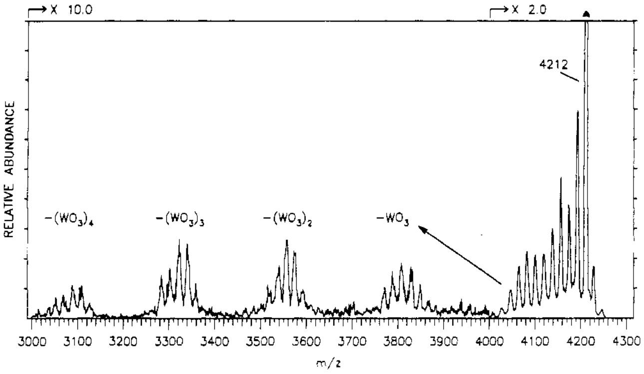

Figure 8. High-mass region in the negative-ion FAB CID MS/MS spectrum of the *m/z* 4212 ion from $(NH_4)_8(FeW_{17}O_{56}F_6NaH_4)\cdot 8H_2O$.

regions than are seen in these spectra.

In order to verify the assignments of the molecular species in the negative-ion spectra, CID mass spectra were obtained for these peaks. The high-mass region of the CID mass spectrum of the cluster centered at *m/z* 4212 in the FAB mass spectrum of the iron complex is shown in Figure 8. The CID mass spectrum for the $(M - H)^-$ of the cobalt complex underwent the appropriate mass shifts but was otherwise very similar. The MS/MS spectrum in Figure 8 clarifies the relationships among the major ions in Figure 6. The CID spectrum has a regular series of abundant fragments, at 18–20-u intervals (average 18.2 u), corresponding to very facile multiple water and HF losses from the molecular ion. This spectrum suggests that accumulation of small-molecule losses leads to the broad maximum observed at *m/z* 4085 (doubly charged, *m/z* 2042.5 in the normal FAB mass spectrum. There are also sequential losses of WO_3. In the CID spectrum, the fine structure due to variations in the total number of oxygens lost is more clear than it is in Figure 6, because the narrow mass window selected by MS-1 limits the width of the isotopic clusters.

These results provide an indication that the MS/MS technique has interesting potential for the elucidation of structural details in large inorganic complexes. The CID mass spectra of these and other types of heteropolytungstate anions are being investigated, and the fragmentation pathways will be discussed more fully elsewhere.

Conclusion

We believe that the structure of the $[XW_{17}O_{56}F_6NaH_4]^{n-}$ anions is that represented in Figure 1.

The X-ray crystallographic determination of the Fe(III) complex located all non-hydrogen atoms of the W_{17} anion. The X-ray powder patterns show that the two compounds are isomorphous. The visible spectrum of the cobalt complex helped us to assign the position of the Co(II) ion as one of the W positions in the two Keggin fragments. Due to the isomorphism of the two compounds, this corresponds to the Fe(III) position in the Fe complex. The electrolytic reduction of the $[CoW_{17}O_{56}F_6NaH_4]^{9-}$ anion substantiates the Keggin-like structure, since only heteropoly complexes with structures closely related to the Keggin structure are known to form heteropoly blues.

The characterization of these two compounds, $(NH_4)_9(CoW_{17}O_{56}F_6NaH_4)\cdot 9H_2O$ and $(NH_4)_8(FeW_{17}O_{56}F_6NaH_4)\cdot 8H_2O$, is another example of the usefulness of fast-atom-bombardment mass spectrometry in the structural determination of heteropolyoxometalate anions. Although chemical analysis indicates the atomic ratio of different elements in the compounds, molecular weight determination by FABMS helped set this ratio at 1:17. The FABMS/MS spectrum verifies the assignment of the molecular anion and demonstrates that the other abundant high-mass ions observed in the spectrum arise from this species by multiple losses of small neutrals.

Acknowledgment. S.H.W. acknowledges support by NIH Grant No. S06-RR08182-09, and C.E.C., support of the MIT Mass Spectrometry Facility under NIH Grant No. RR00317 (to K. Biemann).

Supplementary Material Available: Tables of bond lengths, bond angles, and anisotropic thermal parameters for $(NH_4)_8(FeW_{17}O_{56}F_6NaH_4)\cdot 8H_2O$ (4 pages); a listing of structure factors for the same complex (8 pages). Ordering information is given on any current masthead page.

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Metal Ion Control of Organic Reactivity: Electrophilic and Nucleophilic Reactions of Coordinated 2-Iminopropanoate

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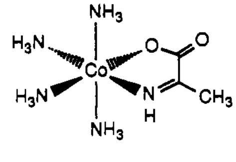
Chelate complexes derived from 2-imino carboxylato ligands contain both electrophilic and nucleophilic sites for reaction. To explore both the utility and control of these properties, reactions of the simple pyruvate imine complex $[(NH_3)_4Co(NH{=}C(CH_3)CO_2)]^{2+}$ with a variety of polyfunctional molecules have been examined. Diethyl oxaloacetate reacts to provide a substituted pyridine, showing that the previously observed reaction of the complex with biacetyl to give a pyrroline can be varied to provide other heterocycles. Reactions with dimethyl acetylenedicarboxylate and methyl vinyl ketone, in contrast, provide branched-chain ligands via cyclization onto the metal center, the pathway for the methyl vinyl ketone reaction being confirmed by a crystal structure determination. Plausible mechanisms for the reactions are discussed in some detail.

Introduction

The simple chelate complex derived from the imine of pyruvate and tetraamminecobalt(III) ion (I) can behave as both an electrophile and a nucleophile.[2] The elementary reactions used to reveal these capacities, however, did not test their exploitation for the formation of more complex organic species. In order to explore them more thoroughly, particularly with regard to heterocycle synthesis, the complex imine has been treated with several bifunctional organic molecules. It is a new way to carry out what is essentially iminium ion chemistry with a remarkably stable



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iminium ion. Previous studies have shown that the metal ion activates the imine carbon atom to attack by a nucleophile as well as making the imine NH and CH_3 groups more acidic. The possibility therefore exists of ready access to the imine nitrogen and methyl carbanion as nucleophiles and the imine carbon as an electrophile in reaction processes with a polyfunctional molecule. Quite complex reactions and syntheses then become possible about the metal ion as a template. Although the reactions described below are exclusively those of the pyruvate imine complex (I), this is largely because of its convenience of synthesis and not because it has properties unlike those of other imino carboxylate chelates. Some preliminary aspects of this work have been published previously.[3,4]

Experimental Section

^1H and ^{13}C NMR spectra were obtained with JEOL MH 100 Minimar and FX60 instruments, respectively. Chemical shifts are given (ppm) relative to tetramethylsilane (TMS), sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DDS), and dioxane. Visible spectra (given as λ_{max} (nm) and ϵ (M^{-1} cm^{-1})) were recorded with a Cary-Varian 118 C spectrophotometer. All evaporations were conducted at ~20-mm pressure by using a Buchi rotary evaporator with a bath temperature always <45 °C.

Salts of the tetraammine(2-iminopropanoato)cobalt(III) ion $\{[(NH_3)_4Co(HN{=}C(CH_3)CO_2)]^{2+}\}$ were prepared as described previously.[2] Acetylacetone, biacetyl, dimethyl acetylenedicarboxylate, methyl vinyl ketone, and sodium diethyl oxaloacetate were all commercial products and were used without purification.

Reaction with Biacetyl. In basic solution in the presence of biacetyl, both reactant and product reduced slowly to Co(II) species. Hence, the preparative procedure was optimized with respect to the product mass even though this mixture was maximized when only ~50% of reactant had been used. The initial report of this synthesis[3] described very basic conditions where decomposition was more extensive.

Carbonate buffer ($[Na_2CO_3]$ = $[NaHCO_3]$ = 0.5 M, pH ~ 10, 5 mL) was added to a solution of biacetyl (5 mL) and $[(NH_3)_4Co(HN{=}C(CH_3)CO_2)]Cl_2$ (3 g) in water (50 mL) and the solution stirred for 60 min at room temperature. Glacial acetic acid (5 mL) was added to quench reaction and the solution then diluted to 200 mL with water and absorbed on H^+ Dowex 50W-X2 resin. The column was washed well with water and eluted with 1 M HCl to remove some Co^{2+} followed by orange Co(III) complexes. The Co(III) eluate was taken to dryness under vacuum and the residue rechromatographed on Na^+ SP Sephadex C25 resin (~60 cm × 7 cm diameter column) by using 0.1 M NaCl as eluant. Two bands were obtained, the complexes in both being recovered as solids by absorbing the eluates on H^+ Dowex 50W-X2, eluting with 1 M HCl, and taking these HCl eluates to dryness under vacuum. The trailing band proved to be reactant (1.5 g). The leading band material (1.0 g) was precipitated as the perchlorate salt by addition of concentrated $HClO_4$ to an aqueous solution of the eluate residue and was then recrystallized from water. Physical characterization has been reported previously.[2]

Reaction with Acetylacetone. The simple procedure previously[4] outlined, precipitation of the perchlorate salt directly from the reaction mixture, is the most convenient method for isolation of the principal reaction product. Several very minor constituents of the reaction mixture can, however, be isolated by chromatography of the whole solution. Because of their low abundance and some apparent reaction during chromatographic separation and isolation, these complexes were not fully characterized. On the basis of comparisons of ^1H NMR spectra, however, at least one component was simply the product of base-catalyzed NH_3 loss from the reactant.[2] Another was most readily isolated in a pure form at early reaction times (~30 min) when unchanged reactant, which preceded it on H^+ Dowex 50W-X2 resin under elution with 1 M HCl, was the only other species detectable. It gave a ^1H NMR spectrum and analyses consistent with the tetraamminecobalt(III) chelate of 2-amino-2-methyl-4-oxopentanoic acid (i.e. the ketone precursor of the final product).[4] Anal. Calcd for $CoC_5H_{22}N_5O_{11}Cl_2$: C, 17.75; H, 5.46; N, 17.25. Found: C, 17.5; H, 5.5; N, 17.2. ^1H NMR δ 1.26 (3 H, CH_3 on saturated carbon), 2.10 (3 H, CH_3 on unsaturated carbon), 2.90 (3 H, NH_3), 3.03, 3.09 (doublet, 2 H, CH_2 group—appears as an AB quartet in D_2O), 2.40, 2.53, 2.83 (each 3 H, 3 NH_3), 5.54, 5.65, 5.86, 5.98 ppm (broad AB quartet, NH_2 group) in DMSO-d_6 vs TMS.

Reaction with Sodium Diethyl Oxaloacetate. As in the reaction with acetylacetone, a number of minor species were detected chromatographically in the reaction mixture along with the principal product. These materials were characterized only by measurement of ^1H NMR spectra of ion-exchange eluate residues.

Sodium diethyl oxaloacetate (8.4 g) was dissolved in a solution of $[(NH_3)_4Co(HN{=}C(CH_3)CO_2)]Cl_2$ (3 g) in water (100 mL). The precipitate, which formed immediately (presumably the salt of the complex cation and the enolate anion), was dissolved by the addition of acetone (40 mL). The solution so formed was allowed to stand for 24 h at room temperature before being acidified to pH 5 with glacial acetic acid, diluted to 500 mL with water, and absorbed on Na^+ SP Sephadex C25 resin. Elution with 0.05 M sodium citrate revealed at least six components, the first being a small quantity of Co(II) and the last a trace of reactant. These complexes were obtained as solids by absorbing the citrate eluate on H^+ Dowex 50W-X2 resin, eluting with 3 M HCl, evaporating the HCl eluates, and crystallizing the residues from dilute HCl by addition of ethanol and acetone. The second fraction gave red platelets (0.9 g), and the fourth, clusters of fine, pink needles (0.6 g). Analyses and NMR spectra were consistent with the two complexes being related as ethyl ester to free carboxylic acid. ^1H NMR: F2, δ 3.89, 4.00 (barely separated broad resonances, 12 H, 4 NH_3), 7.57, 7.60 (sharp, 1 H), 7.86, 7.89 (sharp, 1 H) relative to DSS in 0.1 M DCl; F4, δ 1.34, 1.41, 1.48 (triplet 3 H, CH_3 of ethyl group), 3.90, 4.02 (barely separated broad resonances, total 12 H, 4 NH_3), 4.35, 4.42, 4.49, 4.55 (quartet, 2 H, CH_2 of ethyl group), 7.64, 7.66 (sharp doublet, 1 H), 7.92, 7.94 (sharp doublet, 1 H) relative to DSS in 0.1 M DCl. ^{13}C NMR (F2): Seven distinct resonances at δ 21.5, 24.0, 72.4, 76.7, 93.5, 98.5, and 101.2 in 0.1 M DCl (broad-band proton decoupled). Anal. Calcd for $CoC_7H_{16}N_5O_5Cl_2{\cdot}H_2O$, F2: Co, 14.80; C, 21.12; H, 4.55; N, 17.59. Found: Co, 14.6; C, 21.3; H, 5.1; N, 17.6. Calcd for $Co_9H_{20}N_5O_5Cl_2{\cdot}1^1/^2H_2O$, F4: Co, 13.61; C, 24.97; H, 5.35; N, 16.18. Found: Co, 13.7; C, 24.8; H, 5.0; N, 16.2.

The other components of the reaction mixture partially decomposed during the chromatographic treatment, and because of this and the very small amounts present, they were not fully characterized. ^1H NMR spectra of eluate residues showed, however, broad AB quartet resonances near δ 5.5–6.0 attributable to the NH_2 groups of carbanion addition products.[3]

Reaction with Dimethyl Acetylenedicarboxylate (DMAD). A number of simple preparative procedures were investigated in attempts to minimize reactions between DMAD and the bases used to generate $[(NH_3)_4Co(N{=}C(CH_3)CO_2)]^+$. Use of excess DMAD was nonetheless found necessary in all instances.

NaOH (4 M, 0.63 mL) was added to a solution of $[(NH_3)_4Co(HN{=}C(CH_3)CO_2)](ClO_4)_2$ (1.1 g) in water (40 mL). Methanol (10 mL) and DMAD (1 mL) were added immediately, and the solution was stirred for 5 min as it rapidly became intensely red-brown in color. $HClO_4$ (12 M, 2 mL) was then used to quench reaction and the solution absorbed on a column of H^+ Dowex 50W-X2 resin after dilution to 500 mL with water. The column was washed well with water and then eluted with 1 M HCl. Following removal of a trace of Co^{2+}, a broad orange band was collected and the eluate taken to dryness under vacuum. A ^1H NMR spectrum of the residue (0.7 g) implied the presence of ~30% reactant, and this was separated out by chromatography on Na^+ SP Sephadex C25 using 0.1 M NaCl as eluant. The leading pink band was absorbed on H^+ Dowex 50W-X2 resin and the complex obtained by elution with 1 M HCl and evaporation of the eluate to dryness under vacuum. It was then crystallized as the perchlorate salt by dissolution in water (2 mL), addition of $HClO_4$ (12 M, 0.5 mL), and cooling to 0 °C. Clusters of pink needles, which powdered when washed with ethanol, were obtained. Analyses were consistent with a mixture of di- and unipositive forms, and a method of crystallizing either species pure was not found. ^1H NMR: δ 2.24 (3 H, $=CCH_3$), 3.16 (3 H, broad, NH_3), 3.60 (sharp), ~3.66 (broad ($-CO_2CH_3$ superimposed on 2 NH_3, total 9 H), 6.96 (1 H, sharp).

In some preparations of this complex, a trace orange component was observed to precede it on SP Sephadex columns. The amount of this material present varied depending on the length of time for which the reaction products had been kept in acid solution, and indeed, over a long period (days at room temperature) the pink reaction product could be completely converted to the orange. The orange complex was readily crystallized from water by addition of $HClO_4$. Anal. Calcd for $CoC_6H_{18}N_5O_{12}{\cdot}H_2O$: Co, 11.79; C, 14.41; H, 4.03; N, 14.01; Cl, 14.18. Found: Co, 12.2; C, 14.3; H, 4.0; N, 14.2; Cl, 14.2. ^1H NMR: δ 2.30 (3 H, sharp, $=CCH_3$), 3.06 (3 H, broad, NH_3), 3.60 (6 H, broad, 2 NH_3), 3.86 (3 H, broad, NH_3), 5.88 (1 H, sharp doublet, $=CH$), 6.52 (1 H, sharp doublet, $=CH$) in D_2O relative to DSS.

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Table I. Crystal Data and Details of Data Collection

formula: $CoC_{11}H_{26}I_2N_5O_3$	radiation: Cu Kα_1
appearance: yellow-brown tablets	$\lambda = 1.5405$ Å
cryst system: monoclinic	monochromator: graphite cryst
space group: $P2_1/n$; No. 14	abs coeff = 311.15 cm^{-1}
$a = 7.572$ (5) Å	scan range: $3° \leq 2\theta \leq 125°$
$b = 16.358$ (9) Å	$N = 3812$
$c = 16.610$ (9) Å	$N_o = 2278$
$\beta = 96.03$ (2)°	$R = 0.047$
$V = 2045$ Å^3	$R_w = 0.057$
$Z = 4$	"standard" reflcn indices: $(03\bar{7})$, (431), (095)
$D_{obs} = 1.90$ (1) g mL^{-1}	cryst stability: anisotropic decay of 3.5, 2.0, and 1.7%, respect[a]
$D_{calc} = 1.91$ g mL^{-1}	
specimen size: 0.135 × 0.105 × 0.245 mm	
temp = 20 (1) °C	

[a] For each of the three "standard" reflections.

Reaction with Methyl Vinyl Ketone (MVK). As in all the above reactions, the conditions used to achieve reaction with MVK led to both some loss of NH_3 ligand from the reactant and some reduction of Co(III) to Co(II) species. Thus, although MVK underwent consecutive reactions with $[(NH_3)_4Co(HN{=}C(CH_3)CO_2]^{2+}$, extensive conversion to the second species could not be achieved, although the 1:1 initial adduct could be isolated in good yield. Conditions leading to appreciable amounts of both products were as follows:

MVK (10 mL, 90% aqueous solution) was added to a solution of $[(NH_3)_4Co(HN{=}C(CH_3)CO_2)](ClO_4)_2$ (2.1 g) in water (50 mL) plus carbonate buffer ($[CO_3^{2-}] = [HCO_3] = 0.5$ M, pH ~ 10, 5 mL) and the solution left to stand at room temperature for 90 min. Acetic acid was added to quench reaction (pH 5) and the solution diluted to 200 mL and absorbed on H^+ Dowex 50W-X2 resin. The column was eluted with 1 M HCl, any rapidly removed Co^{2+} being discarded and the slowly eluted yellow products being collected as a single band before evaporation to dryness. The residue was dissolved in water and absorbed on Na^+ SP Sephadex C25 resin, and the column was eluted with 0.1 M NaBr. The first fraction was a minor yellow band, the complex being recovered as the chloride salt by absorption on H^+ Dowex 50W-X2 resin, elution with 1 M HCl, and evaporation of this eluate. It was recrystallized from dilute HCl by slow addition of acetone (0.2 g). Bromide and iodide salts were readily obtained by metathesis with the appropriate sodium salt in water. For structure determination, crystals of the iodide salt were grown by slow evaporation of a dilute aqueous solution. Anal. Calcd for $CoC_{11}H_{26}N_5O_3I_2$: Co, 10.00; C, 22.43; H, 4.45; N, 11.89; I, 43.08. Found: Co, 9.9; C, 22.1; H, 4.5; N, 11.7; I, 43.3. (2:1 adduct.) ^{1}H NMR: δ 1.79, 1.87, 1.95, 2.02, 2.09 (quintet, 2 H), 2.28 (3 H), 2.76 (3 H), 2.84, 2.91, 2.98, 3.03, 3.11, 3.18 (4 H, two triplets), ~3.40 (5 H, broad NH_3 resonance + superimposed triplet), ~4.30 (5 H, broad NH_3 resonance + superimposed triplet), 10.48 ppm (1 H, broad) vs DSS in 1 M DCl. Visible spectrum (λ_{max}, ϵ_{max}): 466, 115 in 1 M HCl.

A second yellow band from the SP Sephadex column contained the bulk of the product. The complex was recovered as the chloride salt as above and converted to the perchlorate by precipitation from aqueous solution with $HClO_4$. Recrystallization from water gave large yellow needles (1.5 g). Anal. Calcd for $CoC_7H_{20}N_5Cl_2O_{10}$: Co, 12.70; C, 18.12; H, 4.34; N, 15.09; Cl, 15.28. Found: Co, 12.8; C, 18.2; H, 4.5; N, 15.0; Cl, 15.0. (1:1 adduct.) ^{1}H NMR: δ ~2.70 (multiplet, 6 H), ~3.4 (5 H, triplet superimposed on broad NH_3 resonance), 4.06, 4.11, 4.17, and 4.26 (5 H, triplet just separated broad NH_3 resonance), 10.1 ppm (1 H, broad) vs DSS in 1 M DCl. Visible spectrum (λ_{max}, ϵ_{max}): 466, 113 in 1 M HCl.

In some preparations, trace amounts of the reactant were detected as a third band from SP Sephadex/0.1 M NaBr.

Collection and Reduction of X-ray Intensity Data. Approximate unit cell dimensions for crystals of $[Co(NH_3)_3\{O_2CC(CH_2CH_2CH_2COCH_3){=}NCH_2CH_2C(CH_3){=}NH\}]I_2$ were obtained from preliminary Weissenberg (*h*0*l*, *h*1*l* data) and precession (0*kl*, 1*kl*, *hk*0, *hk*1 data) photographs, which showed systematic absences corresponding to the space group $P2_1/n$, a nonstandard setting of space group $P2_1/c$ (C_{2h}^5, No. 14). The crystal chosen for data collection was transferred to a Picker FACS-I fully automatic four-circle diffractometer and was aligned in a random orientation. The unit cell dimensions (and estimated standard errors) and crystal orientation matrix were obtained from the least-squares refinement[5] of the 2θ, ω, χ, and ϕ values obtained for 12 carefully centered high-angle reflections ($2\theta > 82°$). Crystal data and details of data collection methods used are given in Table I. Reflection intensities were reduced to values of $|F_o|$, and each reflection was assigned an individual estimated standard deviation $\sigma(F_o)$.[6] For this data set, the instrumental "uncertainty" factor (p)[7] was assigned a value of $(0.002)^{1/2}$. Slight crystal decomposition observed during data collection was assumed to be anisotropic but 2θ independent, and reflection data were corrected for decomposition by using program SETUP3.[8] The reflection data were sorted to a convenient order, equivalent reflection forms were averaged, and those reflections with $I < 3\sigma(I)$ were discarded.[6] The statistical R factor (R_S) for the 2278 reflections of the terminal data set is 0.027.

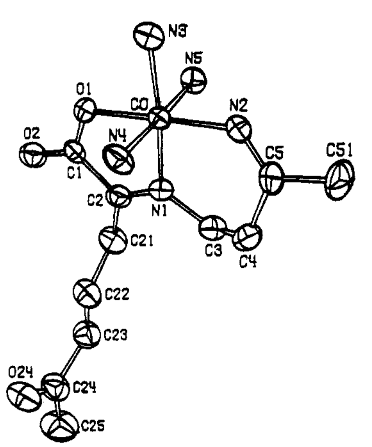

Figure 1. Crystal structure of the complex cation in $[Co(NH_3)_3\{O_2CC(CH_2CH_2CH_2COCH_3){=}NCH_2CH_2C(CH_3{=}NH\}]I_2$. For clarity, hydrogen atoms have been omitted. The unit cell structure is available in the supplementary material.

Solution and Refinement of the Structure. Normalized structure factors were generated by using program EPROG.[9] The structure was solved by using the MULTAN[10] series of programs to calculate a set of five starting phases used to assign phases to 296 reflections with $|E| > 1.40$, which were then used as coefficients in a Fourier synthesis. The resulting "*E* map" showed the cobalt and iodine positions, and the remaining atoms were located from successive difference Fourier syntheses. From data corrected for absorption, the structure was refined by block-diagonal least-squares methods to final unweighted R factors of 0.047 (R) and 0.056 (R_w), respectively.[7] Atomic scattering factors for the non-hydrogen atoms were taken from the compilation of Cromer and Mann[15] and corrected for the real and imaginary parts of anomalous scattering.[16]

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(5) The programs contained in the Picker Corp. FACS-I disk operating system (1972) were used for all phases of diffractometer control and data collection.

(6) The formulas used in data reduction are: Lp (Lorentz–polarization factor) = $(\cos^2 2\theta + \cos^2 2\theta_m)/2 \sin 2\theta$, where θ and θ_m (=13.25°) are the reflection and monochromator Bragg angles, respectively; I (net peak intensity) = $[CT - (t_p/t_b)(B_1 + B_2)]$, where CT is the total peak count in t_p (s) and B_1 and B_2 are the individual background counts in $(t_b/2)$ (s); $\sigma(I)$ (reflection significance) = $[CT + (t_p/t_b)^2(B_1 + B_2)]^{1/2}$; $\sigma(F_o)$ (the reflection esd) = $\{[\sigma(I)/Lp]^2 + (p|F_o|^2)^2\}^{1/2}/2|F_o|$; $\sigma_S(F_o)$ (the reflection esd from counting statistics only) = $\sigma(I)/2(Lp)(|F_o|)$; R_S (statistical R factor) = $\sum\sigma_S(F_o)/\sum|F_o|$.

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(9) Programs SETUP3 and EPROG were written locally for a Univac-1108 computer (P. O. Whimp). The sorting (SORTIE), Fourier (ANUFOR), and block-diagonal least-squares (BLKLSQ) programs used have been described previously.[11] Absorption corrections were carried out by using TOMPAB, a locally modified version of the Brookhaven National Laboratory absorption correction program.[12] Figures were produced by using ORTEP,[13] while bond lengths and angles, together with their estimated standard deviations, were calculated by using ORFFE.[14]

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Table II. Fractional Atomic Positional and Thermal Parameters for $[Co(NH_3)_3\{O_2CC(CH_2CH_2CH_2COCH_3){=}NCH_2CH_2C(CH_3){=}NH\}]I_2$

atom	x/a	y/b	z/c	B, Å^2
		(a) Refined Positional Parameters		
Co	0.16490 (16)	0.16038 (8)	0.00387 (7)	
I(1)	0.74093 (9)	0.33384 (4)	0.07935 (5)	
I(2)	0.30349 (11)	0.21440 (5)	0.28234 (4)	
O(1)	0.2012 (7)	0.0449 (3)	0.0113 (3)	
O(2)	0.3152 (8)	−0.0570 (4)	−0.0534 (4)	
O(24)	0.9472 (9)	0.0205 (5)	−0.1934 (4)	
N(1)	0.2775 (8)	0.1499 (4)	−0.0933 (4)	
N(2)	0.1340 (9)	0.2744 (4)	−0.0068 (4)	
N(3)	0.0425 (9)	0.1571 (4)	0.1027 (4)	
N(4)	0.3956 (9)	0.1768 (4)	0.0694 (4)	
N(5)	−0.0677 (9)	0.1415 (4)	−0.0591 (4)	
C(1)	0.2765 (10)	0.0154 (5)	−0.0469 (5)	
C(2)	0.3128 (11)	0.0756 (5)	−0.1127 (5)	
C(3)	0.2968 (12)	0.2184 (6)	−0.1495 (6)	
C(4)	0.3403 (14)	0.2975 (6)	−0.1058 (6)	
C(5)	0.2074 (13)	0.3252 (5)	−0.0510 (6)	
C(21)	0.3856 (13)	0.0486 (6)	−0.1879 (5)	
C(22)	0.5844 (13)	0.0516 (6)	−0.1815 (5)	
C(23)	0.6541 (13)	0.0293 (6)	−0.2616 (5)	
C(24)	0.8527 (13)	0.0200 (6)	−0.2576 (6)	
C(25)	0.9230 (17)	0.0058 (9)	−0.3369 (6)	
C(51)	0.1664 (17)	0.4172 (6)	−0.0499 (7)	
		(b) Calculated Hydrogen Coordinates and Fixed Isotropic Thermal Parameters[a]		
NH(2)	0.058	0.296	0.023	2.9
H(3A)	0.189	0.225	−0.183	3.8
H(3B)	0.390	0.206	−0.182	3.8
H(4A)	0.350	0.339	−0.145	4.2
H(4B)	0.451	0.291	−0.074	4.2
H(21A)	0.340	0.083	−0.231	3.8
H(21B)	0.348	−0.006	−0.199	3.8
H(22A)	0.631	0.014	−0.141	3.9
H(22B)	0.623	0.105	−0.167	3.9
H(23A)	0.619	0.071	−0.300	4.2
H(23B)	0.601	−0.021	−0.280	4.2

[a] Hydrogen atoms are numbered according to the nitrogen [NH(n)] or carbon [C(n)] atoms to which they are bonded.

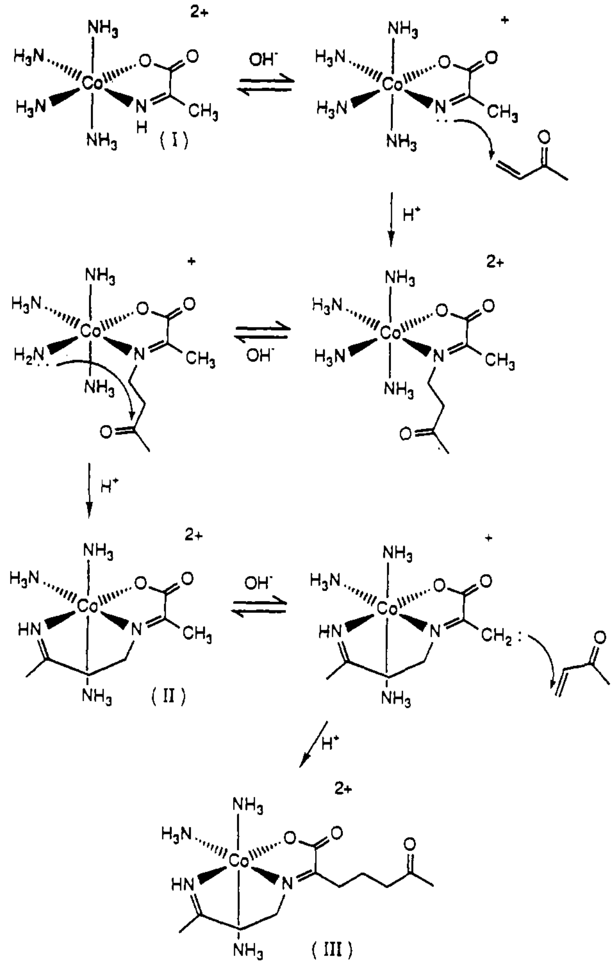
Hydrogen atom scattering factors were taken from the compilation of Stewart et al.[17] A full account of the course of refinement is included in the supplementary material (Table SUP-1).

When fixed hydrogen atom coordinates were included in the scattering model, the C–H and N–H distances were assumed to be 0.95 and 0.87 Å, respectively.[18] The hydrogen atoms were assigned fixed isotropic temperature factors 10% greater than the equivalent isotropic temperature factor of the carbon or nitrogen atom to which they were bonded. Hydrogen atom coordinates were recalculated prior to each refinement cycle. No attempt was made to include either the six methyl hydrogen atoms or the nine ammine hydrogen atoms in the scattering model.

On the final cycle of least-squares refinement, no individual parameter shift was greater than 0.02 of the corresponding parameter esd (estimated standard deviations derived from inversion of the block-diagonal matrices). A final electron-density difference map showed no unusual features, and the largest residual peak on the map was one of 0.9 e/Å^3 close to one of the iodide anions. The standard deviation of an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|^2/(m - n)]^{1/2}$ (where m is the number of observations and n (=100) is the number of parameters varied), is 1.71, cf., an expected value of 1.0 for ideal weighting. Comparison of the final $|F_o|$ and $|F_c|$ values showed no evidence of serious extinction effects, and there is no serious dependence of the minimized function on either $|F_o|$ or $\lambda^{-1}\sin\theta$.

The final atomic positional parameters, together with their estimated standard deviations (where appropriate) are listed in Table II. A listing of observed and calculated structure factor amplitudes [×10 (electrons)] is available along with that of anisotropic thermal parameters and of best least-squares planes[19] as supplementary material (Tables SUP-2–SUP-4).

Scheme I. Reaction Pathways for the Consecutive, Base-Catalyzed Additions of Methyl Vinyl Ketone to $[Co(NH_3)_4(HN{=}C(CH_3)CO_2)]^{2+}$



Results and Discussion

Structure of the Product of Condensation of $[(NH_3)_4CoNH{=}C(CH_3CO_2)]^{2+}$ with Methyl Vinyl Ketone. The crystals contain the complex cation $[Co(NH_3)_3$(7-aza-6 carboxy-10-imino-undec-6-en-2-one)$]^{2+}$ as shown in Figure 1. The complex cation has neither crystallographic nor virtual symmetry higher than C_1 but has essentially octahedral geometry about the central metal ion. Three meridional sites at the cobalt are occupied by coordinated ammonia groups; the three remaining coordination sites are occupied by the carboxyl and two imine centers of the tridentate ligand. In Figure 1 the thermal ellipsoids have been drawn to include 50% of the probability distribution and, for clarity, the hydrogen atoms have been omitted.

Principal bond distances and interbond angles, together with their estimated standard deviations, are listed in Table III. It should be noted that the effects of atom–atom correlations have been neglected both in the block-diagonal least-squares refinement process and also in the subsequent calculation of bond length and interbond angle estimated standard deviations. Consequently, the tabulated values of bond length and angles esd's are almost certainly underestimated.

Scheme I outlines the sequence of reactions believed to be involved in the formation of the 1:1 (II) and structurally characterized 2:1 (III) adducts of methyl vinyl ketone with the imine complex I. Clearly, complex III results from the addition of both nitrogen and carbon nucleophiles from I to the activated olefin but the structure determination does not, of course, establish the order of these additions. The ^{1}H NMR spectrum of II, however, showing the loss of the very low field imine NH resonance typical of 2-imino carboxylate chelates,[2] retention of the original imine methyl resonance, and loss of one ammonia resonance, demonstrates that the first addition must be by the nitrogen nucleophile.

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(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(18) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(19) The method used for calculating weighted least-squares planes is described by: Blow, C. M. *Acta Crystallogr.* **1960**, *13*, 168.

Table III. Bond Lengths and Interbond Angles

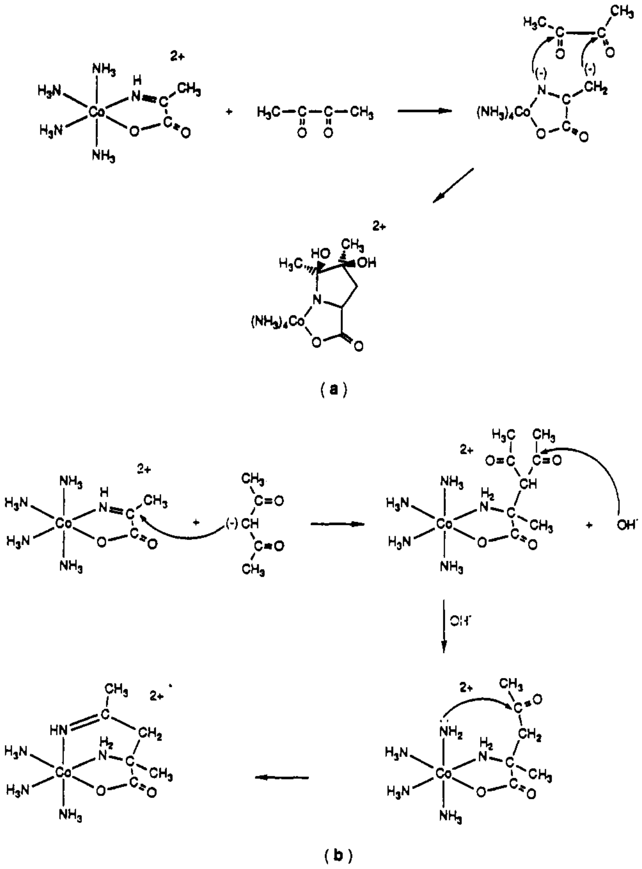
		(a) Bond Lengths, Å			
Co–O(1)	1.911 (5)	Co–N(1)	1.911 (7)	Co–N(2)	1.885 (7)
Co–N(3)	1.969 (7)	Co–N(4)	1.977 (7)	Co–N(5)	1.975 (7)
O(1)–C(1)	1.269 (10)	O(2)–C(1)	1.228 (10)	C(1)–C(2)	1.518 (12)
C(2)–N(1)	1.293 (11)	N(1)–C(3)	1.476 (12)	C(3)–C(4)	1.503 (13)
C(4)–C(5)	1.497 (15)	C(5)–N(2)	1.275 (12)	C(5)–C(51)	1.537 (13)
C(2)–C(21)	1.486 (13)	C(21)–C(22)	1.499 (14)	C(22)–C(23)	1.525 (13)
C(23)–C(24)	1.506 (14)	C(24)–O(24)	1.220 (12)	C(24)–C(25)	1.489 (16)
		(b) Interbond Angles, deg			
O(1)–Co–N(1)	83.8 (3)	O(1)–Co–N(2)	177.9 (3)	O(1)–Co–N(3)	89.8 (3)
O(1)–Co–N(4)	89.2 (3)	O(1)–Co–N(5)	89.6 (3)	N(1)–Co–N(2)	94.1 (3)
N(1)–Co–N(3)	173.1 (3)	N(1)–Co–N(4)	91.7 (3)	N(1)–Co–N(5)	89.5 (3)
N(2)–Co–N(3)	92.3 (3)	N(2)–Co–N(4)	90.6 (3)	N(2)–Co–N(5)	90.6 (3)
N(3)–Co–N(4)	90.6 (3)	N(3)–Co–N(5)	88.0 (3)	N(4)–Co–N(5)	178.2 (3)
Co–O(1)–C(1)	113.6 (5)	Co–N(1)–C(2)	114.7 (6)	Co–N(1)–C(3)	123.3 (5)
Co–N(2)–C(5)	129.9 (6)	O(1)–C(1)–O(2)	124.4 (8)	O(1)–C(1)–C(2)	115.6 (7)
O(2)–C(1)–C(2)	120.0 (7)	C(1)–C(2)–N(1)	111.9 (7)	C(1)–C(2)–C(21)	121.7 (8)
C(21)–C(2)–N(1)	126.4 (8)	C(2)–N(1)–C(3)	121.3 (7)	N(1)–C(3)–C(4)	112.3 (7)
C(3)–C(4)–C(5)	115.3 (8)	C(4)–C(5)–N(2)	121.1 (8)	C(4)–C(5)–C(51)	116.9 (8)
C(51)–C(5)–N(2)	122.0 (9)	C(2)–C(21)–C(22)	112.9 (7)	C(21)–C(22)–C(23)	111.6 (7)
C(22)–C(23)–C(24)	114.9 (8)	C(23)–C(24)–C(25)	115.2 (8)	C(23)–C(24)–O(24)	121.9 (9)
O(24)–C(24)–C(25)	122.9 (9)				

It is not necessary, of course, that this addition be an intermolecular process, since it is conceivable that the carbonyl group of methyl vinyl ketone is first attacked by a deprotonated, coordinated ammine (trans to carboxylate O) and the deprotonated imine NH then adds intramolecularly to the olefinic group. Our studies of intramolecular nucleophilic additions to olefins[20] suggest, however, that such a reaction would actually be slow, and given the great difference in acidity between coordinated imine NH and NH_3,[2] it seems more plausible that intermolecular addition of imine N to the olefin is the first reaction step. An intramolecular condensation giving the tridentate diimine via well-characterized processes would follow, though it is not obvious why this condensation route is preferred to that resulting in a dihydropyridine by attack of the original deprotonated imine methyl carbanion on the ketone carbonyl group. We have no direct information concerning the relative acidity of the NH_3 and CH_3 groups, though, if proton exchange rates are taken as an index,[21,22] the NH_3 group is expected to be more extensively deprotonated at a given pH, and this factor alone may explain the observed reaction pathway.

Compound II, like the reactant I, has both imine NH and CH_3 sites at which potent nucleophiles may be exposed by deprotonation. The imine NH is expected to be much less acidic than in I, however,[2,3] and it is therefore not surprising that reaction of II with methyl vinyl ketone occurs via the methyl group originating from I. Presumably the carbanionic center would be a more reactive nucleophile in any case, and this greater nucleophilicity may even overwhelm unfavorable differences in acidity.

No evidence was obtained for facial forms of the tridentate ligand complex though in the 1:1 adduct the methyl group ^1H NMR resonances displayed a complexity that could not be fully explained. In part, the fine structure of the resonances arose from four-bond coupling of the six-membered ring imine NH to its methyl group protons (demonstrated by both decoupling and deuteration experiments). This effect identifies the new imine methyl group as that with the slightly lower field resonances. Decoupling experiments did not eliminate the poorly resolved multiplicity of the pyruvate imine methyl resonance. The only rationalization we can offer is the possibility of some relatively slow conformational interconversion within the adjacent six-membered ring. The effect is solvent dependent, since in acetone-d_6 both methyl groups appear as sharp singlets.

Scheme II. Reaction Pathways for Condensations of (a) Biacetyl and (b) Acetylacetone with $[Co(NH_3)_4(HN{=}C(CH_3)CO_2)]^{2+}$ in Basic Media



The crystal structure of the 2:1 adduct closely compares with those of related Co(III) complexes.[3,4] The Co–N(NH_3) distances, equal within the error (3σ), average 1.974 Å. The Co–N imine distances are significantly shorter than those of the saturated Co–N and reflect the different σ-bond radii of the sp^2 and sp^3 centers. The Co–O distance also agrees with those observed in related structures,[3,4,23,24] and the carboxyl group is polarized (C(1)–O(1)

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[20] Gahan, L. R.; Harrowfield, J. MacB.; Herlt, A. J.; Lindoy, L. F.; Whimp, P. O.; Sargeson, A. M. *J. Am. Chem. Soc.* **1985**, *107*, 6231.

[21] Jackson, W. G.; Sargeson, A. M. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, Essay II, p 273.

[22] Buckingham, D. A.; Marzilli, P. A.; Sargeson, A. M. *Inorg. Chem.* **1969**, *8*, 1595.

[23] Buckingham, D. A.; Cresswell, P. J.; Dellaca, R. J.; Dwyer, M.; Gainsford, G. J.; Marzilli, L. G.; Maxwell, I. E.; Robinson, W. T.; Sargeson, A. M.; Turnbull, K. R. *J. Am. Chem. Soc.* **1974**, *96*, 1713.

is significantly longer than C(1)–O(2)), unlike uncoordinated carboxyl groups, which are equal within the error.[25]

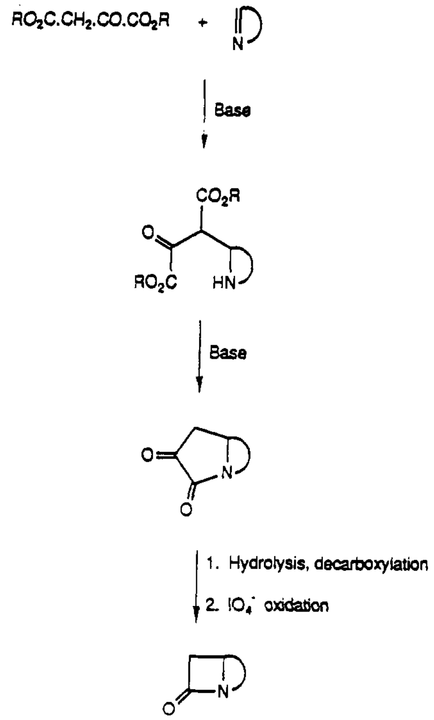
The C=N imine bond lengths are equal within experimental error but are substantially longer than the value of 1.252 (7) Å observed for the $[Co(NH_3)_3\{HN{=}C(CH_3)CH_2C(CH_3)(NH_2)(CO_2)\}]^{2+}$ cation.[4] In $H_2NCH{=}NOH$,[26] where there is evidence that the C–N bond order is significantly less than 2, the C=N distance is 1.30 (1) Å. However, within the tridentate ligand, the remaining C–N and C–O distances are all close to expected values.

Condensations with Biacetyl and Acetylacetone. The essence of the chemistry observed in these reactions has been discussed in previous publications.[3,4] Reaction pathways are depicted in Scheme II. For acetylacetone, it is considered that reaction is initiated by attack of its enolate carbon on the imine center. In the final product, one acetyl group of acetylacetone has been cleaved. It appears that this cleavage must occur prior to condensation of the other acetyl group with coordinated ammonia, since the reaction intermediate isolated in the present work is, on the basis of its ^1H NMR spectrum, the cleaved but uncondensed species. The ready formation of enolates from β-diketones and the resistance of the enolates toward nucleophilic addition may explain both why the initial observed reaction is enolate addition to the imine (and not condensation of coordinated ammonia with acetylacetone carbonyl groups) and why intramolecular condensation rapidly follows cleavage of the initial addition product. Obviously, the interplay of rate and equilibrium acidity factors in reactions such as these is very complex, since we have previously demonstrated that inter- and intramolecular additions of coordinated hydroxide to acetylacetone are very facile. Here, of course, it is possible to generate high concentrations of the coordinated nucleophile under conditions where negligible conversion of acetylacetone to its enolate occurs.[27]

Biacetyl[28] is a considerably weaker acid than acetylacetone and, given the subtleties of the acetylacetone reactions, it is not surprising that those observed with biacetyl are strikingly different. In this case, it appears addition of the deprotonated imine at the carbonyl site must occur first. Once the N-center is alkylated, the imine methyl group can be deprotonated in the alkaline conditions. The carbanion so produced then attacks the remaining carbonyl group intramolecularly to generate the dimethyldihydroxydihydroproline chelate, whose structure has been established previously.[3] The process is stereospecific in that the hydroxyl groups are syn, and this could be explicable in terms of the developing basicity of the carbonyl oxygen atom as the carbanion adds and its ability to hydrogen bond to the adjacent hydroxyl group. The pK_a change in the process is >14, so the interaction in the transition state could be substantial and could readily accommodate the exclusive syn orientation found. The absence of any indication of a pathway involving addition of the biacetyl enolate carbon to the imine center is consistent with differences in ground-state acidity, since the imine would be completely converted to its far less electrophilic conjugate base under conditions where even partial deprotonation of biacetyl occurs.

Condensation with Diethyl Oxaloacetate. One aim in attempting to react a coordinated imine with diethyl oxaloacetate was to achieve the preparation of a coordinated β-lactam through a series of reactions known to occur with the uncomplexed organic molecules[29] (Scheme III),

Scheme III. β-Lactam Formation via Oxaloacetate Addition to Uncoordinated Imines



Though it appeared from the ^1H NMR spectra (vide supra) of some of the very minor products of the coordinated imine reaction that at least some oxaloacetate carbanion addition did occur, this did not seem to be the reaction pathway responsible for the formation of the bulk product, which showed no high-field ^1H magnetic resonance attributable to a saturated methyl group except for that of its ester group. This fact, coupled with the appearance in the ^1H NMR spectrum of broad resonances due to retention of *four* NH_3 ligands and of two low-field, sharp resonances due to two protons attached to unsaturated carbon, could be simply rationalized by identifying the product with either VI or VII, formed as in Scheme IV. Since the heterocyclic ligands in VI and VII both lack symmetry, NMR data for the complex do not distinguish between the alternative structures. An attempt to make this distinction by preparing the chelidamic acid chelate (VII)[30] from chelidamic acid and $[(NH_3)_4CoCO_3]^+$ was unsuccessful because of the reduction of Co(III) by the free ligand. However, when the acid form complex (F2) was decomposed by reduction of Co(III) with BH_4^- in acid solution (when reduction of the metal center is extremely rapid) a white, crystalline precipitate showing two low-field ^1H magnetic resonances (δ 6.92, 7.18 vs TMS in DMSO-d_6) was obtained. This is consistent with structure VI for the complex.

The preferential formation of VI can be rationalized in the following manner: first, acylation of the imine N is more likely than that of the imine methyl carbon because of the far greater ease of exposure of the former nucleophile; second, under the reaction conditions oxaloacetate is entirely in its enolate form and hence the ethoxycarbonyl group more remote from the enol center should be the more susceptible to nucleophilic attack. Reaction parallel to that observed with acetylacetone and involving enolate carbon addition to the imine group may have been the source of minor side products observed with oxaloacetate. These products appeared to partially decompose during workup of the reaction mixture, however, and their characterization was not pursued.

Condensation with Dimethyl Acetylenedicarboxylate (DMAD). Though potentially complicated depending upon both the point[31] and stereochemistry of nucleophilic attack,[32] the reaction between DMAD and $[(NH_3)_4(N{=}C(CH_3)CO_2)]^+$ offered at least the prospect of a substituted pyrroline and thence a substituted proline

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(24) Freeman, H. C.; Marzilli, L. G.; Maxwell, I. E. *Inorg. Chem.* **1970**, *9*, 2408.

(25) Marsh, R. E.; Donohue, J. *Adv. Protein Chem.* **1967**, *22*, 235.

(26) Hall, D.; Llewellyn, F. J. *Acta Crystallogr.* **1956**, *9*, 108.

(27) Buckingham, D. A.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1973**, *95*, 7281.

(28) Sleszynski, N.; Zuman, P. *J. Org. Chem.* **1987**, *52*, 2622.

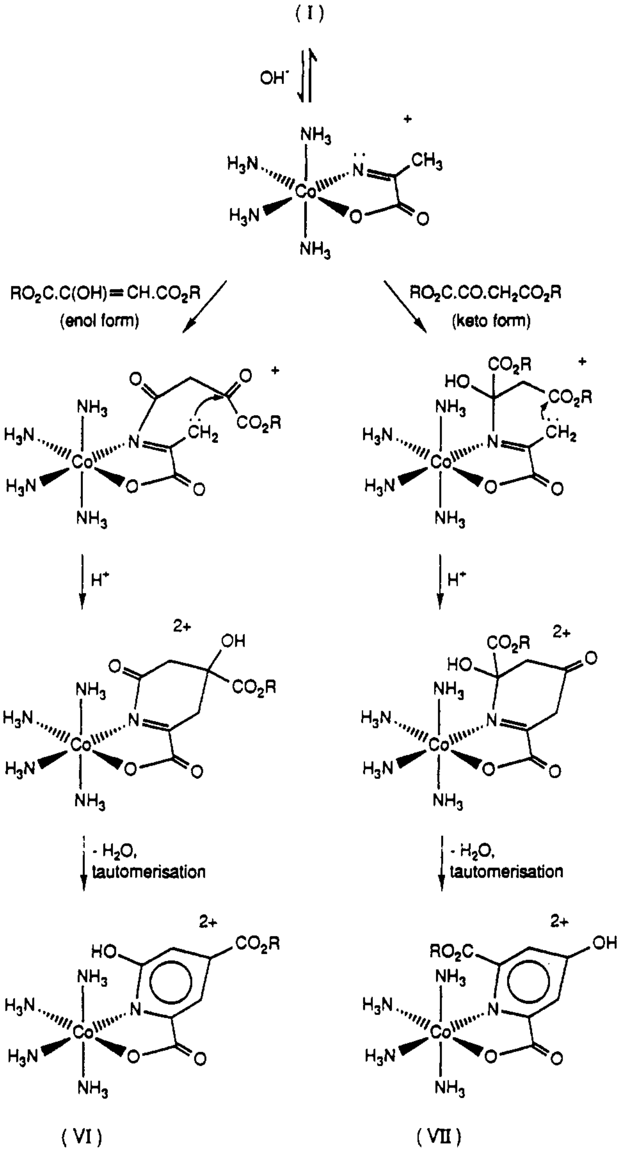
(29) Bender, D. R.; Bjeldanes, L. F.; Knapp, D. R.; Rapoport, H. *J. Org. Chem.* **1975**, *40*, 1265.

(30) Bag, S. P.; Fernando, Q.; Freiser, H. *Inorg. Chem.* **1962**, *1*, 887.

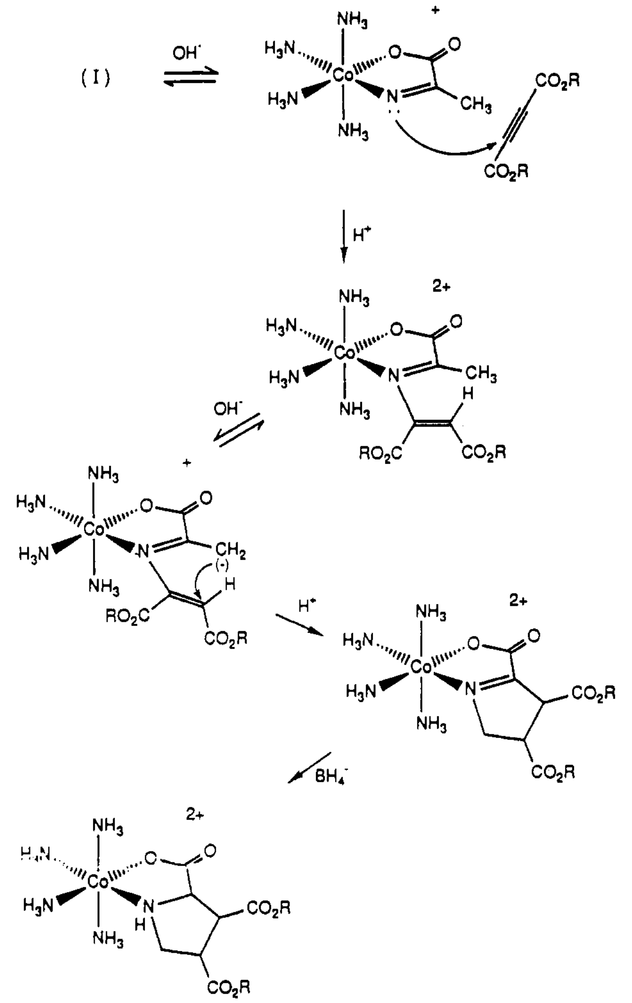
(31) Note that DMAD undergoes attack by $[(NH_3)_5CoOH]^{2+}$ at both carbonyl and acetylenic carbon—see ref 2.

(32) George, M. W.; Khetan, S.; Gupta, R. K. In *Advances in Heterocyclic Chemistry*; Academic Press: New York, 1976; Vol. 19, Chapter 4.

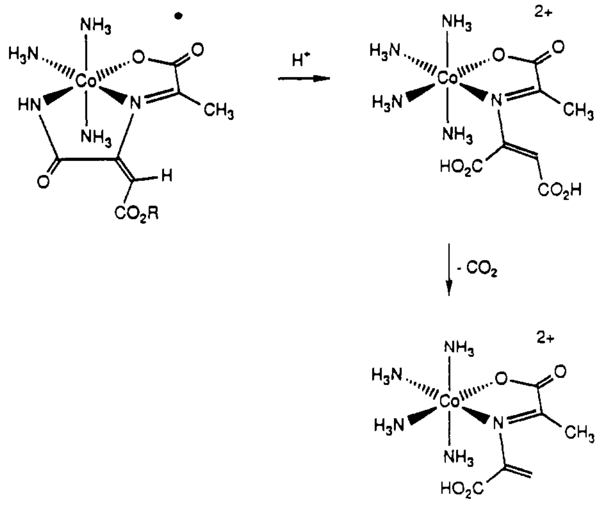
Scheme IV. Reaction Pathways Consistent with the Spectroscopic Properties of the Major Product of the Reaction of Diethyl Oxaloacetate with $[Co(NH_3)_4(HN{=}C(CH_3)CO_2)]^{2+}$



Scheme V. Heterocycle Synthesis Envisaged for Reaction of Dimethyl Acetylenedicarboxylate with $[Co(NH_3)_4(HN{=}C(CH_3)CO_2)]^{2+}$



Scheme VI. Observed Initial Reaction of Dimethyl acetylenedicarboxylate with $[Co(NH_3)_4(HN{=}C(CH_3)CO_2)]^{2+}$ under Basic Conditions



synthesis as in Scheme V. Actually, the reaction gave a single product that was obviously not a pyrroline. The ^{1}H NMR spectrum showed the retention of the imine methyl substituent and the loss of one methoxyl and one ammine group with two of the three remaining ammine groups appearing equivalent (implying the presence of a plane of symmetry incorporating the new ligand). These results are consistent with the reaction pathway in Scheme VI.

It is not necessary to assume cis nucleophilic addition to the triple bond; both stereochemistries in fact are known in DMAD reactions.[32] Trans addition would allow formation of the six-membered ring amide, as well as the five-membered one indicated, but related reactions of metal complexes suggest that the formation of the smaller ring would in fact be so much faster than that of the larger as to be the only path detectable.[33] The slow reaction of this initial product in acid led to the loss of two carbon atoms and reconversion to a tetraammine species (^{1}H NMR) and to the appearance of a second olefinic proton very weakly coupled to the first. These data imply that the reactions in Scheme VII are taking place and are not consistent with a six-membered ring for the cyclization product. The final product therefore appears to contain pyruvate imine in both its imine and enamine forms.

Conclusions

In the limited number of reactions presently described a considerable complexity of pathways is exhibited. At a superficial level, several anomalies are apparent, and in the absence of detailed mechanistic studies of the reactions, complete resolution of these is not presently possible. Thus, the formation of pyrroline and

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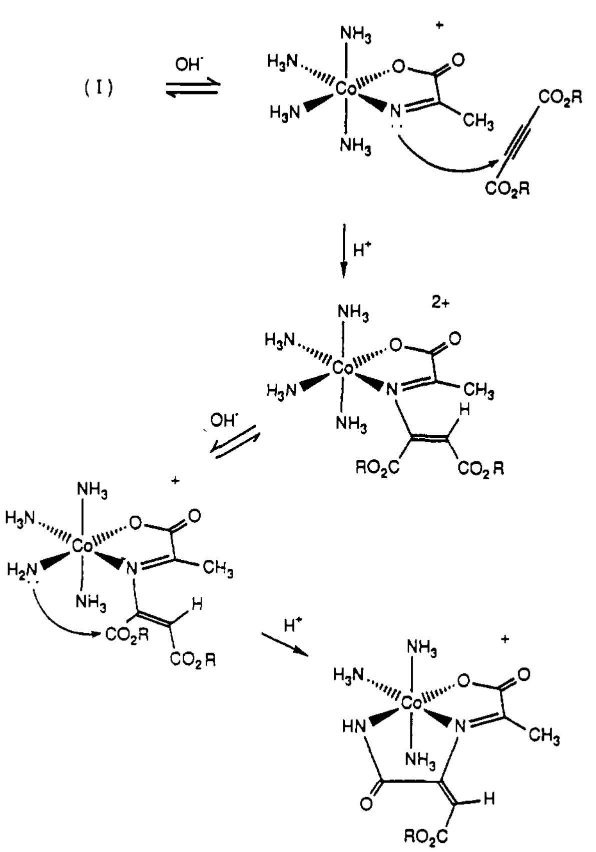
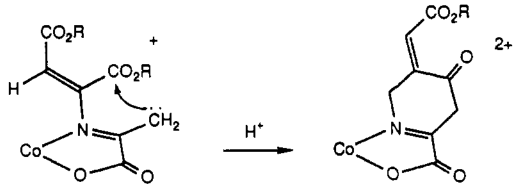
(33) (a) Buckingham, D. A.; Morris, P.; Sargeson, A. M.; Zanella, A. W. *Inorg. Chem.* **1977**, *16*, 1910. (b) Baraniak, E. Ph.D. Thesis, Australian National University, 1973.

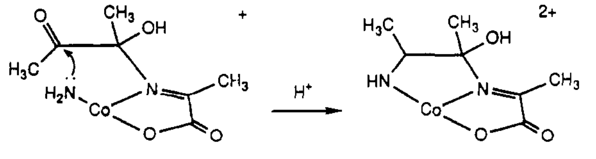
Scheme VII. Reactions of the Initial Product of Addition of $[Co(NH_3)_4(HN{=}C(CH_3)CO_2)]^{2+}$ to Dimethyl Acetylenedicarboxylate



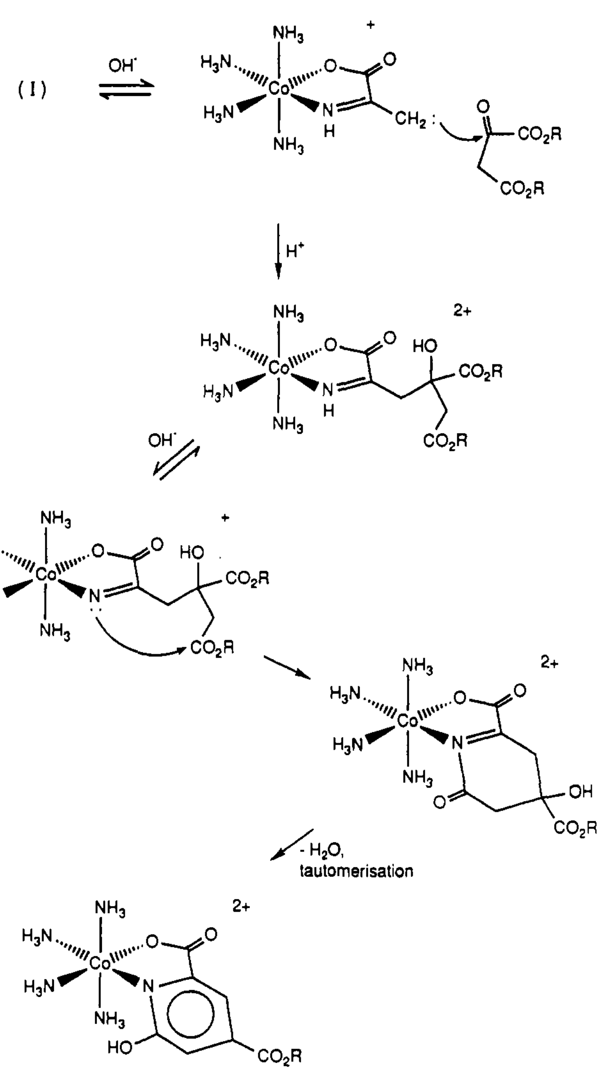
pyridine ligands in the reaction with biacetyl and diethyl oxaloacetate contrasts with the formation of tridentate ligands involving new five- and six-membered chelate rings from dimethyl acetylenedicarboxylate and methyl vinyl ketone. Since all these reactions may be rationalized by reaction schemes involving initial imine nitrogen alkylation, differences presumably arise in the second (cyclization) step, and it is not immediately apparent why that should be so. Although the unusually facile amide C–N bond cleavage[34] observed for the DMAD product suggests that there must be considerable strain in a tridentate ligand with two fused unsaturated five-membered rings, cyclization to this species nonetheless occurs in preference to the following reaction:



In the light of this result, the lack of any tridentate diimine ligand formation in the biacetyl reaction is surprising.



Scheme VIII. Alternative Mechanism for the Formation of an Isomer of Chelidamic Acid in the Reaction of Diethyl Oxaloacetate with $[Co(NH_3)_4(HN{=}C(CH_3)CO_2)]^{2+}$



A possible explanation of these results is that the degree of reversibility in the alternative initial addition steps determines the observed results. This is implied by the fact that, in intramolecular cyclizations on metal ions, addition intermediates are far more readily detected in imine[35,36] than in amide[37] formation. The difficulties in explaining tridentate rather than bidentate heterocyclic ligand formation and vice versa in the reactions of methyl vinyl ketone and diethyl oxaloacetate are greater. Since tridentate ligands involving linked five- and six-membered chelate rings (e.g., salicylideneglycinate[38]) are not uncommon and apparently not greatly strained, and since coordinated NH_3 is considerably more acidic than the methyl group of coordinated pyruvate imine (taking proton exchange rates[21,22] as a measure of acidity), the structure of the 1:1 methyl vinyl ketone adduct is readily rationalized. Similar products from labile metal ion reactions are well-known.[39]

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(34) N-bound amides, as for example, formed in the hydrolysis of coordinated nitriles (Creaser, I. I.; Harrowfield, J. MacB.; Keene, F. R.; Sargeson, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 3559 and references therein) are generally resistant to further reaction, the complexes undergoing slow aquation to aquo species plus free amide and not amine complex plus free acid: Sargeson, A. M. Unpublished work.

(35) Golding, B. T.; Harrowfield, J. MacB.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 3003.

(36) Bell, J. D.; Gainsford, A. R.; Golding, B. T.; Herlt, A. J.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1974**, *1123*, 980.

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Formation of a substituted pyridine from diethyl oxaloacetate is then difficult to understand, since, unlike the comparison of DMAD and biacetyl reactants, the alternative cyclization steps for methyl vinyl ketone and diethyl oxaloacetate are equivalent. A possible explanation of the results may lie in differences in conformational flexibility of the N-alkylated intermediates, though another possibility is that the diethyl oxaloacetate reaction actually involves C alkylation as its initial step (Scheme VIII).

A final, less perplexing, anomaly is the lack of importance of carbanion addition in the diethyl oxaloacetate reaction compared to that of acetylacetone. This may simply be a reflection of the fact that the enolate anion from diethyl oxaloacetate is a weaker base, and hence a poorer nucleophile, than that from acetylacetone.

While strategies for the selective and controlled utilization of coordinated imine reactivity required further clarification,[40] it is quite apparent that all possible reaction sites identified in basic studies may be exploited in facile syntheses of complex organic molecules. Further, these organic products may be species difficult to isolate or unstable in their uncoordinated form. Their generation therefore offers the prospect of increasingly more sophisticated syntheses at metal ion centers.

Supplementary Material Available: Tables SUP-1, SUP-3, and SUP-4, containing solution and refinement procedures, anisotropic thermal parameters, and least-squares planes, and Figure SUP-1, showing a stereodiagram of the unit cell structure of the complex iodide (5 pages); Table SUP-2, listing structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Oxidation of the Bis(1,2-ethanediamine)(sarcosinato)cobalt(III) Ion with Thionyl Chloride

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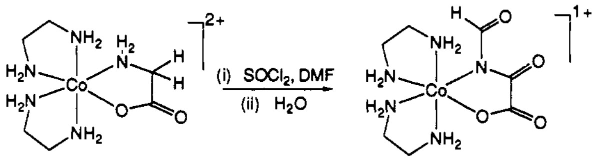
The oxidation of bis(1,2-ethanediamine)(sarcosinato)cobalt(III) ion with $SOCl_2$ in dimethylformamide gave the *N*-methylthiooxamato complex as the final product. The results, along with others, implicate the acid chloride chelate, a sulfine, and the methyl thiooxamato chelate as intermediates en route. The thiooxamato sulfur atom retains a nucleophilic capability and adds readily to cyclohexene in the thionyl chloride–dmf reaction medium to give an unusual imido hydroxycyclohexane thioester complex. Various results, including those in this paper, indicate that the chelated acid chloride readily loses an α-carbon proton and the resulting carbanion captures $SOCl^+$. Elimination of HCl yields the sulfine and further addition of $SOCl^+$, eliminations, and rearrangement yield chelated thiooxamate, which reacts even further under the pseudo-Vilsmeier conditions to the *N*-methyloxamato chelate complex.

Introduction

Previously, the oxidation of a variety of α-amino acidato complexes containing tertiary α-carbon centers with $SOCl_2$ in dimethyl formamide (dmf) to give the corresponding α-imino acidato complexes has been described.[1] That work was undertaken partly in order to shed some light on the path by which the glycinato complex **1** reacts with $SOCl_2$ in dmf to give the *N*-formyloxamato complex **2** and partly to synthesize new imino acid complexes.



(1) (2)

Bidentate, N,O-attachment of an α-amino acid to a metal center such as cobalt(III) serves to protect the ligating groups and to activate the proton(s) on the α-carbon atom. Coordination of the amine gives the nitrogen atom some ammonium ion character, and in addition, the metal-bound carboxylate ion has some ester character. These two features, together with the higher positive charge of the complex overall, combine to activate the proton(s) on the adjacent carbon atom[2,3] and thereby to facilitate carbanion formation. A mechanism for the formation of the α-imino acidato complexes (Scheme I) was proposed,[1] which involved, initially, the formation of the more highly activated chelated α-amino acid chloride and then deprotonation at the α-carbon center. Reaction of the resulting carbanion with $SOCl_2$ gave the α-sulfinyl chloride. Subsequent extrusion of sulfur monoxide and hydrolysis produced the α-imino acidato products. However, the presence of an additional proton on the secondary α-carbon center of the glycinato complex instead of an alkyl substituent allows an alternative path by which the α-sulfinyl chloride species **3** may react (Scheme I, R = H). Loss of the second α-proton and the chloride ion from this molecule would give the chelated sulfine **4**. Thus, it was concluded that the α-amino acidato complexes containing tertiary α-carbon centers could behave differently from the glycinato complex **1**. The sarcosinato complex **5** was therefore employed as an analogue for the study of these oxidation routes. While this complex is structurally similar to the glycinato complex **1**, it was hoped that it would be sufficiently different to allow the isolation or characterization of intermediates, without differing with respect to the mechanism of reaction. Also, the presence of the methyl group on the amine nitrogen atom should prevent the formylation reaction. Any activation of the system resulting from formylation would then be lost, and the intermediates along the reaction path might prove stable enough to be isolated.

Experimental Section

^1H and ^{13}C NMR spectra were recorded in D_2O with a Jeol JNM-FX 200 Fourier transform spectrometer, using sodium 3-(trimethylsilyl)-

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