$SiCl_4$ and other main-group-element halides proceeded with a breakdown of the $(C_2H_5)_2B(pz)_2$ moiety.

As shown in this study, although the poly(1-pyrazolyl)borate ligands have been known for a long time and have been used effectively in coordination chemistry, their chemical character is not yet fully understood. A noteworthy step to explore this situation is a recent X-ray crystal structure determination of M-$[B(pz)_4]\cdot H_2O$ (M = Na, K) as well as detailed NMR studies on $[H_nB(pz)_{4-n}]^-$ (n = 0-2) species. As a result, it has been stated that poly(1-pyrazolyl)borates constitute moderate electron-releasing substituents which are comparable to alkyl groups, but where the electron-releasing ability decreases with increasing number of pz groups bonded to the boron.[17]

Acknowledgment. This work was supported by the Office of Naval Research (K.N.) and Fonds der Chemischen Industrie (A.M.). Travel funds from the North Atlantic Treaty Organization (A.M. and K.N.) are also gratefully acknowledged.

Supplementary Material Available: Complete listings of bond distances and angles, H atom coordinates, and anisotropic thermal parameters for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ and $[B(pz)_4]SnCl(CH_3)_2$ (8 pages); structure factor tables for $[(C_6H_5)_2B(pz)_2]SnCl(CH_3)_2$ and $[B(pz)_4]SnCl(CH_3)_2$ (37 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of the Pentaamminecobalt(III) Linkage Isomers of Succinimide

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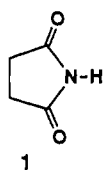
The linkage isomers of (succinimido)pentaamminecobalt(III) have been selectively synthesized and characterized by ^1H and ^{13}C NMR, IR, and UV-visible spectroscopies. The deprotonated imide ligand bonds to the metal through oxygen or nitrogen. The oxygen-bonded isomer is the less stable form. In water (k^s_{ON} = 1.7 × 10^{-4} s^{-1}, 25 °C) and Me_2SO (k^s_{ON} = 5.1 × 10^{-5} s^{-1}) it spontaneously isomerizes to the nitrogen-bonded form; in aqueous acid (pK_a = 2.7, I = 0.1 M, $LiClO_4$) and acidified Me_2SO it protonates and rapidly solvolyzes; the protonated species in water has reactivity comparable (k_H = 2.3 × 10^{-2} s^{-1}, I = 0.1 M, $LiClO_4$, 25 °C) to the most reactive isolable $[(NH_3)_5CoX]^{n+}$ species known. In aqueous base three competing reactions have been detected, namely solvolysis (40%, 25 °C), base-catalyzed O- to N-bonded linkage isomerization (30%), and nucleophilic attack on the coordinated carbonyl group by hydroxide ion leading to the formation of the carboxylate-bonded isomer of (succinamato)-pentaamminecobalt(III) (30%) (k_{OH}(obsd) = 9.0 × 10^{-2} M^{-1} s^{-1}, I = 0.1 M, KF, 25 °C). The individual rates and rate laws for all these reactions have been determined. In acid and base the nitrogen-bonded imido complex is less reactive than the O-bonded form. It is base hydrolyzed relatively slowly, and a term second order with respect to hydroxide ion is dominant in the rate law (k_N = 6.1 × 10^{-3} M^{-2} s^{-1}, I = 1.0 M, $NaClO_4$, 25 °C); ^{18}O studies establish the reversible addition of OH^- in the first step. The product is the nitrogen-bonded succinamato complex, which has been characterized through crystallization in its basic and acidic forms (pK_a = 1.8 (amide) and 3.55 (carboxylic acid), I = 1.0 M, NaCl, 25 °C). The succinimido-*N* complex is protonated in water and Me_2SO only in very strong acid. The protonated species has been crystallized and characterized; it is a strong acid (pK_a < 1), and in acidic solution it solvolyzes very slowly ($t_{1/2}$ = days, 25 °C). A N- to O-bonded isomerization reaction has not been detected. The structure and reactivity of these imide complexes are compared with those of the related amide and urea complexes.

Introduction

This paper describes the syntheses, solution structures, and reactions of oxygen- and nitrogen-bonded (succinimido)pentaamminecobalt(III).[1] There have been complexes of succinimide (**1**) reported since the time of Werner; the ligand has been coordinated to a range of metal ions mostly via nitrogen[2,3] but also via oxygen.[4,5] However, the pentaammine complexes described here are the first examples of an imide bonded to Co(III) and the first pair of imide linkage isomers to be reported. Succinimide forms a planar ring.[6] The imide proton is acidic (pK_a 9.5 in aqueous solution[7]), and the resulting anion **2** has a highly delocalized electronic structure with the potential to coordinate to a metal ion via the endocyclic nitrogen or either of the equivalent exocyclic oxygens. A similar ligand is 1-oxo-3-iminoisoindoline (**3**), whose complexes with cobalt(III) via the exocyclic (**4**) and endocyclic (**5**) nitrogens have been synthesized,[8] but no isomerization or ligand hydrolysis reactions were reported.



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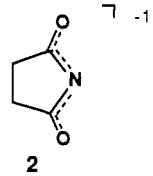

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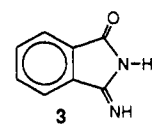

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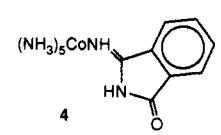

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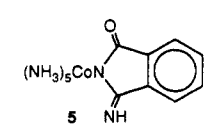

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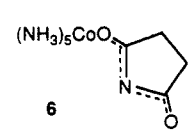
Our studies of the reactions of amide-containing ligands bonded to cobalt(III) have produced, inter alia, the following linkage isomers:



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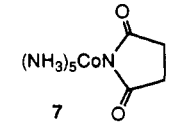

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The reactions of these complexes have been studied in detail for several reasons. First, the oxygen-bonded isomer **6** is novel in that the ligand is coordinated solely via the amide oxygen while the

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Table I. Visible Spectral Data (λ_{max} in nm, ϵ_{max} in M^{-1} cm^{-1}) for (Succinimido-*O*)pentaamminecobalt(III) and Derived Complexes (Perchlorate Salts)

	solvent	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
succinimido-*O*[a]	water	503	90.0	349	74.0
succinimido-*N*	0.10 M Tris	483	61.0	345	55.0
succinimide-*N*	2.0 M HCl	483	62.5	345	61.0
succinamato-*O*	water	500	61.5	350	50.0
succinamato-*N* (deprotonated)	0.10 M Tris	482	49.5	346	44.0
succinamato-*N* (diprotonated)	1.0 M HCl	474	53.0	340	54.0

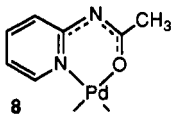
[a] Triflate salt.

Table II. ^1H NMR Spectral Data (δ, ppm) for Succinimide and Its Pentaamminecobalt(III) Complexes at 20 °C[a] in Me_2SO-d_6

	cis-NH_3	*trans*-NH_3	others
succinimide			2.55 ($-CH_2-CH_2-$)
			11.04 (>NH)
succinimido-*O*	3.93	2.29	2.64[b] ($-CH_2-$ adjacent to Co)
			2.51[b] ($-CH_2-$ remote from Co)
succinimido-*N*	3.44	3.11	2.50 ($-CH_2-CH_2-$)
succinimide-*N*[c]	3.27	2.99	2.36 ($-CH_2-CH_2-$)

[a] Shifts downfield from TMS. [b] AA'BB' spectrum, center of multiplet. [c] Recorded with added CF_3SO_3H to prevent deprotonation.

amide nitrogen remains deprotonated. This kind of structure is rare, previously demonstrated conclusively[9] only in a palladium(II) complex of chelated *N*-(2-pyridyl)acetamide **8**, where chelation



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through the amide oxygen and the pyridyl nitrogen has precluded metal bonding to the deprotonated amide nitrogen.[10] Also, by analogy with related amide and urea chemistry, it was anticipated that the oxygen-bonded deprotonated succinimide complex should be less stable than the nitrogen-bonded isomer so evidence for O- to N-bonded linkage isomerization was sought. Finally, it was of interest to compare the coordination chemistry of succinimide, which has a rigid conformation and an additional and strongly electron-withdrawing functional group attached to the amide nitrogen, with that of primary amides and ureas. Studies on complexes of these ligands have revealed pH-dependent linkage isomerization reactions[11-13] and ligand hydrolyses[14,15] as well as metal–ligand cleavage reactions. These acyclic amides and ureas have a certain degree of conformational flexibility, and their reactivity has been shown to vary[15] with the nature of the substituents on the amide carbon and nitrogen.

Results

Synthesis of the succinimido-*O* complex **6** was achieved using $[(NH_3)_5CoOSO_3CF_3](CF_3SO_3)_2$, which allows rapid, kinetically controlled syntheses. Initial attempts to make the O-bonded isomer for the uncharged ligand were unsuccessful, but use of a noncoordinating base resulted in a rapid reaction which produced the deprotonated O-bonded isomer. The succinimido-*O* complex forms a sparingly soluble, bright pink trifluoromethanesulfonate (triflate) salt whose visible (Table I) and ^1H NMR (Table II) spectra are characteristic of the CoN_5O chromophore. Coordination through oxygen rather than through nitrogen means the symmetry of the

Table III. ^{13}C NMR Spectral Data (δ, ppm) for Succinimide and Its Pentaamminecobalt(III) Complexes at 20 °C[a] in Me_2SO-d_6

	C=O	other
succinimide	179.7	29.7 ($-CH_2-CH_2-$)
succinimido-*O*	193.6 (free)	31.4 ($-CH_2-$ remote from Co)
	203.6 (coord)	32.6 ($-CH_2-$ adjacent to Co)
succinimido-*N*	192.5	30.7 ($-CH_2-CH_2-$)

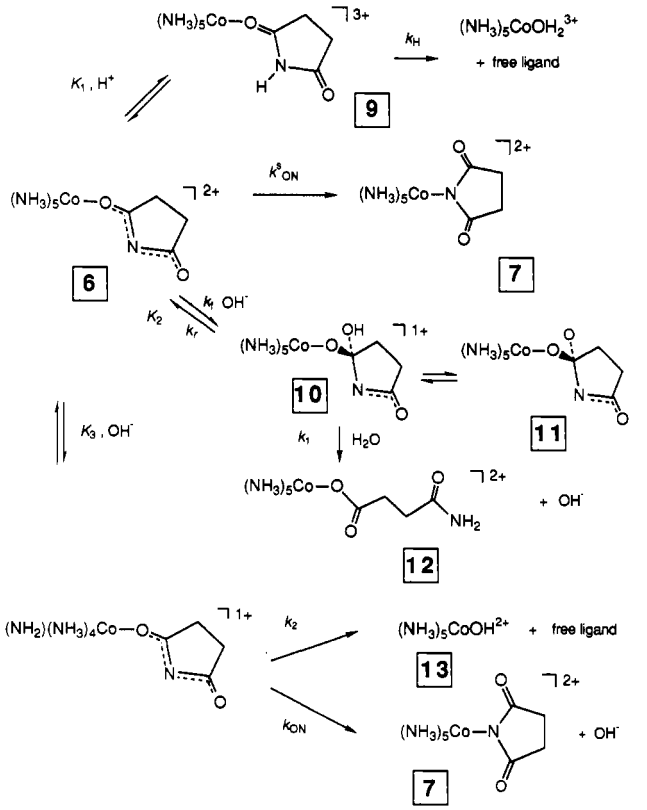
[a] Downfield from TMS.

Table IV. Infrared Spectral Data (cm^{-1}) for Succinimide and Its Pentaamminecobalt(III) Complexes[a]

	C=O str vibrations		C=O str vibrations
succinimide	1780, 1700	succinimido-*N*	1620
succinimido-*O*	1690, 1550	succinimide-*N*	1530 (broad, weak)

[a] Spectra recorded in Nujol mulls with NaCl windows.

Scheme I



structure is reduced compared with that of the free ligand. This is demonstrated by the presence of two methylene signals in the ^1H and ^{13}C NMR (Table III) spectra and of two carbonyl resonances in the ^{13}C spectrum and by the splitting of the C=O stretching vibration in the IR spectrum (Table IV). Deprotonation of the ligand in this complex is inferred from the necessity of using base in the synthesis and from the absence of the imide proton (>NH) signal in the ^1H NMR spectrum of the complex (this NH signal is present in the corresponding spectrum of the free ligand). It also elutes characteristically as a 2+ ion from a cation-exchange column.

The reactions of the succinimido-*O* complex **6** are summarized in Scheme I. In the solid state and in a variety of solvents the succinimido-*O* ion spontaneously reacts to form a pale orange complex which was identified as the succinimido-*N* isomer **7**. Visible and ^1H NMR spectra are consistent with coordination through nitrogen, and the ^1H and ^{13}C NMR spectra show only one methylene peak and the ^{13}C and IR spectra only one carbonyl peak, demonstrating the expected equivalence of these groups. A complex with identical spectroscopic properties was prepared directly from succinimide using a method which produces the

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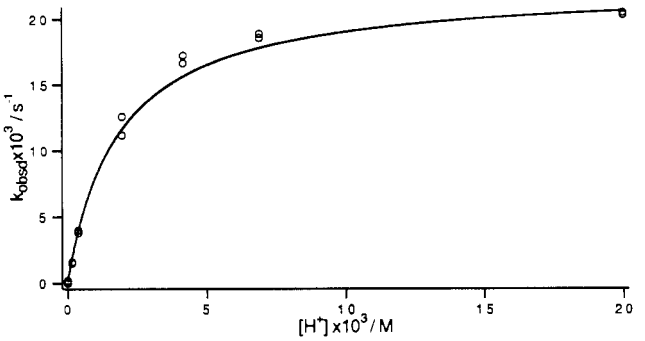

Figure 1. Rate profile (observed and calculated) for the solvolysis of the succinimido-*O* complex in aqueous acid at 25 °C, I = 0.100 M ($LiClO_4$).

Table V. ^{13}C NMR Spectral Data (δ, ppm) for Succinamic Acid and Its $(NH_3)_5Co(III)$ Complexes in Me_2SO-d_6 at 20 °C[a]

	–CON–	–COO–	$-CH_2-$ (acid)	$-CH_2-$ (amide)
$H_2NCO(CH_2)_2COOH$	174.3	173.9	29.3	30.0
$[Co(NH_3)_5NHCO(CH_2)_2COO]^+$	184.6	177.7	35.4	37.0
$[Co(NH_3)_5OCO(CH_2)_2CONH_2]^{2+}$	174.6	182.6	31.5	33.4

[a] Downfield from TMS.

thermodynamically more stable isomer.[16] The spontaneous linkage isomerization is complete (>98% N-bonded isomer) and devoid of competing reactions in solution and also in the solid state. The rates of spontaneous isomerization in solution are recorded in Table VII; they appear to be relatively insensitive to the nature of the supporting electrolyte and to the ionic strength. A crystalline sample of O-bonded isomer was found to contain 80% N-bonded isomer after 16 weeks at 20 °C in an airtight container, corresponding to a half-life of 23 weeks at this temperature; this is clearly much slower than isomerization in solution. Such a difference in solution and solid-state rates is typical.

When the succinimido-*O* complex is dissolved in acid solution (water or Me_2SO), the reaction products are free succinimide and the solvento complex. [The protonated N-bonded isomer (vide infra) is relatively unreactive and if formed would have been detected.] The rate data (Table VIII, supplementary material) were fitted to the rate law

$$k_{obsd} = \frac{k^s_{ON} + k_H K_1[H^+]}{1 + K_1[H^+]}$$

which is consistent with formation of the protonated complex **9** followed by its aquation (Scheme I). The variation of the rate constant (observed and calculated) with $[H^+]$ is shown in Figure 1. From $[H^+]$ = 0.020–0.10 M the rate constant is invariant; $k_H = 2.3 \times 10^{-2}$ s^{-1} and $K_1 = 540$ (I = 0.1 M, $LiClO_4$, 25 °C). The pK_a of coordinated succinimide was determined kinetically as 2.7 and independently (spectrophotometrically; Table IX, supplementary material) as 3.0 under the same conditions. This is a considerable enhancement when compared with pK_a 9.5 for free succinimide.[7]

When the oxygen-bonded isomer **6** was reacted in aqueous base at 25 °C, three reaction products were separated by ion-exchange chromatography after acid quenching—aqua pentaammine, succinimido-*N*, and a bright pink 2+ ion. Repetition of the reaction at 2 °C produced a sufficiently larger proportion of the pink complex to enable it to be crystallized from the eluate. ^1H and ^{13}C NMR spectra (Tables V and VI) of this unknown complex suggested it was succinamato-*O* pentaammine **12** (the carboxylate functional group is bonded to the metal), produced by direct attack of hydroxide ion on the coordinated imide with subsequent ring opening through C–N cleavage. The succinamato-*O* pentaammine complex was then synthesized directly from succinamic acid, and

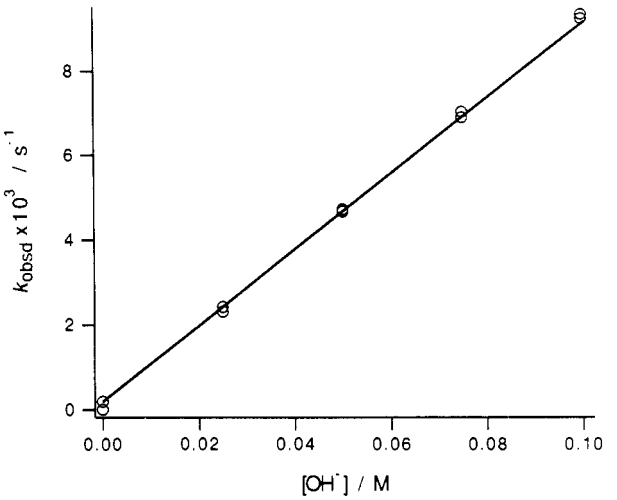

Figure 2. Dependence of k_{obsd} (observed and calculated) on $[OH^-]$ for the base hydrolysis of the succinimido-*O* complex at 25 °C, I = 0.100 M (KF).

the spectra (^1H and ^{13}C NMR and UV–visible) of the two independently synthesized complexes were identical.

The hydroxo pentaammine **13** and succinimido-*N* **7** complexes are produced via the conjugate base of succinimido-*O* pentaammine, that is by base-catalyzed ligand–metal cleavage and isomerization reactions. Since these reactions and the C–N cleavage pathway have markedly different activation enthalpies,[14] the relative rates are quite temperature dependent. Thus, at a lower temperature less hydroxo pentaammine **13** and succinimido-*N* **7** complexes were expected, and this is consistent with observation.

On the basis of the reactions shown in Scheme I and with application of the steady-state approximation to the reactive intermediate **10**, the following rate law for the reactions of the succinimido-*O* complex in base may be derived:

$$k_{obsd} = \frac{k^s_{ON} + [OH^-]\{K_2k_1 + K_3(k_2 + k_{ON})\}}{1 + (K_2 + K_3)[OH^-]}$$

The observed rate constant was found to vary linearly with $[OH^-]$ up to at least 0.10 M (Table X, supplementary material; Figure 2), and this is consistent with $K_2 + K_3 \ll 1$. The rate law then simplifies to

$$k_{obsd} = k^s_{ON} + [OH^-]\{K_2k_1 + K_3(k_2 + k_{ON})\} = k^s_{ON} + [OH^-]\{k_{OH} + k'_{OH} + k^{OH}_{ON})\} = k^s_{ON} + k_{OH}(obsd)[OH^-]$$

where corresponding terms should be obvious. The slope of k(obsd) vs $[OH^-]$ ($=k_{OH}$(obsd)) was evaluated as 0.090 M^{-1} s^{-1}. The rate constants for the individual pathways were obtained from product ratios. The relative amounts were constant at differing [KOH] with 4:3:3 hydroxo pentaammine:succinamato-*O*:succinimido-*N* ratios, consistent with Scheme I where each product arises by a term first order in $[OH^-]$ (the k^s_{ON} path was a negligible contributor at the $[OH^-]$ employed). The individual terms were evaluated as $K_2k_1 = k_{OH} = 0.027$, $K_3k_2 = k'_{OH} = 0.036$, and $K_3k_{ON} = k^{OH}_{ON} = 0.027$ M^{-1} s^{-1}.

In D_2O/OD^- the methylene protons α to the coordinated carbonyl group of the succinimido-*O* complex were observed to exchange at a rate comparable to loss of reactant (^1H NMR); thus, the liberated free succinimide and N-bonded ligand were also partly deuterated, but these species did not undergo independent H/D exchange under the conditions.

The chemistry of succinimido-*N* is summarized in Scheme II. In aqueous base a different orange complex was produced, and its ^1H NMR spectrum (Table V) is consistent with that of an N-bonded amide; so too is the ^{13}C spectrum (Table VI). From these data, and by analogy with the chemistry of free succinimide, we consider this complex to be succinamato-*N* pentaammine **17**, formed by attack of hydroxide on the imide carbonyl group. This complex could not be synthesized directly from succinamic acid,

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Table VI. ^1H NMR Spectral Data (δ, ppm) for Succinamic Acid and Its $(NH_3)_5Co^{III}$ Complexes in Me_2SO-d_6 at 20 °C[a]

	cis-NH_3	*trans*-NH_3	NH/NH_2	$-CH_2-$(amide)[b]	CH_2-(acid)[b]
$H_2NCO(CH_2)_2COOH$			6.82, 7.33	2.27	2.38
$[Co(NH_3)_5NHCO(CH_2)_2COO]^+$	3.41	3.53	3.90	2.36	2.09
$[Co(NH_3)_5NHC(OH)(CH_2)_2COOH]^{3+}$	3.33	3.26	6.78	2.63	2.61
$[Co(NH_3)_5OCO(CH_2)_2CONH_2]^{2+}$	3.70	2.64	6.73, 7.27	2.27	2.21

[a] Downfield from TMS. [b] AA'BB' spectra, center of multiplets.

Table VII. Rates of Spontaneous O–N Isomerization of (Succinimido-*O*)pentaamminecobalt(III) Triflate at 25.0 °C

solvent	$10^5k^s_{ON}$/ s^{-1} [a]	$t_{1/2}$, min	solvent	$10^5k^s_{ON}$/ s^{-1} [a]	$t_{1/2}$, min
dimethyl sulfoxide	5.07	230	0.10 M $LiClO_4$	18.3	63
			0.10 M KF	18.7	62
water	17.8	65			

[a] ±3%.

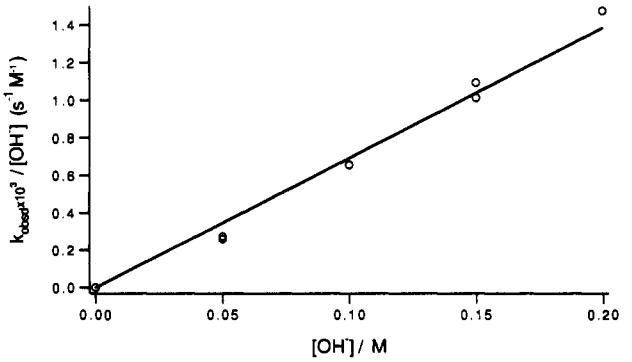
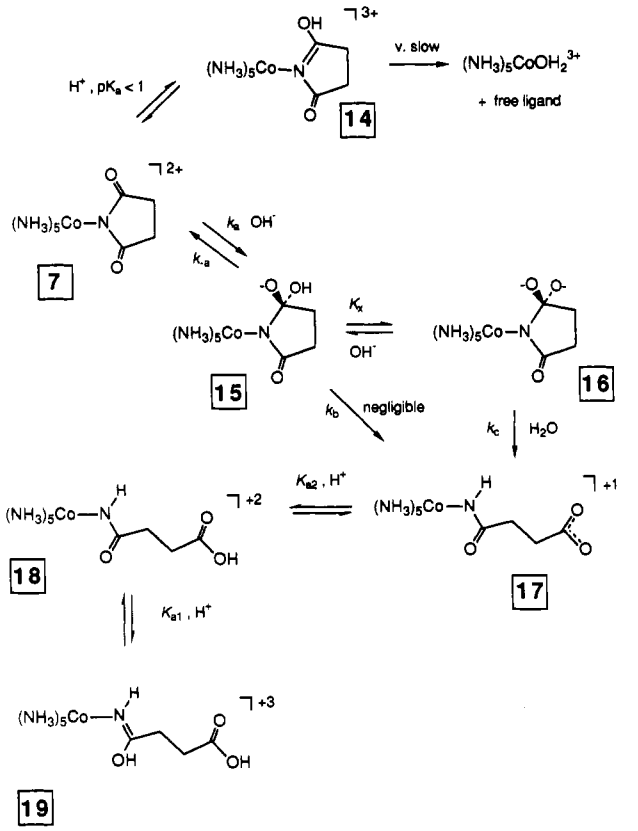


Figure 3. Variation of $k_{obsd}/[OH^-]$ with $[OH^-]$ for the base hydrolysis of the succinimido-*N* complex at 25 °C, I = 1.00 M ($NaClO_4$).

which coordinates preferentially through the carboxylate group in both water and Me_2SO, even with added base. The fully protonated species **19** may be crystallized from acid solution, and it has two acidic groups, the N-coordinated amide group pK_a 1.8 (cf. 3 in acetamide-*N*[17]) and the remote carboxylate group pK_a 3.55 (I = 1.0 M, NaCl, 25 °C). The latter demonstrates the enhanced acidity of the coordinated ligand, even in a group remote from the metal (succinamic acid pK_a 4.52[18]), and is very similar to the pK_a of the remote carboxylate group (3.1) in (succinato)pentaamminecobalt(III).[19] The chemistry of the succinamato-*N* complex will be described in a later paper.[20] Kinetic studies of the base hydrolysis of the succinimido-*N* ion (Table XI, supplementary material) have determined that the rate law is $k_{obsd} = k_N[OH^-]^2$, where k_N = 0.0061 M^{-2} s^{-1} (I = 1.0 M, $NaClO_4$, 25 °C). The variation of $k_{obsd}/[OH^-]$ with $[OH^-]$ is shown in Figure 3. The term first order in hydroxide was negligible ($<10^{-6}$), and this low value is unusual. The complexes of dimethylformamide with Rh(III) and Ir(III)[21] show finite terms both first and second order in hydroxide in their rate laws, but no second-order term was observed for the corresponding cobalt(III) complex.[14] The rate laws for the base hydrolysis of (trichloroacetato)-[22] and (trifluoroacetato)pentaamminecobalt(III)[23] have terms both first and second order in hydroxide in their rate laws. Isotopic tracer studies with the trifluoroacetato complex have shown that ligand hydrolysis (the carbon–oxygen cleavage pathway) proceeds only through the second-order term in the rate law; the term first order in hydroxide accounts for the ligand–metal cleavage reaction.

Scheme II



The succinimido-*N* complex was reacted in $H_2{}^{18}O$ (5 atom %) containing NaOH (0.5 M), and the reaction was quenched with acid after 1 half-life. Residual reactant was recovered and found to be enriched 13% in oxygen-18 relative to the solvent. Since there are two equivalent oxygen atoms in the complex, this means that on average 26% of the complex has one labeled oxygen and clearly addition of hydroxide ion is reversible.

The succinimido-*N* complex protonates in strongly acidic solution (water and Me_2SO), and the conjugate acid may be crystallized. It is a strong acid (pK'_a <1); this was deduced from titration of the complex in solution (pK_a ~0.5) and from chromatographic behavior. In acid solution (water or Me_2SO) it is remarkably inert; it solvolyzes very slowly ($t_{1/2}$ = days). Spectra indicate that the complex is protonated on an oxygen as are N-bonded amide complexes.[12,13,17] No Co–NH peak was detected in the ^1H NMR spectrum, and the methylene and ammine signals are shifted to slightly lower field, as is seen in amide-*N* complexes. The OH peak is not seen, and this is usual; it is in rapid exchange with residual solvent water. It has been detected in the protonated acetamide complex[12] using very dry materials, but attempts to remove lattice water from the succinimide-*N* complex surprisingly resulted in deprotonation. Although the complex is monoprotonated, the methylene and carbonyl signals are equivalent on the NMR time scale, and this is attributed to rapid proton exchange between the imide oxygens in solution.

"Superacid" studies on succinimide[24] have shown that the imide protonates on oxygen; in those extreme conditions diprotonation

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is observed. This is consistent with the electronic structure of the ligand; the imide nitrogen is acidic; its electron pair is extensively delocalized into the ring and is not readily available to bond with a proton.

Discussion

Reactions of the Oxygen-Bonded Succinimide Complex. The deprotonated N-bonded isomer is more stable thermodynamically than the corresponding deprotonated O-bonded isomer, from direct observation (^{1}H and ^{13}C NMR). Also, for the N-bonded form $pK_a < 1$ whereas the O-bonded form is less acidic, pK_a 2.7. The same situation has been observed for urea[11] and amide[12,13] complexes although the acidity difference between the linkage isomers is much smaller in the succinimide system. The spontaneous O–N isomerization reaction for the imide becomes significant when it is deprotonated. When pH ≥ 11 however, the amount of isomerization decreases as base-catalyzed solvolysis and ligand hydrolysis become competitive. Base-catalyzed O–N isomerization occurs and is faster than the spontaneous pathway, but like O–N isomerization reactions in urea and nitrito[25] complexes, it is less efficient. For linkage isomerization reactions this is the norm, and an account has been offered.[11] Further, the O to N pathway must be intramolecular, since the succinimido anion could not compete with the solvent as the incoming ligand once it was completely dissociated from the metal ion.

The O-bonded complex for the unchanged succinimide ligand is quite reactive ($t_{1/2}$ = 30 s, 25 °C), comparable to $[(NH_3)_5CoO_3SCF_3]^{2+}$ ($t_{1/2}$ = 28 s, 25 °C),[26] and if the triflate ion is regarded as a very good leaving group, so also must neutral succinimide-*O*. Base-catalyzed hydrolysis of the triflate complex is, as expected, especially fast ($k_{OH} = 10^5$ M^{-1} s^{-1}), and one would therefore anticipate base-catalyzed *hydrolysis* of the succinimide-*O* complex to be comparable in rate, perhaps even faster because a 3+ ion has more acidic amines than a 2+ ion. Thus, a reasonable estimate for k_{OH} might be 10^6 M^{-1} s^{-1}, and the reactive species in the S_N1CB process would be $[(NH_3)_4(NH_2)Co(succinimide\text{-}O)]^{2+}$. Now the complex in base deprotonates, but the site of deprotonation in the predominant tautomer is on the succinimide rather than NH_3 ligand, and this $[(NH_3)_5Co(succinimido\text{-}O)]^{2+}$ ion is only modesty reactive. However the prospect that reaction procedes via the reactive tautomer $[(NH_3)_4(NH_2)Co(succinimide\text{-}O)]^{2+}$ (the internal conjugate base), albeit in very low abundance, still merits consideration.

The general rate law for base hydrolysis when proton transfer is not rate limiting is $k(obsd) = kK_a[OH^-]/(K_w + K_a[OH^-])$, where K_a is the acidity constant for the complex, usually of the order of 10^{-16}, and k is the specific rate of hydrolysis for the conjugate base, estimated to be as large as 10^7 s^{-1}. Usually, $K_a[OH^-] \ll K_w$, and the rate law reduces to $k(obsd) = kK_a[OH^-]/K_w = k_{OH}[OH^-]$. If the ligand can be deprotonated (K'_a) and the tautomer so generated has a specific rate of reaction k', the rate law is $k(obsd) = (kK_a + k'K'_a)[OH^-]/(K_w + (K_a + K'_a)[OH^-])$. Commonly the ligand is more readily deprotonated than NH_3 ($K'_a \gg K_a$), such as for O-bonded amides and ureas, and the rate simplifies to $k(obsd) = (kK_a + k'K'_a)[OH^-]/(K_w + K'_a[OH^-])$. Indeed in the examples quoted the ligand is sufficiently acidic such that $K_a \gg K_w$, and a limiting rate is achieved at high $[OH^-]$. For our succinimide-*O* complex, K'_a ($=10^{-2.7}$) is so large that the limiting rate is reached even as low as pH 7 [rate increases in the high-pH region are actually associated with a second deprotonation]. This limiting rate is $(kK_a + k'K'_a)/K'_a = kK_a/K'_a + k' = k_{OH}/K_w/K'_a + k'$. In the last expression, the term $k_{OH}K_w/K'_a$ is the contribution to reaction from the aminato conjugate base and k' is the contribution from the other tautomer. Using $K'_a = 10^{-2.7}$ and the estimate $k_{OH} = 10^6$ M^{-1} s^{-1}, the term $k_{OH}K_w/K'_a = 5 \times 10^{-6}$ s^{-1}. This is a factor of 36 smaller than the observed 1.8×10^{-4} s^{-1}, and we conclude that reaction does not procede significantly via the aminato tautomer.

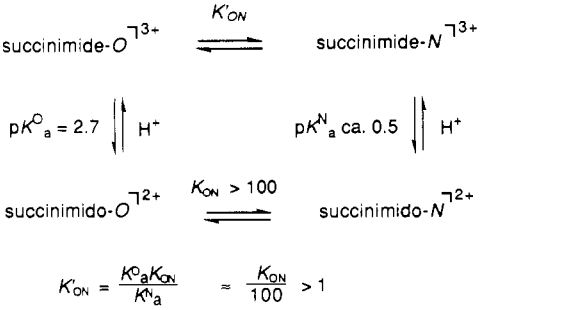
It is striking that the sole reaction product for the succinimido-*O* complex at pH 7 is the N-bonded linkage isomer whereas hydrolysis is the exclusive reaction when protonated. This fact is certainly inconsistent with reaction of the deprotonated form via its $[(NH_3)_4(NH_2)Co(succinimide\text{-}O)]^{2+}$ conjugate base because there should be more rather than less linkage isomerization, compared to hydrolysis, by the corresponding spontaneous reaction, i.e. reaction of $[(NH_3)_5Co(succinimide\text{-}O)]^{3+}$. In a related system $[(NH_3)_4CoOC(S)NHCH_3]^{2+}$,[27] the O to S linkage isomerization reaction is acid catalyzed[28] and the product distribution appears to change with acid. In that system the proton probably adds to the amine which is not the captured functional group, but addition to sulfur has been suggested.[28] Thus, the obvious explanation is that in the reactive form of the succinimide complex the proton resides on the nitrogen and that the other pair of electrons remain effectively delocalized in the ring thereby completely blocking the capture of nitrogen.

In chelated[29] and monodentate[14,15] amide complexes and in ureas,[11] the ligand-deprotonated species is relatively unreactive. In the monodentate systems the conjugate base pathway with a neutral leaving group has been argued to win out over reaction via the tautomer with an anionic leaving group. This is opposite to what we argue for the sucinimide system, and the difference must simply reside in the vastly different values for K'_a, which swap the relative importance of the reactivity terms $k_{OH}K_w/K'_a$ and k'.

Reactions of the Nitrogen-Bonded Succinimide Complex. The succinimido-*N* complex displays a chemistry which differs significantly from N-bonded amides and ureas. First, it is a stable nitrogen-bonded Co(III) complex yet the nitrogen is substituted. The delocalized electronic structure and planar configuration of the imido ligand result in a predominantly sp^2 character at the nitrogen. This contrasts with N-substituted amides and ureas; in those ligands the nitrogen has partial sp^2 character, and thus far we and others have been unable to coordinate them to Co(III) through nitrogen as monodentate ligands.

Another significant difference between the succinimido-*N* complex on the one hand and N-bonded amide and urea complexes on the other is the extreme lack of reactivity of the protonated succinimido-*N* species. Indeed, it is orders of magnitude less reactive than the corresponding protonated succinimido-*O* complex, which, conversely, was singled out for being unusually reactive. In amide and urea complexes the protonated N-bonded isomers undergo N–O isomerization and parallel solvolysis, and the urea complexes, as a class, are more reactive than the amides.[11] The solvolysis of the succinimido-*N* complex occurs very much more slowly ($t_{1/2}$ = days) than even the amides.

N–O isomerization, if it is occurs, would not be detected because the product O-bonded isomer hydrolyzes so rapidly ($t_{1/2}$ = 30 s), although conceivably the reaction could all go via N to O isomerization. To evaluate this prospect, we need to consider first the relative stabilities of the protonated N- and O-bonded forms. The equilibrium constant K'_{ON} governing this may be estimated from the following equilibria:



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(29) Buckingham, D. A.; Davis, C. E.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 5571–5579.

Although acid shifts the O–N equilibrium as it does for amides, ureas, and related ligand systems,[11,12] in the succinimide system the linkage isomer acidity difference is much smaller and consequently the equilibrium shift is diminished. Thus, the O-bonded protonated species may not be the more stable form and the protonated succinimido-*N* complex may be prevented from N–O isomerization and react solely by solvolysis.

N–O isomerization involving the protonated amide bond was first studied in peptide complexes. A general mechanism proposed for this reaction[30] suggested that, although protonation in N-bonded peptides initially occurred at the oxygen, rearrangement to the O-bonded form occurred through a nitrogen-protonated intermediate. In protonated free amides only a small fraction (1:1000) appears to be N-protonated,[31] while in free succinimide,[24] as previously noted, protonation also occurs on the oxygen only, a direct consequence of the very low basicity of the imide nitrogen. In "superacid" diprotonation has been observed and the sites of protonation were the carbonyl oxygens only. The inference is that succinimido-*N* might behave like the amides, with protonation on O.

For monodentate amide-*N* and urea-*N* complexes it has been argued that N–O linkage isomerization occurs via the N-protonated tautomer $Co–NH_2–CO–$, and this is rapid, whereas the O-protonated tautomer $Co–NH{=}C(OH)–$ is relatively unreactive and leads only to hydrolysis. The ureas exist predominantly as the former tautomer, and the amides, as the latter. To be consistent with these data, the succinimido-*N* complex must not only be all O-protonated but its N-protonated tautomer must be essentially inaccessible. Moreover, it must have almost total imine character, since solvolysis and/or the unobserved N-O rearrangement are extremely slow, even slower than the amides. In further support of this, the visible spectrum of the succinimido-*N* complex hardly changes on protonation (Table I), consistent with little disruption to the chromophore on the addition of a proton (cf. amides and ureas). Indeed, while the ^1H NMR spectra in Me_2SO-d_6/CF_3SO_3H indicated that protonation could be achieved (and showed that solvolysis of the protonated form is also extremely slow) and a spectrophotometric titration in H_2O/HCl indicated a pK_a of ca. 0.5, the spectral changes were too small to render this number reliable, especially in this high-acid region. Kinetically, therefore, the protonated form behaves not too differently from the deprotonated form, and this ion is stable (to solvolysis) indefinitely. It seems that ring delocalization does not involve this lone pair on the nitrogen as much as it does for analogous amides and ureas.

Ring-Opening Reactions in Base. As for the oxygen-bonded isomer, the succinimido-*N* ion undergoes addition of hydroxide ion, in this case at an uncoordinated carbonyl group; this process leads solely to carbon–nitrogen bond cleavage and the formation of $[(NH_3)_5CoNHCO(CH_2)_2COO]^+$. Amides and peptides are considered to be deactivated toward ligand hydrolysis when deprotonated and coordinated through nitrogen,[10] but the very polar imide has a sufficiently activated carbonyl group to be susceptible to nucleophilic attack even when N-bonded and deprotonated.

The rate of ligand hydrolysis of the N-bonded complex is of the same magnitude as that of the free ligand; however, the mechanistic details are quite different. Hydrolysis of the free ligand proceeds through the unionized imide,[7] and the process is first order in hydroxide ($k_{OH} = 8 \times 10^{-3}$ M^{-1} s^{-1}). But for the succinimido-*N* complex the rate law shows a second-order dependence on hydroxide and no detectable term which is first order in hydroxide over the range $[OH^-] = 0.050$–0.20 M (we estimate $k_{OH} \leq 2 \times 10^{-6}$ M^{-1} s^{-1}—the intercept of the graph shown in Figure 3). Thus, by the first-order hydroxide term the ligand is more reactive but by the second-order hydroxide term the complex is the more reactive. Assessment of the mechanism can only be speculative, but it does not seem likely that it could involve the tautomer arising from deprotonation of an ammonia ligand. The only activation expected there would be a weakening of the Co–N bond and subsequent solvolysis. No such process has been detected. The most probable mechanism, which has a parallel in the base hydrolysis of anilides[32,33] and is shown in Scheme II, is addition of hydroxide to the carbonyl group forming a tetrahedral intermediate and then deprotonation of this intermediate to produce the reactive species which undergoes ring opening. Imides and anilides have a common factor—each has an electron-withdrawing substituent on the nitrogen. The general rate law for this mechanism is

$$\frac{k_{obsd}}{[OH^-]} = \frac{k_a(k_b + k_cK_x[OH^-])}{k_{-a} + k_b + k_cK_x[OH^-]}$$

Experimentally, $k_{obsd}/[OH^-]$ varied linearly with $[OH^-]$ over 0.050–0.20 M (Figure 3), and the intercept is negligible. Thus, k_cK_x must be larger than k_b but small compared with k_{-a}; since K_x is very likely $\ll 1$, it follows also that $k_c \gg k_b$. The rate law then simplifies to

$$\frac{k_{obsd}}{[OH^-]} = \frac{k_ak_cK_x[OH^-]}{k_{-a}}$$

and the experimental rate constant k_N may be expressed as

$$k_N = \frac{k_ak_cK_x}{k_{-a}}$$

The oxygen-18 analysis showed that recovered unreacted imide complex was significantly (but incompletely) labeled after 1 half-life of reaction. The result is not simply quantified because the extent of labeling depends upon the reaction time. However k_{-a} (regeneration of reactant from intermediate) must be of the same order of magnitude as k_cK_x (irreversible removal of intermediate), and hydroxide ion addition is clearly reversible (Scheme II). Further, the deductions k_cK_x ca. k_{-a} and $k_c \gg k_b$ now require $k_c \gg k_{-a}$.

The kinetics at fixed $[OH^-]$ and at various wavelengths of the spectrophotometric study were always simple pseudo first order, and thus we were not dealing with consecutive reactions where the intermediate **15** (or **16**) accumulated (Scheme II). This is the justification for the steady-state treatment in the derivation of the rate law. Furthermore, since the intermediate is formed through k_a and removed through k_{-a} and k_cK_x paths, and $k_{-a} \approx k_cK_x$, it follows that k_a is much less than k_{-a}. Note also that k_a is, coincidentally, approximately equal in magnitude to the measured k_N (0.006 s^{-1}), and this provides a measure of the specific rate of OH^- addition in the first step.

The form of the rate law suggests that in the succinimido-*N* complex coordination deactivates the ligand to the degree that a highly polar intermediate must be formed before ring opening can occur. With the succinimido-*O* complex the carbonyl group is polarized by coordination and the ring-opening reaction occurs adjacent to this site. Although the rate constants for these two reactions are of similar magnitude, one is first order and the other second so they are not comparable. Also, the observed rate constants are composite and, in the case of the O-bonded isomer, may not directly reflect the efficacy of OH^- addition anyway. For example, a knowledge of the magnitude of K_2 ($=k_f/k_r$) is required to evaluate k_1 from k_{OH} ($=k_{OH}/K_2$; vide supra and Scheme I). Some useful information can however be deduced as follows. By arguments similar to those advanced for the N-bonded isomer, the intermediate **10** does not accumulate and thus $K_2 \ll 1$, or $(k_r + k_1) \gg k_f$. This allows us to estimate that $k_1 \gg |k_{OH}|$, i.e., $\gg 0.027$ s^{-1}. We can also say that $k_f \geq 0.027$ s^{-1}, depending upon the relative magnitudes of k_1 and k_r, thus providing a minimum specific rate of OH^- addition in the first step (Scheme I). The corresponding number for the N-bonded isomer is 0.006 s^{-1}. This analysis indicates that the O-bonded isomer is at least 5-fold more

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reactive than the N-bonded form toward addition of OH^-, but it may well be much greater than this. The N-bonded isomer, ceteris paribus, has a statistical advantage of two, and this fact serves to magnify the intrinsic difference between the nitrogen- and oxygen-bonded ligands in their susceptibilities toward attack by OH^-.

Experimental Section

All new complexes analyzed satisfactorily; the presence of lattice water was confirmed by ^1H NMR spectroscopy for dry Me_2SO-d_6 solutions.[26] Numbers after the complexes below refer to Schemes I and II.

$[(NH_3)_5CoOC(CH_2)_2C(O)N](CF_3SO_3)_2 \cdot H_2O$ (6). $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$ (triflato complex) was prepared by a modification of the original method.[15,34] $NaCF_3SO_3$ used ahead is a byproduct of this synthesis. Succinimide (Fluka, 5 g), triflato complex (3 g), and lutidine (BDH, 0.5 g) were stirred in AR acetone (30 mL) in a covered beaker for 30 min. The ligand gradually dissolved, the solution turned dark red, and finally a pink precipitate was formed. The products were precipitated in chilled AR diethyl ether (500 mL) and filtered off. The residue was treated on the frit with AR methanol (20 mL) to remove excess $[(NH_3)_5CoOH](CF_3SO_3)_2$. The crude complex was then dissolved in a minimum amount of cold water and crystallized with concentrated $NaCF_3SO_3$ solution. The bright pink crystals were washed with ether, air-dried (yield 0.35 g, 12%), and stored at 0 °C in an airtight container to inhibit isomerization. The complex may also be crystallized as the dithionate or perchlorate salts, but the usefulness of these salts is limited by their very low solubility in both water and Me_2SO.

$[(NH_3)_5CoNC(O)(CH_2)_2CO](ClO_4)_2 \cdot H_2O$ (7). This complex was prepared using a general synthesis of deprotonated nitrogen-bonded complexes.[16] Succinimide (5 g) and $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3$[35] (3 g) were heated in Me_2SO (30 mL) and tetramethylpiperidine (Merck, 0.5 g) in a sealed flask at 60 °C for 1 h. The resultant red solution was diluted with 2-butanol (50 mL) and then added to diethyl ether (400 mL). The crude complex precipitated and was isolated by filtration. The pure product was obtained by recrystallization from aqueous Tris with cold concentrated $NaClO_4$ solution. The orange crystals were washed with absolute ethanol and ether and air-dried (yield 1.0 g, 50%).

$[(NH_3)_5CoNC(OH)(CH_2)_2CO](ClO_4)_3 \cdot H_2O$ (14). A concentrated solution of the succinimido-*N* complex was acidified gradually with 6 M $HClO_4$. The solution turned yellow, and after excess acid was added bright yellow crystals separated and were filtered off, washed copiously with ether, dried, and stored at 0 °C in an airtight container to inhibit deprotonation.

$[(NH_3)_5CoNHCO(CH_2)_2COO]ClO_4 \cdot H_2O$ (17). The succinimido-*N* complex (0.50 g) was dissolved in 0.1 M NaOH (30 mL), and the solution was stirred for 5 h. The crude complex was crystallized by adding solid $NaClO_4$ followed by a drop of 6 M $HClO_4$. The pure product was obtained by recrystallization from aqueous Tris with cold concentrated $NaClO_4$ solution and ethanol. The pale orange crystals were washed with absolute ethanol and ether (yield 0.22 g, 54%). This complex may also be crystallized as the diprotonated species. Acidification of a solution of the complex with 6 M $HClO_4$ produced $[(NH_3)_5CoNHC(OH)(CH_2)_2COOH](ClO_4)_3 \cdot H_2O$ (**19**), a yellow salt which was filtered off and washed with copious amounts of ether.

$[(NH_3)_5CoOCO(CH_2)_2CONH_2](ClO_4)_2 \cdot H_2O$ (12). Succinamic acid was prepared by modification of a synthesis of phthalamic acid.[36] Succinic anhydride (40 g, Ajax) was added gradually with stirring to warm concentrated ammonia solution (200 mL). The resulting solution was chilled and acetone added to precipitate ammonium succinamate, which was filtered off and dissolved in minimum water. Succinamic acid was obtained by the addition of concentrated perchloric acid. The white solid (14 g) was washed with ether and air-dried. $[(NH_3)_5CoOH_2](ClO_4)_3$ was prepared from $[(NH_3)_5CoOCO_2]NO_3 \cdot {}^1/_2H_2O$.[37] The title complex was prepared using a standard method for carboxylato complexes,[22] i.e. heating a mixture of $[(NH_3)_5CoOH_2](ClO_4)_3$ (3 g), succinamic acid (5 g), and $NaHCO_3$ (0.5 g) in 50 mL of water overnight at 60 °C. The resulting dark pink solution was diluted to 250 mL with water and chromatographed on Dowex (50WX2; Na^+ form, 200–400 mesh) to separate the complex from unreacted succinamic acid and other impurities. It was eluted with $NaClO_4$ solution (1 M, pH 3). The crude complex was recovered from the eluate by rotary evaporation and was recrystallized from water with concentrated $NaClO_4$ solution and ethanol (yield 0.5 g, 20%).

Spectra. UV–visible spectra were obtained with a Cary 210 spectrophotometer using quartz cells. IR spectra were measured with a Jasco A-100 spectrophotometer in Nujol mulls with NaCl windows. ^1H and ^{13}C NMR spectra were obtained with a Varian XL 300 spectrometer with a probe temperature of 20 °C using Me_2SO-d_6 and D_2O (Aldrich) as solvents.

Kinetic Data. Pseudo-first-order rate constants were obtained by measuring the changes in absorbance over time of solutions of isomers using Cary 210 and 2300 spectrophotometers; each was fitted with a cell block connected to a circulating Lauda bath which maintained the temperature at 25.0 ± 0.1 °C. Reactions were followed over at least 5 half-lives. The oxygen-bonded isomer has a low solubility which necessitated using solutions of low ionic strength (0.10 M). Its reactions in basic solution were followed at 510 nm by dissolving the complex directly in solutions of KOH (0.025–0.10 M) using KF to maintain the ionic strength. F^- mimics the activity of OH^-.[38] Reactions in acid were monitored at 290 nm in the same way using solutions of $HClO_4$ (0.02–0.10 M) and also buffer solutions (pH 2–4) made from succinic, citric, and oxalic acids partially neutralized with LiOH, using $LiClO_4 \cdot 3H_2O$ as the supporting electrolyte. The pH of the buffer solutions was determined as follows: a solution of 0.010 M HCl (ConVol), I = 0.100 M ($LiClO_4$), was titrated under a nitrogen atmosphere with 2.00 M NaOH (ConVol) solution from a Metrohm 655 Dosimat 5-mL buret. The base had been standardized with potassium hydrogen phthalate (BDH). During the titration the potential of the solution was measured continuously with an Orion Ross combination pH electrode and a Metrohm 654 pH meter. The potential of the buffer solutions was measured under the same conditions. A graph of potential versus $p[H^+]$ was used to determine the acidity of each buffer solution. For the base hydrolysis of succinimido-*N*, samples of the isomer were dissolved directly in NaOH solutions (ConVol) of 0.050 – 0.20 M, I = 1.00 M ($NaClO_4$), and the reaction monitored at 310 nm. Rate constants were determined by nonlinear least-squares analysis using the FORTRAN program KINCAL adapted for the Macintosh computer. Rate constant–pH data were fitted to the relevant expressions using weighted nonlinear least-squares analysis by means of the same program.

Product Distribution Data. Products from the reaction(s) of succinimido-*O* in aqueous base (0.4-g samples in 0.05 and 0.1 M KOH, I = 0.10 M (KF)) were analyzed spectrophotometrically after chromatographic separation using a Cary 210 spectrophotometer and a 10-cm quartz cell. Secondary reactions are significant but were minimized by quenching the reaction with 6 M $HClO_4$ at $4t_{1/2}$. The solution was diluted with water and chromatographed onto SP Sephadex C-25 resin (Na^+ form; Pharmacia). We were unable to separate cleanly the succinimido-*N* and succinamato-*O* ions so they were eluted together with 0.25 M NaCl at pH 5 (NaH_2PO_4) and the eluate diluted to 250 mL in a volumetric flask. The concentration of the complexes was determined by measuring the absorbance of the solution at 500, 490, and 480 nm and using the following spectral data: isosbestic point ϵ_{490} 59.0 M^{-1} cm^{-1}; succinamato-*O* ϵ_{480} 53.0, ϵ_{500} 61.0 M^{-1} cm^{-1}; succinimido-*N* ϵ_{480} 61.0, ϵ_{500} 52.5 M^{-1} cm^{-1}. The aqua pentaammine band was eluted separately with 0.75 M NaCl at pH 7 (NaH_2PO_4/Na_2HPO_4) and analyzed similarly, ϵ_{492} 50.5 M^{-1} cm^{-1}.[11]

The other reactions studied, H^+-catalyzed hydrolysis of the succinimide-*O* species, OH^--catalyzed reaction of succinimido-*N*, and the spontaneous isomerization of succinimido-*O* all gave single products and were shown to be irreversible reactions, either by direct monitoring (^1H NMR) or chromatography (after acid quenching for the OH^- reactions) on Sephadex resin as detailed above.

Determination of Acidity Constants. pK_a values for the diprotonated N-bonded complex of succinamic acid were determined by automated spectrophotometric titration of a solution of the complex in 1.0 M HCl with 2.0 M NaOH/1.0 M NaCl (ConVol solutions) using a Varian DMS 300 spectrophotometer, a Metrohm 655 Dosimat instrument fitted with a 20-mL buret, a Metrohm 654 pH meter, and an Orion Ross combination pH electrode. The temperature was maintained at 25 °C with a circulating Lauda bath. Absorbance (300–500 nm) and potential (mV) data were recorded during the titration and stored on the computer. The pH for each spectrophotometric measurement was determined by a potentiometric titration of the acid with the base and construction of a graph of potential versus pH. These data were added to the computer file. The data were processed using the computer program SPECFIT,[39,40]

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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. $[(NH_3)_5CoNCO(CH_2)_2CO](ClO_4)_2$ 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.

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

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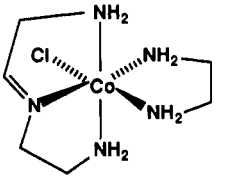
The complex *mer*-[Co(dienim)(en)Cl]$ZnCl_4$ (dienim = $NH_2(CH_2)_2N{=}CHCH_2NH_2$) has been synthesized from NH_2CH_2CHO, $NH_2(CH_2)_2NH_2$, and $Co^{II}Cl_2$ by H_2O_2 oxidation; it is identical to the material isolated by House et al.[1,2] as a side product in the synthesis of *trans*-$[Co(en)_2Cl_2]Cl$. 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(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(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



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

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.

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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