Inorg. Chem. **2003**, *42*, 3822–3834

A Unique Mechanism for Base Catalyzed Hydrolysis of Pentaaminecobalt(III) Complexes Containing Picolyl Residues

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Received December 3, 2002

A novel $[Co(pentaamine)Cl]^{2+}$ complex having all tertiary amine or pyridine donors has been synthesized (pentaamine = 1,4-bis(2′-pyridyl)-7-methyl-1,4,7-triazacyclononane). This *asym*-$[Co(dmpmetacn)Cl]^{2+}$ species has been completely characterized through 1D and 2D NMR studies, and through the X-ray structure for the $ZnCl_4^{2-}$ salt. Despite the lack of an activating NH center, remarkably its hydrolysis to $[Co(pentaamine)OH]^{2+}$ is base catalyzed (k_{OH} 0.70 M^{-1} s^{-1}, 25 °C, I = 1.0 M, NaCl). Detailed NMR studies reveal that the base catalyzed substitution leads to the exchange of just one deuterium in one of the two $-CH_2-$ pyridyl arms, that is approximately trans to the leaving group, and this occurs during and not after base hydrolysis. Quenching experiments for the reaction of *asym*-$[Co(dmpmetacn)Cl]^{2+}$ and control experiments on H/D exchange for the product *asym*-$[Co(dmpmetacn)OD]^{2+}$ in OD^- show that each act of deprotonation at the acidic methylene leads to loss of Cl^-. This is the first established case of base catalyzed substitution for a complex where the effective site of deprotonation is at a pyridyl group. A pronounced kinetic isotope effect is observed for the species perdeuterated at the pyridyl methylenes (k_H/k_D = 5.0), consistent with rate limiting deprotonation which is a rare event in Co(III) substitution chemistry. The activation afforded by the carbanion is discussed in terms of a new process coined the pseudo-aminate mechanism.

Introduction

Pyridine containing cobalt(III) complexes have long attracted the attention of groups interested in octahedral substitution mechanisms.[1−8] Pyridine does not quite parallel the coordination chemistry of a simple aliphatic amine such as NH_3,[1,2,5,9] and the reasons for the different behavior of pyridine and pyridine containing ligands such as bipy, picen, and picdien remain not well understood (Figure 1).

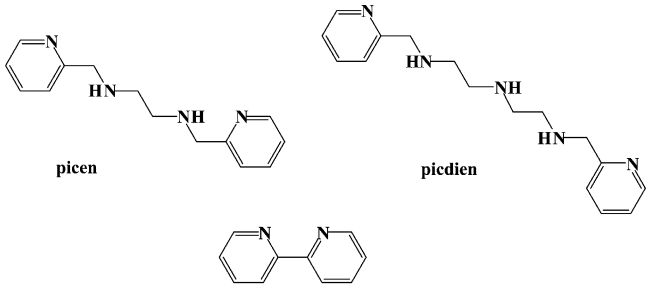

Figure 1. Ligand abbreviations.

Tobe has suggested a "covalent-hydration" or "pseudo-base" mechanism to accommodate the apparently unusual reactivity of pyridine metal complexes in base,[1] a proposal vigorously supported by Gillard (Figure 2).[10] However, House et al. could find no evidence in favor of the proposal,[5] in observing a negligible secondary isotope effect for the base hydrolysis of *cis*-$[Co(en)_2(py\text{-}d_5)Cl]^{2+}$. Now that pyri-

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10.1021/ic0206995 CCC: $25.00
Published on Web 05/13/2003

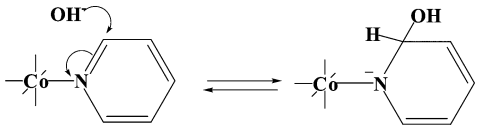

Figure 2. Covalent hydration of coordinated pyridine.

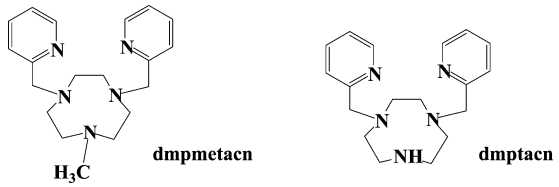

Figure 3. Tacn derived quinquedentate ligands.

dine and pyridyl complexes are no longer considered unusually reactive per se,[2,5,11] there seems to be no reason to sustain a belief in this mechanism for which there is no direct experimental evidence.

Spiccia et al. have synthesized the pyridine containing quinquedentate ligand dmptacn (di(2-methylenepyridine)-tacn), having two picolyl "arms" (picolyl = 2-methylenepyridine), which bears just the one NH donor (Figure 3). The mononuclear Co(III) complex $[Co(dmptacn)Cl]^{2+}$ base hydrolyzes normally (first-order in $[OH^-]$),[12] albeit slowly, and it was thought that that the reaction went via the aminato species derived from this −NH−. We reasoned that having the NH center of dmptacn blocked by a methyl group would provide a simple pyridine-all-tertiary-amine ligand (dmpmetacn, Figure 3) which might be complexed to provide a mononuclear $[Co(pentaamine)Cl]^{2+}$ complex with no NH protons. Such a $[Co(dmpmetacn)Cl]^{2+}$ complex is a rare species;[2] indeed, this is one of only a few pentaaminecobalt(III) complexes of which we are aware that is totally lacking in an NH site and which, ostensibly, prevents base catalyzed substitution.

Thus, we expected a hydrolysis rate for $[Co(dmpmetacn)Cl]^{2+}$ independent of $[OH^-]$, but to our chagrin, we observed the normal rate law for base catalysis, first-order in $[OH^-]$. Moreover, the complex hydrolyzed more rapidly than its $[Co(dmptacn)Cl]^{2+}$ analogue which does have an NH site.

Herein we report a detailed study of this reaction, identifying a new and unique mechanism for base hydrolysis of metal ion complexes.

Results and Discussion

Ligand Synthesis. The synthesis followed that described for the dmptacn analogue[11] (Figure 4) but commenced with metacn. Metacn (Figure 5) was synthesized as described later; other routes using dual protecting groups look promising but were not explored.[13] Dmptacn could in principle be methylated directly by the standard method (HCHO/HCOOH), since the picolyl groups protect the other amine sites (Figure 4). However, because tacn is normally synthesized as its

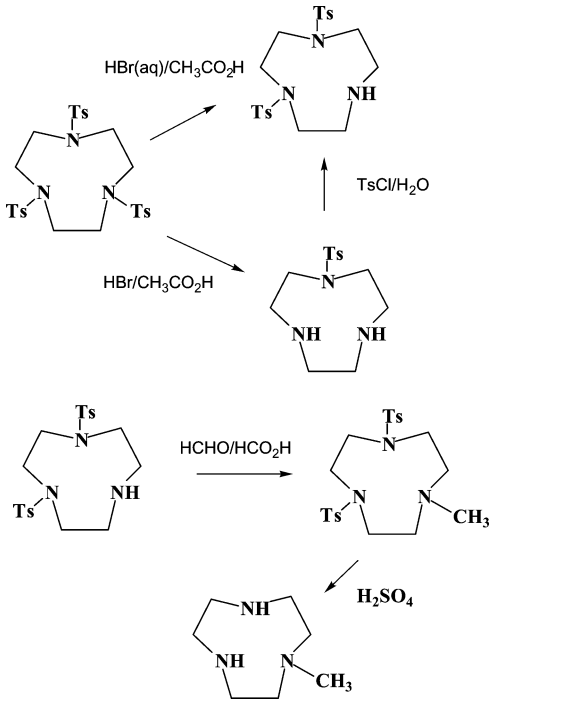

Figure 4. Synthesis of metacn.

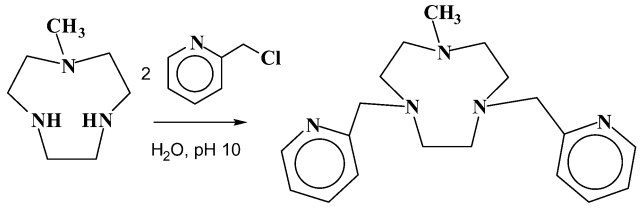

Figure 5. Synthesis of dmpmetacn.

tritosylate, we chose to monodetosylate and methylate before totally deprotecting the secondary amines and introducing the two methylenepyridyl arms. For tacn itself, the control of pH and equivalents of reagents is crucial, and even when optimized for the addition of just two arms, the dmptacn is contaminated with both mono- and trisubstituted products.[12] The chosen strategy had a clear advantage in yield over the alternative, since metacn can be forced to react with 2 equiv of picolyl chloride (and using I^- as a catalyst) without fear of addition of a third. However, caution is required because we have observed that quaternization of the desired ligand can occur using excess picolyl chloride.

In passing, we discovered a clean one-pot synthesis of ditosylated tacn, with use of aqueous HBr rather than HBr(g) in acetic acid. The new procedure removes just the one tosyl group. The former procedure strips off two protecting groups, and the product then has to be monotosylated to give the desired material.

The new dmpmetacn (Figure 5) ligand was characterized by its ^{13}C NMR spectrum, and through its complexes of Co(III) described in following paragraphs. Indeed, the free ligand was not usually isolated from its aqueous synthetic mixture, but it was complexed directly using a slight excess of $Co^{II}Cl_2$, aerial oxidation to Co(III), and subsequent quantitative recovery as $[Co(dmpmetacn)X]^{n+}$ by ion exchange chromatography (IEC).

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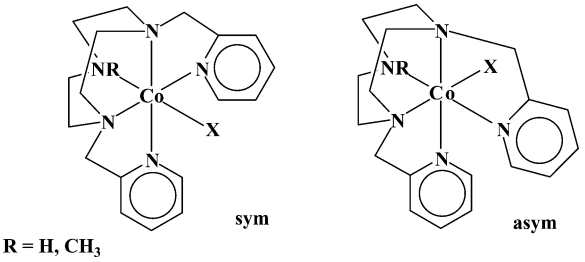

Figure 6. The two geometric isomers of $[Co(dmptacn)X]^{n+}$ and $[Co(dmpmetacn)X]^{n+}$.

Complexes. The oxidized (air or H_2O_2) mixture of a Co(II) salt and free ligand yielded $[Co(dmpmetacn)X]^{n+}$ ($X = Cl^-$, NO_2^-, N_3^-, and others) in good yield. With $CoCl_2$, both orange $[Co(dmpmetacn)OH_2]^{3+}$ and pink $[Co(dmpmetacn)Cl]^{2+}$ were obtained, with the 3+ ion curiously eluting in front of the 2+ chloro complex on Dowex; the analogous $[Co(dmptacn)X]^{2+}$ ions are also anomalous in this regard.[14] The complexes easily crystallized as ClO_4^- salts; they are less soluble in water than their corresponding dmptacn salts. Other synthetic routes using Co(III) reactants ($Na_3[Co(OCO_2)_3]$ and *trans*-$[Co(py)_4Cl_2]Cl$) and free ligand were similarly successful.

The $[Co(dmpmetacn)Cl]^{2+}$ complex is slow to hydrolyze to $[Co(dmpmetacn)OH_2]^{3+}$, while the latter is anated slowly but completely back to the chloro ion in strong HCl. This is typical pentaaminecobalt(III) chemistry, but the rates of these reactions appear to be slower than for the prototype pentaammine complexes, $[Co(NH_3)_5X]^{n+}$. The visible absorption spectra are typical for CoN_5O and CoN_5Cl chromophores (Experimental Section), while the IR spectra are devoid of the peak for the NH stretch observed at around 3090 cm^{-1} (Nujol) in the salts of the $[Co(dmptacn)X]^{n+}$ ions.

These complexes can exist in two isomeric forms, a symmetrical form (mirror symmetry) and one with no symmetry (Figure 6). We were particularly interested in obtaining both isomers, since for R = H they provide a pair of ions bearing only one NH, either cis or trans to the leaving group X, and potentially enabling a resolution of a long standing problem in the base hydrolysis mechanism:[2,15] which is the effective deprotonated center, that cis or that trans to the departing group?

The asymmetric form is the only one we have obtained thus far, for a variety of derivatives,[12] and we have confirmed that the total product eluted from the column contains only the asym form. All attempts to isomerize the asym form to the sym isomer, using a variety of strategies, have thus far failed.

The asym form is also the exclusive isomer obtained for a range of $[Co(pentaamine)Cl]^{2+}$ complexes for related ligands derived from tacn, with both two and three carbon backbone "arms" (e.g., datn, dasn, daptacn).[16,17] Also, the bis(picolyl) derivative of S-, O-, and Se-substituted tacn gives rise to just the asym isomer.[18] Molecular mechanics calculations have thus far given no clue to the exclusive preference for the asym form. However, these calculations (and molecular models) suggest that interaction of the pyridine hydrogens across the two rings is strongly exacerbated in the sym form (much like in the twisted biphenyls), making the preference for the asym isomer even stronger. All the asym isomers are of course chiral, but as yet, we have not attempted to optically resolve any of the complexes. The sym form might also be chiral and potentially resolvable, given the twisting of the pyridyls (C_2-sym).

A purely empirical analysis of the $[Co(dmptacn)Cl]^{2+}$ and $[Co(dmpmetacn)Cl]^{2+}$ structures compared to related configurations known for trien, trenen, and tetraen complexes is potentially informative. Figure 7S (in the Supporting Information) illustrates the topological relationship between these, for both the sym and asym isomers, and the following comments refer to thermodynamic rather than kinetic isomer preferences. Perhaps the most telling observation is the fact that, of the five configurations possible for a $[Co(trien)X_2]^{n+}$ complex, the trans-meso form is the only one never to have been observed,[19] and it is that analogous to the putative *sym*-dmpmetacn and *sym*-dmptacn species. The implication, however, has to be tempered by the fact that the other comparisons do not all tell the same story. The stable trenen isomer is the s form,[15,19] but others have been observed: one of the p forms, and the t isomer.[20] For metrenen, the t isomer is the more stable isomer.[21] For tetraen, there are eight possible configurations,[22] six of which are known. The $\alpha\alpha$, α antiβ, and α synβ are the more stable forms. Until all the facts on the relative stability of isomers in these structurally related systems are known, comparisons of topologically analogous complexes are of limited usefulness. These considerations do show, however, that the energy differences between alternative isomeric forms are subtle: the nitrogen configurations are clearly important, and even *N*-methylation has a profound effect.

The crystal structures of two complexes of the dmptacn analogues[14,23] confirm the prevalence of the asym configuration, and the very close similarity of the ^1H and ^{13}C NMR spectra of the dmptacn and dmpmetacn complexes indicates that they have the same configuration. These data, together with the 2D NMR spectra and the crystal structure, eliminate the prospect of the sym form with twisted pyridyls.

Single Crystal X-ray Structure of $[Co(dmpmetacn)Cl](ClO_4)_2$. The structure (Figure 7) is very similar to that reported for the $[Co(dmptacn)OH_2](ClO_4)_3$ complex.[14] The present structure was determined for a complex obtained

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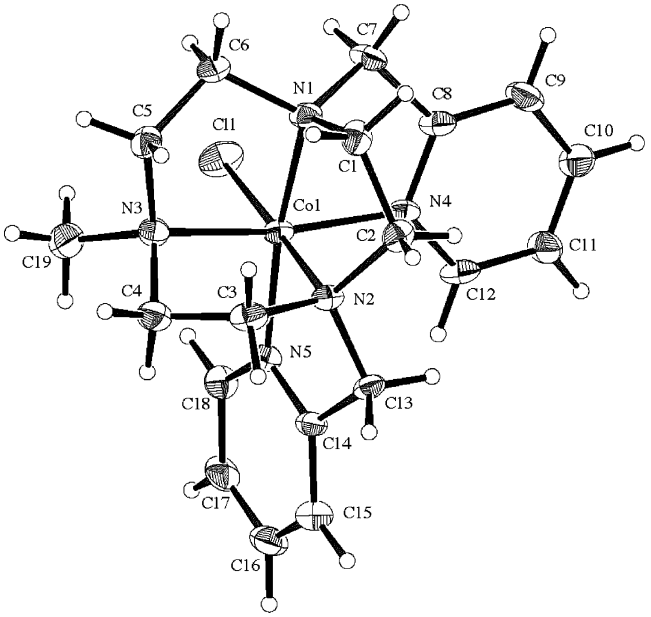


Figure 7. ORTEP diagram for *asym*-[Co(dmpmetacn)Cl]$^{2+}$ with 30% thermal ellipsoids.

through an unexpected reaction, that of [Co(dmpmetacn)(ONO)]$(ClO_4)_2$ isomerized in Me_2SO, which led to reduction of perchlorate to chloride and its subsequent incorporation into the coordination sphere.[24] Controlled reduction of ClO_4^- is rare, it is normally explosive, but there is a precedent in the similar reaction of *cis*-[Co$(en)_2(OSMe_2)_2$]$(ClO_4)_2NO_3$ with N_3^- in Me_2SO, in which *cis*-[Co$(en)_2(OSMe_2)$Cl]ClO_4·NO_3 is a significant product along with *cis*-[Co$(en)_2(OSMe_2)$-N_3]ClO_4·NO_3,[25] and we are pursuing this chemistry in another arena.

Principal bond lengths are presented in Table 1, and bond angles are in Tables 2 and 3. Atomic coordinates (Table 1S), anisotropic displacement parameters (Table 2S), torsion angles (Table 7S), and nonbonded contacts (Table 8S) are included in Supporting Information.

The complex crystallizes as a racemate, and the X-ray result confirms the asym configuration. There are no outstanding structural features, save for the through-space proximity of the methyl group (C-19, Figure 7) and the pyridyl C−H at C-18. This gives rise to a significant NOE in the ^{1}H NMR spectra which forms the basis for a complete assignment of the proton (and carbon) spectra.

NMR Spectra and Assignment of Nuclei. The assignment of NMR signals to particular nuclei in both the [Co(dmpmetacn)Cl]$^{2+}$ and [Co(dmpmetacn)OH_2]$^{3+}$ complexes, the protons in particular, is important to the detailed interpretation of the mechanism of base hydolysis.

The ^{1}H NMR spectra of the two chloro complexes are shown in Figure 9, and those of the aqua are shown in Figure 10. For each, all protons are inequivalent, consistent with the asymmetry. The four pyridyl C−H protons in each arm of the ligand appear, at 400 MHz, as two sets of doublets and two sets of triplets, with essentially first-order couplings and very similar H−H coupling constants (ca. 7 Hz) typical for sustituted pyridines. The triplets are clearly the "inner" protons, and the doublets, the "outer" C−H protons. The two sets of four multiplets are overlaid, but only one proton

Table 1. Bond Lengths (Å) and Angles (deg)

Zn(l)	Cl(2)	2.250(3)	Zn(1)	Cl(3)	2.263(3)
Zn(l)	Cl(4)	2.253(3)	Zn(1)	Cl(5)	2.291(3)
Co(l)	Cl(l)	2.232(3)	Co(l)	N(l)	1.955(7)
Co(l)	N(2)	1.964(7)	Co(l)	N(3)	2.005(7)
Co(l)	N(4)	1.983(8)	Co(l)	N(5)	1.962(7)
N(1)	C(l)	1.53(l)	N(1)	C(6)	1.49(l)
N(l)	C(7)	1.51(l)	N(2)	C(2)	1.47(l)
N(2)	C(3)	1.51(l)	N(2)	C(13)	1.49(l)
N(3)	C(4)	1.51(l)	N(3)	C(5)	1.52(l)
N(3)	C(19)	1.52(l)	N(4)	C(8)	1.36(l)
N(4)	C(12)	1.37(l)	N(5)	C(14)	1.34(l)
N(5)	C(18)	1.34(l)	C(l)	C(2)	1.52(l)
C(3)	C(4)	1.52(l)	C(5)	C(6)	1.51(l)
C(7)	C(8)	1.52(l)	C(8)	C(9)	1.39(l)
C(9)	C(10)	1.37(l)	C(10)	C(11)	1.34(l)
C(11)	C(12)	1.36(l)	C(13)	C(14)	1.52(l)
C(14)	C(15)	1.36(l)	C(15)	C(16)	1.36(l)
C(16)	C(17)	1.38(l)	C(17)	C(18)	1.38(l)
C(l)	H(la)	0.95	C(l)	H(lb)	0.95
C(2)	H(2a)	0.95	C(2)	H(2b)	0.95
C(3)	H(3a)	0.95	C(3)	H(3b)	0.95
C(4)	H(4a)	0.95	C(4)	H(4b)	0.95
C(5)	H(5a)	0.95	C(5)	H(5b)	0.95
C(6)	H(6a)	0.95	C(6)	H(6b)	0.95
C(7)	H(7a)	0.95	C(7)	H(7b)	0.95
C(9)	H(9)	0.95	C(10)	H(10)	0.95
C(11)	H(11)	0.95	C(12)	H(12)	0.95
C(13)	H(13a)	0.95	C(13)	H(13b)	0.95
C(15)	H(15)	0.95	C(16)	H(16)	0.95
C(17)	H(17)	0.95	C(18)	H(18)	0.95
C(19)	H(19a)	0.95	C(19)	H(19b)	0.95
C(19)	H(19c)	0.95			

Cl(2)	Zn(l)	Cl(3)	113.5(l)	Cl(2)	Zn(1)	Cl(4)	111.9(1)
Cl(2)	Zn(l)	Cl(5)	107.1(1)	Cl(3)	Zn(l)	Cl(4)	107.2(l)
Cl(3)	Zn(l)	Cl(5)	110.0(l)	Cl(4)	Zn(l)	Cl(5)	106.9(l)
Cl(1)	Co(l)	N(l)	93.9(3)	Cl(1)	Co(1)	N(2)	179.1(2)
Ci(i)	Co(l)	N(3)	92.6(2)	Cl(1)	Co(l)	N(4)	86.6(2)
Ci(i)	Co(l)	N(5)	94.3(2)	N(1)	Co(l)	N(2)	86.8(3)
N(1)	Co(l)	N(3)	87.2(3)	N(1)	Co(l)	N(4)	83.9(3)
N(l)	Co(l)	N(5)	171.0(3)	N(2)	Co(l)	N(3)	86.8(3)
N(2)	Co(l)	N(4)	94.1(3)	N(2)	Co(l)	N(5)	85.0(3)
N(3)	Co(l)	N(4)	171.0(3)	N(3)	Co(l)	N(5)	96.0(3)
N(4)	Co(l)	N(5)	93.1(3)	Co(l)	N(1)	C(l)	109.4(6)
Co(l)	N(1)	C(6)	106.7(6)	Co(l)	N(1)	C(7)	106.8(6)
C(l)	N(1)	C(6)	111.1(7)	C(1)	N(1)	C(7)	110.1(8)
C(6)	N(1)	C(7)	112.5(8)	Co(l)	N(2)	C(2)	107.2(6)
CO(l)	N(2)	C(3)	109.8(6)	Co(l)	N(2)	C(13)	106.8(5)
C(2)	N(2)	C(3)	110.3(7)	C(2)	N(2)	C(13)	112.0(7)
C(3)	N(2)	C(13)	110.6(7)	CO(l)	N(3)	C(4)	105.9(6)
Co(l)	N(3)	C(5)	108.0(5)	CO(l)	N(3)	C(19)	118.0(6)
C(4)	N(3)	C(5)	110.3(8)	C(4)	N(3)	C(19)	106.3(8)
C(5)	N(3)	C(19)	108.3(7)	CO(l)	N(4)	C(8)	113.5(7)
Co(l)	N(4)	C(12)	130.0(7)	C(8)	N(4)	C(12)	116.5(9)
Co(l)	N(5)	C(14)	113.3(6)	CO(l)	N(5)	C(18)	127.8(7)
C(14)	N(5)	C(18)	118.8(9)	N(1)	C(1)	C(2)	110.1(7)
N(2)	C(2)	C(l)	107.4(7)	N(2)	C(3)	C(4)	110.7(8)

Table 2. Bond Angles (deg)

N(3)	C(4)	C(3)	107.1(8)	N(3)	C(5)	C(6)	110.5(8)
N(l)	C(6)	C(5)	108.3(8)	N(l)	C(7)	C(8)	108.1(8)
N(4)	C(8)	C(7)	113.8(9)	N(4)	C(8)	C(9)	121.5(9)
C(7)	C(8)	C(9)	125(l)	C(8)	C(9)	C(10)	119(l)
C(9)	C(10)	C(11)	121(l)	C(10)	C(11)	C(12)	118(l)
N(4)	C(12)	C(11)	123.4(9)	N(2)	C(13)	C(14)	109.2(7)
N(5)	C(14)	C(13)	114.6(8)	N(5)	C(14)	C(15)	123(l)
C(13)	C(14)	C(15)	122(l)	C(14)	C(15)	C(16)	118(l)
C(15)	C(16)	C(17)	120(l)	C(16)	C(17)	C(18)	119(1)
N(5)	C(18)	C(17)	121(l)				

(24) Jackson, W. G. Unpublished results, 1999.
(25) Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1978**, *17*, 1348.

Table 3. Bond Angles (deg)

N(1)	C(l)	H(1a)	109.3	N(1)	C(l)	H(lb)	109.3
C(2)	C(I)	H(la)	109.3	C(2)	C(I)	H(1b)	109.3
H(la)	C(l)	H(lb)	109.5	N(2)	C(2)	H(2a)	110.0
N(2)	C(2)	H(2b)	110.0	C(l)	C(2)	H(2a)	110.0
C(1)	C(2)	H(2b)	110.0	H(2a)	C(2)	H(2b)	109.5
N(2)	C(3)	H(3a)	109.2	N(2)	C(3)	H(3b)	109.2
C(4)	C(3)	H(3a)	109.2	C(4)	C(3)	H(3b)	109.2
H(3a)	C(3)	H(3b)	109.5	N(3)	C(4)	H(4a)	110.1
N(3)	C(4)	H(4b)	110.1	C(3)	C(4)	H(4a)	110.1
C(3)	C(4)	H(4b)	110.1	H(4a)	C(4)	H(4b)	109.5
N(3)	C(5)	H(5a)	109.2	N(3)	C(5)	H(5b)	109.2
C(6)	C(5)	H(5a)	109.2	C(6)	C(5)	H(5b)	109.2
H(5a)	C(5)	H(5b)	109.5	N(1)	C(6)	H(6a)	109.8
N(1)	C(6)	H(6b)	109.8	C(5)	C(6)	H(6a)	109.8
C(5)	C(6)	H(6b)	109.8	H(6a)	C(6)	H(6b)	109.5
N(1)	C(7)	H(7a)	109.8	N(l)	C(7)	H(7b)	109.8
C(8)	C(7)	H(7a)	109.8	C(8)	C(7)	H(7b)	109.8
H(7a)	C(7)	H(7b)	109.5	C(8)	C(9)	H(9)	120.6
C(10)	C(9)	H(9)	120.6	C(9)	C(10)	H(10)	119.4
C(11)	C(10)	H(10)	119.4	C(10)	C(11)	H(11)	120.8
C(12)	C(11)	H(11)	120.8	N(4)	C(12)	H(12)	118.3
C(11)	C(12)	H(12)	118.3	N(2)	C(13)	H(13a)	109.5
N(2)	C(13)	H(13b)	109.5	C(14)	C(13)	H(13a)	109.5
C(14)	C(13)	H(13b)	109.5	H(13a)	C(13)	H(13b)	109.5
C(14)	C(15)	H(15)	120.8	C(16)	C(15)	H(15)	120.8
C(15)	C(16)	H(16)	120.0	C(17)	C(16)	H(16)	120.0
C(16)	C(17)	H(17)	120.5	C(18)	C(17)	H(17)	120.5
N(5)	C(18)	H(18)	119.5	C(17)	C(18)	H(18)	119.5
N(3)	C(19)	H(19a)	109.5	N(3)	C(19)	H(19b)	109.5
N(3)	C(19)	H(19c)	109.5	H(19a)	C(19)	H(19b)	109.5
H(19a)	C(19)	H(19c)	109.5	H(19b)	C(19)	H(19c)	109.5

from each set is actually almost coincident with another (a doublet with a triplet, Figure 9). The tacn CH_2 signals, δ 1.9−4.3, are complex multiplets and are not of particular interest. They appear as ABMX and as the more complex spin systems ABCD. However, the resolution is sufficient at 400 MHz to clearly identify all 12 proton multiplets. The assignment of the methyl signal for the dmpmetacn complexes around δ 2.5 is clear, as are the AB quartets for the two picolyl $-CH_2-$ groups, one at δ 4.6 ($J \sim \Delta\delta$), and the other centered at δ 4.85 (a doublet of doublets ($J < \Delta\delta$) rather than an AB quartet). The latter assignments were confirmed through deuteration of these methylenes, described ahead.

Important questions remained: Which AB quartet belongs to which arm of the ligand (one can be designated cis to the $N-CH_3$ group in $[Co(dmpmetacn)X]^{n+}$ ligand, the other trans), and which proton is which within each arm? The 2D NMR data unambiguously resolved these issues.

The absence of an NH signal for the two dmpmetacn complexes was apparent from the ^{1}H NMR spectroscopy. In Me_2SO-d_6, the NHs are seen clearly in the dmptacn complexes as ^{14}N broadened singlets at δ 7.42 ppm (aqua; Figure 10), and δ 8.16 ppm (Cl; Figure 9). In addition, the aqua dmpmetacn and dmptacn complexes (Figure 10) show a characteristic $Co-OH_2$ signal, coincidentally at δ 7.42 ppm for each.

The 1D proton-decoupled ^{13}C NMR spectra for the chloro and aqua complexes are shown in Figures 12S and 13S, respectively (Supporting Information). Each spectrum of the aqua and chloro complexes displays the 10 pyridine carbons at low field, the 6 tacn carbons at higher field, and the methyl group at ca. δ 2.5 ppm. The distinction between the CH_3 and CH_2 carbons at higher field was clear, given the close

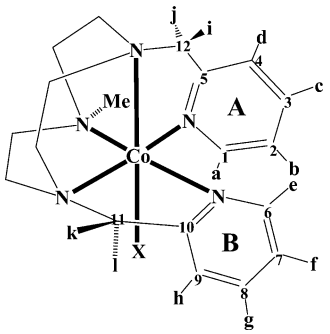


Figure 8. Carbon and proton numbering scheme for *asym*-[Co(dmpmetacn)X]$^{n+}$.

similarity between the dmptacn and dmpmetacn spectra for the CH and CH_2 carbons, and the fact that the dmptacn complex is devoid of a methyl group. The assignments were confirmed by the DEPT spectra (not shown) which clearly distinguished CH, CH_2, and CH_3 carbons.

Amine Deuteration Studies. The parent $[Co(dmptacn)Cl]^{2+}$ complex in D_2O undergoes slow exchange at the sole *sec*-NH center, and this is evident from the loss of the NH signal in the ^{1}H NMR spectrum but also apparent from the ^{13}C NMR spectra which show that the two carbons α to this center diminish in time, while a new pair of signals appears for the deuterated species, each new line 10 Hz upfield from the original (the characteristic isotopomer shift[26,27] at 300 MHz field strength). In contrast, the corresponding $[Co(dmpmetacn)Cl]^{2+}$ complex shows no changes in ^{13}C NMR spectra over a similar period; indeed, a 50:50 mixture of protic reactant, and reactant subject to the usual NH perdeuteration treatment (D_2O, pD ca. 6), shows no characteristic doubling of any C signals, clear evidence that there are no NH protons present, as the IR and ^{1}H NMR data had indicated. This was an important fact to confirm, given that the hydolysis reaction was base catalyzed, and hitherto, this has always associated with the presence of $-NH-$ centers.

2D NMR Studies. The key to the complete assignment of signals was the recognition that the *N*-methyl group is within ca. 3 Å of a unique pyridine C−H, adjacent to the nitrogen on just one of the two arms of the ligand (H-a, Figure 8). This was evident from models of the asym isomer, and this structural feature showed up clearly in a difference NOE experiment (the methyl also interacts with several tacn $-CH_2-$ species, Figure 8). The two signals involved for the chloro complex are the doublet at δ 9.0 ppm (C−H) and the methyl singlet at δ 2.5 ppm, and the same two signals in the spectrum of the aqua species (lowest field C−H, and the methyl).

The following discussion now focuses on the chloro complex.

A ^{1}H−^{1}H COSY experiment (Figure 14S, Supporting Information) revealed which four of the eight pyridine signals were vicinal CH protons belonging to this same ring (B, Figure 8), and since the H-a proton (doublet) is assigned unambiguously, that for the triplet H-b followed. For the

(26) Jackson, W. G. *Inorg. Chem.* **1991**, *30*, 1570.
(27) Jackson, W. G. *Inorg. Chem.* **1993**, *32*, 4168.

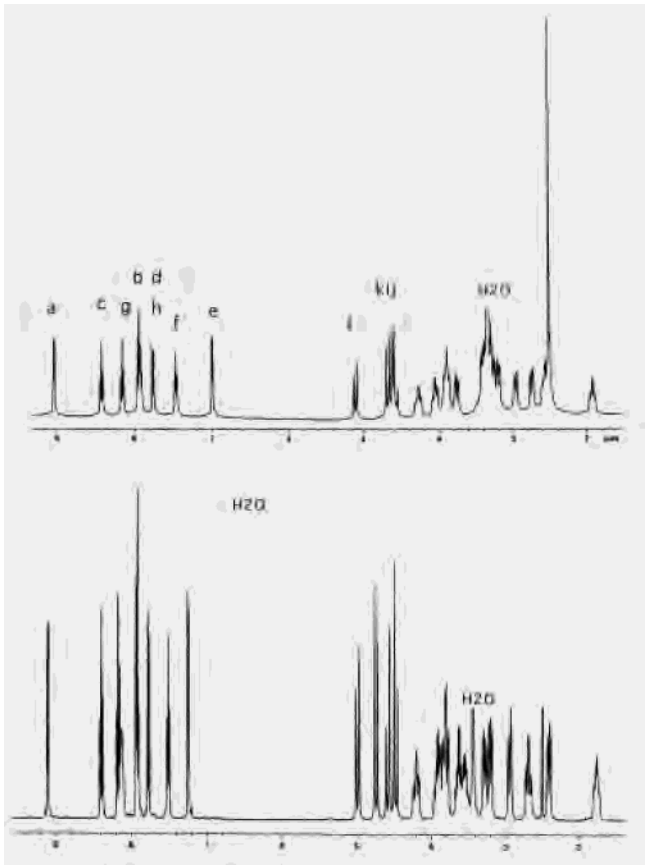


Figure 9. ^{1}H NMR spectra for *asym*-[Co(dmpmetacn)Cl](ClO$_4$)$_2$ (top) and *asym*-[Co(dmptacn)Cl](ClO$_4$)$_2$ in Me$_2$SO-d_6; the proton numbering scheme is in Figure 8.

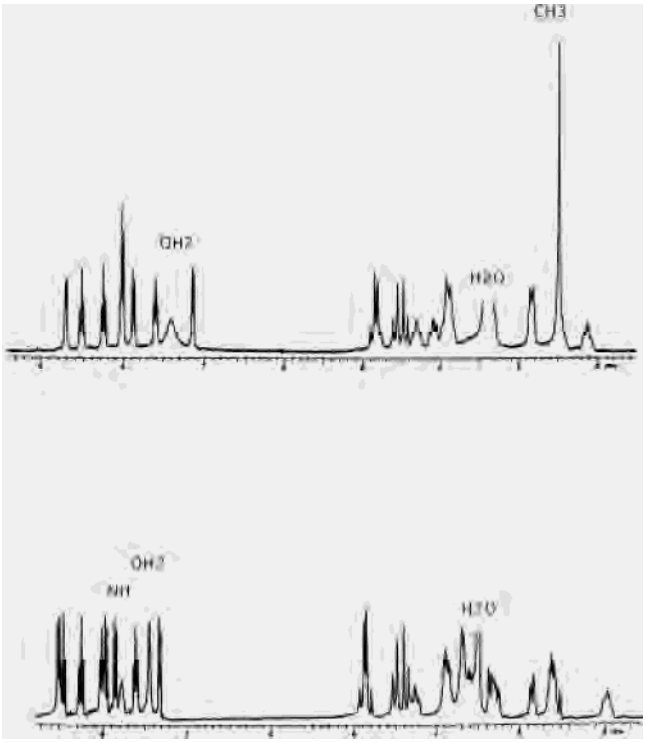


Figure 10. ^{1}H NMR spectra for *asym*-[Co(dmpmetacn)OH$_2$](ClO$_4$)$_3$ (top) and *asym*-[Co(dmptacn)OH$_2$](ClO$_4$)$_3$ in Me$_2$SO-d_6; the proton numbering scheme is in Figure 8.

other vicinal pair, the triplet must therefore be H-c and the doublet H-d.

The four CH multiplets for the other ring (A, Figure 8) are clearly H-f, H-g (triplets) and H-e, H-h (doublets). Which is which, however, needed to be established.

With all protons on the B-ring assigned, the ^{1}H−^{13}C HETCOR NMR spectrum (Figure 15S, Supporting Information) permitted the unambiguous carbon assignments for the same ring (C-1 to C-4, Figure 8). The carbons are grouped in closely spaced pairs in the 1D ^{13}C spectrum (Figure 12S); i.e., C-1 is grouped with C-6, C-4 with C-9, and so on. By this argument, the A-ring carbons, and hence their directly attached protons, can then be assigned using the HETCOR spectrum.

The highest field pyridine A-ring signal is thus H-e, and the other is H-g, while the other two are H-f (δ 7.5) and H-h (δ 7.8). These assignments are consistent with their observed multiplicities (doublet or triplet).

There is no consistent chemical shift pattern for the inner and outer CH protons for the two rings. Indeed, corresponding ring protons H-a (A) and H-e (B) are at the lowest and highest field of all eight protons, separated by ca. 1.5 ppm. This can be understood given the chemical environment of the two rings (Figure 8). There is, however, a systematic chemical shift pattern for the ring carbons in the ^{13}C NMR spectra (Figure 12S). Thus, carbons α to N in the A- and B-pyridine rings are much further downfield than the β carbons, and this shift is much larger than the difference between the other corresponding carbons in the two rings. Nonetheless, the corresponding pair C-1, C-6 (Figure 8) shows the greater difference, as do their attached protons (H-a, H-e).

Two TOCSY NMR experiments (one long and one short delay time, Figure 16S) enabled the identification of the methylene protons H-k, H-l on C-11 adjacent to the B-ring, and H-j, H-i on C-12 next to the A-ring. Our experience with this technique for complexes of this size is that, with a short (0.01 s) delay, relayed proton interactions across three or even four bonds are detected, while for longer delays (0.1 s), protons up to five bonds apart show cross-peaks in the 2D TOCSY spectrum. Thus, for methylene protons H-i, H-j, there should be cross-peaks with H-d (4 bonds), H-a (5 bonds), and H-c (5 bonds), but not H-b, in the 0.1 s delay spectrum, and the two 5-bond and one 4-bond cross-peaks should drop out in the 0.01 s delay spectrum. This is precisely what is observed for the AB quartet at δ 4.6 (Figure 9); this multiplet therefore corresponds to the "elbow" methylenes of ring A. For the other "elbow" CH_2 protons (ring B), a pair of doublets at δ 4.7 and 5.1 (Figure 9) can therefore be assigned as H-k, H-l. The expected cross-peaks for these protons are confirmed by the two TOCSY spectra (Figure 16S). The long delay TOCSY spectrum shows cross-peaks with H-e, H-h, and H-g, but not H-f which is 6 bonds removed, and these observations are consistent with the initially difficult assignment of H-e, H-f as discussed. No cross-peaks are observed for any of the "elbow" methylenes in the short delay spectrum, since there are no protons less than 4 bonds away. Finally, we note that the relay in the

TOCSY experiments is carried across the pyridine nitrogens which bear no protons.

These assignments for the "elbow" protons were further supported by the NOESY spectrum (Figure 17S). For each H-k and H-l, a through-space interaction with H-h was observed, while for the H-i, H-j pair, an interaction with only H-d was detected. These facts are in accord with expectations based on molecular models. Further, there is a significant NOE interaction of H-i with H-e on the other ring, and given that it is the only proton of the pair H-i, H-j which can possibly show an NOE to H-e, its assignment seems secure on this basis (Figure 8); it is the doublet to the lower field of the AB quartet centered at δ 4.6 (Figure 9). These observations not only corroborate all the assignments but permit individual assignments of the elbow proton peaks to H-i and H-j, and H-k and H-l. We assign the δ 5.1 doublet to H-l, since this is closer to H-d and one would expect the bigger NOE. In summary, the low to high field "elbow" proton assignments for the chloro complex are H-l, H-k, H-i, and H-j.

The 2D NMR studies were also conducted on the [Co(dmpmetacn)OH_2]$^{3+}$ complex. The results were similar; only the chemical shifts and AB quartet patterns for the "elbow" $-CH_2-$ protons were different, but the relativities were largely the same. For example, the A-ring methylenes were at higher field than those of the B-ring, and the chemical shift sequences for the A- and B-ring pyridine protons were the same. A partially deuterated d_2-aqua sample (see later) was anated by heating in 10 M HCl to give the chloro complex having the upper but not the lower α-CHD singlet in the same relative positions; thus, H-k and H-l are reversed for the aqua and chloro ions (Figure 8). This also followed from observations on 60:40 mixtures of h_2- and d_2-complexes (Figure 18S). In the ^{13}C NMR spectra, however, the upper α-CH_2 carbon is C-12 for both the chloro and aqua ions (Figures 19S and 20S). These results are consistent with the 2D NMR assignments.

Reaction Stoichiometry and Base Hydrolysis Kinetics. The base hydrolysis reaction of the [Co(dmpmetacn)Cl]$^{2+}$ complex was followed spectrophotometrically in a range of triethanolamine buffers (I = 1.0 M; NaCl; pH 9.3−10.7). Good pseudo-first-order kinetics at least up to 4 half-lives were observed at all wavelengths in the range investigated (300−600 nm), and in all buffers.

The same sharp isosbestic points (406, 523, and 557 nm) were observed in each buffer. The absorbance−time traces for the hydroxo product were horizontal over hours, even in 1 M NaOH. This attests to the stability of the [Co(dmpmetacn)OH]$^{2+}$ product; the corresponding datn complex has been reported[16] to lose one of its 2-aminomethyl arms following base hydrolysis, and at quite an appreciable rate. Although pyridine nitrogen is a better leaving group than a primary amine, we can find no evidence for such a process in our [Co(dmpmetacn)OH]$^{2+}$ complex. Indeed, acidification with strong HCl and anation (95 °C, 60 min) regenerates the [Co(dmpmetacn)Cl]$^{2+}$ complex quantitatively. One would have expected a protonated dangling pyridyl arm to resist rechelation on heating; moreover, such a [Co(dmpmetacn)-

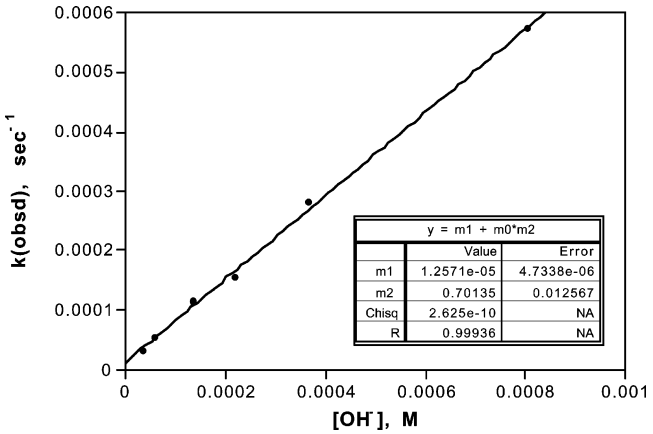


Figure 11. Plot of k(obsd) versus [OH^-] for the base catalyzed hydrolysis of *asym*-[Co(dmpmetacn)Cl]$^{2+}$ showing the linear behavior and nonzero intercept.

$(OH)_2$]$^+$ complex would consume 3 equiv of acid on titration. In the present reaction, just 1 equiv was consumed, consistent with clean formation of [Co(dmpmetacn)OH]$^{2+}$, and no subsequent reaction.

Rate Law. Remarkably, the kinetics were first-order rather than zero-order in [OH^-], with $k_{OH} = 0.70 \pm 0.1$ M^{-1} s^{-1} at 25 °C (Figure 11; Table 7S, Supporting Information); the small but real nonzero intercept ($(1.3 \pm 0.5) \times 10^{-5}$ s^{-1}) is the spontaneous or acid hydrolysis rate constant, normally of this magnitude for a pentaaminecobalt(III) complex. The base hydrolysis is faster than that for the parent [Co(dmptacn)Cl]$^{2+}$ complex (k_{OH} = 0.040 M^{-1} s^{-1})[12] which bears an ionizable NH proton. The complex *s*-[Co(metrenen)Cl]$^{2+}$ also base hydrolyzes faster than its NH analogue *s*-[Co(trenen)Cl]$^{2+}$, and both react via the same mechanism.[28] These results suggests that there is some special mechanism operating, and possibly this same mechanism operates for the complex bearing an NH proton as well; i.e., base catalysis is not associated with the amine NH.

Partial Base Hydrolysis Experiments. A saturated solution of the *asym*-[CoCl(dmpmetacn)]$^{2+}$ complex in D_2O containing NaOD was reacted for one half-life and then quenched with $HClO_4$. On cooling, unreacted starting material precipitated and was filtered off. Later, after addition of 2-propanol, the aqua product precipitated. The NMR spectra of starting material, recovered starting material, and product were obtained. A similar experiment was conducted for the reaction of the chloro complex over 5 half-lives.

The spectroscopy (^1H and ^{13}C NMR) revealed that the recovered chloro reactant showed negligible exchange for any of the four "elbow" methylene protons (Figure 22S). However, for the product aqua complex (Figure 20S), exchange was observed. This occurred for only the one α-CH_2 site (the higher field AB quartet in the ^1H NMR spectrum), assigned as H-i (Figure 8), and under conditions of either one or five half-lives of base hydrolysis for the chloro complex.

Control experiments were conducted on the aqua (hydroxo) complex under identical conditions (0.01 M NaOD). The

(28) Cresswell, P. J. Doctoral thesis, **1974**, Australian National University.

recovered material was unchanged: no D incorporation into either methylene arm. In fact, there was <5% exchange for a time corresponding to $5t_{1/2}$ reaction for the chloro hydrolysis. This result established that the incorporation of just the one deuteron of the pyridyl $-CH_2-$ of the $[Co(dmpmetacn)OD]^{2+}$ product of base hydrolysis must have arisen during base hydrolysis.

These results demonstrate unequivocally that the reactant $[Co(dmpmetacn)Cl]^{2+}$ complex, on deprotonation at one ot the two pyridyl arms, loses Cl^- substantially faster (at least 20-fold) than it reprotonates.

In hindsight, it is not surprising that the methylene protons of the pyridyl groups exchange in base. The ortho and para methyl protons of *C*-methylpyridine are not appreciably acidic, but in the quaternized *N*-alkyl-*C*-methylpyridinium derivatives, these protons exchange readily in base; there is a clear analogy here between N-alkylation and N-binding to Co(III).

The $[Co(dmpmetacn)Cl]^{2+}$ ion base hydrolyzes via deprotonation at an "elbow" $-CH_2-$ proton much faster than the similarly charged $[Co(dmpmetacn)OH]^{2+}$ complex exchanges at the "elbow" $-CH_2-$ centers, and this warrants comment. There are two germane points. First, and the major point, NH exchange rates in the classic $[Co(NH_3)_5X]^{n+}$ ions are known to be quite sensitive to the X group, as well as to the charge on the ion.[29] Second, while exchange rates are normally measured by the rate of abstraction by OH^- (since proton return is much faster and usually diffusion controlled),[19] in the case of $[Co(dmpmetacn)Cl]^{2+}$, the exchange rate is not the rate of abstraction by OH^- of the "elbow" proton because the deprotonated complex loses the Cl^- faster than proton return. As the data have indicated, the true exchange rate for the chloro complex is at least 20-fold less than the measured rate of base hydrolysis, and the normal exchange process is "undercut" by this unusual circumstance. As for the $[Co(dmpmetacn)OH]^{2+}$ complex, proton exchange can also occur by two mechanisms, the first, through simple deprotonation and reprotonation, and the second, through a substitution process[30] involving loss of OH^- and re-entry of water. Given that OH^- is a poorer leaving group than Cl^-, it seems likely that the former is operative. In any event, none of these considerations impinge upon the facts nor conclusions drawn from them. It is pertinent to note, however, that, for the corresponding $[Co(dmptacn)Cl]^{2+}$ complex, proton exchange in the reactant and product is competitive with base hydrolysis,[12] and the case for rate limiting deprotonation cannot be made on the basis of these D labeling experiments alone. The problem with the dmptacn system can be resolved by using an improved leaving group, e.g., the triflate ion, and this prospect is under active pursuit.

Dissociation and rechelation of one arm of the ligand as a means to exchange in the elbow protons need also be considered. The "elbow" protons remain inequivalent in the dangling arm, although they are not in the free ligand. We find no evidence for this possibility, arguing that activation to deprotonation requires the pyridine to be coordinated; indeed, the free ligand does not exchange its methylenes readily, even in strong base. Moreover, such a process cannot accommodate the observation of exchange during the act of base hydrolysis, being much faster than exchange in either reactant or product.

In summary, the $[Co(dmpmetacn)Cl]^{2+}$ complex, which contains no NH protons, base hydrolyzes by a path that is first-order in $[OH^-]$, and the base catalysis arises from deprotonation at a specific pyridyl methylene center which has been identified as H-i in the A-arm (Figure 8). Further, the deprotonated substrate is extraordinarily effective in permitting the substitution of Cl^- by H_2O. Each act of deprotonation leads to substitution, with only a trace of detectable competition from reprotonation.

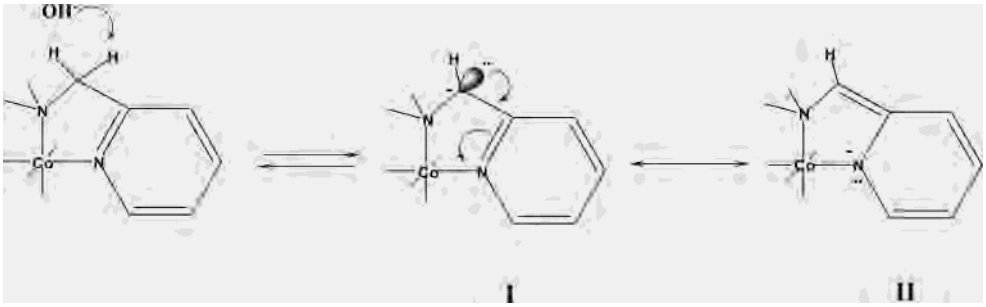
Deuteration at the Methylene "Elbows" of the $[Co(dmpmetacn)OH]^{2+}$ Complex. The $[Co(dmpmetacn)OH]^{2+}$ complex in 0.01 M NaOD exchanges protons at the α-CH_2- arms only very slowly, but in stronger OD^-, sequential exchange of all four inequivalent protons is observed. In 0.1 M NaOD, the second uppermost CH is first exchanged, in minutes; this is the same proton exchanged during base hydrolysis of the chloro complex, and presumably, it is the most acidic in both the hydroxo and chloro ions. Next, the second lowest field proton (in the other "elbow") is exchanged. After several minutes, the dideuterated species is obtained cleanly. Each AB quartet had collapsed to a singlet, with a slight upfield isotopic shift for the $-CHD-$ signal compared to the center of the $-CH_2-$ AB quartet. After acid quenching and isolation, this $[Co(dmpmetacn)OD_2](ClO_4)_3$ complex showed ^1H NMR and ^{13}C NMR spectra (Me_2SO-d_6) identical to those shown in Figure 23S for the dideuterated aqua complex obtained after reaction of the $[Co(dmpmetacn)Cl]^{2+}$ ion in 1 M NaOD for 5 min (>100 half-lives). Retentive anation of this complex in HCl was used in NMR experiments to corroborate the CH assignments in the chloro and aqua species.

The third proton of the hydroxo species, the second of the two lower field CH protons, exchanged in much stronger NaOD (1 M) with a half-life of ca. 15 min at 20 °C. The last proton, in the higher field "elbow" was very much slower to exchange, but had disappeared after 2 h in 2 M NaOD. This fully deuterated species was isolated, converted to chloro complex by heating in 10 M HCl without proton incorporation (Figure 24S), and used in the kinetic isotope effect experiments described in following paragraphs.

The exchange process was also followed by ^{13}C NMR spectroscopy. The inequivalent "elbow" carbons of the aqua complex are closely spaced but are resolved in the broadband decoupled spectrum. Deuteration of the higher field CH leads to collapse of this signal into a weak 1:1:1 triplet ($-CHD-$; (J_{CD} ca. 20 Hz for each)), and similarly for the second proton to exchange (Figure 23S, lower). The ^{13}C NMR data displayed the expected upfield isotopic shifts for C−D compared to C−H. Isotopic shifts were also clearly observed for the pyridyl tertiary carbons, α to the $-CHD-$ centers (C-5, C-10; Figure 8), and even for the pyridyl CHs β to

(29) Buckingham, D. A.; Durham, L.; Sargeson, A. M. *Aust. J. Chem.* **1967**, *20*, 257.
(30) Comba, P. C.; Jackson, W. G.; Marty, W.; Zipper, L. *Helv. Chim. Acta* **1992**, *75*, 1172.

Scheme 1



this center (C-4 and C-9), consistent with the assignments for these carbons. The α and smaller β shifts were on the order of 10−20 Hz at 100 MHz (^{13}C) and not immediately apparent, but for a mixture of the undeuterated and dideuterated aqua complexes, the shifts were seen clearly as doubling in two pyridine carbons for each ring (Figures 25S and 26S). Two tacn carbons β to each −CHD− group also revealed this doubling.

Stereochemistry of Substitution. NMR studies established that the asym configuration is retained on base hydrolysis. Anation after acidifaction (HCl) and heating regenerates asym reactant. Although we have not studied the optically resolved ion, we can assert that the achiral sym configuration is not involved, even transiently (either through a symmetrical pentacoordinate intermediate, or the six coordinate *sym*-[Co(dmpmetacn)OH]$^{2+}$ complex). The [Co(dmpmetacn)OH]$^{2+}$ complex was both regio- and stereoselectively labeled with deuterium at two of the four inequivalent picolyl methylenes already discussed, and these positions are retained on anation in HCl. They are also retained on repetitive cycling of the resultant chloro complex in OH^-. The dideuterated complex exchanges one of its deuteriums in OH^-, but this is inconsequential in OD^-. The important point is that the D does not migrate from one arm to the other to become site scrambled, which the formation of sym isomer (or the described intermediate) requires. Site scrambing within the one arm, however, is still possible, since even for the sym isomer the protons are inequivalent but have the opportunity to become interchanged in the deprotonation/reprotonation process (see ahead) through inversion at the methylene carbon while in the carbanion state. This does not occur, however.

The structurally related *asym*-[Co(datn)Cl]$^{2+}$ and *asym*-[Co(dasn)Cl]$^{2+}$ ions have been optically resolved and it is known that their base hydrolysis proceeds without appreciable loss of optical activity and that the product is also 100% *asym*-[Co(dat*x*)OH]$^{2+}$ (x = n or s).[16]

Kinetic Isotope Effect and General Base Catalysis. Rate limiting deprotonation is rare in base hydrolysis reactions of Co(III) complexes,[2] and general base catalysis is expected rather than the more usual specific base catalysis. Other than for triethanolamine, this prospect has not been extensively explored. Triethanolamine, one of the buffer components, is at the 0.018 M level at the low pH end and 0.18 M at the top end. Upward curvature would therefore be expected in the plot of k(obsd) versus [OH^-], but it is not apparent; the linearity is excellent. Hydroxide ion is clearly superior to triethanolamine as a base, despite its overwhelming concentration advantage in the pH region in question (9.3−10.7).

A substantial kinetic isotope effect is expected for rate limiting cleavage of C−H versus C−D.[31] We carried out parallel kinetic runs on h_4-[Co(dmpmetacn)Cl]$^{2+}$ and d_4-[Co(dmpmetacn)Cl]$^{2+}$. The perdeuterated complex (2 D at each of the picolyl methylenes) was synthesized by anation (HCl) of the aqua complex which had been left in 2 M NaOD for some hours. NMR confirmed the complete exchange of the "elbow" $-CH_2-$ protons (Figure 24S) and also confirmed that back-exchange does not occur in protic acid. Runs were conducted in two basic media; for h_4-Cl in triethanolamine buffer ([OH^-] = 8.04×10^{-4} M), k(obsd) = 5.85×10^{-4} s^{-1}, while for d_4-Cl, k(obsd) = 1.19×10^{-4} s^{-1}. These values correspond to k_{OH} values of 0.73 and 0.15 M^{-1} s^{-1}. For 0.1 M NaOD (I = 1.0 M, NaCl), corresponding k(obsd) values were 9.7×10^{-2} and 2.25×10^{-2} s^{-1}, corresponding to k_{OH} values of 0.97 and 0.225 M^{-1} s^{-1}, respectively. Clearly, the deuterated species is significantly less reactive (5-fold) in each medium. The magnitude of the effect is entirely consistent with rate limiting C−H(D) cleavage. Figure 27S gives an indication of how much slower the deuterated species is to base hydrolyze.

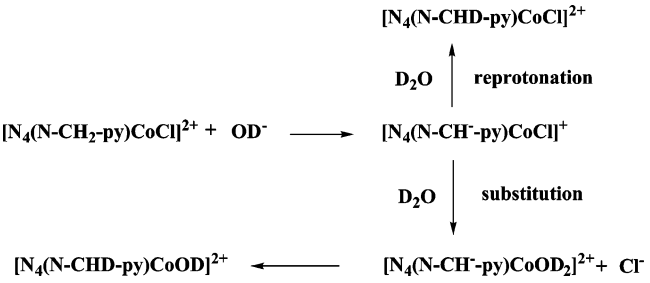
Summary and Conclusions

Picolyl (not pyridine) complexes can indeed form pseudo-bases that are effective in base catalyzed hydrolysis reactions. The essential idea is abstraction of a proton from the 2-methylene group by base, with e^- delocalization leading to a pseudo-base or more accurately termed a pseudo-aminate ion, Scheme 1. This proposal stemmed initially from observations on base-catalyzed deuteration in D_2O/OD^- of the α-methylene centers in the [Co(tmptacn)]$^{3+}$ ion (Figure 1), and its rearrangement.[32] It was then reasoned that if the pseudo-aminate is the effective site of deprotonation in the base hydrolysis of a pyridyl complex, say [Co(pentaamine)Cl]$^{2+}$ where one or more arms of the pentaamine ligand are pyridyl groups, e.g., [Co(picdien)Cl]$^{2+}$ (Figure 1),[6] then the product must be deuterated at the α-methylene as a result of base hydrolysis. To our knowledge, this prospect has never been tested before, Scheme 2.

The D-labeling experiments, extensive 2D NMR work, and chemical correlation of the *asym*-chloro and aqua complexes

(31) Espenson, J. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1995; p 281.
(32) Jackson, W. G.; McKeon, J. A. Paper presented at the IC'96 Conference (Royal Australian Chemical Institute), Townsville, Queensland; Abs. IC'96, P65/A, 1996.

Scheme 2



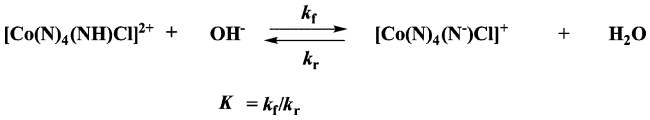
have permitted the unambiguous assignment of the four picolyl methylene protons, and we know which one is effective in the base hydrolysis reaction (H-i, Figure 8). But do we? Inspection of Scheme 2 implies labilization by an aminate generated at the pyridine nitrogen. Each of the two pyridines is cis to the leaving group, and we know which of these is the active form. However, delocalization requires the carbanion generated through deprotonation from this arm to be essentially flat; i.e., the carbanion chirality is lost in the first step. Loss of either proton in the chloro reactant can generate this same species, and therefore, which proton in the reactant is that actually deprotonated remains a moot point. However, we can be certain from which "elbow" the proton is abstracted, and this is the one from the A-ring (Figure 8).

The effectiveness of the pyridyl-derived pseudo-aminate to realize an enhanced rate of substitution at the metal ion brings one to explore the detailed reasons. First, we note that it is not meaningful to distinguish carbanion **I** from pseudo-base **II** where the N is more aminate-like, since these are simply canonical forms. The labilizing effect through the deprotonation is clear, although the magnitude of k_{OH} is certainly not great. Indeed, the $[Co(dmpmetacn)Cl]^{2+}$ ion (and its dmptacn analogue) is among the least reactive ever observed for macrocyclic pentaaminecobalt(III) complexes, and it is quite likely the reason we have been able to exploit these systems to establish the pseudo-aminate mechanism. We return to this important point ahead.

Normally, in base hydrolysis reactions of pentaaminecobalt(III) systems, deprotonation at one of the amine centers leads to proton exchange in both the reactant and base hydrolysis product, and almost invariably, reprotonation is faster than loss of the leaving group.[2,19] This general result only serves to emphasize just how reactive the aminate derivative from a simple amine complex can be, given that only a fraction of the acts of deprotonation lead to base hydrolysis, because k_{OH} values usually reflect not only the intrinsic reactivity of the conjugate base (k) but also the acidity of the active site (K_a); $k_{OH} = kK_a/K_w$. However, if deprotonation is rate determining, as certainly is the case here, then the reactivity of the deprotonated species does not impinge upon the magnitude of k_{OH}; the conjugate base simply disappears to give substituted product faster than it reprotonates.

An analysis of the kinetic data for the hydrolysis of the $[Co(dmptacn)Cl]^{2+}$ complex up to 1 M $[OH^-]$ reveals no significant departure from linearity,[12] a fact consistent with

Scheme 3



little if any net deprotonation at either the amine or methylene centers, and it is reasonable to assume the same pertains for the very similar $[Co(dmpmetacn)Cl]^{2+}$ complex. Probably 10% net deprotonation at the uppermost $[OH^-]$ would be detectable, and so, we can estimate that K is 0.1 or smaller; this acidity limit is likely to apply to the methyl derivative as well. For rate determining deprotonation, the measured k_{OH} value (0.70 M^{-1} s^{-1}) is k_f in Scheme 3. From the acidity argument, it follows that k_r is greater than 7.0 s^{-1} if $K < 0.1$, and this is not surprising for a reprotonation process (usually diffusion controlled). The intrinsic reactivity of the conjugate base can also be assessed from this analysis. Since $k > 20\ k_r$, k must be >140 s^{-1}. This is not large compared to the reactivities normally assigned to aminatecobalt(III) species, but it does at least set a minimum reactivity for the pseudo-aminate complex, an activation of at least 10^7-fold, given an estimated specific rate of aquation of ca. 10^{-5} s^{-1} typical of $[Co(amine)_5Cl]^{2+}$ species.

These considerations lead one to ask whether an aminate derived from a regular amine is more effective in base hydrolysis where a pyridyl methylene center is also present. The $[Co(picdien)X]^{2+}$ and $[Co(picditn)X]^{2+}$ complexes are cases in point;[6,7] others are to be found in an earlier review[2] and the more recent literature. A recent report of base catalysis in the chemistry of Cr(III) pyridyl complexes also warrants attention.[33] These studies are currently under active pursuit.

Finally, it would be useful to know the activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) for the base hydrolysis of both $[Co(dmptacn)Cl]^{2+}$ and $[Co(dmpmetacn)Cl]^{2+}$ in order to more fully ascertain whether base hydrolysis occurs for the former ion by CH_2 rather than NH deprotonation. Activation parameters are normally strikingly different for "normal" base hydrolysis as opposed to the rarer rate limiting deprotonation.[34]

Experimental Section

All chemicals were AnalaR or an equivalent grade. Carbon-13 and proton NMR spectra were recorded on Varian XL-300 and Unity Plus 400 MHz instruments at 20 °C. Solvents used were D_2O with dioxane as the internal reference (^1H, δ 3.75; ^{13}C, δ 69.27 relative to DSS) and Me_2SO-d_6 with the central peak of the CD_3 multiplet as the reference (^1H, δ 2.50; ^{13}C, δ 39.37 relative to $SiMe_4$). Full visible absorption spectra and absorbance−time traces were recorded on a HP8452A diode array UV−vis spectrophotometer thermostated to 25.00 ± 0.05 °C with use of a Lauda RM6 circulating water bath. Infrared spectra were obtained for KBr disks on a Biorad FTIR instrument. Cation exchange media used were Dowex 50Wx2 (H^+ form, 200−400 mesh; Biorad) and SP-Sephadex C25 (Na^+ form; Pharmacia). Carbon dioxide free Milli-Q water was used for all physical measurements.

(33) Tekut, T. F.; Holwerda, R. A. *Inorg. Chem.* **1994**, *33*, 5254.

Ligand Synthesis. The tacn-based ligand dmpmetacn was prepared commencing with tacn purchased from Aldrich or synthesized as described, or directly from *N*-methyltacn. The standard Richman−Atkins method[35] involves cyclization of the disodium salt of di-N tosylated dien (1,5-diamino-3-aza-pentane) with di-O tosylated ethyleneglycol, or the converse, cyclization of fully tosylated (di-O, mono-N) dithanolamine (bis(2-hydroxyethyl)-amine) by reacting with the disodium salt of the di-N tosylated ethylenediamine (1,2-diaminoethane).[36] The former method, used by Searle and Geue,[37] was preferred.

Tritosylate of Dien (Dientt). The synthesis followed the published procedure.[37] ^{13}C NMR (Me_2SO-d_6): δ 143.4 (2C), 135.2 (2C), 129.8 (4C), 126.8 (4C), (terminal aromatic); 142.7 (1C), 137.2 (1C), 129.6 (2C), 126.5 (2C), (central aromatic); 48.3 (2C, CH_2); 41.5 (2C, CH_2); 20.9 (3C, CH_3) ppm.

Ditosylate of Ethylene Glycol.[37] ^{13}C NMR ($CDCl_3$): δ 145.3 (1C), 132.2 (1C), 130.0 (2C), 127.9 (2C), (aromatic); 66.8 (2C, CH_2); 21.6 (2C, CH_3) ppm.

Tritosylate of Tacn (Tacntt). The procedure used for the cyclization is an optimized combination of a number of procedures.[35,37,38] A solution of sodium metal (8.62 g) in ethanol was added to a well stirred slurry of dientt (106.3 g) in ethanol (250 mL) under dry nitrogen. After the mixture was heated to reflux and cooled overnight, a precipitate formed. This, the disodium salt of dientt, was filtered off under nitrogen and washed with ethanol. It was immediately dissolved in dry DMF (500 mL), and 1 mol equiv of $TsOCH_2CH_2OTs$ dissolved in DMF (250 mL) was added dropwise at 100 °C over 1.5 h under dry nitrogen. Heating at 100 °C was continued for a further 2 h before cooling and adding water (500 mL) to form a white precipitate. This was filtered and recrystallized from hot ethanol. Yield: 80%, based on dientt. ^{13}C NMR ($CDCl_3$): δ 143.9 (3C), 134.5 (3C), 129.9 (6C), 127.5 (6C) (aromatic); 51.9 (6C, CH_2); 21.5 (3C, CH_3) ppm.

Detosylation. The tacntt in excess concentrated H_2SO_4 was heated at 100 °C for 3−4 days. After cooling, an equal volume of ethanol/ether (50:50) was added, and more cooling precipitated a tacky gray solid. The mother liquor was decanted and the solid washed with ethanol and ether. Two methods were then used to purify the resultant crude tacn·$1.5H_2SO_4$.

Method 1. The gray solid was dissolved in excess aqueous 5 M NaOH and extracted with three portions of chloroform. After removal of solvent, a yellow oil resulted which solidified on standing. Yield: 60%. ^{13}C NMR ($CDCl_3$): δ 47.3 (6C, CH_2) ppm.

Method 2. The gray solid was dissolved in water, diluted, loaded onto a Dowex cation exchange column, and eluted with HCl.[37] After removal of solvent, the crystalline hydrochloride salt was obtained.

Ditosylate of Tacn (as Tacndt·Hbr). To a mixture of glacial acetic acid (350 g) and aqueous 48% HBr (319 g) was added phenol (22 g) and tacntt (16.5 g). The solution was heated on a steam bath under reflux (85−90 °C) for 42 h. After cooling, twice the volume of ether (ca. 800 mL) was added, and then sufficient ethanol was added to bring about a single liquid phase. A white precipitate resulted which was collected by filtration. Yield: 10.5 g (62%). ^{13}C NMR (Me_2SO-d_6): δ 143.9 (2C), 133.4 (2C), 130.0 (4C), 127.0 (4C), (aromatic); 51.0 (2C, CH_2); 47.2 (2C, CH_2); 44.3 (2C, CH_2); 20.8 (2C, CH_3) ppm.

Ditosylate of *N*-Methyl Tacn (Metacndt). The methylation procedure is an optimized combination of published methods.[39,40] To formic acid (98%, 40 mL) and formaldehyde (40%, 40 mL) was added tacndt·2HBr (9.5 g), and the mixture was heated at 90 °C on an oil bath overnight. The addition of HCl (12 M) and evaporation to dryness yielded the product as a white solid (8.9 g). ^{13}C NMR (Me_2SO-d_6): δ 144.1 (2C), 133.9 (2C), 130.2 (4C), 127.0 (4C), (aromatic); 50.7, (2C, CH_2); 50.6, (2C, CH_2); 45.0 (2C, CH_2); 41.0 (1C, CH_3); 21.0 (2C, CH_3) ppm.

***N*-Methyl Tacn (Metacn).** The procedure for detosylation of metacndt followed the described method 1 for tacn[37] Yield: ca. 60%. ^{13}C NMR ($CDCl_3$): δ 54.4 (2C, CH_2); 46.4 (2C, CH_2); 46.0 (2C, CH_2); 45.1 (1C, CH_3) ppm.

Monotosylate of Tacn (Tacnt). The method of Sessler et al. was used on a 10−50% scale, with a comparable % yield.[36] ^{13}C NMR ($CDCl_3$): δ 143.3 (1C), 135.4 (1C), 129.7 (2C), 127.1(2C), (aromatic); 53.8 (2C, CH_2); 49.4 (4C, CH_2); 21.5 (1C, CH_3) ppm.

Dmpmetacn. The method was analogous to that for the synthesis of dmptacn.[11,14] To an aqueous solution containing metacn (1.0 g, free base) was added 2 equiv of picolyl chloride and the pH adjusted to about 11. Over 3 days, the pH was continually adjusted with 2 M NaOH to ca. 11. The workup was the same as that described for dmptacn, and it resulted in a yellow oil. Yield: 80%. ^{13}C NMR ($CDCl_3$): 160.5 (2C), 148.9 (2C), 136.2 (2C), 123.3 (2C), 121.8 (2C), (aromatic); 65.0 (2C, CH_2); 56.7 (2C, CH_2); 56.0 (2C, CH_2); 55.9 (2C, CH_2); 46.3 (1C, CH_3) ppm.

[CoCl(dmpmetacn)]Z_2 (Z = ClO_4^-, Cl^-, 0.5$ZnCl_4$). Method 1. Dmpmetacn (0.6 g, free base) was dissolved in 1:1 water/methanol (50 mL), and 1 mol equiv of $CoCl_2·6H_2O$ was added. Enough hydrogen peroxide (30% w/w) was added dropwise to completely oxidize the Co(II) to Co(III), and a brown color developed (bridging peroxo species). An equal volume of 10 M HCl was added, and the now orange solution was heated on a steam bath for 1 h before dilution and sorption onto a Dowex column. Elution with 2 M and then 3 M HCl yielded an orange band (aqua) followed by a red product (chloro). By heating the aqua product at 90 °C in HCl (10 M) for 4 h, more chloro product was obtained. Eluates were taken to dryness. The perchlorate salt of the chloro product was crystallized from a saturated aqueous solution of the residue by addition of a fifth volume of $HClO_4$ (70%); it is sparingly soluble in water. It was collected, washed with ethanol and ether, and air-dried. ^{13}C NMR (Me_2SO-d_6): 164.8 (1C), 163.7 (1C), 152.9 (1C), 149.7 (1C), 141.8 (1C), 140.6 (1C), 126.9 (1C), 126.8 (1C), 125.0 (1C), 123.8 (1C) (aromatic); 69.4 (1C), 67.4 (1C) (elbow CH_2); 64.5 (1C), 63.5 (1C), 62.8 (1C), 61.7 (1C), 61.0 (1C), 52.5 (1C), (ring CH_2); 51.3 (1C, CH_3) ppm.

Method 2. By dissolving the free base dmpmetacn (1.44 g) in excess aqueous HCl and evaporating to dryness under reduced pressure the hydrochloride salt was obtained. This was then dissolved in water and sodium triscarbonatocobaltate(III) (1.5 g)[41,42] added. Heating for 15 min and then adding HCl (3 M) to remove unreacted triscarbonatocobaltate(III) resulted in a clear orange/red solution; heating at 90 °C for several hours completed the reaction. After the reaction mixture cooled, the addition of concentrated perchloric acid yielded 1.25 g of pink-red product as the perchlorate salt. The mother liquor was an orange color, and the aqua product was recovered by anation (HCl) as in method 1 to give more chloro complex.

Method 3. To a solution of *trans*-$[Co(py)_4Cl_2]Cl·6H_2O$ (2.0 g, 3.4 mmol)[43,44] in methanol was added free base dmpmetacn, (1.1 g, 3.4 mmol) in methanol (5 mL), and the mixture was heated to

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(41) Bauer, H. F.; Drinkard, W. C. *J. Am. Chem. Soc.* **1960**, *82*, 5031.
(42) Bauer, H. F.; Drinkard, W. C. *Inorg. Synth.* **1966**, *8*, 202.

60 °C for 15 min. The product mixture was quenched with 1 M HCl, diluted with water, and sorbed on and eluted from Dowex as before. It was crystallized as the perchlorate or tetrachlorozincate salts from water using $HClO_4$ or "H_2ZnCl_4" as precipitants. Yield: 1.71 g (80%). Anal. Calcd for $CoC_{19}H_{27}N_5Cl{\cdot}ZnCl_4$: C, 36.39; H, 4.34; N, 11.17; Cl, 28.27. Found: C, 36.0; H, 4.3; N, 11.0; Cl, 28.3%. Calcd for $CoC_{19}H_{27}N_5Cl{\cdot}(ClO_4)_2{\cdot}0.5H_2O$: C, 35.23; H, 4.27; N, 11.41; Cl, 17.33. Found: C, 34.8; H, 4.1; N, 11.2; Cl, 17.3%. UV−vis (0.01 M $HClO_4$): ϵ_{375}(max) 207.5, ϵ_{510}(max) 157.5.

The quite soluble chloride salt was conveniently obtained from the purified perchlorate by adding some HCl (10 M) to a slurry of the salt in acetone/water (1:1), and then carefully diluting with excess acetone.

[Co(dmpmetacn)OH$_2$](ClO$_4$)$_3$. A slurry of the chloro derivative (perchlorate) in a minimum volume of 2 M NaOH was warmed to effect dissolution and hydrolysis. The solution was filtered and acidified by addition of an equal volume of $HClO_4$ (70%). On cooling, orange crystals deposited. These were filtered, washed with *i*-PrOH and ether, and air-dried. Yield: ca. 70%. Anal. Calcd for $CoC_{19}H_{27}N_5OH_2{\cdot}(ClO_4)_3$: C, 32.56; H, 4.17; N, 10.00; Cl, 15.18. Found: C, 32.4; H, 4.31; N, 9.9%. UV−vis (0.01 M $HClO_4$): ϵ_{357}(max) 156.5, ϵ_{489}(max) 197.5.

Steric Course of Base Hydrolysis. A sample (ca. 80 mg) of *asym*-[Co(dmpmetacn)Cl]$^{2+}$ (Cl^- or ClO_4^- salt) was dissolved in D_2O, containing dioxane as an internal reference, and the ^{13}C NMR spectrum was recorded. Two drops of NaOD (10 M) were then added, and the ^{13}C NMR spectrum was recorded for the hydroxo ion which was formed within seconds (established in control experiments). The product solution was acidified by addition of a few drops of DCl (10 M) until the solution just became orange. The ^{13}C NMR spectrum was recorded immediately. Isomer distributions for both the hydroxy and the aqua ions were determined from the relevant peak areas; individual isomers were easily identified from their characteristic and unique ^{13}C NMR patterns. The results obtained from the hydroxo spectra agreed with those deduced from the spectra for the corresponding aqua ions, and the results from both sets of spectra were averaged; protonation of the ligand does not involve rearrangement about the metal ion.

Buffer Solutions. Buffers employed triethanolamine (0.40 M), partly neutralized (0.1 to 0.9 equiv) with HCl, with the ionic strength adjusted to 2.00 M with NaCl. They were diluted 1:1 for use. The pH determinations were performed using a Metrohm 654 digital pH meter as part of a Metrohm autotitration system, with a jacketed 25 mL capacity cell thermostated pH vessel to 25.00 ± 0.05 °C with use of a Lauda RM6 circulating water bath. This vessel was covered with a blanket of N_2, saturated with water vapor from a Dreschel bottle containing aqueous NaCl of the same ionic strength and temperature as the buffers (1 M, 25 °C). The temperature was measured with an Orion 100 Ω platinum resistance thermometer attached to the Metrohm instrument. A Ross combination "Sure-flow" electrode was used (internal electrolyte 1.00 M NaCl). The calibration of the instrumentation employed 0.1000 M NaOH (Volucon; I = 1.0 M, $NaClO_4$), standardized against potassium hydrogen phthalate, and then titrated against 0.1 M $HClO_4$ (I = 1.0 M; $NaClO_4$) using the electrode to provide millivolt versus p[OH^-] values; "pH" or p[H^+] values were then obtained using pK_w = 13.77, the value obtained from the data analysis of complete titration curves using Superquad.

Base Hydrolysis Kinetics. The kinetics for the chloro species were measured in a series of buffers at 25.00 ± 0.05 °C. All rates were measured as absorbance versus time traces, with at least three runs per complex and reaction, using the in situ method (1 cm cell). Either the chloride or perchlorate salts (ca. 0.01 g) were used for all kinetic runs. This was carried out by thermally equilibrating equal volumes (1.00 mL) of each of a solution of the complex and the double concentration buffer (2 M) in a bifurcated 1 cm cell, and mixing rapidly to initiate reaction. Kinetic data were analyzed by weighted nonlinear regression on a Macintosh with the usual package, or by importing the HP mkd files into Specfit and carrying out global spectral analysis (SVD data reduction) to a first-order rate law.

Partially Deuterated Complexes. A solution of *asym*-[Co(dmpmetacn)Cl]Cl$_2$ (0.5 g) in D_2O (20 mL) was mixed with 0.5 M NaOD in D_2O (15 mL), using an inverted Y-tube,[45] and allowed to react at 25 °C for 2.0 min before quenching with $HClO_4$ (5 mL). On cooling, the d_2-aqua complex crystallized. A similar reaction in 2 M NaOD but with a 2 h reaction time afforded the d_4-aqua complex. The corresponding d_2- and d_4-chloro ions were made by heating samples of the aqua species in HCl (10 M; steam bath, 2 h). They were crystallized as perchlorates and recrystallized from water/$HClO_4$ to remove traces of the aqua complex.

Partial Base Hydrolysis Experiments. The half-life for the base hydrolysis of [Co(dmpmetacn)Cl]$^{2+}$ (0.002 M in D_2O) diluted 1:1 with a solution of NaOD (0.02 M, I approximately equal to 2.0 M NaCl) was measured spectrophotometrically at 25.0 °C ($t_{1/2}$ ca. 82 s). The experiment was repeated on a preparative scale; 5.0 mL of both complex (ClO_4^-, or better, Cl^- salt) solution in D_2O and the NaOD solution were placed in an inverted Y-tube[45] and, after temperature equilibration, mixed. After 100 s, the reaction was quenched with excess perchloric acid (5 mL; 70%). On cooling, unreacted starting material precipitated and was filtered off. Later, after addition of 2-propanol, the aqua product precipitated.

Kinetic Isotope Effect Measurements. These were performed as described under kinetics but using both h_4- and d_4-*asym*-[Co(dmpmetacn)Cl]$(ClO_4)_2$ as reactants, with runs performed in parallel to provide a direct comparison of k_H/k_D. Two media were employed (a triethanolamine buffer, and 0.1 M NaOH, both I = 1.0 M (NaCl)).

Crystallography. A pink plate crystal of $C_{19}H_{27}Cl_5CoN_5Zn$ having approximate dimensions of 0.44 × 0.04 × 0.04 mm^3 was mounted on a glass fiber. All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 19 carefully centered reflections in the range 12.25° < 2θ < 14.98° corresponding to an orthorhombic cell with dimensions a = 17.723(5) Å, b = 15.130(6) Å, c = 18.350(6) Å, V = 4921(5) Å^3. For Z = 8 and fw = 627.03, the calculated density is 1.69 g/cm^3. The systematic absences of 0kl, $k \neq 2n$; $h0l$, $l \neq 2n$; and $hk0$, $h \neq 2n$ uniquely determine the space group as *Pbca* (No. 61).

The data were collected at a temperature of 23 ± 1 °C using the ω−2θ scan technique to a maximum 2θ value of 50.10°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a takeoff angle of 6.0°. Scans of (0.80 + 0.34 tan θ)° were made at a speed of 2.0°/min (in ω). The weak reflections (I < 10.0σ(I)) were rescanned (maximum of 4 scans), and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the

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incident beam collimator was 0.5 mm, the crystal to detector distance was 200 mm, and the detector aperture was 3.5 × 3.5 mm^2 (horizontal *x* vertical).

A total of 4854 reflections were collected. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, for Mo Kα radiation is 22.1 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.74 to 0.92. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SIR92[46]) and expanded using Fourier techniques (DIRDIF94[47]). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement (function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + (p^2/4)F_o^2]^{-1}$; $\sigma_c(F_o)$ = esd based on counting statistics; p = *p*-factor) was based on 2071 observed reflections ($I > 3.00\sigma(I)$) and 280 variable parameters and converged (largest parameter shift was <0.01 times its su) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.043$ and $R_w = \sqrt{[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]} = 0.040$, respectively. The standard deviation of an observation of unit weight was 2.08. The weighting scheme was based on counting statistics and included a factor ($p = 0.007$) to downweight the intense reflections. Plots of $\sqrt{[\sum w(|F_o| - |F_c|)}$ versus $|F_o|$, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.47 and −0.57 e/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[48] Anomalous dispersion effects were included in F_{calc};[49] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[50] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[51] All calculations were performed using the teXsan[52] crystallographic software package of Molecular Structure Corporation.

Acknowledgment. We are grateful to the Australian Research Council for financial support, and to Dr. Leone Spiccia and Susanne Brudenell for alerting us to their pioneering work with dmptacn, and for helpful discussions. Assistance with the 2D NMR experiments from Drs. J. Grant Collins and Barry Gray and Ms. Kerri Wells was appreciated.

Supporting Information Available: Tables of atomic coordinates (Table 1S), anisotropic displacement parameters (Table 2S), torsion angles (Table 7S), and nonbonded contacts (Table 8S); kinetic data (Table 7S). Crystallographic file in CIF format for *asym*-[Co(dmpmetacn)Cl]$ZnCl_4$. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0206995

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