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Synthesis and Reactivity of Coordinated Imines Derived from 2-Keto Acids

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Abstract: The synthesis of a series of $[Co(NH_3)_5OCOCOR]^{2+}$ ions (R = H, CH_3, C_6H_5, COOH, $-CH_2C_6H_5$, $C(CH_3)_3$, $CH_2CH_2CO_2^-$) and a number of derivatives is described. In aqueous base most of these ions undergo cyclization to tetraammine iminocarboxylato chelates which undergo a variety of reactions: alkylation of the deprotonated imine N center, addition of nucleophiles at the imine C center, reduction of the imine to give an amino acid, and intramolecular condensations after the addition of the nucleophile. The compounds illustrate the potential of the metal ion to protect and activate organic molecules as well as to organize such intramolecular condensations. The kinetics of the imine cyclization are also discussed.

Introduction

The imine functional group, >C=N–, plays a near-ubiquitous role in synthetic organic, biological, and coordination chemistry. Nonetheless, while there is a vast literature concerning the effects of Schiff base ligands on metal ion properties, only for complexes of Schiff bases derived from pyridoxal has there been any systematic and thorough investigation of the properties of imine containing ligands as affected by a metal ion.[1] The reactivity of simple coordinated imines is essentially unknown. Further, while an extremely large number of so-called "template" reactions[2] involve imine formation, no detailed study of the kinetics of genuine intramolecular condensations is available. It might well be anticipated from the behavior of related systems[3] that the (carbinolamine) addition intermediate involved in imine formation would be stabilized by metal ion coordination and that the kinetics of its formation and decomposition would therefore be amenable to investigation. It is frequently difficult to detect and therefore to understand factors controlling the stability of carbinolamine intermediates in simple organic systems.[4] In preliminary publications[5] we have outlined the synthesis and some aspects of the chemistry of simple cobalt(III) imine complexes and in related work detailed studies of the kinetics of genuine intramolecular imine formation with cobalt(III) have been made.[6] The present work describes the synthesis, formation kinetics and basic physical and chemical properties of a variety of α-iminocarboxylate complexes of cobalt(III).

Experimental Section

pH measurements were made under nitrogen at 25 °C using a Radiometer PHM26 meter with G202B glass electrode. Infrared spectra of KBr disk, Nujol mull (NaCl plates), and solution (D_2O, CaF_2 cell) samples were recorded with a Perkin-Elmer Model 337 instrument. Visible spectra and slower reaction rates were measured with a Cary-Varian 118C UV–visible spectrophotometer while reaction rates corresponding to half-lives of <2 s were measured with a Durrum-Gibson stopped flow kinetics spectrophotometer. Separate solutions of complex in 1 M $NaClO_4$ and NaOH (plus $NaClO_4$ to an ionic strength of 1.0) were degassed under water pump vacuum prior to thermal equilibration in the reservoirs of the stopped-flow apparatus. NMR spectra were recorded with JEOL "Minimar" MH 100 (proton) and FX-60 (^{13}C) instruments using tetramethylsilane (Me_4Si) in dimethyl-d_6 sulfoxide (Me_2SO-d_6) and sodium trimethylsilylpropanesulfonate in D_2O as references for ^1H spectra and dioxane (in D_2O) for ^{13}C.

Syntheses. 1. α-Ketocarboxylatopentaamminecobalt(III) Complexes. Trimethylpyruvic acid,[7] phenylglyoxylic acid,[8] and phenylpyruvic acid[9] were prepared by literature methods. Glyoxylic acid (BDH), ketomalonic (mesoxalic) acid (Lights), sodium pyruvate (Sigma), and α-ketoglutaric acid (ROC-R1C) were commercial products, though disodium ketomalonate was also prepared by base hydrolysis of dibromomalonic acid.[10] $[(NH_3)_5CoO_2CCOCH_3](ClO_4)_2$, $[(NH_3)_5CoO_2C{\cdot}CHO](ClO_4)_2$ $[(NH_3)_5CoO_2C{\cdot}CO{\cdot}C_6H_5](ClO_4)_2$, and $[(NH_3)_5CoO_2C{\cdot}CO{\cdot}C(CH_3)_3](ClO_4)_2$ were prepared by reaction of $[(NH_3)_5CoOH_2]^{3+}$ in a buffer of the ligand following the general procedure of Taube and Price[11] (though a 90-min reaction period was found sufficient. Note that full characterization of only the glyoxylatopentamminecobalt(III) complex is reported therein. Data for the related new species[12] are given below.) Anal. Calcd for $[Co(NH_3)_5OCOCOCH_3](ClO_4)_2$: Co, 13.71; C, 8.38; H, 4.22; N, 16.29; Cl, 16.49. Found: Co, 13.91; C, 8.74; H, 4.63; N, 16.12; Cl, 16.31.

^{13}C NMR (NB. The generally low solubility of the α-ketocarboxylatopentaamminecobalt(III) complexes meant that ^{13}C NMR spectra could be conveniently obtained for only a few species.): Consistent with the known ^1H NMR spectrum,[11,12] the ^{13}C spectrum showed resonances attributable to both keto and *gem*-diol forms of the complex. Relative to dioxane in 10^{-3} M DCl: +1976 (>C=O), +1736 (CO_2H, hydrate form), +1576 (CO_2H, keto form), +394 ($>C(OH)_2$), −597 (CH_3, keto), −619 Hz (CH_3, hydrate) (assignments tentative).

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl): 500 nm, 71.5 M^{-1} cm^{-1}.

Anal. Calcd for $[Co(NH_3)_5OCOCOC_6H_5](ClO_4)_2$: Co, 11.98; C, 19.53; H, 4.10; N, 14.23; Cl, 14.41. Found: Co, 12.0; C, 19.6; H, 4.2; N, 14.1; Cl, 14.2.

^{13}C NMR: +2880 (>C=O), +2751 (CO_2H, approximately twice the intensity of the 2880-Hz resonance), +2148, 2087, 2068, 2053 Hz (C_6H_5 group) relative to dioxane in 10^{-3} M DCl.

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl) 498 nm, 77.1 M^{-1} cm^{-1}.

Anal. Calcd for $[Co(NH_3)_5OCOCOC(CH_3)_3](ClO_4)_2$: Co, 12.48;

0002-7863/79/1501-1514$01.00/0

C, 15.26; H, 5.12; N, 14.83; Cl, 15.02. Found: Co, 12.4; C, 15.3; H, 5.2; N, 14.9; Cl, 14.9.

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl) 502 nm, 73.7 M^{-1} cm^{-1}.

Preparations of other $[(NH_3)_5CoO_2C{\cdot}COR]^{2+}$ complexes involved sufficient modifications of this procedure to justify more detailed description.

$[(NH_3)_5CoO_2C{\cdot}C(OH)_2{\cdot}CO_2]Cl$. The principal difficulty associated with the preparation of this complex was its isolation from the preparative mixture. The protonated form, $[(NH_3)_5CoO_2C{\cdot}C(OH)_2{\cdot}CO_2H]^{2+}$, is extremely soluble in water (as Cl^- or ClO_4^- salts), whereas the deprotonated form, though readily precipitated with Cl^- or ClO_4^-, is present at a pH where excess sodium ketomalonate is also readily deposited. In addition, several minor complex ion species contaminated the desired product if isolated by direct precipitation and hence it was simplest to isolate it by cation exchange chromatography. Sodium ketomalonate (25 g) was added in portions to a hot (80 °C) solution of $[(NH_3)_5CoOH_2](ClO_4)_3$ (32 g) and $HClO_4$ (70%, 12.5 mL) in H_2O (300 mL), the mixture being well stirred to ensure rapid dissolution. The final solution was heated on a steam bath for 2 h and cooled and a small amount of red precipitate (apparently $[(NH_3)_5CoC_2O_4H](ClO_4)_2$) filtered off. The filtrate was diluted to ~3 L and absorbed on a large column (approximately 30 × 12 cm diameter) of Li^+ form SP Sephadex C25 resin. The column was washed well with water and eluted with 0.2 M LiCl to reveal at least seven components. The major (red) band, which was preceded by two very weak, pink bands, was collected and the eluate volume reduced to ~50 mL on a rotary evaporator at water pump pressure. Pyridine was then added dropwise until the pH of the solution rose to approximately 5, at which stage rapid deposition of red crystals began. After the mixture was cooled for 30 min on ice, the crystals were filtered off and washed with methanol and ether (yield 10 g). The complex was recrystallized by adding concentrated HCl to its aqueous slurry (5 mL/g) until dissolution just occurred, filtering, raising the pH to 5 with pyridine, and cooling the solution on ice. The perchlorate salt was obtained by metathesis with $NaClO_4$ in aqueous solution.

Anal. Calcd for $CoC_3H_{17}N_5O_6Cl{\cdot}2H_2O$: Co, 18.79; C, 11.49; H, 5.46; N, 22.33; Cl, 11.31. Found: Co, 18.3; C, 11.3; H, 5.9; N, 21.3; Cl, 11.8.

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl): 501 nm, 70.3 M^{-1} cm^{-1}.

^1H NMR: Ammine group proton resonances in dilute DCl at δ 2.9 (3 H, NH_3 trans to O) and 3.9 (12 H, $4NH_3$ cis to O) typify the present complexes and are as expected[13] for carboxylatopentaamminecobalt(III) species.

$[(NH_3)_5CoO_2C{\cdot}CO{\cdot}CH_2{\cdot}C_6H_5](ClO_4)_2$. A slurry of $C_6H_5CH_2CO{\cdot}CO_2H$ (9 g) and $[(NH_3)_5CoOH](ClO_4)_2$ (7 g) in water (100 mL) was heated on a steam bath for 90 min. $NaClO_4$ (10 g) was dissolved in the hot solution, which was then cooled on ice for 30 min. The pink precipitate formed was filtered off, sucked well dry in air, and twice extracted with a mixture of ether (100 mL) and ethanol (10 mL) to free the complex of coprecipitated phenylpyruvic acid. The complex was recrystallized from water (200 mL, 80 °C) slightly acidified with $HClO_4$ (5 drops, 12 M) by filtering, adding $HClO_4$ (5 mL, 12 M), and cooling on ice. The lustrous, pink flakes were washed with ethanol and ether (yield 6 g).

Anal. Calcd for $CoC_9H_{22}N_5O_{11}Cl_2$: Co, 11.64; C, 21.36; H, 4.38; N, 13.84; Cl, 14.01. Found: Co, 11.7; C, 21.6; H, 4.7; N, 13.6; Cl, 14.1.

^1H NMR: δ 2.58 (3 H, trans NH_3), 3.70 (12 H, cis NH_3 groups), 3.91 (2 H, CH_2), and ~7.0 (5 H, multiplet, C_6H_5) in Me_2SO-d_6 vs. Me_4Si.

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl): 500 nm, 71.0 M^{-1} cm^{-1}.

$[(NH_3)_5CoO_2C{\cdot}COCH_2CH_2CO_2]ClO_4$. A mixture of $[(NH_3)_5CoCO_3]NO_3$ (30 g) and 2-oxoglutaric acid (60 g) in water (200 mL) was heated on the steam bath for 2 h. The deep red solution was cooled to 0 °C and $HClO_4$ (12 M, 50 mL) added to precipitate a mass of pink crystals, which were collected and washed with ethanol and ether (yield ~50 g). As this diperchlorate salt tended to occlude large quantities of water when crystallized, it was more convenient to isolate the monoperchlorate of the carboxyl deprotonated species from neutral solution. Thus, the crude diperchlorate was dissolved in the minimum volume of water, the pH of the solution raised to approximately 7 by addition of pyridine, and excess $NaClO_4$ added to cause slow separation of large, red crystals. Note that ion exchange chromatography of the whole initial reaction mixture provided no evidence for more than one isomer in the product.

Anal. Calcd for $CoC_5H_{19}N_5O_9Cl{\cdot}H_2O$: Co, 14.53; C, 14.81; H, 5.22; N, 17.27; Cl, 8.74. Found: Co, 14.3; C, 14.6; H, 5.1; N, 16.8; Cl, 9.2.

Visible spectrum (λ_{max}, ϵ_{max}): 500 nm, 69.2 M^{-1} cm^{-1}.

2. Formation of Imine Chelate Tetraamminecobalt(III) Complexes. Conversion of the ketocarboxylatopentaammine complexes to the imine chelate tetraammine species was generally achieved by reacting the complex for 30 s with a slight excess (~1.1:1 molar ratio) of dilute aqueous NaOH. Isolation of the products presented various minor problems except for the phenylglyoxylate and trimethylpyruvate derivatives, where quenching of the reaction mixture with concentrated $HClO_4$ led to ready precipitation of perchlorate salts, and for the ketomalonate derivative, where quenching with concentrated HCl provided the slightly soluble Cl^- salt. (Note that this last imine chelate is so acidic that it is essential to add at least a 10% excess of NaOH to ensure complete cyclization of the pentaammine precursor within 30 s. This is not so crucial a requirement for the other species, which also cyclize more rapidly.)

Anal. Calcd for $[Co(NH_3)_4(NH{=}C(C_6H_5)COO)](ClO_4)_2$: Co, 12.43; C, 20.27; H, 3.83; N, 14.77; Cl, 14.9. Found: Co, 12.4; C, 20.6; H, 4.2; N, 14.9; Cl, 14.7.

^1H NMR: δ 2.82 (3 H, NH_3), 3.26 (6 H, 2 NH_3), 3.86 (3 H, NH_3), ~7.46; 7.90 (5 H, multiplets, C_6H_5), 12.65 (1 H, =NH) in Me_2SO-d_6 acidified with a trace of D_2SO_4, Me_4Si reference.

IR: $\nu_{C=N}$ 1680 cm^{-1} (N-deuterated complex).

Visible spectrum (λ_{max}, ϵ_{max}, in 1 M HCl): 480 nm, 94.0 M^{-1} cm^{-1}.

Anal. Calcd for $[Co(NH_3)_4NH{=}C(C(CH_3)_3)COO](ClO_4)_2$: Co, 12.98; C, 15.87; H, 4.88; N, 15.42; Cl, 15.61. Found: Co, 12.8; C, 15.9; H, 4.8; N, 15.2; Cl, 15.6.

^1H NMR: δ 2.80 (3 H, NH_3), 3.07 (6 H, 2 NH_3), 3.67 (3 H, NH_3), 11.37 (1 H, =NH), 1.19 (9 H, $C(CH_3)_3$) in Me_2SO-d_6 + D_2SO_4, Me_4Si reference. (NB. =NH resonance is rather sensitive to the amount of D_2SO_4 in the Me_2SO-d_6. Apparent differences between complexes may therefore be due largely to this effect).

IR: $\nu_{C=N}$ 1680 cm^{-1}.

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl): 483 nm, 80.5 M^{-1} cm^{-1}.

Anal. Calcd for $CoC_3H_{13}N_5ClO_4{\cdot}2H_2O$: C, 11.40; H, 5.46; N, 22.33. Found: C, 11.7; H, 5.8; N, 22.3.

^1H NMR: δ 2.94 (3 H, NH_3), 3.38 (6 H, 2 NH_3), 3.98 (3 H, NH_3), 13.80 (1 H, =NH) in Me_2SO-d_3 + D_2SO_4, Me_4Si reference.

IR: $\nu_{C=N}$ 1680 cm^{-1}.

Visible spectrum (λ_{max}, ϵ_{max}): 484 nm, 92.9 M^{-1} cm^{-1} (1 M HCl); 486 nm, 85.1 M^{-1} cm^{-1} (H_2O).

The pyruvate imine complex could also be directly precipitated from the quenched reaction mixture as its ClO_4^- salt, but in the concentrated media required for efficient precipitation the base cyclization step led to production of considerable amounts of dimerized product as a contaminant. It was therefore preferable to use very dilute base (<0.1 M) for the cyclization, to absorb the reaction mixture on H^+ form Dowex 50WX2 resin after acid quenching, and to selectively elute the desired product with 1 M HCl. On evaporation of the eluate to dryness, both choride and perchlorate salts could be readily crystallized from the residue (the former by addition of ethanol to a solution of the residue in water). Physical characterization has been reported previously[5a] (except for the visible spectrum: λ_{max} 485 nm, ϵ_{max} 81.5 M^{-1} cm^{-1} in 1 M HCl).

The 2-oxoglutarate imine chelate was most conveniently crystallized as its chloride salt, obtained by addition of ethanol to a dilute HCl solution of the complex. To avoid contamination with NaCl, which would have resulted on applying this precipitation procedure to the quenched reaction mixture, the complex was first purified by absorbing the reaction on H^+ form Dowex 50WX2 resin and eluting with 1 M HCl.

Anal. Calcd for $CoC_5H_{18}N_5O_4Cl_2{\cdot}H_2O$: Co, 16.37; C, 16.68; H, 5.60; N, 19.45; Cl, 19.69. Found: Co, 16.4; C, 17.2; H, 5.7; N, 19.7; Cl, 20.7.

Visible spectrum (λ_{max}, ϵ_{max}, 1 M HCl): 485 nm, 78.6 M^{-1} cm^{-1}.

^1H NMR: δ 2.82 (3 H, NH_3), 3.14 (6 H, 2 NH_3), 3.77 (3 H, NH_3), 12.01 (1 H, =NH), 2.4–2.8 (multiplet, 4 H, CH_2CH_2) in Me_2SO-d_6 + D_2SO_4, Me_4Si reference.

IR: $\nu_{C=N}$ 1680 cm^{-1}.

Because of its sensitivity to base, the phenylpyruvate imine chelate could not be isolated in high yield. The following procedure was the most efficient developed.

NaOH (1 M, 5 mL) was added to a vigorously stirred solution of $[(NH_3)_5CoO_2C{\cdot}CO{\cdot}CH_2C_6H_5](ClO_4)_2$ (1.0 g) in water (100 mL). After 5 s, in which time the solution had become almost black in color and some flocculent precipitate had begun to form, $HClO_4$ (12 M, 5 mL) was added and the now orange solution filtered. It was absorbed on H^+ form Dowex 50WX2 cation exchange resin and the column washed with H_2O and 1 M HCl (100 mL). The orange complex was then eluted with 3 M HCl and this eluate taken to dryness under vacuum. The residue was triturated with H_2O (20 mL) and some insoluble pink-violet material (probably $[(NH_3)_5CoCl]Cl_2$) filtered out. Addition of $HClO_4$(12 M, 5 mL) to the filtrate and cooling on ice precipitated shiny, orange flakes (0.4 g).

Anal. Calcd for $CoC_9H_{20}N_5Cl_2O_{10}$: Co, 12.07; C, 22.15; H, 4.13; N, 14.35; Cl, 14.53. Found: Co, 12.1; C, 22.4; H, 4.4; N, 14.5; Cl, 14.7.

Visible spectrum (λ_{max}, ϵ_{max} in 1 M HCl): 486 nm, 81.0 M^{-1} cm^{-1}.

^1H NMR: δ 2.92 (3 H, NH_3), 3.24 (6 H, 2 NH_3), 3.77 (3 H, NH_3), 11.17 (1 H, -NH), 3.92 (2 H, CH_2), 7.24 (5 H, C_6H_5, sharp) in Me_2SO-d_6 + D_2SO_4, Me_4Si reference.

IR: $\nu_{C=N}$ 1680 cm^{-1}.

All imine chelate complexes, once isolated, were readily recrystallized from water.

3. Isolation of Deprotonated Imine Chelates. With the exception of the phenylglyoxylate derivative, all deprotonated imine chelate derivatives were exceedingly soluble in water (and/or were very unstable). The pyruvate compound was therefore the only one of these soluble species to be analytically characterized.

$[(NH_3)_4Co(N{=}C(C_6H_5)CO_2)]ClO_4$. NaOH (1 M, 15 mL) was added to a solution of $[(NH_3)_4Co(NH{=}C(C_6H_5)CO_2)](ClO_4)_2$ (4.7 g) in water (100 mL). $NaClO_4$ (15 g) was added to the deep red-brown solution formed, causing immediate precipitation of small, brown needles. After cooling for 15 min on ice the precipitate was collected and washed with a little ice-cold water, then ethanol and ether. Recrystallization from dilute (~10^{-3} M) NaOH by the addition of $NaClO_4$ gave large, deep brown-red needles (3.6 g).

Anal. Calcd for $CoC_8H_{17}N_5ClO_4{\cdot}H_2O$: Co, 15.05; C, 24.53; H, 4.89; N, 17.88; Cl, 9.05. Found: Co, 15.2; C, 24.8; H, 5.2; N, 18.0; Cl, 9.2.

Visible spectrum (λ_{max}, ϵ_{max} in Me_2SO) 539 nm, 211 M^{-1} cm^{-1}.

^1H NMR: δ 2.05 (2 NH_3), 2.17 (NH_3), 3.9 (NH_3), 7.3, 8.1 (C_6H_5 multiplets) in Me_2SO-d_6, Me_4Si reference.

$[(NH_3)_4Co(N{=}C(CH_3)CO_2)]ClO_4$. The protonated complex $[(NH_3)_4Co(HN{=}C(CH_3)CO_2)](ClO_4)_2$ (2 g) was added to ice-cooled NaOH (1 M, 10 mL). As soon as dissolution was complete, $NaClO_4$ (15 g) was added and the solution stirred vigorously to initiate product precipitation. After 10 min of ice cooling the solid was filtered off and washed with ethanol and ether. Microscopic examination showed the crystals to be uniform but rather transparent. No convenient method of recrystallization was discovered (yield 1.9 g). (NB. A chloride salt could be precipitated from water by addition of acetone, but was unstable for more than a few hours at room temperature.)

Anal. Calcd for $CoC_3H_{15}N_5ClO_6{\cdot}2NaClO_4{\cdot}4H_2O$: Co, 9.38; C, 5.74; H, 3.69; N, 11.15; Cl, 16.93. Found: Co, 9.3; C, 6.2; H, 3.7; N, 11.5; Cl, 17.9.

Visible spectrum (0.1 M NaOH, approximate): λ_{max} 530 nm, ϵ_{max} ~155 M^{-1} cm^{-1}.

4. Preparation of N-Alkylated Imine Chelates. Direct alkylation of the imine chelate complexes was achieved through reaction in Me_2SO with an alkylating agent in the presence of Na_2CO_3. Even with a very large excess of as active an alkylating agent as methyl iodide, however, rather poor yields (<40%) resulted and separation of the components of the product solution often proved difficult. Use of the isolated deprotonated imine chelates was a far superior method. Thus, reaction of $[(NH_3)_4Co(N{=}C(CH_3)CO_2)](ClO_4)$, for example, with a two- to threefold excess of CH_3I, $CH_2{=}CHCH_2Br$, or $C_6H_5CH_2Cl$ in Me_2SO for 15, 60, or 60 min, respectively, gave essentially quantitative yields of the *N*-methyl, *N*-allyl, and *N*-benzyl complexes.

Anal. Calcd for $CoC_4H_{18}N_5Cl_2O_{10}$: Co, 13.83; C, 11.28; H, 4.26; N, 16.44; Cl, 16.64. Found: Co, 13.8; C, 11.4; H, 4.9; N, 17.0; Cl, 16.4.

^1H NMR: δ 2.3 ($C{-}CH_3$), 3.05 (NH_3), 3.3 ($N{-}CH_3$), 3.35 (2 NH_3), 3.75 (NH_3).

Anal. Calcd for $CoC_6H_{20}N_5Cl_2O_{10}$: C, 15.94; H, 4.66; N, 15.49. Found: C, 15.7; H, 4.3; N, 15.1.

^1H NMR: δ 2.35 ($C{-}CH_3$), 3.05 (NH_3), 3.5 (2 NH_3), 4.3 (NCH_2-broadened doublet), 5.5 ($CH{=}CH_2$, ABC system).

Anal. Calcd for $CoC_{10}H_{22}N_5Cl_2O_6$: Co, 12.92; C, 26.33; H, 5.30; N, 15.35; Cl, 15.54. Found: Co, 12.9; C, 26.2; H, 5.2; N, 15.1; Cl, 15.4.

^1H NMR: δ 2.41 (3 H, CH_3), 3.19 (3 H, NH_3), 3.56 (6 H, 2 NH_3), 3.98 (3 H, NH_3), 5.12 (2 H, CH_2), 7.41 (5 H, C_6H_5, sharp) in Me_2SO-d_6, Me_4Si reference.

5. Nucleophilic Additions to Imine Chelate Complexes. Additions of hydride (as BH_4^-) and nitromethane anion to the imine carbon center of the pyruvate imine chelate complex have been described previously.[5a] Details of the BH_4^- reduction, which requires fairly closely controlled conditions, are as follows.

$NaBH_4$ (0.1 g) was added to a solution of $[(NH_3)_4Co(N{=}C(CH_3)CO_2)](ClO_4)_2$ (0.4 g) in H_2O (30 mL) rendered weakly alkaline by the addition of a few drops of carbonate buffer (in acid solution BH_4^- instantly reduces the metal center). The mixture was stirred vigorously for 30 s, then absorbed as quickly as possible (under suction) on a short column (2 × 2 cm) of Na^+ form Dowex 50WX2 resin. The column was thoroughly washed with water (again under suction) and with 0.5 M HCl to remove all Na^+ ions. The complex was then eluted with 1 M HCl, the eluate taken to dryness under vacuum, and the residue crystallized from water by addition of ethanol (yield 0.25 g). After N-deuteration the ^1H NMR spectrum showed simply a methine quartet (δ 4.1 in D_2O) and methyl doublet (δ 1.85).

Another simple reaction typical of the carbon-nitrogen double bond is the addition of CN^-.[14] For the coordinated imines, however, reaction proceeded beyond simple addition.

$(NH_3)_3NHCoNH_2C(CH_3)(CNH_2)(CO_2)(ClO_4)_2$. $NaHCO_3$ (0.84 g) and NaCN (0.25 g) were added to a slurry of $[(NH_3)_4Co(N{=}C(CH_3)CO_2)](ClO_4)_2$ (2.06 g) in H_2O (40 mL). The mixture was magnetically stirred in a stoppered flask for 2 h, giving a clear red-orange solution. This was acidified with $HClO_4$ (12 M, 5 mL) and stirred for another 30 min (fume hood). Reduction of the volume to ~10 mL under vacuum induced product crystallization and this was completed by the addition of ethanol. The complex was recrystallized from methanol by the addition of ether (yield 1.8 g).

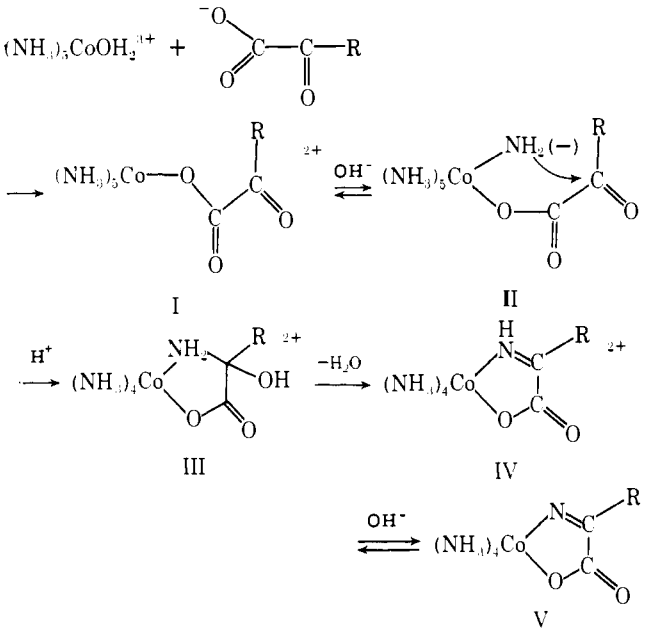
Anal. Calcd for $CoC_4H_{17}N_6Cl_2O_{10}$: C, 10.94; H, 3.90; N, 19.14. Found: C, 11.0; H, 4.6; N, 18.7.

^1H NMR: δ 1.45 ($C{-}CH_3$), 2.6 (NH_3), 3.42 (NH_3), 3.6 (NH_3), 5.9 (NH_2, broad AB doublet pair), 6.3 (NH_2, amidine), 8.0 (NH amidine broad).

Results and Discussion

1. Synthesis. Essentially identical behavior in basic solution is shown by all but one of the present set of $[(NH_3)_5CoO_2C{\cdot}COR]^{2+}$ complexes (I). Thus the intramolecular cyclization to the imine chelate (IV) is signaled by a dramatic color change from the pink of the reactant to the intense red-brown of the deprotonated product (V). Acidification of the reaction mixture causes a similar marked color change of the solution to a light orange characteristic of the protonated imine chelates (Figure 1). All the deprotonated complexes underwent fairly rapid decomposition in solution in the presence of excess base, the color of the solution fading to pink and a gelatinous brown precipitate slowly forming. Even in the solid state their stability was not greatly enhanced. The pyruvate imine (R = CH_3) derivative, for example, could be kept for only a few hours at 25 °C as its chloride salt before ammonia loss was detectable. In the formation of the chelate from the complex of phenylpyruvic acid the color changes described above were largely overlaid by redox phenomena leading to formation of deeply colored organic products, which were strongly absorbed by Dowex 50 cation exchange resin and on which they underwent further slow reactions. These processes are presumably related to those observed in the facile formation of the dimer of benzyl cyanide by the Co(III) oxidation of the coordinated benzyl

Scheme I



cyanide carbanion.[15] Only for the glyoxylatopentaammine complex (R = H) were no dramatic color changes observed on base treatment. Instead, rapid total decomposition, leading to formation of a Co(II)-containing precipitate, occurred. For the analogous bis(ethylenediamine) complexes, which are of considerably greater hydrolytic and redox stability than the tetraamine, formation of hydrolytically unstable carbinolamine, but not the imine, from glyoxylate was detectable. Therefore it was assumed that an internal (base-catalyzed) redox process occurred on formation of the carbinolamine from $[(NH_3)_5CoC_2C{\cdot}CH(OH)_2]^{2+}$. Some evidence that the glyoxylate imine chelate itself was of moderate stability was obtained from attempts to decarboxylate the mesoxalato imine (IV, R = COOH) in dilute acid. Chromatographic separation and NMR and analytical characterization indicated the formation of similar amounts of $[(NH_3)_4CoO_2C{\cdot}C(NH_2)(OH)CO_2]^+$, $[(NH_3)_4Co(NH{=}C(H)CO_2)]^{2+}$, $[(NH_3)_4Co(NH{=}C(OH)(H)CO_2)]^{2+}$, and Co^{2+} after 60 min at 80 °C in 1 M HCl. This did not seem to offer an acceptable overall pathway to the potentially synthetically valuable (vide infra) glyoxylate imine chelate.

Alternate general syntheses were investigated to a limited extent. The phenylglyoxylate imine complex was also prepared from $(NH_3)_5CoO_2C{\cdot}CO{\cdot}C_6H_5^{2+}$ obtained by chromic acid oxidation of the mandelatopentaammine complex, but the overall yield compared poorly with that of the method given above, and difficulties were anticipated for complexes less readily isolated from chromic acid and containing functional groups (other than -OH) sensitive to this reagent. In confirmation, chromic acid oxidation of $(NH_3)_5CoO_2C{\cdot}CH(OH){-}CH_2CO_2CH_3^{2+}$ (obtained via reaction between $(NH_3)_5CoOH^{2+}$ and methyl malate chloralide[16] in Me_2SO[17]) provided none of the desired methyl oxaloacetate complex. Other procedures investigated for the preparation of oxaloacetate complexes also failed. Thus, reaction between $(NH_3)_5CoOH^{2+}$ and diethyl oxaloacetate proceeded extremely slowly and even after a period of weeks gave no product identifiable as $(NH_3)_5CoO_2C{\cdot}CO{\cdot}CH_2COOC_2H_5^{2+}$ (or its enolate). Attempted base-catalyzed cyclization of $(NH_3)_5CoO_2C{\cdot}C{\equiv}C{\cdot}CO_2CH_3^{2+}$ [18] provided several materials, $(NH_3)_5CoO_2C{\cdot}C{\equiv}CH^{2+}$ being predominant, but $(NH_3)_4Co(N{=}C(CH_2CO_2CH_3)CO_2)^{2+}$ (or its enamine) was not among them. Efforts were made to prepare ketomalonate imine derivatives by base-catalyzed cyclization of $(NH_3)_5CoNHCO{\cdot}CBr_2{\cdot}CO_2Et^{2+}$ and $(NH_3)_5CONHCOC(=N{\cdot}OH){\cdot}CO_2Et^{2+}$, formed by bromination and nitrosation, respectively, of $(NH_3)_5CoNC{\cdot}CH_2CO_2Et^{3+}$. The former complex, however, provided only $(NH_3)_5CoNHCOCHBr_2^{2+}$ while the latter merely underwent slow redox decomposition. A fortuitous discovery made during an investigation of the Michael addition of nitromethane to the ketomalonate imine complex was that this reaction led to formation of the pyruvate imine complex. This was interpreted as due to elimination of NO_2^- from the β-nitroalanine complex formed by decarboxylation of the initial addition product as in Scheme II.

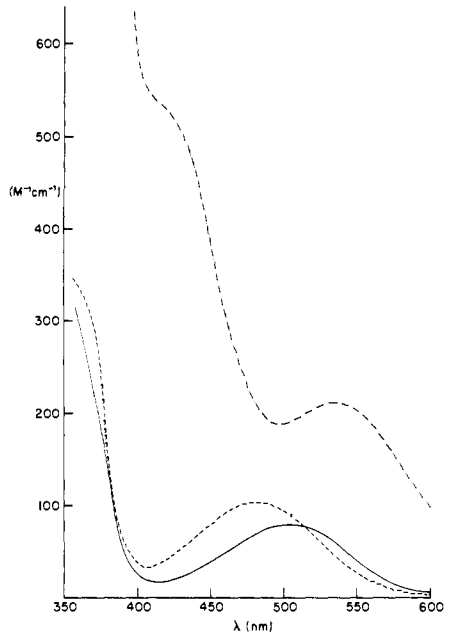
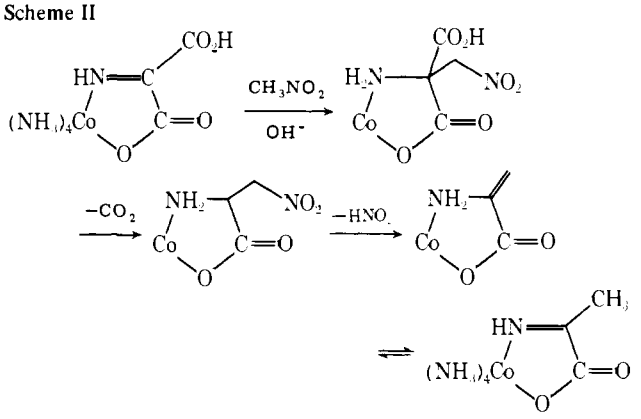


Figure 1. Visible absorption spectra in Me_2SO of $[(NH_3)_5CoO_2C{-}COC_6H_5](ClO_4)_2$ (———), $[(NH_3)_4Co(NH{=}C(C_6H_5)CO_2)](ClO_4)_2$ (- - - -), and $[(NH_3)_4Co(N{=}C(C_6H_5)CO_2)]ClO_4$ (·····).

Scheme II



Subsequent exploitation of related reactions has provided an especially convenient route to the preparation of α-iminocarboxylatobis(ethylenediamine)cobalt(III) chelates.

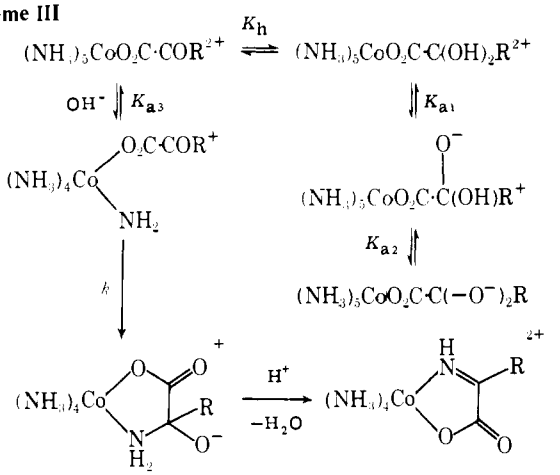
2. Characterization. The overall process occurring on treatment of the α-oxocarboxylatopentaammine complexes with base was clearly defined from ^1H NMR spectra, the spectra of all complexes showing the basic features of that of the pyruvate imine chelate (IV).[5b] Thus, ammine group resonances revealed the drop from (effective) C_{4v} symmetry of the reactants to the C_s product symmetry and the concomitant loss of one ammine group. Very low field ^1H resonances attributable to *one* imine NH proton were seen in all cases. In no cases were resonances attributable to the diastereotopic protons of a carbinolamine NH_2 group seen (note that the product of

addition of nitromethane to the pyruvate imine chelate gave a ^{1}H NMR spectrum showing a well-resolved AB quartet for its NH_2 resonances), nor did the pattern of ammine group resonances indicate a complete lack of molecular symmetry, though these resonances were quite broad. Other physical data supported identification of the reaction products as imine chelates. Thus, whether for paraffin mulls, KBr disks, or D_2O solutions, an IR absorption at 1680 cm^{-1}, typical of C=N[14] and absent in reactant spectra, was seen. ^{13}C NMR spectra also showed resonances in a region close to that of carboxyl carbon and attributable to C of C=N. Finally, crystal structure determinations[5a,19] revealed the 2-iminocarboxylate chelate moiety to be intact in some products of further reactions of the pyruvate imine complex.

Chemical evidence as to the nature of the complexes was also compelling. Nucleophilic attack by species such as BH_4^-, $CH_2NO_2^-$, and CN^- (see below) is a reaction characteristic of imines.[14] Such behavior would also be shown by a carbinolamine in rapid equilibrium with its imine, but the available evidence indicates that such an equilibrium would be achieved very slowly. Thus, two of the products obtained by heating the ketomalonate imine chelate in acid were the glyoxylate imine chelate and its hydrate (carbinolamine); examination of NH proton exchange by D incorporation in these two complexes showed that exchange of the imine NH was orders of magnitude faster than that of either of the carbinolamine NH_2 protons. Moreover, the latter exchanged at a rate similar to that for a simple NH_2 group such as chelated alanine. Rapid H_2O elimination and D_2O addition could therefore be excluded as a special path for the NH_2 group exchange. All the above evidence, coupled with the failure of attempts to observe any change in structure (i.e., hydration) of any complex, other than the ketomalonate derivative, in acidic solution leads to the conclusion that the α-iminocarboxylate form is strongly preferred for all.

3. Formation Kinetics. Preliminary observations revealed that for the pyruvate, phenylglyoxylate, and possibly the ketomalonate pentaammine complexes spectral changes in basic solution (with $[OH^-]$ in large excess) corresponded to a single first-order process, whereas for the other complexes consecutive reactions were involved. In fact, extended observations showed that for all complexes one rapid and at least one (perhaps several) slow processes(es) were involved. Eventually, all the complexes underwent complete decomposition in base, with formation of a brown precipitate. Experiments in which the reaction mixtures were quenched with acid after the intrusion of the first slow process was obvious, and the mixture of materials was separated by ion exchange chromatography, showed that a pink complex containing imine chelate but only three ammine groups (as established by ^{1}H NMR) was present. This species was also formed as the initial product when the isolated imine chelates were allowed to react in basic solution and it has been noted previously that the deprotonated pyruvate imine complex underwent rather rapid NH_3 loss even in the solid state. Hence, it was concluded that in all reactions any nonlinearity in simple first-order kinetic plots[20] could be attributed to product decomposition rather than to the detection of a carbinolamine intermediate. Attempts to follow the cyclization reaction by ^{1}H NMR were complicated by various factors (complex insolubility, an alternative reaction path in concentrated solution[5a]) but also provided no evidence for a species intervening between reactant and tetraammine imine chelate. In a closely related reaction, the cyclization of the aminoacetonepentaamine complex $[(NH_3)_5CoNH_2CH_2COCH_3]^{3+}$,[21] ^{1}H NMR spectroscopy can be very conveniently used to detect the carbinolamine intermediate. The wavelength independence of the present measurements also supports the interpretation offered.[20] Finally, therefore, detailed rate measurements were made only for those complexes (the pyruvate and phenylglyoxylate species) where a sensibly constant absorbance was attained following the initial rapid change. Some more limited data were obtained for the ketomalonate system, where the intrusion of a subsequent reaction was sufficiently insignificant for the minimum absorbance to be used as an "infinity" value giving first-order rate plots linear for at least 3 half-lives. All data are shown in Table I.

Scheme III



It is obvious that the observed pseudo-first-order rate constants do not show a simple linear dependence on hydroxide ion concentration. Nonlinearity of double reciprocal plots ($1/k_{obsd}$ vs. $1/[OH^-]$) of the pyruvate and phenylglyoxylate data also showed that the apparent approach of the rate to independence of base concentration could not be ascribed simply to saturation of a single base-dependent preequilibrium (a reaction mechanism which would lead to the expression $k_{obsd} = a[OH^-]/(1 + b[OH^-])$). The relationship between k_{obsd} and $[OH^-]$ was in fact found to be adequately described by the expression $k_{obsd} = a[OH^-]/(1 + b[OH^-] + c[OH^-]^2)$ for these two systems. The ketomalonate complex data could also be described thus but were too limited to justify fitting to an expression more complicated than $k_{obsd} = a[OH^-]/(1 + b[OH^-])$. Table I shows the agreement between calculated and experimental (k_{obsd}) rate constants for the pyruvate and phenylglyoxylate complexes. Experimental error (greatest in the phenylglyoxylate data as rates in the more concentrated base solutions were close to the limit of instrumental capabilities) was too great to justify close analysis of the values of a, b, and c. A reaction scheme (Scheme III) leading to the given rate law follows.

$$k_{obsd} = \frac{kK_{a3}[OH^-]}{K_W(1 + K_h)} \Bigg/ \left\{1 + \frac{(K_{a3} + K_{a1}K_h)[OH^-]}{K_W(1 + K_h)} + \frac{K_{a1}K_{a2}K_h[OH^-]^2}{K_W^2(1 + K_h)}\right\}$$

Several plausible alternative reaction schemes may, of course, be envisaged. That described is, however, supported by several lines of evidence. The presence of reactant hydrate in the system is readily established. ^{1}H NMR has been used previously to detect ~36% hydrate in the pyruvate complex[11,12] and present measurements of the ^{13}C NMR of the phenylglyoxylate species suggest that approximately equal amounts of the carbonyl form and its hydrate are present in aqueous solution. Acidity constants for several simple carbonyl compound hydrates have been measured and found to be in the range 10^{-10}–10^{-14}.[22] It would be expected that Co(III) would enhance this acidity, probably by a factor $\gtrsim 10^2$ for a site so removed from the metal ion.[23] It would thus be anticipated that saturation of the hydrate OH deprotonation equilibria would occur in preference to saturation of the Co–NH_3 deprotonation

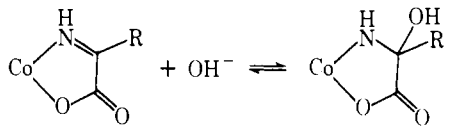
Table I. Observed First-Order Rate Constants for Base-Catalyzed Cyclization of $(NH_3)_5CoO_2C{\cdot}CO{\cdot}R^{2+}$, μ = 1.0 ($NaClO_4$), 25 °C

R	$[OH^-]$, M	10^2k_{obsd}, s^{-1} [a]	10^2k_{calcd}, s^{-1} [f]
$-CO_2^-$	0.100	18.4 (4)[b]	
	0.010	6.86 (3)[b,c]	
	0.001	0.79 (3)[c]	
$-C_6H_5$	0.500	1970 (3)[d]	2000
	0.250	2150 (3)[d]	2041
	0.100	1630 (3)[d]	1724
	0.050	1310 (3)[d]	1300
	0.010	421 (3)[d]	423
	0.001	44.5 (3)[c]	49
$-CH_3$	1.00[e]	294 (1)[c]	300
	0.500	292 (3)[d]	300
		292 (3)[d]	
	0.250	292 (3)[d]	273
		279 (5)[c]	
	0.100	226 (3)[d]	203
		190 (4)[c]	
	0.050	151 (3)[d]	140
		135 (3)[c]	
	0.010	36.0 (2)[d]	40
		37.1 (9)[c]	
	0.001	4.12 (4)[c]	4.4

[a] Average precision better than ±3%. Figures in parentheses indicate number of separate runs. [b] λ 270 nm. [c] λ 280 nm. [d] λ 530 nm. [e] Ionic strength 1.5. [f] Calculated values of the rate constants assuming rate laws: for $-C_6H_5$ $k = 500[OH^-]/(1 + 18[OH^-] + 10[OH^-]^2)$; for $-CH_3$ $k = 45[OH^-]/(1 + 12[OH^-] + 2[OH^-]^2)$.

equilibrium (pK_{a3} = 16).[24] The only possibly anomalous feature of the suggested interpretation is that the values obtained for the parameters *b* and *c* indicate (for both systems) that K_{a1} and K_{a2} are approximately the same.

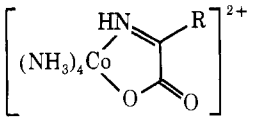
4. Reactivity of the Imine. The most remarkable property of the imine chelates was their ready reaction with base to give



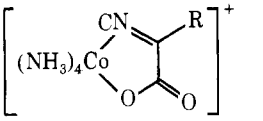
the deeply colored imine NH deprotonated species. That the reaction was one of deprotonation rather than OH^- addition to give a deprotonated carbinolamine was suggested by its rapidity (immeasurably fast for all available equipment, while additions of potent carbon nucleophiles such as CN^- and $CH_2NO_2^-$ were quite slow) and the lack of major shifts in R group ^1H NMR resonances. The methyl signal of the pyruvate derivative, for example, shifts upfield by only ~0.1 ppm in basic solution. Formation of a saturated C center by OH^- addition would presumably cause a much larger upfield shift, the methyl resonances in the carbonyl and hydrate forms of $(NH_3)_5CoO_2CCOCH_3^{2+}$, for comparison, being separated by ~1 ppm. In addition the ^1H NMR spectrum in Me_2SO-d_6 of the only readily isolated base product, V, R = C_6H_5, showed resonances attributable to the phenyl group and four ammine groups only.

Original pK_a measurements[5a] on $[(NH_3)_4\overline{CoNH{=}C(CH_3)CO_2}]^{2+}$ used spectrophotometric methods requiring rapid mixing of complex and buffer solutions and back-extrapolation to determine initial absorbance values. Later measurements were made by simply determining the pH of a 1:1 buffer of the complex and its conjugate base (freshly prepared in N_2-saturated solution). pH readings were found to be stable over at least 2 min, a period in which spectral scanning indicated considerable decomposition. The lower sensitivity of the pH measurement to decomposition was apparently due to the fact that the initial reaction was loss of an NH_3 ligand, a base of similar strength to the complex itself. pK_a values obtained by buffer pH measurement for a range of complexes are given in Table II. These values are all similar but do vary in a manner consistent with the basic electronic properties of the groups R.

Table II. pH Values (25 °C, I = 0.10 ($NaClO_4$)) for 1:1 Buffer Mixtures of i and ii



i



ii

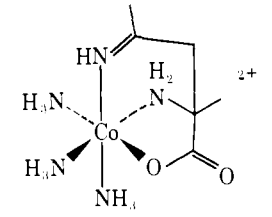
R	pH	R	pH
CH_3-	10.36[a]	$-CO_2$-	9.04
C_6H_5-	9.50	$-CH_2CH_2CO_2$-	10.43
$(CH_3)_3C$-	10.56		

[a] Previous spectrophotometric measurements gave pK_a = 10.5 (I = 1.0, $NaClO_4$, 25 °C).

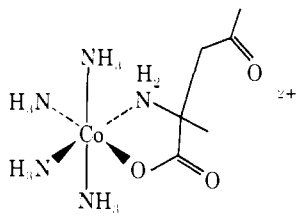
The nitrogen nucleophile exposed on deprotonation of the imine center, where R = CH_3, reacted readily with the active alkylating agents CH_3I, $C_6H_5CH_2Br$, and $CH_2{=}CHCH_2Br$, its reactivity being similar to that of $[(NH_3)_5Co$ imidazolato$]^{2+}$ (pK_a = 10.0).[23]

The reaction was cleaner when the isolated solid deprotonated complexes were used in place of the protonated form plus base and the derivatives isolable in best (nigh quantitative) yield were therefore those of the pyruvate and phenylglyoxylate species. The failure of these N-alkylated complexes to react with base to give an intensely colored solution was additional evidence that the reaction of the NH form with base was one of deprotonation. The complexes did decompose in base, perhaps via the OH^- addition product, and, because of this reaction, accurate rate data on a base-catalyzed reaction of those species with β CH protons (e.g., exchange of β protons of the pyruvate compound with those of solvent) could not be obtained. For $[(NH_3)_4\overline{CoN(CH_3){=}C(CH_3)CO_2}]^{2+}$, however, the approximate half-life for the C-methyl proton exchange at pH 10 and 25 °C was 5 min. The analogous bis(ethylenediamine) complexes are both more acidic and less sensitive to base and therefore provide a much more suitable system for the collection of such data.

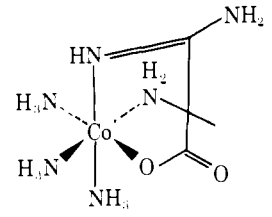
Although rate data for reactions of the free ligand are unknown, it was anticipated (vide supra) that the electrophilic capacities of the imine group carbon would be enhanced by coordination. Indeed, borohydride reduction of and nitromethane addition to the coordinated imines occurred with considerable facility. The BH_4^- reduction provides an efficient preparation of $(NH_3)_4Co$ aa^{2+} complexes (aa = amino acid), which are difficult to prepare in good yield by conventional means. It should be noted that pH control is important in BH_4^- reduction, in that below pH ~6 direct reduction of the Co(III) center (presumably by B_2H_6) is very much faster than reduction of the imine moiety. Also, the addition of CH_3NO_2 is faster than addition of other nitroalkanes. For the most extensively investigated complex, the pyruvate imine chelate, only the reactions with BH_4^- and nitroalkanes provided the simple addition products. With other nucleophiles subsequent intramolecular reactions were observed and the nature of the rate-determining steps remains to be established. Thus, reaction with acetylacetonate ion led to formation of the tridentate ligand complex (X) characterized by X-ray crystallography. Though the intermediate species (Y) is isolable by ion-exchange chromatography of quenched reaction mixtures, in the case of CN^- addition no species has been observed to intervene between the reactant and the amidine product (Z).[25] If the intramolecular attack of coordinated NH_2^- on the $-C{\equiv}N$ of the initial addition product occurs at a rate comparable to that



X



Y



Z

observed for intramolecular amidine formation from aminoacetonitrile complexes,[26] then such is the expected observation. Though the structure of the CN^- reaction product has not been established by X-ray crystallography for the tetraammine complex, this has been done for the (bis(ethylenediamine) analogue[25] and the assignment of the amidine structure to the tetraammine species is based on that result and a ready interpretation of its ^1H NMR spectrum in such terms (see Experimental Section).

Conclusions

The formation of chelated imines by base-catalyzed cyclization of *cis*-ammine(α-ketocarboxylato) complexes provides another example of genuine intramolecular capture of a coordinated nucleophile by unsaturated carbon. An important feature of these reactions is that chelation to a metal is an especially convenient path to isolation of carbonyl compound–ammonia condensation products in the true imine form. Products of the direct organic reaction using simple carbonyl compounds are frequently polymeric (e.g., "aldehyde ammonias") or difficult to isolate. The metal ion may therefore be considered to have a useful role in affecting the stability as well as the reactivity of simple organic molecules. In their Co(III) complexes α-iminocarboxylates show up to three sites of synthetically useful reactivity. Deprotonation of the relatively acidic =NH exposes an active nucleophile which, when consideration is given to the ease of reduction of the C=N moiety, may be considered as equivalent to an especially readily generated amide ion. The imine carbon appears to be a relatively weak electrophile and generation of a carbanion at the α carbon is, of course, limited to species possessing an α-CH, but both offer a potential for exploitation in cyclization reactions also involving the imine nitrogen. Further, the ready juxtaposition of reactive moieties at metal-ion coordination sites not occupied by the imine chelate adds another dimension to considerations of the synthetic utility of the sites of reactivity within the imine. The product of the reaction between the tetraammine pyruvate imine chelate and acetylacetone demonstrates the operation of this fourth factor. In subsequent publications we shall report the results of attempts to systematically evaluate the possibilities for synthetic utilization of the multiple sites of reactivity in α-iminocarboxylate chelates.

References and Notes

(1) This generalization is inaccurate if imine-containing macrocycles (especially highly conjugated species) only are considered. Ligand-centered redox processes have been quite extensively studied with macrocyclic polyimines; see, e. g., N. Takvoryan, K. Farmery, V. Katovic, F. V. Lovecchio, E. S. Gore, L. B. Anderson, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 73i, 3109 (1974); J. C. Dabrowiak and D. H. Busch, *Inorg. Chem.*, **14**, 1881 (1975); M. C. Weiss and V. L. Goedken, *J. Am. Chem. Soc.*, **98**, 3389 (1976). Few simple nucleophilic additions to coordinated imines, macrocyclic or not, have, however, been investigated; see E. D. McKenzie, M. Cressey, and S. Yates, *J. Chem. Soc. A*, 2677 (1971); L. T. Taylor, F. L. Urbach, and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 1072 (1969); V. Katovic, L. T. Taylor, and D. H. Busch, *Inorg. Chem.*, **10**, 458 (1971); E. K. Barefield and F. Wagner, *ibid.*, **12**, 2435 (1973) (footnote 6). For a recent review of reactions of pyridoxaldimine complexes see D. L. Leussing in "Metal Ions in Biological Systems", Vol. 6, H. Sigel, Ed., Marcel Dekker, New York, N.Y., 1975.

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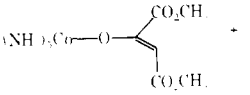
(18) Prepared from reaction between $(NH_3)_5CoOH^{2+}$ and dimethyl acetylenedicarboxylate (DMAD) in Me_2SO. This reaction provided approximately equal amounts of $(NH_3)_5CoO_2C{\cdot}C{\equiv}C{\cdot}OO_2CH_3^{2+}$ and $(NH_3)_5CoMe_2SO^+$, the latter presumably forming via



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