In keeping with the assumption of nonselective photoinduced Co–Co bond homolysis, we assumed the photochemical first-order rate constants k_1–k_3 to be equal, at a value that reproduces the observed pseudo-first-order behavior. Numerical values for k_4 and k_6 were obtained from flash photolysis experiments.[29] The recombination rate constant, k_5, was varied from 1.0×10^8 to 1.0×10^9 M^{-1} s^{-1}. An optimal fit with the observed rate data, as illustrated in Figure 1, was achieved with k_5 equal to 7×10^8 M^{-1} s^{-1}, close to the value derived from eq 19.

It is noteworthy that the approach to a photostationary state is first order in $[Co_2(CO)_8]$ when L = P(*n*-Bu)$_3$. This behavior results from the strong internal filter effect created by the presence of $Co_2(CO)_7L$ and $Co_2(CO)_6L_2$ in addition to $Co_2(CO)_8$.[32,33]

Except for the case of L = P(*t*-Bu)$_3$ the thermal reactions of $Co_2(CO)_8$ and $Co_2(CO)_6L_2$ are extremely slow. No attempt was made to study the kinetics of the thermal reactions in detail. It is tempting to suggest that the thermal reaction proceeds via a mechanism analogous to Scheme I with steps 2–4 proceeding by thermal bond homolysis. The equilibration in such a case is rate limited by the slower rate of metal–metal bond rupture in $Co_2(CO)_8$ and $Co_2(CO)_6L_2$. Certain thermal reactions involving dinuclear cobalt carbonyl compounds have been postulated to occur via Co–Co bond homolysis.[34,35] The slow rates of thermal equilibration for L other than P(*t*-Bu)$_3$ are not inconsistent with what is known of this process in $Co_2(CO)_8$ and the $Co_2(CO)_6L_2$ compound involved. However, the very rapid rate of equilibration of $Co_2(CO)_8$ with $Co_2(CO)_6[P(t\text{-}Bu)_3]_2$ is inconsistent with this mechanism. Co–Co bond rupture in $Co_2(CO)_6[P(t\text{-}Bu)_3]_2$ is likely to be comparatively rapid as a result of steric strain created by the phosphine ligands.[36] In that event, Co–Co bond rupture in $Co_2(CO)_8$ would be rate determining. However, equilibration occurs at a rate much faster than the estimated rate of metal–metal bond homolysis in $Co_2(CO)_8$.[37]

A process involving rate-determining loss of L from $Co_2(CO)_6L_2$, eq 21–23, can also be ruled out. The kinetics of the

$$Co_2(CO)_6L_2 \rightarrow Co_2(CO)_6L + L \qquad (21)$$

$$Co_2(CO)_8 + L \rightarrow Co_2(CO)_7L + CO \qquad (22)$$

$$Co_2(CO)_6L + CO \rightarrow Co_2(CO)_7L \qquad (23)$$

reaction of $Co_2(CO)_8$ with P(*t*-Bu)$_3$ have recently been studied.[38] The results show that the reaction is too slow to account for the present results. Our observations can be accommodated by a postulated rapid electron-transfer process, as shown in eq 24–27. The slow process in this mechanism could be either

$$Co_2(CO)_6L_2 \rightleftharpoons 2Co(CO)_3L\cdot \qquad (24)$$

$$Co(CO)_3L\cdot + Co_2(CO)_8 \rightarrow Co_2(CO)_8^{-}\cdot + Co(CO)_3L^+ \qquad (25)$$

$$Co_2(CO)_8^{-}\cdot \rightarrow Co(CO)_4\cdot + Co(CO)_4^- \qquad (26)$$

$$Co(CO)_4^- + Co(CO)_3L^+ \rightarrow Co_2(CO)_7L \qquad (27)$$

step 24 or step 25. There is precedent for an electron-transfer process such as 25 in the reactions of $Co_2(CO)_8$ with phosphines.[37,38] Steps 26 and 27 would be expected to be rapid.[39]

Registry No. $Co_2(CO)_8$, 10210-68-1; $Co_2(CO)_6(P(n\text{-}Bu)_3)_2$, 14911-28-5; $Co_2(CO)_6(P(t\text{-}Bu)_3)_2$, 70623-28-8; $Co_2(CO)_6(P(OPh)_3)_2$, 21118-36-5; $Co_2(CO)_6(PPh_3)_2$, 1010-27-1; $Co_2(CO)_6(P(CH_3)_2Ph)_2$, 21407-17-0; $Co_2(CO)_6(P(CH_3)Ph_2)_2$, 31224-11-0; $Co_2(CO)_7(P(n\text{-}Bu)_3)$, 19298-62-5; $Co_2(CO)_7(P(CH_3)_2Ph)$, 83746-88-7; $Co_2(CO)_7(P(OPh)_3)$, 19298-61-4.

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Imine Formation and Stability and Interligand Condensation with Cobalt(III) 1,2-Ethanediamine Complexes

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The isolation of imine complexes formed by the condensation of acetaldehyde with Co(III) 1,2-ethanediamine complexes is described. In one instance two such acetaldimine moieties condense relatively stereospecifically. The X-ray crystal structures of this product and another acetaldimine product derived from the Λ-$[Co(en)_2((S)\text{-}Tyr)]^{2+}$ ion are also described. The results indicate something of the reactivity and stability of such coordinated imines and have implications for the manner in which macrocyclic ligands are formed on metal ions.

Introduction

The reactions that occur between carbonyl compounds and amines or amine derivatives in the presence of metal ions have been widely exploited and form the basis of many quite extensive studies in inorganic chemistry.[1,2] One of the simplest reactions of this kind is the so-called "Curtis reaction" between acetone and nickel(II) ethylenediamine complexes, the ultimate products being the very well-known macrocyclic diimine ligand complexes **1** and **2**. Several intermediates, including isopropylidene amine ligand complexes such as **3**, have been

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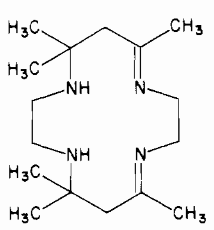

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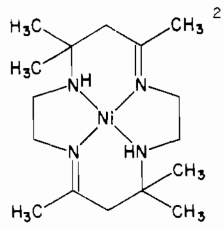

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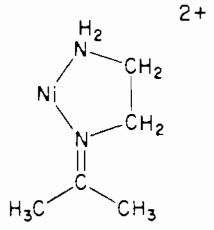

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identified in these reactions, and a plausible mechanism has been advanced for their occurrence.[1] An unambiguous demonstration that the widely-accepted "template" mechanism of intramolecular reaction between coordinated ligands[2] does apply is, however, not readily produced for labile metal ion systems. With inert metal ion complexes, one possible step in a template process, intramolecular condensation between coordinated-ligand amine and carbonyl functional groups, has been observed to occur with facility,[3–5] but other possible steps in a template reaction remain to be characterized in this way. Even the reactivity of a coordinated simple imine can only be inferred from the study of relatively complex systems.[5–7]

Similarly, although reactions between amino acid complexes and carbonyl compounds have been frequently studied[8–16] and synthetically exploited,[17–19] in only a few instances[13,20,21] has evidence relating directly to the species involved in the reactions been obtained. Because the reactions would appear to have a greater synthetic utility than has currently been realized, a more detailed understanding of their mechanisms would seem desirable. In principle, considerable detail should be obtained from the study of inert metal complexes for which it is certain that donor atoms remain attached to the metal ions throughout a reaction sequence. The readily prepared amino acid complexes $[Co(en)_2aa]^{2+}$ are suitable in this regard. Since they contain both amine and amino acid (aa) ligands, reactions with carbonyl compounds could occur at centers of different kinds, so that observed product distributions should give valuable information on relative reactivity.

As part of a general program of investigation of the formation and reactions of coordinated imines and of reactions of coordinated ligands with carbonyl compounds,[3,4,5,21,22] the synthesis and characterization of some products of the reactions between $[Co(en)_2((S)\text{-Tyr})]^{2+}$ and $[Co(en)_2ox]^+$ ((*S*)-Tyr = (*S*)-tyrosinato; ox = oxalato) and acetaldehyde in basic solutions are reported. The given reactant complexes merely represent species for which the particular products are readily isolated, and these products are regarded as typical of the materials that may be formed from related complexes.

Results

$[Co(en)_2((S)\text{-Tyr})]^{2+}$ + CH_3CHO at pH 10–12.5. The reaction between the diastereoisomeric mixture of Δ- and Λ-$[Co(en)_2((S)\text{-Tyr})]^{2+}$ ions and acetaldehyde (pH 10–12.5, CO_3^- buffer) was investigated to see if the aldehyde condensed at the amino acid or at the ethylenediamine amino groups. The reactions were carried out over the range 0–20 °C for reaction times varying between 20 min and 7 h. All of the complex appeared to react within 1 h. The products were separated with use of ion-exchange chromatography and between five and nine bands were observed over all the conditions examined. The results indicated that the products for pH 10.5 and 20 °C were similar to those formed at pH 12.5 and 0 °C, although with a different distribution. The latter reaction conditions yielded five bands after 30 min of reaction time. The first two products were isolated as perchlorate salts and assigned structures, but the remaining products were not crystallized. ^1H NMR spectra of these products indicated they were isomeric mixtures.

The first isolated product (3%) was analyzed for two molecules of acetaldehyde condensed, and the ^1H NMR spectra (analyzed below) indicated that the imines were condensed on the ethylenediamine ligands, rather than at the amino acid amino group. The second product (35%) was analyzed for one molecule of acetaldehyde condensed, and the ^1H NMR spectrum also indicated that this had occurred with the formation of a stable imine on the ethylenediamine chelate. Both compounds were stable over hours in 3 M DCl at 25 °C.

The ^1H NMR data and assignments for spectra in D_2O relative to external tetramethylsilane are summarized (all resonances in ppm). *Diimine*: CH_3, 2 doublets centered about 2.15 and 2.3 (J = 6 Hz); $-C\mathit{H}_2-NH_2$, ~2.6; $CH_2-N=$, 3.6; $C\mathit{H}_2-CH$, 3.1 (2 doublets); $C\mathit{H}-CH_2$, 4.0 (triplet); CH=N, 7.5 (broad); aromatic H, ~7 (quartet); tyrosine NH_2, 6.0; en NH_2 5.7 and 4.8 (two broad resonances of equal integrated value). Monoimine: CH_3, *doublet* centered about 2.0 (J = 6 Hz); $C\mathit{H}_2-NH_2$, ~2.6; $C\mathit{H}_2-N$, 3.6; $C\mathit{H}_2-CH$, 3.1 (2 *doublets*); $C\mathit{H}-CH_2$, 4.0 (triplet);, CH=N, 7.3 (broad); aromatic H, 7.0–7.3 (quartet); tyrosine NH_2, 6.0; en NH_2, ~4.5–5.5. The integration of the various signals was in agreement with these assignments. The -CH=N and aromatic proton signals in D_2O overlapped for the diimine and monoimine complexes, but both sets of signals were observed separately with dimethyl-d_6 sulfoxide as solvent. The integrated signals were also consistent with two and one imine protons, respectively.

Crystal Structure of Λ-[((*S*)-Tyrosinato)(2-acetaldimino-1-ethanamine)(1,2-ethanediamine)cobalt(III)] Diperchlorate

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Table I. Final Atomic Coordinates ($\times 10^4$) with Estimated Standard Deviations for Λ-[((*S*)-Tyrosinato)(2-acetaldimino-1-ethanamine)(1,2-ethanediamine)cobalt(III)] Diperchlorate Dihydrate

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Co	8087 (1)	6250	1785 (1)	C(10)	9273 (3)	6123 (9)	1071 (5)
O(1)	7696 (2)	7651 (4)	839 (3)	C(11)	9304 (3)	7401 (7)	1635 (6)
N(1)	7270 (2)	5325 (5)	975 (4)	C(12)	8256 (5)	4883 (10)	3815 (8)
N(2)	8559 (2)	5727 (5)	666 (4)	C(13)	7744 (6)	5757 (8)	3825 (6)
N(3)	8883 (2)	7306 (5)	2468 (4)	C(14)	7440 (3)	7820 (6)	3078 (5)
N(4)	8435 (2)	4778 (5)	2740 (4)	C(15)	7187 (4)	8260 (8)	4057 (5)
N(5)	7693 (2)	6737 (5)	2973 (3)	Cl(1)	1554 (1)	6968 (2)	2229 (1)
C(1)	7166 (3)	7401 (5)	33 (4)	O(11)	1690 (7)	7068 (22)	3274 (7)
C(2)	6909 (3)	6036 (6)	−50 (4)	O(12)	1840 (6)	7784 (11)	1711 (16)
O(2)	6881 (2)	8207 (4)	−662 (3)	O(13)	1849 (6)	5821 (9)	1893 (8)
C(3)	6123 (3)	5970 (6)	−258 (5)	O(14)	901 (4)	7047 (14)	1645 (10)
C(4)	5900 (2)	6437 (6)	734 (5)	Cl(2)	3791 (1)	5772 (2)	3727 (2)
C(5)	5760 (3)	5600 (7)	1509 (7)	O(21)	3544 (6)	5047 (9)	2786 (6)
C(6)	5568 (4)	5994 (9)	2415 (7)	O(22)	3701 (12)	6977 (11)	3453 (16)
C(7)	5524 (4)	7273 (9)	2618 (7)	O(23)	3541 (6)	5367 (15)	4625 (7)
O(3)	5380 (4)	7723 (9)	3579 (6)	O(24)	4438 (6)	5655 (27)	4113 (14)
C(8)	5661 (3)	8137 (7)	1892 (7)	$O_w(1)$	9939 (3)	5216 (8)	3812 (5)
C(9)	5831 (3)	7734 (7)	947 (6)	$O_w(2)$	650 (7)	7708 (11)	4706 (9)

Dihydrate. Collection and Reduction of X-ray Data. A single crystal of the monoimine product, isolated as the hydrated perchlorate salt, was mounted on a quartz fiber and coated with an epoxy cement. An initial X-ray photographic examination established the crystal class with the systematic absences, limiting the choice of space groups to centric C_2/m and noncentric C_2 and Cm. The anticipated presence of the chiral (*S*)-(−)-tyrosine moiety in the molecular structure, together with the requirement of only four molecules in the unit cell, strongly suggested the correct space group to be C_2 (C_2^3, No. 5). This choice was later confirmed from the noncentrosymmetric distribution of *E* values for (*hkl*) reflections and a centrosymmetric distribution for (*h0l*) reflections. Reflection intensity data were measured on a Picker FACS-I diffractometer by $\theta/2\theta$ moving-crystal/counter technique. The method of data collection and reduction to observed structure factors has been presented in detail elsewhere,[23] and only details relevant to this structure determination are summarized below.

Crystal Data: $C_{15}H_{28}Cl_2CoN_5O_{11}\cdot 2H_2O$; $M_r = 620.3$; monoclinic; $a = 20.591$ (2), $b = 10.461$ (1), $c = 12.263$ (1) Å; $\beta = 106.21$ (1)°; $V = 2536.5$ Å^3; $d_{obsd} = 1.61$, $d_{calcd} = 1.63$ g cm^{-3}; $Z = 4$; space group C_2 (C_2^3, No. 5); $\mu = 11.5$ cm^{-1}; transmission factors 0.843–0.912.

Data Collection: Mo Kα radiation; $\lambda = 0.7107$ Å; graphite-crystal monochromator; $2\theta_m = 12.0°$; takeoff angle 3.0°; data collected at 2θ speed of 2° min^{-1} over 2θ scan range 3 60° for ($\pm h,-k,l$), 3–35° for (hkl), and 3–35° for ($\pm h,-k,-l$); individual 2θ scan width ($1.80 + 0.692 \tan \theta$)°; total background count time 20 s; standard reflection intensities remeasured every 100 reflections with no significant variation; number of data collected 5216, number of unique data (C_2 space group) with $I \leq 3\sigma(I)$ 3449; $\rho = 0.040$ (the constant ρ is used in the calculation of $\sigma(F_0)$); $R_s = 0.024$.

Solution and Refinement of the Structure. The structure was solved by direct methods (MULTAN 74). Examination of the *E* map calculated by using the phasing set with the lowest ψ_0 index readily revealed the position of the cobalt atom, but it had two superimposed and mirror-related coordination octahedra. One enantiomer was arbitrarily chosen and used to phase a difference Fourier synthesis from which the remainder of the structure was apparent. The atomic positional and thermal parameters were subjected to full-matrix least-squares refinement with reflection data weighted according to $[\sigma(F_0)]^{-2}$. Methylene and methyne hydrogen atoms were added to the scattering model at a fixed C–H distance of 0.95 Å. Refinement converged at $R = 0.051$ and $R_w = 0.063$ with no parameter shift/esd being greater than 0.10. Residual electron density in the final difference Fourier was in the range 1.5 to −1.4 e/Å^3 with the major peaks and troughs being located in close proximity to the cobalt atom. The choice of absolute configuration was confirmed both from refinement of the other enantiomer ($R = 0.062$) and from the chirality of the (*S*)-(−)-tyrosine species used for the synthesis. The structure is depicted in Figure 1.

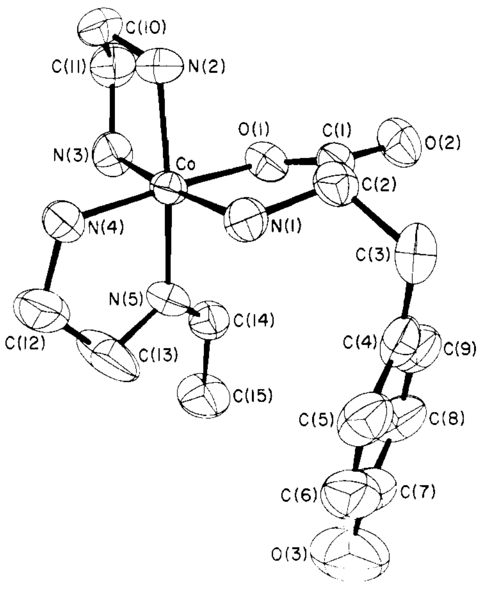

Figure 1. Molecular structure of the cation in Λ-[((*S*)-tyrosinato)(2-acetaldimino-1-ethanamine)(1,2-ethanediamine)cobalt(III)] diperchlorate dihydrate.

Atomic scattering factors[24] were corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[25] All calculations were performed on the Univac-1108 computer of the Australian National University using the ANUCRYS (1975) suite of crystallographic programs. The final atomic positional parameters are given in Table I. Atomic thermal parameters, calculated hydrogen atom positions, and structure factors are available as supplementary material. Bond lengths and principal interbond angles are presented in Tables II and III, respectively.

$[Co(en)_2(C_2O_4)]^+$ + CH_3CHO at pH 10. The reaction between the racemic bis(ethylenediamine)oxalatocobalt(III) ion and acetaldehyde (pH 10.0, CO_3^{2-}, HCO_3^-, buffer, 25 °C) was

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Table II. Interatomic Bond Lengths (Å) for Λ-[((*S*)-Tyrosinato)(2-acetaldimino-1-ethanamine)-(1,2-ethanediamine)cobalt(III)] Diperchlorate Dihydrate

Co–N(1)	1.955 (4)	C(5)–C(6)	1.345 (13)
Co–O(1)	1.903 (4)	C(6)–C(7)	1.368 (13)
Co–N(2)	1.968 (6)	C(7)–C(8)	1.353 (13)
Co–N(3)	1.959 (5)	C(7)–O(3)	1.376 (12)
Co–N(4)	1.946 (5)	C(8)–C(9)	1.368 (12)
Co–N(5)	1.924 (5)	N(2)–C(10)	1.473 (8)
C(1)–O(1)	1.278 (6)	N(3)–C(11)	1.516 (9)
C(2)–N(1)	1.472 (7)	C(10)–C(11)	1.499 (11)
C(1)–O(2)	1.227 (6)	N(4)–C(12)	1.468 (12)
C(1)–C(2)	1.516 (8)	C(12)–C(13)	1.398 (15)
C(2)–C(3)	1.568 (8)	C(13)–N(5)	1.447 (9)
C(3)–C(4)	1.498 (10)	N(5)–C(14)	1.267 (8)
C(4)–C(5)	1.380 (11)	C(14)–C(15)	1.509 (10)
C(4)–C(9)	1.396 (9)		
Cl(1)–O(11)	1.238 (9)	Cl(2)–O(21)	1.365 (8)
Cl(1)–O(12)	1.299 (16)	Cl(2)–O(22)	1.305 (12)
Cl(1)–O(13)	1.337 (8)	Cl(2)–O(23)	1.405 (12)
Cl(1)–O(14)	1.455 (11)	Cl(2)–O(24)	1.288 (11)

Table III. Principal Interbond Angles (deg) for Λ-[((*S*)-Tyrosinato)(2-acetaldimino-1-ethanamine)-(1,2-ethanediamine)cobalt(III)] Diperchlorate Dihydrate

O(1)–Co–N(1)	85.0 (2)	C(2)–C(3)–C(4)	113.0 (4)
N(2)–Co–N(3)	86.5 (2)	C(3)–C(4)–C(5)	121.5 (6)
N(4)–Co–N(5)	85.2 (2)	C(3)–C(4)–C(9)	122.6 (6)
O(1)–Co–N(4)	176.7 (2)	C(5)–C(4)–C(9)	115.9 (7)
N(1)–Co–N(3)	174.0 (2)	C(4)–C(5)–C(6)	122.7 (7)
N(2)–Co–N(5)	175.4 (2)	C(5)–C(6)–C(7)	120.0 (8)
O(1)–Co–N(2)	89.8 (2)	C(6)–C(7)–C(8)	119.9 (8)
O(1)–Co–N(3)	89.3 (2)	C(7)–C(8)–C(9)	120.1 (7)
O(1)–Co–N(5)	93.5 (2)	C(8)–C(9)–C(4)	121.4 (7)
N(1)–Co–N(2)	91.7 (2)	C(6)–C(7)–O(3)	122.1 (9)
N(1)–Co–N(4)	91.9 (2)	C(8)–C(7)–O(3)	118.0 (9)
N(1)–Co–N(5)	91.8 (2)	Co–N(2)–C(10)	109.1 (4)
N(2)–Co–N(4)	91.7 (2)	Co–N(3)–C(11)	108.4 (4)
N(3)–Co–N(4)	93.8 (2)	N(2)–C(10)–C(11)	108.4 (6)
N(3)–Co–N(5)	90.4 (2)	N(3)–C(11)–C(10)	107.1 (6)
Co–O(1)–C(1)	116.0 (3)	Co–N(4)–C(12)	109.8 (5)
Co–N(1)–C(2)	110.0 (4)	N(4)–C(12)–C(13)	115.8 (7)
O(1)–C(1)–C(2)	116.9 (4)	C(12)–C(13)–N(5)	111.1 (9)
O(1)–C(1)–O(2)	122.5 (5)	Co–N(5)–C(13)	113.4 (5)
O(2)–C(1)–C(2)	120.6 (4)	Co–N(5)–C(14)	125.8 (4)
N(1)–C(2)–C(1)	109.6 (4)	C(13)–N(5)–C(14)	120.6 (6)
N(1)–C(2)–C(3)	111.7 (5)	N(5)–C(14)–C(15)	126.6 (6)
C(1)–C(2)–C(3)	112.2 (5)		
O(11)–Co(1)–O(12)	116.6 (12)	O(21)–Cl(2)–O(22)	109.2 (9)
O(11)–Cl(1)–O(13)	111.8 (11)	O(21)–Cl(2)–O(23)	111.5 (7)
O(11)–Cl(1)–O(14)	116.9 (9)	O(21)–Cl(2)–O(24)	111.4 (11)
O(12)–Cl(1)–O(13)	97.0 (8)	O(22)–Cl(2)–O(23)	115.8 (13)
O(12)–Cl(1)–O(14)	102.8 (8)	O(22)–Cl(2)–O(24)	104.1 (16)
O(13)–Cl(1)–O(14)	109.6 (7)	O(23)–Cl(2)–O(24)	104.5 (10)

investigated to explore further the formation of stable imines and the prospects of intramolecular self-condensation between two such imines. This choice of cation reduced the number of potential isomers compared with that for the tyrosine complex, thereby simplifying the study. Experiments over 2 and 30–40 h of reaction time were carried out. For the experiment with 2 h of reaction time essentially only one product was formed. This was isolated as its chloride after purification by cation-exchange chromatography. The product was analyzed for 1 mol of acetaldehyde condensed. The ^{1}H NMR spectrum of this complex shows a methyl doublet resonance (2.6 ppm $J = 6$ Hz), which is ascribed to a methyl group split by an imine proton attached to carbon. It appears that only one of the four possible imine isomers is produced. Also the spectrum shows a resonance for one imine proton attached to carbon (8.05 ppm, broad). Complex signals around 3.0 and 4.0 ppm are ascribed to the ethylenediamine carbon protons. The latter signal is attributed to $-CH_2-$ adjacent to the imine group. All integrations are in agreement with these assignments. The complex is stable in 3 M DCl for hours at 25 °C.

For the 30–40-h reaction the ^{1}H NMR spectrum of the crude product mixture indicated that a substantial part of the initially formed monoimine had condensed with another mole of acetaldehyde, and the new product was isolated pure as its hexafluorophosphate salt. The salt analyzed for 2 mol of acetaldehyde condensed, and this result is supported by the ^{1}H NMR spectrum, which also indicates the self-condensation of the two acetaldehyde entities in a stereospecific manner.

The ^{1}H NMR spectra showed a high-field methyl doublet resonance (δ 1.37, $J = 6$ Hz), ascribed to a methyl group split by a proton attached to a saturated carbon atom. Also the spectrum indicated an imine proton attached to carbon (δ 7.9). Complex signals (at δ 2.6, 2.8, 3.2) were ascribed to the ethylenediamine carbon protons and a methylene group, respectively. All integrations were in agreement with these assignments.

The same synthesis was conducted with chiral $[Co(en)_2ox]^+$ to give the same enal product (enal = 2-acetaldimino-1-ethanamine) identified by its ^{1}H NMR spectrum primarily. Unfortunately, we were not able to crystallize the chiral enal product, but its spectroscopic properties were established along with the chiral nature of the product.

Crystal Structure of the Condensation Product between $[Co(en)_2ox]^+$ + $2CH_3CHO$: $[Co^{III}(enal)ox](PF_6)_2 \cdot 2H_2O$. Crystal Data. Suitable crystals of the reaction product of $[Co(en)_2ox]^+$ with 2 mol of acetaldehyde as the PF_6 salt, $[Co(enal)ox]PF_6 \cdot 2H_2O$, were obtained by evaporation from water over silica gel. Preliminary precession photographs showed them to be monoclinic with space group $P2_1/c$. A hexagonal block with dimensions 0.36 × 0.36 × 0.38 mm was mounted about b on a glass fiber and smeared with epoxy resin. The cell constants at 21 °C were obtained from axial reflections by ω ($h00$, $00l$) and μ ($0k0$) scans on a Stoe-Weissenberg diffractometer using Mo Kα radiation and a graphite monochromator. The crystal data for $[Co(enal)ox]PF_6 \cdot 2H_2O$ are as follows: $C_{10}H_{24}CoF_6N_4O_6P$; $M_r = 500.1$; $Z = 4$; $d_{obsd} = 1.76$ (2), $d_{calcd} = 1.729$ g cm^{-3}; μ(Mo Kα) = 10.00 cm^{-1}; $F(000)$ 1072 e; space group $P2_1/c$; $a = 12.731$ (7), $b = 12.00$ (1), $c = 14.928$ (8) Å; $\beta = 122.6$ (1)°; $V = 1921.3$ Å^3; $\lambda = 0.7107$ Å. Intensity data were collected for the levels $h0l$ to $h9l$ in the range $0 < 2\theta < 55°$ with use of the ω-scan technique. Lorentz, polarization, and absorption corrections were applied to give 2314 nonzero structure factors with $I > 2.5\sigma(I)$. The maximum and minimum transmission factors were 0.83 and 0.69.

Solution and Refinement of the Structure.[26] The structure was solved by the heavy-atom method and refined with use of block-matrix least-squares techniques. The PF_6^- group is well-ordered, but a small additional peak, refined as F(7) with an occupancy of 0.17, appeared 1.65 (3) Å from the phosphorus. The water hydrogens of only one of the water molecules could be found. The remaining hydrogen atoms were included in calculated positions and were made to ride in subsequent cycles of refinement on the atoms to which they were attached (C–H = 0.99, N–H = 0.91 Å).[27] The final refinement sequence was organized in blocks, which ensured that all refined parameters were able to interact. The individual scale factors were adjusted in the isotropic phase of the refinement, which also employed unit weights. The weighting scheme was later refined and converged at $w = 1.8351/(\sigma^2(F) + 0.000608F^2)$. The final error in an observation of unit weight was 1.55. R was 0.0538 on F for 2314 nonzero reflections. The largest residuals in the final difference map, 0.5–0.3 e/Å^3, are in the vicinity of the anion. All scattering

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(26) Programs used included local data reduction (AUPTP), structure solution and refinement (SHELX) by G. M. Sheldrick), and thermal ellipsoid plots (ORTEP by G. K. Johnson).

(27) Geue, R. J.; Snow, M. R. *Inorg. Chem.* **1977**, *16*, 231.

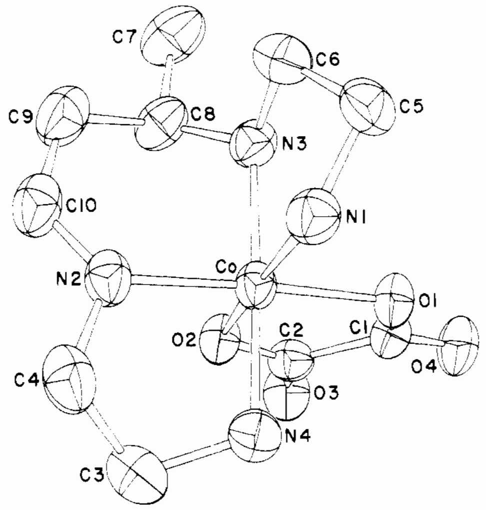

Figure 2. Molecular structure of the cation in [Co(enal)ox]$PF_6 \cdot 2H_2O$ (ellipsoids enclose 50% probability, and hydrogens have been omitted for clarity).

Table IV. Final Atomic Coordinates (×10^4) with Estimated Standard Deviations for [Co^{III}(enal)(ox)]$PF_6 \cdot 2H_2O$

atom	*x*	*y*	*z*
Co	1175 (1)	1866 (1)	1874 (0)
P	6674 (1)	1808 (2)	1526 (1)
F(1)	5450 (4)	2529 (4)	1076 (4)
F(2)	2484 (5)	−2135 (4)	2967 (5)
F(3)	6626 (5)	2079 (6)	485 (4)
F(4)	5823 (5)	773 (4)	1032 (4)
F(5)	6675 (5)	1690 (6)	2576 (4)
F(6)	7925 (5)	1174 (5)	1950 (6)
F(7)	7277 (33)	807 (29)	2424 (27)
O(1)	1285 (3)	1497 (3)	3175 (2)
O(2)	361 (3)	455 (3)	1372 (2)
O(3)	−337 (3)	−934 (3)	1906 (3)
O(4)	804 (4)	97 (3)	3877 (3)
O(5)	2630 (5)	4480 (5)	1015 (4)
O(6)	3712 (5)	−92 (4)	4491 (5)
N(1)	2055 (3)	3252 (3)	2509 (3)
N(2)	967 (4)	2219 (3)	543 (3)
N(3)	2845 (3)	1232 (3)	2435 (3)
N(4)	−465 (3)	2534 (3)	1282 (3)
C(1)	808 (4)	543 (4)	3139 (3)
C(2)	206 (4)	−56 (4)	2046 (4)
C(3)	−1112 (5)	2546 (5)	106 (4)
C(4)	−145 (5)	2928 (5)	−119 (4)
C(5)	3339 (5)	2977 (5)	3383 (4)
C(6)	3798 (5)	2116 (5)	2931 (4)
C(7)	4139 (6)	−138 (5)	2170 (6)
C(8)	2925 (5)	502 (5)	1651 (4)
C(9)	2729 (6)	1192 (5)	707 (5)
C(10)	1626 (5)	1939 (5)	163 (4)

factors (Co for Co^+) were taken from ref 28. A thermal ellipsoid plot of the cation is shown in Figure 2, and Tables V and VI contain the molecular geometry. The final atomic parameters are given in Table IV.

Table V. Interatomic Distances (Å) for [Co(enal)ox]$PF_6 \cdot 2H_2O$[a]

Co–O(1)	1.922 (4)	C(9)–C(10)	1.485 (8)
Co–O(2)	1.915 (3)	P–F(1)	1.580 (5)
Co–N(1)	1.944 (4)	P–F(2)^{IV}	1.568 (6)
Co–N(2)	1.905 (5)	P–F(3)	1.556 (7)
Co–N(3)	1.969 (4)	P–F(4)	1.549 (5)
Co–N(4)	1.948 (4)	P–F(5)	1.573 (7)
C(1)–C(2)	1.555 (7)	P–F(6)	1.559 (6)
C(1)–O(1)	1.284 (6)	P–F(7)	1.649 (34)
C(1)–O(4)	1.228 (7)	N(1)···O(5)	3.073
C(2)–O(2)	1.281 (7)	N(2)···O(5)	3.276
C(2)–O(3)	1.215 (6)	F(5)···O(5)^{I}	3.200
N(1)–C(5)	1.479 (5)	F(7)···O(5)^{I}	2.773
N(2)–C(4)	1.482 (6)	O(4)···O(5)^{II}	2.802
N(2)–C(10)	1.285 (9)	O(6)···O(5)^{II}	3.315
N(3)–C(6)	1.476 (6)	F(2)···O(6)	3.130
N(3)–C(8)	1.508 (8)	O(1)···O(6)	3.241
N(4)–C(3)	1.483 (7)	O(4)···O(6)	3.308
C(3)–C(4)	1.512 (10)	N(3)···O(6)	3.084
C(5)–C(6)	1.512 (9)	C(1)···O(6)	3.206
C(7)–C(8)	1.514 (9)	O(6)···O(6)^{III}	2.783
C(8)–C(9)	1.535 (10)		

[a] Symmetry is indicated by the following superscripts: I, $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; II, x, $-\frac{1}{2}-y$, $\frac{1}{2}-z$; III, $1-x$, $1-y$, $1-z$; IV, $1-x$, $1-y$, $\frac{1}{2}-z$.

Table VI. Bond Angles (deg) of the [Co(enal)ox]$^+$ Cation

O(1)–Co–O(2)	85.5 (2)	C(4)–N(2)–C(10)	118.1 (5)
N(4)–Co–N(2)	85.6 (2)	Co–N(3)–C(6)	110.0 (3)
N(2)–Co–N(3)	92.4 (2)	Co–N(3)–C(8)	113.8 (3)
N(3)–Co–N(1)	85.2 (2)	C(6)–N(3)–C(8)	115.2 (5)
C(1)–O(1)–Co	112.8 (3)	Co–N(4)–C(3)	108.5 (4)
C(2)–O(2)–Co	113.3 (3)	C(4)–C(3)–N(4)	105.5 (4)
O(1)–C(1)–O(4)	125.6 (4)	C(3)–C(4)–N(2)	106.1 (5)
O(3)–C(2)–O(2)	126.4 (5)	C(6)–C(5)–N(1)	105.5 (4)
C(1)–C(2)–O(2)	114.0 (4)	C(5)–C(6)–N(3)	107.7 (5)
C(1)–C(2)–O(3)	119.6 (5)	C(7)–C(8)–N(3)	112.1 (4)
C(2)–C(1)–O(1)	114.2 (5)	C(9)–C(8)–N(3)	110.7 (5)
C(2)–C(1)–O(4)	120.2 (4)	C(9)–C(8)–C(7)	111.1 (7)
Co–N(1)–C(5)	108.2 (3)	C(10)–C(9)–C(8)	117.8 (7)
Co–N(2)–C(4)	111.7 (4)	C(9)–C(10)–N(2)	124.5 (6)
Co–N(2)–C(10)	130.2 (3)		

The structure confirms the stereospecificity at the enal chiral center arising from the internal condensation of the imine functions discussed above. Nitrogen 2 retains the imine character as expected and has a Co–N(2) bond length in the range reported for Co to amide (1.917 (4) Å[29]) and Co to amidine (1.90 (1) and 1.88 (1) Å[30]). The atoms Co, N(2), C(4), and C(10) are coplanar; their angles at N(2) add to exactly 360.0°. The geometry of the oxalate and ethylenediamine ring sections are not unusual, but the six-membered ring is strained. The angles at N(2), C(10), and C(9) in this ring are at least 5° in excess of normal values. The water molecules are involved in hydrogen bonding between themselves, the PF_6 anion, and the oxygens and nitrogens of the cation (see Table IV). Both water molecules have six contacts at distances compatible with hydrogen bonding. In the case of O(6) the hydrogens are most probably disordered over several sites. For O(5) the hydrogens are hydrogen bonded to O(4), an oxalate exo-oxygen, and the minor fluoride site, F(7).

Discussion

The condensation of the coordinated amino groups with the aldehyde is believed to proceed through the deprotonated amine attacking the carbonyl groups to give the carbinolamine which then eliminates water to give the imine[3,31] (**4**–**7**). Separate studies[31] have shown that in this type of compound both the addition (**5**–**6**) and elimination (**6**–**7**) paths are catalyzed by OH^- and that N proton exchange is a preequilibrium step.

At least 35% of the initial reaction of the parent tyrosinato complex proceeds through this path since the crystallographic analysis establishes the structure of the product as **7** with a short C(14)–N(5) imine bond of 1.267 (8) Å attached to the octahedral Co center. It is also likely that the product con-

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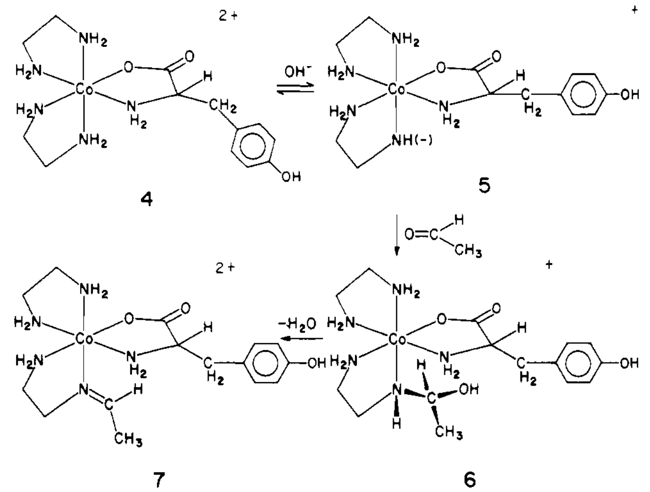
(28) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99, 149.

(29) Petri, W.; Snow, M. R.; Sargeson, A. M., to be submitted for publication.

(30) Springborg, J.; Geue, R. J.; Sargeson, A. M.; Taylor, D.; Snow, M. R. *J. Chem. Soc., Chem. Commun.* **1978**, 647.

(31) Gainsford, A. R.; Pizer, R. D.; Sargeson, A. M.; Whimp, P. O. *J. Am. Chem. Soc.* **1981**, *103*, 792.



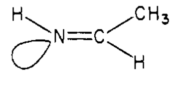
4 5 7 6

taining two acetaldehyde molecules condensed has the imines formed trans to each other following the addition of a second aldehyde to **7** since its NMR spectrum and that of **7** are closely related.

The remaining products, which were not characterized and which were formed in lesser amounts, presumably involve condensation at the other NH_2 positions, four in all excluding the Δ and Λ configurations of the chelates about the Co(III) ion. It is not obvious why condensation at the position shown in isomer **7** is preferred over the other sites for condensation. There appears to be no special steric reason for the preference, and in fact some preference might have been expected for condensation at the tyrosine amino group since this site could be expected to be more acidic than those on ethylenediamine.[32] At the same time the reduced basicity could lead to a reduced stability of the carbinolamine or imine formed. Similarly condensation at the amine center trans to that observed would seem equally likely, and presumably it occurs for the diimine complex. Some of the other fractions are not yet identified, but they clearly form in lesser amounts (see Experimental Section).

The other source of isomerism is the cis/trans relationship of the substituents on the imine relative to Co. The structure shows that the fraction (35%) of monoimine isolated contains the orientation with the methyl group trans to cobalt, and this specificity needs to be accounted for. The addition of the coordinated amide ion to the carbonyl center of acetaldehyde generates two new chiral centers at the N and C, respectively, and the Newman projections of the possible rotamers are depicted in Figure 3. Rotamers a and e appear to be the most stabilized in terms of minimum interaction with the groups on the chiral N center and the remaining chelate atoms. Of these rotamer a should be stabilized relative to rotamer e since the CH_3 group interacts minimally, and the hydroxyl group may hydrogen bond to the adjacent oxygen of the tyrosine. This configuration is relevant now to the elimination reaction, which can be accepted as being OH^- catalyzed.[31] The obvious role for the base is to remove a proton from the carbinolamine amino group, which allows OH^- to depart from the negative moiety and leave the neutral imine. The process essentially involves a cis elimination of H_2O to produce the observed configuration of the imine. The same mechanism allows isomerization of the imine by addition and elimination of H_2O, which is needed for some of the condensations which follow.

A remarkable feature of the coordinated imine is its stability toward acids. Normally imines **8** hydrolyze readily in such media presumably via the formation of the iminium salt **9**.



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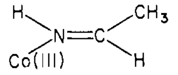

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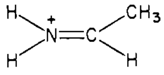

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This assists attack of a nucleophile such as water at the imine carbon atom and hydrolysis of the resulting protonated carbinolamine. The unprotonated imine is, therefore, relatively much more stable to attack from nucleophiles, and the Co(III) complex **10** should be intermediate in stability. First, the Co(III)–imine N bond is kinetically inert and the Co(III) protects the N atom from protonation even in concentrated acid. The imine is clearly stabilized since it remains intact; even so the Co(III) ion must activate the imine to attack by a nucleophile although to a lesser extent than a proton. Evidence for the reactivity of such coordinated imines is to be found for the addition of carbanions, CN^-, and reduction by BH_4^-.[5,33] The coordinated imine is, therefore, intermediate between the imine and protonated imine, activated to nucleophilic attack somewhat but protected from protonation. This role for the metal should be followed by all the first-row transition metal ions except maybe low-spin Fe(II). In most instances, however, a proton will replace the metal on the imine since the metal–N bonds are mostly kinetically labile; low-spin complexes of Co(III), Cr(III), Fe(III), Fe(II), and V(II) are the obvious exceptions. It cannot be expected; therefore, that all imine complexes will be stabilized in strong acid. However, they should be stable in dilute acids if the stability constant is much greater than the pK_a for the protonated imine and they should be activated to attack by nucleophiles. Exceptional cases arise when the filled d orbitals on the metal ion put electron density back into empty π^* orbitals of suitable symmetry on the imine.[34] For Ru(II) bound to such an imine the overlap is sufficient to render the imine immune to nucleophilic attack and it also prevents the reduction of the imine to the saturated amine by BH_4^- ion.[35] The same effect might be anticipated for hexaimine complexes of Fe(II), although to a lesser extent, and for other low-valency d^6 second- and third-row metal ions.

The condensation observed between the two imine groups of the oxalato complex presumably takes place in the manner shown in Figure 4, and an X-ray crystallographic examination of the $[Co(enal)(ox)]PF_6{\cdot}2H_2O$ product adds support for the proposal and demonstrates the specificity of the addition. One diastereoisomer is preferred over the other to the extent of at least 4:1.

Two imines are required to condense at adjacent sites, and an intramolecular condensation between the carbanion generated at one imine methyl group and the imine carbon of the other leads to the product. The Co^{3+} ion activates the imine methyl group to deprotonation,[5] and the ethylenediamine chelates orientate the imines especially well for the condensation to occur. The requirement is that the imines must be cis to each other but not both trans to the oxygen atoms, and the imine methyl group forming the carbanion must be in the less stable orientation cis to the Co atom to provide the nucleophile. This latter species could be in a lower concentration, which would account for the relatively slow reaction. A low concentration of carbanion would also accommodate the slow condensation.

Addition of aldol or mesityl oxide to the $[Co(en)_2(ox)]^+$ ion under the same conditions did not lead to any condensation,

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(32) Halpern, B.; Sargeson, A. M.; Turnbull, K. R. *J. Am. Chem. Soc.* **1966**, *88*, 4630 and references therein.

(33) Taylor, L. T.; Urbach, F. L.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 1072 and references therein. Cressey, M.; McKenzie, E. D.; Yates, S. *J. Chem. Soc. A* **1971**, 2677. Katovic, V.; Taylor, L. T.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 2122.

(34) Taube, H. *Surv. Prog. Chem.* **1973**, *6*.

(35) Evans, I. P.; Everett, G. W.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 8041.

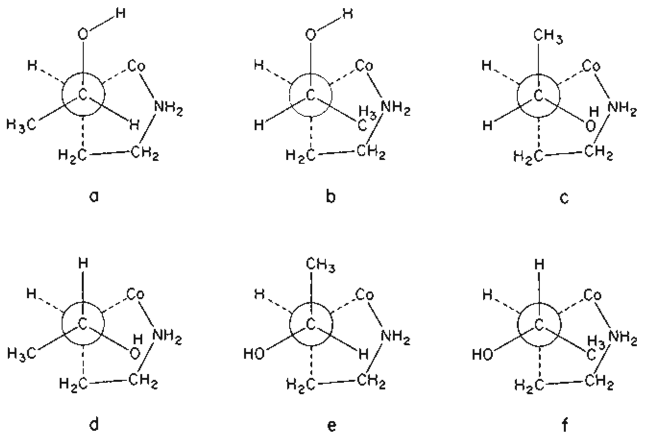


Figure 3. Newman projections of the rotamers involved in the formation of the carbinolamine.

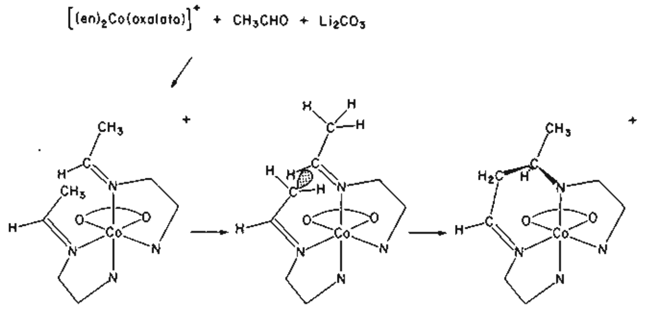
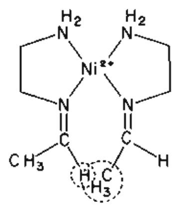


Figure 4. Proposed mechanism for the intraligand condensation between the acetaldimine moieties to yield the $[Co(enal)ox]^+$ cation.

and this path, therefore, can be excluded as a route to this type of condensed ligand at least for complexes where the diamine moieties are not dissociated from the metal ion. Also the synthesis using the chiral $[Co(en)_2ox]^+$ ion to produce chiral enal product demonstrates that the ligand condensations did not occur free of the metal ion and were not incorporated subsequently by electron transfer between inert Co(III) and labile Co(II) complexes. Such a route would be expected to produce racemic products and with certainty both chiralities of the carbon center where the condensation occurs.

Note that the carbanion addition gives a chiral carbon center and, if the assertions about the stable configurations of the imines are correct, then the addition should be substantially stereospecific. The addition shown and that related by the C_2 axis will be preferred. The ^1H NMR spectra of the isolated condensed product and the reaction mixture isolated in total from the ion-exchange column indicated a substantial excess of one diastereoisomer (>80%), and the structure of the ion has been established as that depicted by the reaction sequence. The specificity also implies that the reaction has not taken place by condensation of an acetaldehyde carbanion at the coordinated imine through an intermolecular reaction and subsequent condensation of the dangling carbonyl group with a coordinated amine center. Such a process would not be expected to be so specific, and in any event the concentration of acetaldehyde must be miniscule over most of the reaction time required to effect the ligand condensation because of the rate of the competing organic condensations in solution.[36]

There may be some consequences arising from this condensation for the manner in which the Curtis complexes are formed. If the diimines are cis to each other when the two ethylenediamine ligands are bound in the trans configuration on the nickel(II) ion (**11**), a substantial steric interaction arises. In fact one imine H atom is eclipsed by the neighboring imine methyl C atom. This restriction requires the imine groups to be skewed in order for them to condense or the condensation to occur either when the ligands are not bonded or only monodentate with a free NH_2 group ion or when the ethylenediamine entities are cis to each other as for the Co(III) complex examined here. Clearly the first three factors are less favorable than the cis orientation of the ligands and activation of the imine methyl by the metal ion to deprotonation.



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The pK_a of the coordinated tyrosine and ethylenediamine amino groups is around 14–16,[31,32] so the concentration of the bound amido ion is not high even in the basic reaction mixture (pH 10, $\sim 10^{-4}$–10^{-6} M). Possibly it is this factor that accounts for the relatively slow condensation to give the imines. The imine methyl groups are even less acidic although proton exchange is readily observed in basic solution.[33] Both factors could accommodate the slow interligand condensations in this case and for the Curtis complexes (in the presence of the metal ion), but the latter might also arise from a concentration of monodentate ethylenediamine condensing with a carbonyl group in solution.

Experimental Section

Analytical reagents were used for all purposes without further purification. $[Co(en)_2(ox)]Cl$,[37] *trans*-$[Co(en)_2(H_2O)(OH)](ClO_4)_2 \cdot H_2O$,[38] and $[Co(en)_2CO_3]Cl$[39] were synthesized with use of standard procedures.

Both Sephadex Na^+ SP C25 and Dowex H^+ 50W-X2 (200–400 mesh) cation-exchange resins were used for separation of the complexes studied.

NMR spectroscopy was carried out with a JEOL JNM 100-MHz Minimar instrument with sodium (trimethylsilyl)propanesulfonate (Na-TPS) as internal reference and with tetramethylsilane (Me_4Si) as external reference. All evaporations were carried out under reduced pressure (~20 mmHg) with use of Buchi rotary evaporators under conditions where the solution did not exceed 25 °C.

Synthesis of $[(en)_2Co((S)\text{-Tyr})]Cl_2$. (*S*)-Tyrosine (36.2 g) was added to a solution of *trans*-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$ (82.6 g) in Me_2SO (500 mL). The solution was stirred and heated at 80 °C for 45 min. The orange solution was diluted to 3 L with H_2O and sorbed on Dowex 50W-X2 (H^+) cation-exchange resin. The column was eluted with 3 M HCl to give a single large orange band, the front of which was perceptibly yellow [presumably $Co(en)_3^{3+}$]. When the eluate was reduced under vacuum, considerable pink precipitate deposited, and at a volume of 200 mL this was collected. Both methanol (200 mL) and acetone (200 mL) were added to the filtrate. When the solution was cooled in ice (30 min), $[Co(en)_3]Cl_3$ deposited (7 g) and was removed. Gradual addition of acetone to the filtrate deposited an orange flocculent solid, which was collected, dissolved in water (200 mL), filtered, and treated with acetone to the point of turbidity. When the solution stood, orange crystals were deposited, and when the supernatant liquor had cleared, acetone was again added to turbidity. By the repetition of this procedure all the tyrosinato complex, a mixture of Δ and Λ diastereoisomers, was eventually isolated as a crystalline solid (59 g).

Reaction of $[(en)_2Co((S)\text{-Tyr})]Cl_2$ with CH_3CHO. Acetaldehyde (20 mL, 356 mmol, 0 °C) was added, with stirring and cooling in ice, to an ice-cold solution of Δ,Λ-$[Co(en)_2((S)\text{-Tyr})]Cl_2$ (5.0 g, 11.6 mmol) in a mixture of water (220 mL) and 1.00 M NaOH (35 mL).

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CH_3CO_2H in the acetaldehyde was previously neutralized with 1 M NaOH. After addition of acetaldehyde the solution instantaneously changed from orange to brown and the temperature increased to ~10 °C. After 0.5 h with continued cooling the brown solution was acidified with acetic acid, diluted with water ($2^1/_2$), and sorbed on a Sephadex SP-C25 ion-exchange column (6 × 25 cm, Na^+ form). After elution with 0.05 M trisodium citrate at least five orange-yellow bands appeared, but only the first two were collected and characterized. The first band was eluted with ~600 mL of 0.05 M citrate, which was sorbed on a short Dowex 50W-X2 column and then eluted with 3 M HCl, and the eluate was evaporated (40 °C) to dryness in vacuo, giving yellow crystals of the diimine chloride salt. The chloride, dissolved in water, was treated with a small volume of a saturated solution of sodium perchlorate at room temperature. This gave nearly a quantitative precipitation of the perchlorate salt. The precipitate was washed with 96% ethanol and dried in air; yield ~0.29 g (3%). Anal. Calcd for $[CoC_{17}N_5H_{30}O_3](ClO_4)_2{\cdot}H_2O$: Co, 9.41; C, 32.59; N, 11.18; H, 4.83; Cl, 11.32. Found: Co, 9.20; C, 32.52; N, 11.11; H, 4.84; Cl, 11.23. This salt is only slightly soluble in water.

The second band (eluted with approximately 1400 mL of 0.05 M citrate) was isolated as its chloride by the same method, which yielded 2.4 g (35%) of the chloride of the monoimine. This chloride (1.4 g) was dissolved in water (6 mL), and the filtered solution was treated at 0 °C with a saturated solution of sodium perchlorate (3 mL). After $^1/_2$ h the precipitate was collected and washed with 96% ethanol (1.05 g). Drying in vacuo over P_2O_5 caused the crystals to effloresce partly. Anal. Calcd for $[CoC_{15}N_5O_3H_{28}](ClO_4)_2{\cdot}H_2O$: Co, 9.79; C, 29.91; N, 11.63; H, 5.02; Cl, 11.77. Found: Co, 9.72; C, 30.26; N, 11.61; H, 4.89; Cl, 11.91. The product, recrystallized from a saturated aqueous solution at room temperature over 2 days, was used for the crystallographic investigation.

Each of the last three bands was isolated as the chloride, but crystalline products were not obtained. The CH_3 signals in the ^1H NMR spectra showed clearly that each fraction was a mixture.

Reaction of $[(en)_2Co(ox)]Cl$ with CH_3CHO. Two experiments, differing only in reaction times (2 and 30 h), are described.

$[Co(en)_2(ox)]Cl$ (4.5 g) was dissolved in 0.64 M Na_2CO_3, 0.071 M $NaHCO_3$ buffer (60 mL) and then added to an ice-cold mixture of acetaldehyde (15 mL, 267 mmol, neutralized with Na_2CO_3) and water (25 mL). The suspension was stirred at 20 °C for 2 or 30 h, respectively. All the complex had dissolved within 45 min.

Reaction Time 2 h. The reaction mixture was treated with excess acetic acid, diluted to 600 mL with water, and sorbed on Dowex 50W-X2 (5 × 10 cm). Elution with 1 M HCl gave two bands, a large front-running band and a rather small following band. The eluate containing the large band was evaporated to near dryness and then precipitated with 96% ethanol. The precipitate was collected (the filtrate was rather colored), washed with 96% ethanol, and dried in air (yield 1.6 g). Analysis showed a C:N ratio equal to 2.05.

The crude product (0.5 g) was then dissolved in water, sorbed on Dowex 50W-X2 (3 × 24 cm), and eluted with 0.5 M HCl. This gave one broad band most concentrated in the middle. The middle fraction (~50%) was collected and evaporated to dryness to give a crystalline precipitate. This was dissolved in water, the solution was treated with solid lithium chloride, and the product then crystallized by addition of 96% ethanol. Drying in air gave ~150 mg of product. Anal. Calcd for the monoimine $[Co(C_8N_4O_4H_{18})]Cl{\cdot}1.5H_2O$: C, 27.01; N, 15.75; Cl, 9.97. Found: C, 27.2; N, 15.4; Cl, 10.3.

Reaction Time 30–40 h. The reaction mixture was treated with excess CH_3COOH, diluted to 600 mL with H_2O, and sorbed on Dowex 50W-X2 (5 × 10 cm). Elution with 0.5 M HCl gave a large front-running band, which was evaporated to dryness. The red product, largely reactant, was extracted with a small amount of water. $NaPF_6$ was then added to this solution in excess. Fractional crystallization of the product gave the pure enal complex in low yield in the most soluble fractions. Anal. Calcd for $[CoC_{10}H_{20}N_4O_4]PF_6{\cdot}2H_2O$: C, 24.00; N, 11.21; H, 4.84. Found: C, 25.0; N, 11.4; H, 4.6.

The condensation was also carried out with the chiral complex $(+)_D$-$[Co(en)_2ox]Br_2$ (20 g), with the conditions scaled up appropriately. After 30 h the reaction mixture was neutralized with excess acetic acid, and the solution was extracted five times with $CHCl_3$ to remove the organic byproducts. This solution was now sorbed on Dowex 50W-X2 ion-exchange resin and eluted with 0.5 M HCl as before. The fraction containing unreacted $[Co(en)_2ox]^+$ and other products was evaporated to dryness and the least soluble $[Co(en)_2ox]Cl$ removed. The final soluble fraction was then eluted from Biogel P_2 with water, and this treatment removed the last traces of $[Co(en)_2ox]$ as the slowest moving fraction. The fastest moving fraction contained a monoimine product, and the middle fraction contained the enal complex, which was recovered by evaporation under reduced pressure. Unfortunately we were unable to crystallize the chiral product, but ^1H NMR spectra of D_2O solutions indicated it was composed largely of the diastereoisomer found in the achiral synthesis (>80%). Atomic absorption spectroscopy established the cobalt concentration, and the visible spectrum gave maximum molar absorptivities of $\epsilon^{25}{}_{494} = 103$ $M^{-1}\ cm^{-1}$ and $\epsilon^{25}{}_{355} = 129$ $M^{-1}\ cm^{-1}$ and maximum molar rotations of $[M]^{25}{}_{560} = +1990°$ $M^{-1}\ cm^{-1}$ and $[M]^{25}{}_{496} = -4630°$ $M^{-1}\ cm^{-1}$.

Reaction of $[(en)_2Co(ox)]Cl$ with Aldol. $[(en)_2Co(ox)]Cl$ (4.5 g) dissolved in 0.64 M Na_2CO_3, 0.071 $NaHCO_3$ buffer (60 mL) was treated with aldol (9 mL), and the mixture was stirred at 20 °C for 30 h. The reaction mixture was then treated in a manner identical with that described for the acetaldehyde experiment, but only reactant was recovered. An analogous experiment with mesityl oxide also gave unreacted complex.

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Supplementary Material Available: Listings of least-squares positional and thermal parameters and calculated hydrogen atom positions for $[Co^{III}(enal)ox](PF_6)_2{\cdot}H_2O$, final calculated hydrogen atom positions and anisotropic thermal parameters for non-hydrogen atoms for Λ-$[Co(en)_2((S)\text{-}Tyr)]^{2+}$, and observed and calculated structure factors for both structures (35 pages). Ordering information is given on any current masthead page.