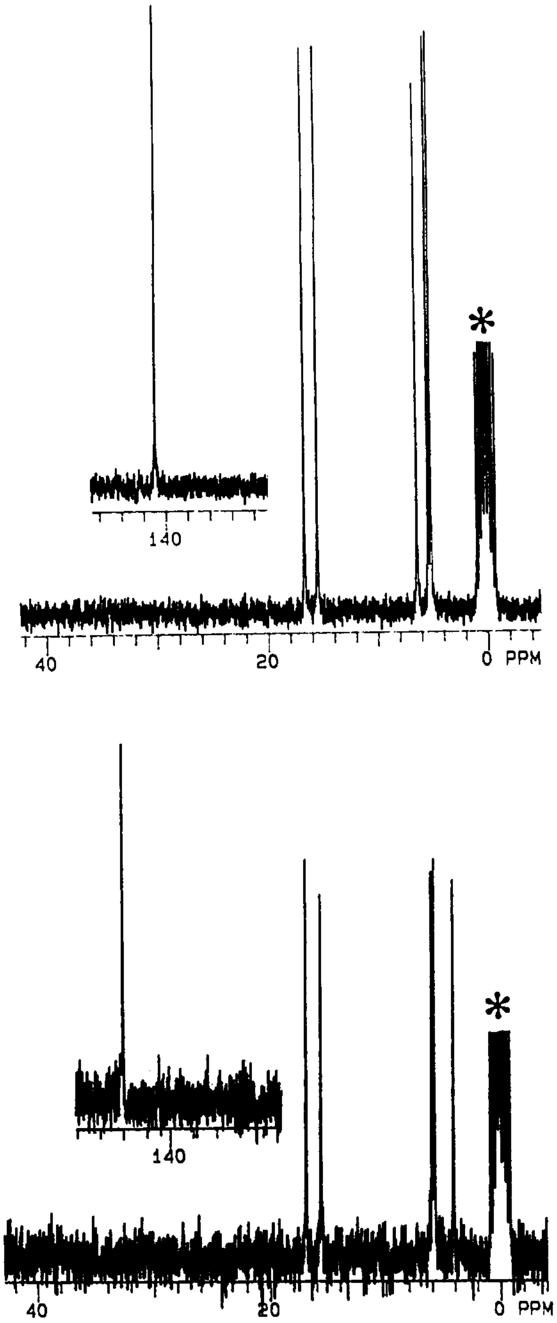


Figure 3. ^{13}C NMR spectra of *mer*-$[Co(dienim)(en)Cl]ZnCl_4$ (upper) and *mer*-$[Co(dienim)(en)OH_2]Cl_3{\cdot}H_2O$ (lower) in Me_2SO-d_6 illustrating the close similarity. The lowest field carbon (inset) is the imine. An asterisk denotes Me_2SO-d_6.

Under controlled conditions only *mer-exo*-$[Co(dien)(en)Cl]^{2+}$ was produced, confirmed by comparison with an authentic[14] specimen (^1H, ^{13}C, vis/UV spectra), and thus the *mer* configuration for the precursor imine is established. Interestingly, no *mer-endo* isomer was observed, suggesting a pronounced specificity

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(11) Buckingham, D. A.; Clark, C. R.; Foxman, B. M.; Gainsford, G. J.; Sargeson, A. M.; Wein, M.; Zanella, A. *Inorg. Chem.* **1982**, *21*, 1986.
(12) Gainsford, A. R.; House, D. A. *Inorg. Chim. Acta* **1969**, *3*, 367.
(13) Gainsford, A. R.; House, D. A. *Inorg. Chim. Acta* **1971**, *5*, 544.
(14) Gainsford, A. R.; House, D. A.; Robinson, W. T. *Inorg. Chim. Acta* **1971**, *5*, 595.
(15) Johnston, J. M.Sc. Thesis, Victoria University of Wellington, New Zealand, 1969; *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.* **1970**, *131*, 155.
(16) The "missing" isomers *mer-endo*-$[Co(dien)(en)Cl]^{2+}$ and *mer-endo*-$[Co(dien)(tn)Cl]^{2+}$ have recently been synthesized.[17]
(17) Jackson, W. G.; Walsh, R. J. Results to be published.
(18) Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1514.

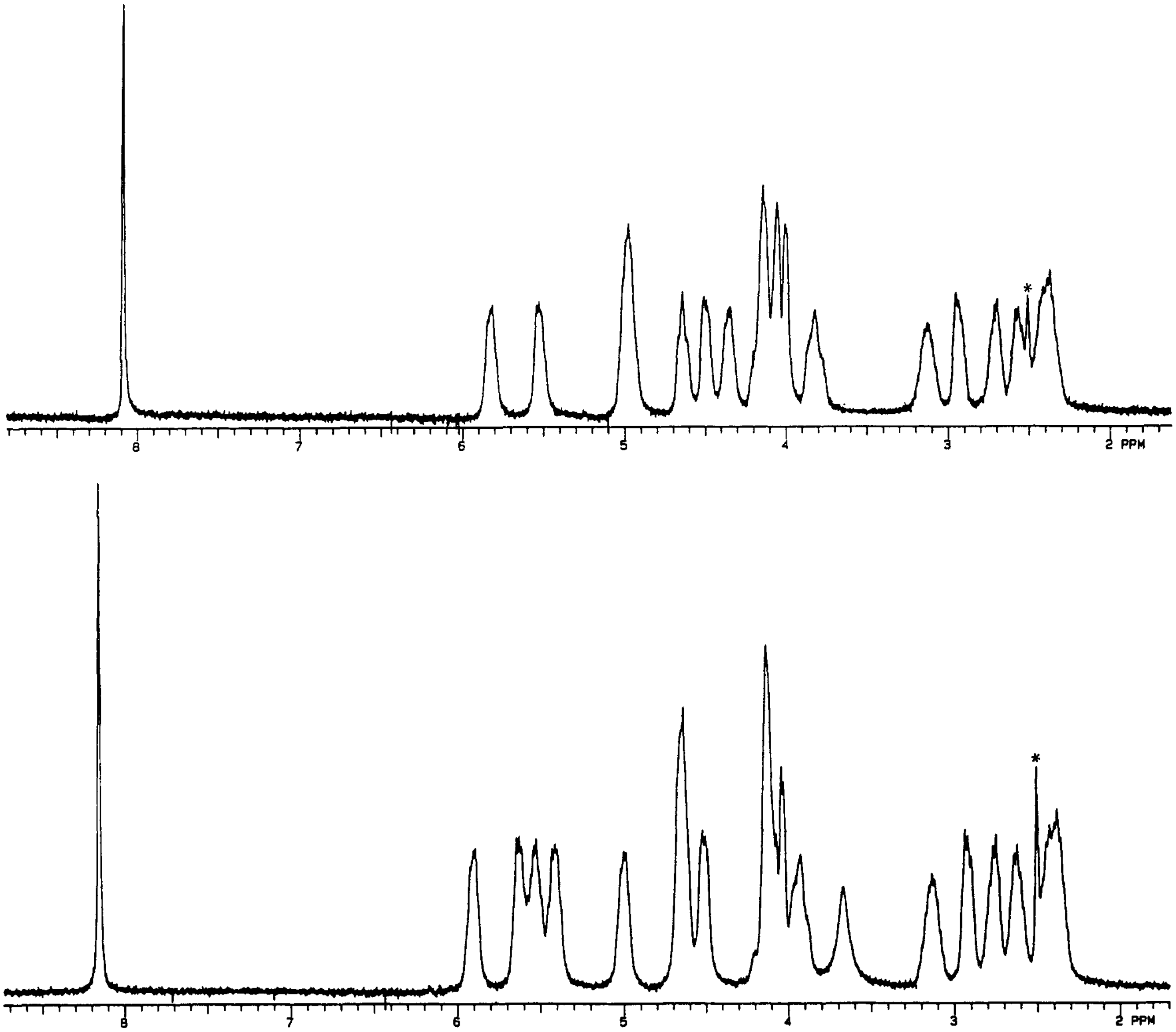

Figure 4. ^1H NMR spectra of *mer*-[Co(dienim)(en)Cl]$ZnCl_4$ (lower) and *mer*-[Co(dienim)(en)Cl]$(ClO_4)_2$ (upper) in Me_2SO-d_6 showing the significant differences between salts, especially at lower field (amine signals). An asterisk denotes Me_2SO-d_5.

for reduction at the imine. Conceivably the more stable[16] exo isomer may have resulted from inversion at the *s*-NH center in base, but the pH was insufficiently high for this. In any event, base hydrolysis is much faster than epimerization, yet the chloro amine product largely survived the conditions of BH_4^- addition.

The existence of optical isomers for this complex is not diagnostic of structure—all possible isomers are chiral. However, the chiroptical properties should perhaps be smallest in magnitude for the *mer* form, which owes its asymmetry simply to the imine function on just one side rather than both sides of the "flat" tridentate. Small molar rotations have been observed for the species resolved using arsenyl-(+)-tartrate,[2] but a new method using hydrogen L-dibenzoyltartrate (DBHT$^-$) as the resolving agent proved more successful. It resulted in molar rotations 3 times those reported, although still of a magnitude not inconsistent with the asymmetric *mer* structure. Optical purity was indicated by equal and opposite molar rotations obtained for exhaustively refractionated (+) and (−) forms.

Several methods for producing the aqua product were found, but in only one was the optical activity retained. The aquation of an active sample of the chloro complex was induced by the addition of mercuric ion.[19] The chloride ion is consumed by the mercuric ion (as $HgCl^+$) and the $[Co(dienim)(en)OH_2]^{3+}$ is formed with geometric and optical retention. This chemistry is typical[8,19,20] of halogenopentaaminecobalt(III) species and is a well-known strategy for the synthesis of chiral complexes of this kind.

The six-line pattern for the ^{13}C NMR spectrum for the aqua complex was very similar to that for the chloro complex (Figure 3), consistent with it being the pure *mer* form. The active aqua complex was relatively stable in acid solution (hours to days, 25 °C) but racemized in minutes in basic solution. In HCl (5 M), it is anated slowly back to the chloro complex, and the activity of the product chloro ion was the same as that of the active chloro complex used in its synthesis, thus confirming the retention of activity in both the forward and reverse directions

$$(+)\text{-}mer\text{-}[Co(dienim)(en)Cl]^{2+} \xrightleftharpoons[Cl^-]{Hg^{2+}} (+)\text{-}mer\text{-}[Co(dienim)(en)OH_2]^{3+}$$

and its optical purity. Again, this is typical pentaaminecobalt(III) chemistry.[8,9,19,20]

These dienim–cobalt(III) complexes are not especially stable in base, and are fairly readily reduced. Thus reaction with azide ion at the synthetic level led to a mixture of products, including

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[19] Posey, F. A.; Taube, H. *J. Am. Chem. Soc.* **1957**, *79*, 255.

[20] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6654.

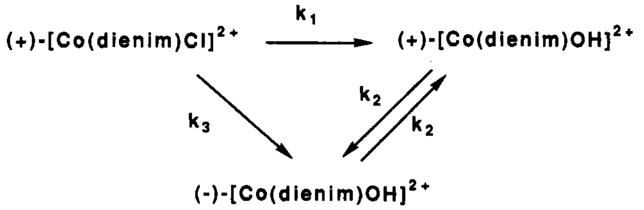
Table III. Specific Rates Determined Polarimetrically and Spectrophotometrically for the Reactions of $[Co(dienim)(en)X]^{2+}$ (X = Cl^-, OH^-) in a 1.0 M NaN_3 Buffer (pH ~7 at 25 °C)

	10^4k(obsd), s^{-1}	
X	polarimetric	spectrophotometric
Cl^-	6.3 ± 0.2	2.17 ± 0.15
OH^-	5.4 ± 0.3	4.7 ± 0.3

$[Co(en)_2(N_3)_2]^+$, and clearly disproportionation via Co(II) catalysis has come about. Azide ion anation could however be observed cleanly in situ by NMR, and although we did not isolate the azido complex we could record its ^{13}C NMR spectrum; anation went to completion under the conditions. Indeed, in a buffer which was 1 M in N_3^-, hydrolysis of $[Co(dienim)(en)Cl]^{2+}$ and subsequent anation of any $[Co(dienim)(en)OH]^{2+}$ surprisingly proved comparable in rate (Table III, spectrophotometric and polarimetric data), and thus any active $[Co(dien)(en)N_3]^{2+}$ formed by azide ion capture would have been quickly diluted by racemic azido complex via the hydroxo complex. These experiments were therefore not pursued.

Kinetics of Base Hydrolysis of (+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$. Both the polarimetric and spectrophotometric data for the base hydrolysis of (+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$ could be fitted to a single exponential function satisfactorily. Because the spectrophotometric results are intrinsically the more accurate of the two, the two values were not expected to be identical. The differences however were too large to be explained simply by experimental error. Particularly in the lower pH region, the polarimetric values for the rate constants for the hydrolysis was generally found to be lower of the two. At higher pH values, the values were close (Table II).

How then can each data set fit single exponentials yet give different results? The answer lies in the fact that a true double exponential fit can be very well approximated by a single exponential under certain circumstances, and yet give spurious results for the specific rate.[6] We have confirmed that the only reaction that the spectrophotometer detects is the conversion of the *mer*-chloro to the *mer*-hydroxo complex, regardless of optical activity. Thus the spectrophotometric rate determined for this reaction accurately describes the base hydrolysis. The explanation for the different polarimetric value must lie in the existence of a second reaction, in this case racemization, and this we have confirmed by directly observing the activity of first-formed (+)-*mer*-$[Co(dienim)(en)OH]^{2+}$ (and its subsequent decay).



$$k(\text{obsd}) = k_1 + k_3 \qquad k_r(\text{obsd}) = 2k_2$$

Refitting the data to a double exponential, which included a correction term for the second racemization step, yielded acceptable k(obsd) values, and thus the polarimetric data are in fact consistent with this reaction scheme. Except at the lowest pH where the rates for the primary and secondary steps are not far apart (vide infra), the spectrophotometric and corrected polarimetric hydrolysis rates were very similar. Furthermore the computed preexponential factors from such an analysis, which give the optical rotation for the first-formed hydroxo product[21] and thus relate directly to the proportion (k_1/k_3) of hydrolysis giving (+)- or (−)-*mer*-$[Co(dienim)(en)OH]^{2+}$, were used to estimate this ratio, using [α] determined at the same wavelength for the optically pure material; the result (approximately 3:1) was in good agreement with that determined directly, 49.5% activity (i.e. 75% (+) and 25% (−)).

At the lowest pH, the *corrected* polarimetric rate was less than half of the spectrophotometric value. This is an artifact and illustrates the often unappreciated point that when the rates of each step of a consecutive reaction are close, and within a factor of 2 is close enough (as they are at this particular pH), there is considerable flexibility in the rate values that can be fitted to the rate data, *without significant differences in the fits*.[6,21] The specific rates need to be separately determined under such a circumstance, as we have done. Nonetheless we could still check the consistency of the α, t data by fitting to a double exponential but confining both k(obsd) and k_r(obsd) to their independently determined values. The fits predictably were as good, and from the preexponential factors[21] the result again emerged that the first-formed product was partly racemized.

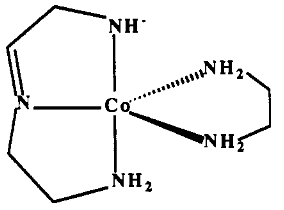
Apart from the above results, a number of other coincidences explain the satisfactory fit of the polarimetric data to one exponential function when two should have been required. The optical rotation of fully active hydroxo complex turned out to be quite low compared with that of the chloro ion. As a result, the change in rotation for the second step, racemization of the hydroxo ion, was so small it was barely detected when one commenced with the active chloro complex, making it appear as though only one reaction was occurring, namely hydrolysis. Interestingly, the relative activities of the (+)-chloro complex at 578 and 546 nm are +230 and +289°, whereas the corresponding values for the (+)-hydroxo complex of the same optical purity are +148 and +45°, a much greater change with wavelength (and in the reverse sense). This is consistent with the "distortion" referred to immediately above being more prominent at 578 nm as attested to in the results; e.g., at pH 8.88, $k(\text{obsd}) = 6.87 \times 10^{-3}$ (578 nm) and $k(\text{obsd}) = 7.43 \times 10^{-3}\ s^{-1}$ (546 nm) from the polarimetric data, while the spectrophotometric value for k(obsd) was $8.20 \times 10^{-3}\ s^{-1}$.

At the higher pH, there is a 5-fold difference in rate for the fast–slow reaction sequence. Not enough data were collected polarimetrically to observe much more than 1 half-life of the slower racemization reaction, although over the same period of time, this corresponds to 3 half-lives of data for the hydrolysis reaction of interest. This meant that the racemization reaction was again only manifested as a distortion of the data for the first step and resulted in an accurate hydrolysis rate. Also of course the result depends on the α(infinity) value used in the kinetic analysis, zero, or α(infinity) corresponding to the first-formed (+)-hydroxo product, which is nonzero.

Conclusions

It is universally accepted that hydroxide functions as a base rather than a nucleophile and one of the amines on the complex is deprotonated to give the reactive form of the complex.[7] Also we adopt the view that a five-coordinate intermediate forms and its structure is dependent upon the site of initial deprotonation.

One prospect is the formation of a symmetrical intermediate during base hydrolysis arising from deprotonation on the dienim ligand:



This permits racemization, but is contrary to the principle[7,22] that the aminate ion should occupy the trigonal plane of the intermediate for maximum p_π–d_π ligand-to-metal π bonding. On the basis of our assumptions, our results rule this out.

The second possibility is the formation of an intermediate arising from deprotonation on the en ligand (I or II), at either of two inequivalent sites. A common symmetrical intermediate III results if reprotonation occurs before the entry of the H_2O, and conse-

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(21) Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348.

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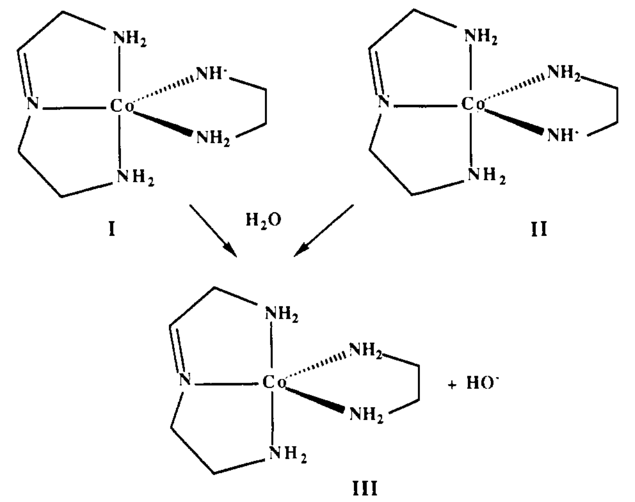
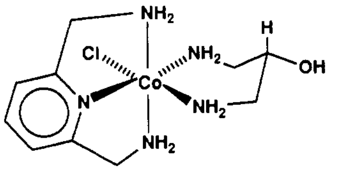
quently, the hydroxo complex formed is racemic:



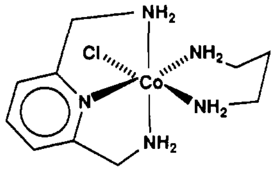
Again, our results eliminate this prospect, and it is interesting to note that such a proposal can be argued to be inconsistent with the principle of microscopic reversibility (PMR). The point is important because the stage of reprotonation in the general S_N1CB process has never been established; it appears to have been tacitly assumed to occur *after* the entry of nucleophile into the intermediate. In hindsight this was probably a safe assumption because if we look at the hypothetical case of base-catalyzed substitution of $[(NH_3)_5CoN_3]^{2+}$ in the presence of excess N_3^-, for example, then if loss of N_3^- occurs after deprotonation (as other data require), then by the PMR reentry of N_3^- *must* precede reprotonation. The extension of entering groups other than N_3^- is obvious, albeit the strict PMR requirement is gone.

Another is that suggested originally.[2] A symmetrical intermediate was believed to be formed through scrambling of the NH^- site across the trigonal plane, after deprotonation of the en ligand (I $\rightleftharpoons$ II, above). Again, our results preclude this possibility, thus preserving the belief[23] that aminate ion scrambling is relatively slow in these complexes.

Base hydrolysis studies[24,25] of *mer*-$[Co(bamp)(tn)Cl]^{2+}$ and *mer*-$[Co(bamp)(dapo)Cl]^{2+}$ are those closest to the present system.



mer-$[Co(bamp)(dapo)Cl]^{2+}$



mer-$[Co(bamp)(tn)Cl]^{2+}$

The complex is rendered optically active by removing the plane of symmetry with the replacement of the tn ligand by the dapo ligand, and the optically active $[Co(bamp)(dapo)Cl]^{2+}$ ion fully retains its optical activity when it undergoes base hydrolysis.[25] This implies that in this system there is no symmetrical intermediate formed.

There are several sites for deprotonation on the $[Co(bamp)(dapo)Cl]^{2+}$ ion (all NH protons are inequivalent), and the proton abstracted could be one of the primary amines of the dapo ligand or one of the terminal amines of the bamp ligand. If deprotonation occurs on the bamp ligand, a symmetrical trigonal-bipyramidal intermediate is formed, and racemization would take place. If instead deprotonation occurs on the dapo ligand and the aminate site is *not* scrambled across the trigonal plane of an otherwise symmetrical trigonal bipyramid, there would be a degree of retention of the chirality because of preferred sites for water attack in the trigonal plane; this is consistent with the facts.

In summary, we believe that in the base hydrolysis of the (+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$ complex, deprotonation occurs on the en ligand and a trigonal bipyramid is formed, analogous to that proposed for the structurally related (+)-*mer*-$[Co(bamp)(dapo)Cl]^{2+}$ system, having the aminate ion in the trigonal plane but not scrambled across the two sites (I *or* II, above). In these molecules the asymmetry arises from the top–bottom difference in the dienim or dapo ligands, coupled with the left–right difference in the deprotonated amine chelate.

It is interesting to note that, for the two possible deprotonation sites, one cis and the other trans to the leaving group, the alternative intermediates I and II are enantiomeric (the same is true of the (+)-*mer*-$[Co(bamp)(dapo)Cl]^{2+}$ system[25]). We have shown predominant retention of optical configuration for the base hydrolysis reaction, suggesting that cis deprotonation is effective if water enters *preferentially* adjacent to the NH^- in the trigonal plane of intermediate II, i.e., from where the Cl^- departed; a similar view has been canvassed[26] in interpreting the stereochemistry of base hydrolysis of *trans*-$[Co(NH_3)_4(^{15}NH_3)X]^{2+}$.[27] Alternatively, both ends of the en amine could be effective sites of deprotonation, with two separate intermediates, one leading to (+)- and the other to (−)-hydroxo forms by preferred attack adjacent to $Co-NH^-$. The rate of generation of the two intermediates would therefore be quite sensitive to the relative acidities of the two sites for deprotonation and the reactivities of the resultant conjugate bases. This latter explanation can account for the sharp difference between the (+)-*mer*-$[Co(dien)(dapo)Cl]^{2+}$ system, which gives a zero loss in activity, and the present (+)-*mer*-$[Co(dienim)(en)Cl]^{2+}$ system, which gives a 25% loss. Experiments are continuing[28] with structurally related complexes having blocked cis or trans deprotonation sites (using 2-(aminomethyl)pyridine in place of en, for example) to provide more information on this problem.

Finally we should comment on the unusual reactivity of the (+)-$[Co(dienim)(en)OH]^{2+}$ ion. It racemizes by a base-catalyzed route with $k_{OH} = 69\ M^{-1}\ s^{-1}$, only about 10-fold less rapid than the (+)-$[Co(dienim)(en)Cl]^{2+}$ ion hydrolyzing by the analogous route ($k_{OH} = 603\ M^{-1}\ s^{-1}$). It seems likely that the (+)-$[Co(dienim)(en)OH]^{2+}$ ion generates the same intermediate or intermediates I or II, by base-catalyzed loss of OH^-, and that water entry into the intermediate in this case not only generates (−)-$[Co(dienim)(en)OH]^{2+}$ but also regenerates the (+)-$[Co(dienim)(en)OH]^{2+}$ reactant (in the ratio 1:3 if the analogy to the chloro ion holds). Since three out of four acts of OH^- dissociation regenerate reactant, it follows that k_{OH} for the *dissociation* of OH^- is actually 4-fold larger than the observed constant for racemization, i.e., 276 $M^{-1}\ s^{-1}$ (cf. 603 $M^{-1}\ s^{-1}$ for dissociation of Cl^-), emphasizing that OH^- is not much poorer a leaving group than Cl^- here. The reason is far from clear, since there is no reason to believe that the amine acidities for the hydroxo complex are any different to the equally charged chloro complex.

The second point concerns the relatively large contribution to reaction in base from the "spontaneous" racemization of (+)-$[Co(dienim)(en)OH]^{2+}$, $k^s_r = 4.8 \times 10^{-4}\ s^{-1}$. This is quite fast for a hydroxopentaaminecobalt(III) complex, because OH^- is usually regarded as a poor leaving group, but in the light of the comments above perhaps it does not bind to Co(III) as tightly when one of the amines is replaced by an imine, as here. Alternatively, the hydroxo complex could react via its internal conjugate base (+)-$[Co(dienimH)(en)OH_2]^{2+}$, where the dienim is deprotonated (dienimH) and the leaving group is now H_2O (which is a better leaving group). By the same argument advanced above, the rate of OH^- dissociation (actually OH^--catalyzed H_2O dissociation) would then actually be about 4 times the observed value, i.e. $1.9 \times 10^{-3}\ s^{-1}$. The internal conjugate base process has been shown[9,29,30] to be viable for several reactive [Co-

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(23) Jackson, W. G. *Inorg. Chim. Acta* **1987**, *187*, 105.
(24) Tinner, U.; Marty, W. *Helv. Chim. Acta* **1977**, *60*, 1629.
(25) Tinner, U.; Marty, W. *Inorg. Chem.* **1981**, *20*, 3750.
(26) Nordmeyer, F. R. *Inorg. Chem.* **1969**, *8*, 2780.
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(28) Jackson, W. G.; Zhu, T. Work in progress.
(29) Comba, P. C.; Jackson, W. G.; Marty, W.; Zipper, L. *Helv. Chim. Acta*, submitted for publication.

(amine)$_5$OH]$^{2+}$ species, notably those where base hydrolysis of the chloro complex is especially rapid, and indeed for *mer*-[Co(dien)(dapo)OH]$^{2+}$ ($k_{OH} = 10^5$ M^{-1} s^{-1} for its chloro derivative),[9,29] for example, the internal base process actually swamps the OH$^-$-catalyzed route (for OH$^-$ loss) below pH 10. For the less reactive (ca. 200-fold) *mer*-[Co(dienim)(en)X]$^{2+}$ species ($k_{OH} = 6 \times 10^2$ M^{-1} s^{-1} for the chloro ion), one might therefore expect k to be reduced from the observed 0.036 s^{-1} for (+)-*mer*-[Co(dien)(dapo)OH]$^{2+}$ to, all else being equal, 1.8×10^{-4} s^{-1} (= 0.036/200). This is close to and actually lower than the observed value, consistent with reaction via its internal conjugate base. The facility of azide ion anation reported earlier, reflected in an unusually rapid anation reaction for the hydroxo ion, is also consistent with such a process because in base-catalyzed substitution azide ion competes well with H$_2$O.

Experimental Section

All chemicals were AnalaR or an equivalent grade. Visible/UV absorption spectra (650–300 nm) and absorbance–time traces were recorded on a Cary 210 spectrophotometer, thermostated to 25.00 ± 0.05 °C. A Perkin Elmer spectropolarimeter, Model 241, thermostated to 25.00 ± 0.05 °C with use of a Lauda Model RM6 circulating water bath, was used to determine optical rotations. Kinetic data in the form of optical rotation versus time traces were also obtained on this instrument using a 1 dm cell. Molar rotations were calculated using the formula $[M]_\lambda^{25} = (\alpha/cl)(\mathrm{FW}/100)$, where α = optical rotation (degrees), FW = formula weight, c = concentration (mol L^{-1}), l = path length (dm), and λ = wavelength (nm). Kinetic data were analyzed by nonlinear regression using the appropriate functions from the Fortran program Kincal adapted to run on a Macintosh computer.[31] Carbon-13 and proton NMR spectra were obtained with a Varian XL-300 instrument at 20 °C, for either D$_2$O solvent with dioxane as the internal reference (δ 69.27 relative to DSS) or Me$_2$SO-d_6 with the central peak of the CD$_3$ septet as the internal reference (δ 39.37 relative to TMS). All evaporations were carried out on a Büchi rotary evaporator at about 50 °C. The cation-exchange media were SP-Sephadex C25 (Pharmacia) and Dowex 50WX2 (H$^+$ or Na$^+$ form, 200–400 mesh, Biorad). All complexes were washed with ethanol and diethyl ether and air dried, unless otherwise specified. All new complexes analyzed satisfactorily. "H$_2$ZnCl$_4$" (2 M) was ZnCl$_2$ (2 M) in HCl (5 M) solution. A solution of Hg(trif)$_2$ was prepared as HgO (0.1 mol) in 4 M triflic acid (CF$_3$SO$_3$H) (100 mL) and Millipore filtered. The pH's of buffers were determined using a Metrohm 654 digital pH meter, with a jacketed 25-mL capacity cell as a thermostated pH vessel. This vessel was covered with a blanket of N$_2$, saturated with water vapor derived from a Dreschel bottle containing some aqueous NaCl of the same ionic strength and temperature as the buffers (0.1 M, 25 °C). The temperature was measured with an Orion 100-Ω platinum resistance thermometer, which was attached to the Metrohm instrument. A Ross combination "Sureflow" electrode was used (internal electrolyte 1.00 M NaCl). Standards (I = 0.1 M also) used to measure p[H$^+$] were HCl (1.000×10^{-3} M, Volucon) and NaOH (1.000×10^{-3} M, Volucon); milli-Q water (CO$_2$ free) was used in all of these solutions. p[H$^+$] was converted to p[OH$^-$] using pK_w = 13.78 at 25 °C.[32]

The modified or new[17] synthesis of all four isomers of [Co(dien)(en)Cl]ZnCl$_4$ (*mer,exo*, *mer,endo*, *unsym,fac*, *sym,fac*)[12-15] will be reported shortly.

***mer*-[Co(dienim)(en)Cl]ZnCl$_4$.** Hydrochloric acid (10.7 M, 90 mL) was added dropwise with stirring and cooling, to a mixture of aminoacetaldehyde diethyl acetal (66.6 g, 0.5 mol) and ice (240 g) . This was then placed in a sealed container and left overnight. CoCl$_2$·6H$_2$O (120 g, 0.5 mol) was then added and mixed in well before addition of ethylenediamine (81 g, 1.35 mol) in 150 g of ice. Finally, H$_2$O$_2$ (99 mL, 30% w/w, "100 vol") was added dropwise while stirring in ice. The solution was heated at 60 °C for 15 min and HCl (12 M, 240 mL) was then added. Heating was continued for a further 10 min, and the solution was left to cool to room temperature. After the solution was left overnight, one-fifth volume of H$_2$ZnCl$_4$ was added. Stirring in ice produced red-brown crystals of crude *mer*-[Co(dienim)(en)Cl]ZnCl$_4$. Yield: 30 g, 14% (based on the amount of cobalt(II) used). The brown color was an unidentified stain, which was not readily eliminated by recrystallization but was eliminated by chromatography on a Dowex column; HCl (2 M) eluted the desired product, leaving the brown residue on the top of the column. The pure product is orange-red. ^{13}C NMR (Me$_2$SO-d_6): δ 180.13 (N=*C*H), 55.94, 54.77 (*C*—N=, N=CH—*C*), 45.66, 44.66, 44.38 (*C*—NH$_2$). ^{13}C NMR (D$_2$O/DCl, 0.01 M): δ 183.61 (N=*C*H), 59.05, 57.87 (*C*—N=, N=CH—*C*), 49.09, 48.08, 47.67 (*C*—NH$_2$). ^{1}H NMR (Me$_2$SO-d_6): δ 8.14 (*H*C=N); see Figure 4. Vis (0.01 M HClO$_4$): ϵ_{470}(max) = 108.0, ϵ_{404} (min) = 37.5, ϵ_{358}(max) = 95.5.

In a separate small-scale experiment, the entire red 2+ band from the Dowex column (2 M HCl) was freeze dried and the ^{13}C NMR spectrum recorded; only a single isomer (*mer*) was observed.

***mer*-[Co(dienim)(en)Cl](ClO$_4$)$_2$.** (1) A sample of *mer*-[Co(dienim)(en)Cl]ZnCl$_4$ was dissolved in the minimum volume of water and had one-fifth volume of HClO$_4$ (70%) added to it. The product tends to supersaturate, but crystallization is accelerated by cooling and stirring. After several days, a reasonable yield of *mer*-[Co(dienim)(en)Cl](ClO$_4$)$_2$ was obtained. ^{1}H NMR (Me$_2$SO-d_6): δ 8.09 (*H*C=N); see Figure 4. Vis (0.01 M HClO$_4$): ϵ_{470}(max) = 108.1.

(2) A sample of *mer*-[Co(dienim)(en)Cl]Cl$_2$ was dissolved in the minimum volume of water and had one-fifth volume of HClO$_4$ (70%) added to it. Several hours of stirring in ice produced a high yield of *mer*-[Co(dienim)(en)Cl](ClO$_4$)$_2$.

***mer*-[Co(dienim)(en)Cl]Cl$_2$.** A sample of *mer*-[Co(dienim)(en)Cl]ZnCl$_4$ or *mer*-[Co(dienim)(en)Cl](ClO$_4$)$_2$ was sorbed onto a Dowex cation-exchange column and eluted with HCl (2 M) after washing with water. The eluate was rotary evaporated to dryness and then dissolved in the minimum volume of HCl (5 M). Acetone was slowly added until the point of permanent cloudiness, and the *mer*-[[Co(dienim)(en)Cl]Cl$_2$ crystallized slowly but quantitatively. Vis (0.01 M HClO$_4$): ϵ_{470}(max) = 107.9.

Optical Resolution of [Co(dienim)(en)Cl]$^{2+}$. The perchlorate salt (0.5 g, 1.1 mmol) was dissolved in a water/acetone mixture (20 mL of each) and 1 equiv of a tris(hydroxymethyl)methylamine (Tris)/dibenzoyltartaric acid (DBH$_2$T) solution (2.87 mL) was added. [The Tris–DBHT solution consisted of Tris (5.28 g, 0.044 mol) in water (50 mL) and DBH$_2$T·H$_2$O (16.4 g) in ethanol (50 mL).] The solution was stirred in ice (stirring accelerated the crystallization), and several fractions were collected as they deposited. After conversion of the less soluble diastereomer to the chloride salt, as described below, optical rotations were recorded for each fraction. All were levorotatory at 589 nm. [Note: the bis(hydrogen dibenzoyltartrate) salt formed is insoluble in water but readily soluble in ethanol or 2-propanol so that 1-butanol or cold water was used for washing.] After several days, another equivalent of the Tris–DBHT solution was added, and when all further fractions had been collected, one-fifth volume of H$_2$ZnCl$_4$ solution was added to the filtrate. The final fraction was collected and converted to the chloride salt via cation-exchange chromatography using 2 M HCl as the eluent. After rotary evaporation, the chloride was crystallized using HCl and acetone. The highest specific rotation $[\alpha]_\lambda$ obtained was +88.5° at 546 nm ($[\alpha]_\lambda = \alpha/cl$, where $[\alpha]_\lambda$ = specific rotation at wavelength λ, α = optical rotation, c = concentration and l = path length) (concentrations used were 0.001 35 g mL^{-1}). This corresponds to a molar rotation of +289 deg mol^{-1} dm^2 at 546 nm.

Removal of the Resolving Agent from (−)-[Co(dienim)(en)Cl](L-dibenzoylHtart)$_2$. Acetone (ca. 10 mL) followed by concentrated HCl (ca. 2.5 mL) was added to the DBHT salt (0.3 g) stirring in water (ca. 1.5 mL). This solution was left stirring for around 10 minutes during which time the tartrate dissolved. More acetone (ca. 100 mL) was then added to crystallize the chloride salt. This was recrystallized by dissolving the salt in the minimum volume of water and adding acetone until a faint permanent cloudiness was apparent. Crystals deposited slowly but quantitatively overnight at 2°. If a sample of active complex was dissolved in the minimum volume of water as the chloride salt and fractionally crystallized by slowly adding acetone, it was found that specific rotations were increased by up to 60% for later fractions; $[\alpha]^{20}_{546}$ = −88.5° was the maximum obtained, numerically as for the other enantiomer. The first and less soluble fractions tended to be racemate. $[M]_{589} = -199$, $[M]_{578} = -230$, $[M]_{546} = -289$, $[M]_{436} = +382$, $[M]_{365} = +186$ (lit.[2] $[M]_{589} = -62$, in 0.1 M HNO$_3$).

(+)-*mer*-[Co(dienim)(en)Cl](ClO$_4$)$_2$. A sample of (+)-*mer*-[Co(dienim)(en)Cl]Cl$_2$ was dissolved in the minimum volume of water and had one-fifth volume of HClO$_4$ added to it. After several days, crystals of (+)-*mer*-[Co(dienim)(en)Cl](ClO$_4$)$_2$ were collected in good yield.

(+)-*mer*-[Co(dienim)(en)Cl]ZnCl$_4$. A sample of (+)-*mer*-[Co(dienim)(en)Cl]Cl$_2$ was dissolved in the minimum volume of water and had one-fifth volume of H$_2$ZnCl$_4$ added to it. The formation of the tetrachlorozincate salt was completed by cooling. A high yield of (+)-*mer*-[CoCl(en)(dienim)]ZnCl$_4$ was collected in fractions over several days.

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Reduction of *mer*-[Co(dienim)(en)Cl]$^{2+}$ to *mer*-[Co(dien)(en)Cl]$^{2+}$. (1) Solid $NaBH_4$ (0.05 g, 0.5 equiv) was added to [Co(dienim)(en)Cl]$ZnCl_4$ (1.0 g, 0.002 16 mol), which was dissolved in the minimum volume of water. One-fifth volume of Li_2ZnCl_4 solution (2 M) was then immediately added and the precipitate was collected. The ^{13}C NMR spectrum revealed a mixture of *mer*-[Co(dien)(en)Cl]$^{2+}$ and some unreacted *mer*-[Co(dienim)(en)Cl]$^{2+}$.

(2) Sodium borohydride (0.08 g) was added in small portions to a well-stirred solution of [Co(dienim)(en)Cl]$ZnCl_4$ (1.0 g) in a minimum volume of water. This was filtered and the mother liquor was diluted, sorbed onto an ion-exchange column, which was washed with water, and eluted with HCl (2 M). Two bands were collected. The first was red and the second, orange. They were separately rotary evaporated, and ^{13}C spectra revealed that the first band contained the starting material and a mixture of the *mer,exo*, π, and ω isomers[12-15] of [Co(dien)(en)Cl]$^{2+}$; the second band contained *mer-exo*-[Co(dien)(en)OH_2]$^{3+}$.[17]

(3) This experiment was carried out as in part 2 above but using an acetate buffer (0.1 M, pH 4.8), with edta (0.02 M) neutralized (NaOH) to the same pH. For this experiment the results were quite different in that there was no aqua band, and the first chloro band contained only the *mer* isomer of [Co(dien)(en)Cl]$^{2+}$, together with a little unreacted *mer*-[Co(dienim)(en)Cl]$^{2+}$.

Synthesis of *mer*-[Co(dienim)(tn)Cl]$ZnCl_4$ and Observation of *mer*-[Co(tnenim)(tn)Cl]$^{2+}$. Concentrated hydrochloric acid (37.5 mL, 0.45 mol), was added dropwise to a solution of aminoacetaldehyde diethyl acetal (30 g, 0.224 mol) in 100 g of ice. This was sealed and left overnight. Following this, $CoCl_2 \cdot 6H_2O$ (53 g, 0.224 mol) dissolved in the minimum volume of water and ethylenediamine (13.25 g, 0.224 mol), were successively added to the stirring solution. After $^1/_2$ h, NaOH (8.8 g, 0.224 mol) was added followed by 1,3-diaminopropane (16.3 g, 0.224 mol). Before the solution was heated to 60 °C, H_2O_2 (50 mL, 30% w/w) was carefully added dropwise. When the solution was at 60 °C, concentrated HCl (100 mL) was added and heating continued for a further 10 min. After being cooled and diluted with H_2O, the solution was sorbed on a Dowex cation-exchange column. After the column was washed, the thick red-orange band was collected (HCl, 2 M), rechromatographed on a longer column, and collected as three red-orange bands. The first band decomposed upon rotary evaporation. The second band consisted largely of [Co(dienim)(en)Cl]$^{2+}$, which crystallized with addition of H_2ZnCl_4. About 80% of the third band was the desired product [Co(dienim)(tn)Cl]$^{2+}$, and the other 20% was made up of [Co(tnenim)(tn)Cl]$^{2+}$ and residual [Co(dienim)(en)Cl]$^{2+}$ (^{13}C NMR). The desired product was selectively crystallized by addition of H_2ZnCl_4 (2 M). The yield was low (<10%).

^{13}C NMR (D_2O/DCl, 0.01 M): δ 185.29 (N═*C*H), 59.23, 52.94 (*C*—N═, N═CH—*C*), 47.78, 47.03, 42.34 (*C*—NH_2), 28.66 (C—*C*—C).

Salts of *rac*- and (+)-[Co(dienim)(en)OH_2]$^{3+}$. A solution of 1 M Hg(trif)$_2$ (ca. 1 mL) was added dropwise to a sample of *rac*- or (+)-[Co(dienim)(en)Cl]$^{2+}$ complex (0.1 g), as either the chloride or the perchlorate salt, dissolved in the minimum volume of water. The solution changed from red to orange within a few minutes. If this solution is left in the cold for days, the orange triflate salt *rac*- or (+)-[Co(dienim)(en)OH_2]$(CF_3SO_3)_3$ forms (ϵ_{457}(max) = 125.5, 0.01 M $HClO_4$). To obtain the chloride salt, concentrated HCl (ca. 2 mL) was added to freshly generated (30 min) aqua complex, followed by addition of acetone until the point of permanent cloudiness. Crystals were formed slowly but quantitatively. ^{13}C NMR (Me_2SO-d_6): δ 183.20 (N═*C*H), 56.14, 54.87 (*C*—N═, N═CH—*C*), 45.28, 45.05, 43.40 (*C*—NH_2). ^{13}C NMR (D_2O/DCl, 0.01 M): δ 187.09 (N═*C*H), 59.04, 58.11 (*C*—N═, N═CH—*C*), 49.0, 48.47, 46.61 (*C*—NH_2). ^1H NMR (Me_2SO-d_6): δ 8.36 (*H*C═N), 6.10 (Co—OH_2); see Figure 4. Vis (0.01 M $HClO_4$): ϵ_{457}(max) = 126.5, ϵ_{391}(max) = 32.5, ϵ_{345}(max) = 88; $[M]_{589}$ = +138, $[M]_{578}$ = +193, $[M]_{546}$ = +343 (lit.[2] ϵ_{458}(max) = 122, $[M]_{589}$ = +72, in 0.9 M HNO_3).

Generation of *rac*- or (+)-[Co(dienim)(en)OH]$^{2+}$. The hydroxo ion was generated in situ in the buffers from the isolated aqua complex. ^{13}C NMR (D_2O/Na_3PO_4(trace), 1 M NaN_3): δ 182.83 (N═*C*H), 58.63, 57.41 (*C*—N═, N═CH—*C*), 48.51, 47.62, 46.56 (*C*—NH_2). Vis ($HClO_4$, I = 0.1 M ($NaClO_4$), pH 8): ϵ_{471}(max) = 134.5, ϵ_{406}(min) = 46.5, ϵ_{340}(max) = 102; $[M]_{589}$ = +151, $[M]_{578}$ = +148, $[M]_{546}$ = +45.

Azide Ion Anation of *mer*-[Co(dienim)(en)OH]$^{2+}$. The reaction of the aqua complex in 1 M NaN_3/D_2O was followed by ^{13}C NMR, and shown to go to completion. The final spectrum was indicative of a single *mer* species: δ 186.32 (N═*C*H), 58.96, 58.03 (*C*—N═, N═CH—*C*), 48.75, 48.29, 46.42 (*C*—NH_2).

Kinetics. Rates of base hydrolysis of [Co(dienim)(en)Cl]$^{2+}$ (as either the chloride or the perchlorate salt—the $ZnCl_4^{2-}$ salt precipitates as $Zn(OH)_2$ in the presence of the basic Tris buffers used) were measured in five basic buffers (Tris/$HClO_4$/$NaClO_4$, [total base] = 0.1 M, ionic strength 0.1 M). All kinetic runs are weighted ($1/\sigma^2$) averages of at least three determinations. The rates were measured on the Cary 210 instrument, from absorbance–time traces at 520 nm at 25 °C, using the in situ (1 cm cell);[31] some runs were performed at other wavelengths. Rates of change of optical activity during the base hydrolysis of (+)-[Co(dienim)(en)Cl]$^{2+}$ (578 and 546 nm) and the rate of loss of optical activity of (+)-[Co(dienim)(en)OH]$^{2+}$ (578 nm), were recorded as optical rotation versus time traces at 25 °C on the Perkin–Elmer spectropolarimeter using a modified in situ method (because the 1-dm cell did not facilitate mixing). Here a Y-tube that was thermally preequilibrated (solid complex in one arm and buffer in the other) was used to initiate the reaction. The same five buffers were used for the spectrophotometric and polarimetric studies. Rates of reaction of *rac*-[Co(dienim)(en)Cl]$^{2+}$ and [Co(dienim)(en)OH]$^{2+}$ in a Tris buffer containing 1 M azide ion (I = 1.1 M) were also measured (25 °C) on the Cary 210 instrument as absorption versus time traces. The corresponding losses of optical activity of the (+)-[Co(dienim)(en)Cl]$^{2+}$ and the (+)-[Co(dienim)(en)OH]$^{2+}$ ions in the same buffer were measured as optical rotation versus time traces on the spectropolarimeter. The D, t and α, t data were fitted to a single exponential (representing a single-step reaction) and the α, t data were also fitted to a double exponential (representing a two-step reaction sequence) using the Kincal program. Final data fits for k(obsd) vs [OH^-] were carried out using the weighted ($1/\sigma^2$) linear regression function in Kincal.

Partial Base Hydrolysis Experiment. A sample of (+)-[Co(dienim)(en)Cl]Cl_2 (0.12 g) was reacted in a Tris buffer (15 mL, pH 8.9) until about half of the sample had base hydrolyzed (the half life for the reaction (135 s) was obtained through independent spectrophotometric rate determination); the Y-tube mixing method was employed. The reaction was then quenched with HCl (5 mL, 11 M). The solution was diluted (to 300 mL with H_2O) and then sorbed onto an H^+ ion exchange column (Dowex) and both the first-formed hydroxo product, which appeared as a yellow-orange aqua band, and the unreacted chloro complex, which appeared as a red-orange band, were eluted using HCl (2 M). The volumes, visible spectral data, and optical rotations were recorded on both solutions. In a control experiment, another sample of the same batch of (+)-[Co(dienim)(en)Cl]Cl_2 was treated with excess $Hg(CF_3SO_3)_2$ to generate (+)-[Co(dienim)(en)OH_2]$^{3+}$. This was chromatographed identically, and visible spectra and optical rotations were recorded.

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Registry No. *mer*-[CoCl(en)(dienim)]$ZnCl_4$, 100788-30-5; *mer*-[Co(dienim)(en)Cl]$(ClO_4)_2$, 83444-51-3; *mer*-[CoCl(en)(dienim)]Cl_2, 136882-01-4; (−)-[Co(dienim)(en)Cl](L-dibenzoylHtart)$_2$, 136910-94-6; (−)-[Co(dienim)(en)Cl]Cl_2, 136910-95-7; (+)-*mer*-[Co(dienim)(en)Cl]$(ClO_4)_2$, 136910-97-9; (+)-*mer*-[Co(dienim)(en)Cl]Cl_2, 136910-96-8; (+)-*mer*-[Co(dienim)(en)Cl]$ZnCl_4$, 104419-55-8; *mer*-[Co(dien)(en)Cl]$ZnCl_4$, 24771-18-4; *mer*-[Co(dienim)(tn)Cl]$ZnCl_4$, 136910-99-1; *mer*-[Co(tnenim)(tn)Cl]$ZnCl_4$, 136911-01-8; [Co(dienim)(en)OH_2]$(CF_3SO_3)_3$, 136983-75-0; (+)-[Co(dienim)(en)OH_2]$(CF_3SO_3)_3$, 136911-02-9; [Co(dienim)(en)OH_2]Cl_3, 136983-76-1; (+)-[Co(dienim)(en)OH_2]Cl_3, 136911-03-0; [Co(dienim)(en)OH]$^{2+}$, 136911-04-1; (+)-[Co(dienim)(en)OH]$^{2+}$, 136983-77-2; aminoacetaldehyde diethyl acetal, 645-36-3; ethylenediamine, 107-15-3; 1,3-diaminopropane, 109-76-2.

Supplementary Material Available: Figures 1 and 2, showing graphical representations of the data in Tables I and II (2 pages). Ordering information is given on any current masthead page.