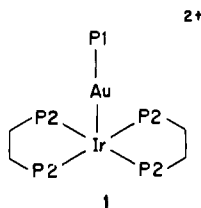


Figure 1. ORTEP drawing of the coordination core of $[\text{Ir}(\text{dppe})_2\text{Au}(\text{PPh}_3)](\text{BF}_4)_2$ (**1**) including selected distances (Å) and angles (deg). The thermal ellipsoids show 50% probability surfaces. The esd's in Ir–Au and M–P distances and M–M–P and P–Ir–P angles are 1, 5, 1, and 2, respectively, in the last significant figure. Some additional angles (deg): Au–Ir–P2 = 89.9 (1); Au–Ir–P5 = 83.3 (1); P3–Ir–P4 = 94.2 (2); P2–Ir–P4 = 177.8 (2); P3–Ir–P5 = 167.8 (2).

is presented in Figure 1 and as supplementary material.¹⁹

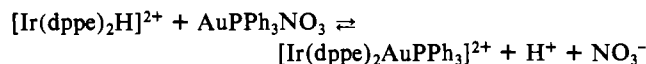
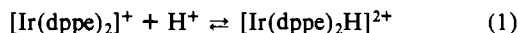
Results and Discussion

The addition of $\text{AuPPh}_3\text{NO}_3$ to an acetone solution of $[\text{Ir}(\text{dppe})_2]\text{BF}_4$ in the presence of HBF_4 gave a mixture of $[\text{Ir}(\text{dppe})_2\text{H}]^{2+}$ and the binuclear complex $[\text{Ir}(\text{dppe})_2\text{AuPPh}_3]^{2+}$ (**1**). **1** was isolated in moderate yield from this solution and was characterized by ^{31}P $\{^1\text{H}\}$ NMR spectroscopy and in the solid state by a single-crystal X-ray analysis.



As shown in the drawing, **1** has an approximately square-pyramidal geometry about the Ir atom. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is consistent with the solid-state structure and consists of a doublet and a quintet, attributable to P2 and P1, respectively: δ 41.4 (P2, d, $J_{\text{PP}} = 6$ Hz, intens 4), -4.75 (P1, quint, $J_{\text{PP}} = 6$, intens 1). No evidence for a hydride ligand was found in either the ^1H NMR or IR spectrum of **1**.

$[\text{Ir}(\text{dppe})_2]\text{BF}_4$ was rapidly protonated in acetone solution by the addition of HBF_4 to form an equilibrium mixture of $[\text{Ir}(\text{dppe})_2]^+$ and $[\text{Ir}(\text{dppe})_2\text{H}]^{2+}$ as determined by ^{31}P and ^1H NMR spectroscopy.¹⁵ The low-temperature ^1H NMR spectrum of $[\text{Ir}(\text{dppe})_2\text{H}]^{2+}$ (-95 °C) displayed a quintet resonance at -25.5 ppm ($J_{\text{PH}} = 12$ Hz), also consistent with a square-pyramidal structure. It is this protonated species, apparently, that reacted with $\text{AuPPh}_3\text{NO}_3$ to form **1**. A mixture of $\text{AuPPh}_3\text{NO}_3$ and $[\text{Ir}(\text{dppe})_2]^+$ in acetone solution, for example, did not form a detectable amount of **1**. The formation of **1** is also reversible. Addition of HBF_4 to acetone solutions of **1** generated mixtures of **1** and $[\text{Ir}(\text{dppe})_2\text{H}]^{2+}$ as evidenced by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Thus, the proton plays a kinetic role in activating the Ir complex, a perhaps surprising result in light of the increased charge of the protonated Ir species (eq 1). Presumably, a bridged Ir–H–Au intermediate or transition state is involved in the formation of **1**.



The structure of **1** consists of well-separated dication and BF_4^- anions. Figure 1 shows an ORTEP drawing of the $[\text{Ir}(\text{dppe})_2\text{AuPPh}_3]^{2+}$ core and includes atom labels and selected distances and angles. An ORTEP drawing of the entire dication and a table of all distances

and angles are included as supplementary material.¹⁹

The geometry of the coordination core around the iridium atom is approximately square pyramidal. There are significant distortions from this idealized geometry; however, they are most likely due to a combination of nonbonded repulsions between the phenyl rings, crystal packing forces, and constraints imposed by the chelating nature of the dppe ligand. The chelate P–Ir–P "bite" angles are 85.0 (2) and 80.5 (2)° (average 82.8°) and are similar to the values found in $[\text{Ir}_3(\mu_3\text{-AuNO}_3)\text{H}_6(\text{dppe})_3]^+$ (average 84.7 (2)°),¹ the nonchelated cis P–Ir–P angles average 97.5 (2)°, and the trans P–Ir–P angles are 177.8 (2) and 167.8 (2)°, respectively, for phosphorus atoms 2,4 and 3,5. These values show the slight distortion in the basal square plane. The dihedral angle between the IrP2P3 and IrP4P5 planes is 11°. The Ir–Au vector is approximately orthogonal to the IrP4 basal plane (average Au–Ir–P angle is 92.3 (1)° with maximum and minimum values of 107.6 (1) and 83.3 (1)°, respectively). The Au–Ir separation (2.625 (1) Å) is short compared with values in other complexes (average 2.685 (1) Å in $[\text{IrAu}_2(\text{H})(\text{PPh}_3)_4\text{NO}_3]\text{BF}_4$,¹³ average 2.641 (1) Å in $[\text{IrAu}_3(\text{PPh}_3)_5(\text{NO}_3)]\text{BF}_4$,¹ average 2.705 (1) Å in $[\text{Ir}(\mu_3\text{-AuNO}_3)\text{H}_6(\text{dppe})_3]^+$,¹ and 2.765 (1) Å in $[\text{Ir}(\text{PPh}_3)_3\text{H}_2(\mu\text{-H})\text{AuPPh}_3]^+$).⁶ The average Ir–P distance of 2.357 (5) Å is comparable to values found in other complexes that contain trans phosphorus atoms;^{1,6} however, the Ir–P2 and Ir–P4 separations (2.277 (5) and 2.431 (5) Å) deviate significantly from the average. The large difference in the distances of these trans Ir–P bonds is unusual, but a similar phenomenon has been observed in $[\text{Rh}(\text{dppb})_2]^+$ ²⁰ and is most likely due to nonbonded repulsions between phenyl rings. The Au–P distance in **1** (2.219 (5) Å) is short compared with values observed in other Au–Ir phosphine clusters (average 2.272 (4) Å in $[\text{IrAu}_2(\text{H})(\text{PPh}_3)_4\text{NO}_3]\text{BF}_4$,¹³ average 2.266 (4) Å in $[\text{IrAu}_3(\text{PPh}_3)_5(\text{NO}_3)]\text{BF}_4$,¹ and 2.265 (5) Å in $[\text{Ir}(\text{PPh}_3)_3\text{H}_2(\mu\text{-H})\text{AuPPh}_3]^+$).⁶

The distances and angles within the dppe ligands and the BF_4^- anions are normal and are included as supplementary material.¹⁹

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Registry No. 1-0.4 CH_2Cl_2 , 93895-64-8; $\text{Ir}(\text{dppe})_2\text{BF}_4$, 15130-28-6; $\text{AuPPh}_3\text{NO}_3$, 14897-32-6; Au, 7440-57-5; Ir, 7439-88-5.

Supplementary Material Available: A figure of the molecular structure and tables of positional and thermal parameters, distances and angles, least-squares planes, calculated hydrogen positional parameters, and observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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Cerium(IV)-Induced Electron Transfer in Pentaamminecobalt(III) Complexes of α -Amino Acids. Evidence for the Fraction of Reaction with Synchronous N–H and C–C Bond Fissions

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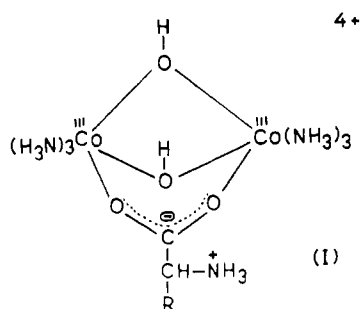
Studies on Ce(IV) oxidations of cobalt(III) complexes of pyridinemethanols¹ and pyridinecarboxaldehyde² evidenced the

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partition of an intermediate depending on the initial concentration of Ce(IV). However, the study on Co(III) complexes of α -hydroxy acids³ showed no such partition in the reaction paths at all concentrations of Ce(IV). Such behavior observed in Ce(IV) oxidation of pentaamminecobalt(III) complexes has been used in the present work on Ce(IV) oxidation of pentaamminecobalt(III) complexes of α -amino acids as a diagnostic tool to find out the fraction proceeding by synchronous cleavages of N-H and C-C bonds.

Experimental Section

Ammonium cerium(IV) nitrate (British Drug House, AnalaR grade) (Anal. Calcd for $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$: Ce, 25.5. Found (ignition of CeO_2): Ce, 25.5) and α -amino acids employed as ligands (Aldrich products) were used as obtained. *N*-Acetyl- and *N*-benzoylglycine and *N*-benzoylalanine were prepared by following the procedure of Vogel.⁴ The $(\text{NH}_3)_5\text{Co}^{\text{III}}$ complexes of glycine, α -alanine, *N*-acetyl- and *N*-benzoylglycine, and *N*-benzoylalanine were prepared as their perchlorates by the method of Fan.⁵ The tris(μ -hydroxo) complex $(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3(\text{ClO}_4)_3$ (trio) has been prepared by the modified procedure of Siebert and co-workers.^{6,7} The following modified procedure was used for the conversion to the carboxylato-bridged dimeric cobalt(III) complex of type I since an earlier method⁶ was unsuccessful in this case: A 10-mmol



sample of ligand was dissolved in 10 mL of 1 M HClO_4 at 50–60 °C, 1 g of trio was added, and the mixture was maintained at 60 °C for 0.5 h. The solution was filtered off, and 10 mL of 12 M HClO_4 was added to filtrate. The mixture was then kept at 0 °C for about 12 h, during which crystals of the dimeric cobalt(III) complex precipitated. These were filtered and dried under vacuum. The cobalt analysis performed on this complex gave results that agreed with the expected value for the structure assigned.

The reaction between Ce(IV) and Co(III) complexes was carried out at 50.0 \pm 0.2 °C in a thermostated bath. The concentrations of unreacted Ce(IV) were determined both iodometrically and spectrophotometrically at 400 nm. The disappearance of Co(III) was followed spectrophotometrically by following the decrease in absorbance at 502 nm (for the monomeric Co(III) complex) and at 520 nm (for the dimeric Co(III) complex). The specific rates estimated from the optical density measurements agree with the values from the volumetric procedure within \pm 5%. Curiously, the change in absorbance observed at 502 nm or 520 nm for the Co(III) complexes of glycine corresponds to very nearly 20% of the initial concentration of Co(III), while the change in optical density at 400 nm for Ce(IV) corresponds to 180% of $[\text{Co(III)}]_i$ (i = initial).

Co(II) was estimated after the completion of reaction, by diluting the reaction mixture 10-fold with concentrated HCl, allowing evolution of chlorine to cease, and then measuring the absorbance at 692 nm (ϵ = 560).⁸ The amount of Co(II) estimated in all these cases corresponds to nearly 20% of $[\text{Co(III)}]_i$. After 48 h, the product was extracted with ether and analyzed iodometrically⁹ for the amount of HCHO formed in

Table I. Kinetic Data for Ce(IV) Oxidation of α -Amino Acids^{a,c}

compd	$10^2 \times$ [substrate], M	$10^3 k_1$, ^d min^{-1}	$10^3 k_1$, ^{b,d} min^{-1}	$10^3 \times$ k_{calcd} , ^f min^{-1}
glycine	1.5	2.0	1.3	1.50
	2.0	2.2	1.6	1.64
	3.0 ^e	2.5	1.8	1.77
	5.0	2.3	2.2	1.90
	10.0	2.5	2.3	2.00
α -alanine	1.0	1.15	0.92	0.97
	2.0	2.7	1.2	1.20
	3.0	2.8	1.5	1.60
	5.0	3.4	2.3	1.90
	10.0	3.5	2.4	2.30
<i>N</i> -acetylglycine	1.0	15.6	9.4	10.50
	1.5	20.0		
	2.0	19.0	10.7	11.00
	3.0	17.0	11.4	11.60
	5.0	18.0	11.9	12.20
<i>N</i> -benzoylglycine	10.0	18.0	12.2	12.50
	1.0	11.0	11.1	12.10
	1.5	13.0		
	3.0	12.0	13.2	13.40
	5.0	14.0	14.6	14.10
	10.0	15.0	14.4	14.40

^a Reactions were carried out at 50 \pm 0.2 °C in both 0.24 and 0.10 M HClO_4 . ^b The specific rates given correspond to 0.10 M HClO_4 . ^c Concentration of Ce(IV) used was $(2.0\text{--}2.2) \times 10^{-3}$ M unless otherwise mentioned. ^d $-\text{d} \ln [\text{Ce(IV)}]/\text{d}t = k_1$ (min^{-1}). ^e At $[\text{Ce(IV)}] = 4.1 \times 10^{-3}$ M. ^f Specific rates were calculated from the k_{lim} and formation constant (K) values given in Table II at 1.10 M HClO_4 .

Table II. Ce(IV) Complexes of α -Amino Acids

substrate	$10^{-2} K$, ^a M^{-1}	$10^3 k_{\text{lim}}$, ^b min^{-1}	correln coeff (r)
glycine	1.80	2.1	1.00
α -alanine	0.46	2.8	0.970
<i>N</i> -acetylglycine	2.8	13.0	0.999
<i>N</i> -benzoylglycine	2.7	15.0	0.984

^a Formation constant, K , for the Ce(IV)- α -amino acid complex was calculated as the ratio of intercept to slope from the plot of $1/k_{\text{obsd}}$ vs. $1/[\text{amino acid}]$ at 0.10 M HClO_4 at 50 °C. ^b The limiting specific rate was calculated from the intercept of the $1/k_{\text{obsd}}$ vs. $1/[\text{amino acid}]$ plot at 0.10 M HClO_4 .

the case of the (glycinato)- and (*N*-acetylglycinato)cobalt(III) complexes, the dimeric Co(III) complex, and unbound glycine. The yield of HCHO in all these cases is nearly 20% of $[\text{Co(III)}]_i$ (Table III). After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.5, and the aqueous layer was separated by filtration in the case of both the free ligands and the corresponding complexes, viz. the (glycinato)- and (*N*-acetylglycinato)cobalt(III) complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated. Though the yield of glyoxalic acid was nearly quantitative, the estimation of glyoxalic acid complex was less nearly quantitative. In both the cases the IR spectra of the product agreed with the IR spectra of authentic samples of glyoxalic acid or the (glyoxalato)cobalt(III) complex.

Results and Discussion

Table I summarizes the kinetic data for the Ce(IV) oxidation of α -amino acids at both 0.24 and 0.10 M HClO_4 at 50 \pm 0.2 °C. Though the reaction exhibits first-order dependence on Ce(IV), kinetic saturation has been observed with respect to substrate concentration, suggesting a complex formation between Ce(IV) and α -amino acids.

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- (a) Under the present reaction conditions, the consumption of Ce(IV) by HCHO is less than 5%. (b) The oxidation of α -amino acids by Co(III) salts in aqueous perchloric acid yields about 15%–20% of aldehyde. (Sheikh, R. A.; Waters, W. A. *J. Chem. Soc. B* **1970**, 988).

Table III. Comparative Rates of Ce(IV) Oxidation of α -Amino Acids and Corresponding Co(III) Complexes^a

ligand	$10^3 k_{\text{ligand}}$, min ⁻¹	$10^3 k_{\text{Co-L}^{2+}}$, ^{b,c} min ⁻¹	$10^3 k_{\text{Co}_2\text{-L}^{3+}}$, ^{b,c} min ⁻¹
glycine	3.0	3.3	1.4
<i>N</i> -acetyl glycine	26.0	12.0	
<i>N</i> -benzoyl glycine	27.0	12.0	
α -alanine	4.2	4.5	
<i>N</i> -benzoylalanine	26.0	11.5	

^a Reactions were carried out at $50 \pm 0.2^\circ\text{C}$ in 1.2 M HClO_4 .
^b The concentration of Co(III) complexes used was $(1.0\text{--}2.0) \times 10^{-3}$ M with $[\text{Ce(IV)}] = 1.5 \times 10^{-3}$ M. ^c $-\text{d} \ln [\text{Ce(IV)}]/\text{d}t = k$ (min⁻¹).

Assuming a 1:1 complex involving Ce(IV) and α -amino acid, the following rate law has been deduced for this reaction:

$$\frac{\text{rate}}{[\text{Ce(IV)}]} = k_{\text{obsd}} = \frac{k_{\text{lim}}[\alpha\text{-amino acid}]}{K^{-1} + [\alpha\text{-amino acid}]}$$

where k_{lim} is the limiting specific rate observed at higher $[\alpha\text{-amino acid}]/[\text{Ce(IV)}]$ ratios and K is the formation constant for the cerium- α -amino acid complex.

Hence, from the plot of $1/k_{\text{obsd}}$ vs. $1/[\text{amino acid}]$ the slope and intercept can be evaluated.

Table II lists the formation constants for Ce(IV)- α -amino acid complexes along with the limiting specific rates.

Such complex formation seems to be absent when the carbonyl end is tied up by Co(III) and the reactions between Ce(IV) and Co(III) complexes of α -amino acids exhibit uncomplicated second-order kinetics.

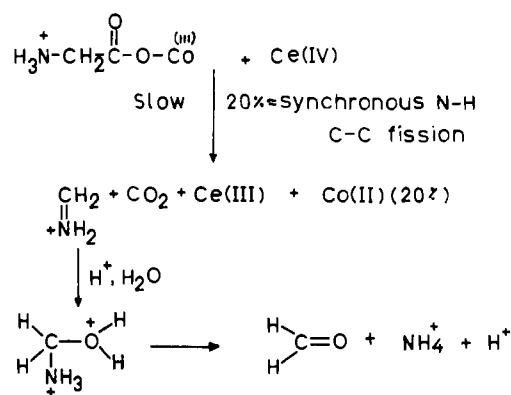
From a comparison of the specific rates for Ce(IV) oxidation of the respective Co(III) complexes and the dimeric Co(III) glycine complex (Table III), one can infer that the oxidation rates of α -amino acids are not significantly affected by complex formation. This may be because the seat of attack lies away from the Co(III) center so that its electrostatic influence is less felt on the position of attack. There is, however, a considerable change in the specific rate of Ce(IV) oxidation of the Co^{III}_2 -glycine complex as the two Co^{III} centers can exert greater electrostatic influence over the reacting center. This suggests that Ce(IV) attacks the $-\text{NH}_2$ or $-\text{NH}$ center in the slow step of the reaction, leading to the formation of a radical $-\dot{\text{N}}\text{H}$ or $-\dot{\text{N}}$. The reduction in the specific rate of Ce(IV) oxidation of Co(III) complexes of *N*-acetyl- and *N*-benzoyl glycine and *N*-benzoylalanine, compared to that for the unbound ligands, points to significant electronic influence of the acyl group and also the electrostatic influence of the Co(III) center at the seat of attack, viz. the $-\text{NH}$ group. Such an electrostatic influence due to ligation of α -amino acids to the Co(III) center (in the monomer only) seems to be absent as the amino nitrogen is protonated both in the complex and in the unbound ligand, exerting possibly the same electrostatic influence at the seat of attack.

Table IV. Stoichiometric Data for Ce(IV) Oxidation of α -Amino Acids and Corresponding Co(III) Complexes

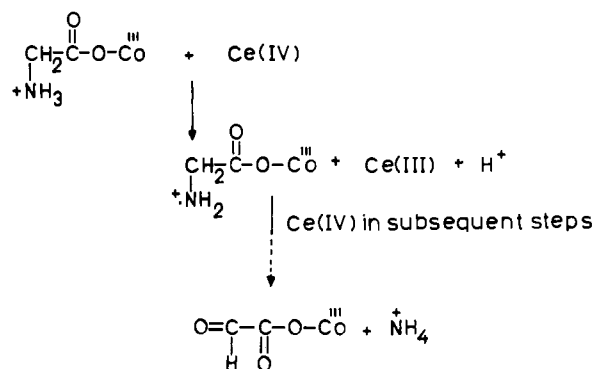
	[compd] _i , M	[Ce(IV)] _i , M	$\Delta[\text{Ce(IV)}]:$ $[\text{Co(III)}]_i^e$	[Co(II)], mM (%)	[HCHO], ^d mM (%)	[glyoxalic acid], mM (%)
glycine	0.010	0.050	2.3 ^a :1		1.92 (19.2)	7.6 (76)
<i>N</i> -acetyl glycine	0.010	0.050	2.2 ^a :1		2.1 (21)	7.1 (71)
α -alanine	0.010	0.050	2.2 ^a :1			
$(\text{NH}_3)_2\text{Co}^{\text{III}}\text{-L}^{2+}$						
L = glycine	0.010	0.049	1.8 ^a :1	2.1 (21)	2.0 (20) ^f	
L = glycine	0.0026	0.0060	1.9 ^b :1	0.50 (19.5)	0.49 (19) ^f	
L = <i>N</i> -acetyl glycine	0.010	0.050	1.8 ^a :1	2.0 (20)	2.1 (21)	
L = α -alanine	0.010	0.052	1.8 ^a :1	2.1 (21)		
L = α -alanine	0.0025	0.0080	1.84 ^b :1	0.49 (19.6)		
$\text{Co}^{\text{III}}_2(\text{gly})^e$	0.010	0.050			2.3 (23)	

^a $[\text{Ce(IV)}]_{\text{final}}$ was estimated iodometrically after 100 h at 50°C , and $\Delta[\text{Ce(IV)}]$ was calculated. ^b The change in concentration of Ce(IV) was determined from the change in optical density at 400 nm measured spectrophotometrically. ^c Suitable blank reactions were done and correction for the hydrolysis of the Co(III) complex was applied. ^d HCHO and glyoxalic acid were estimated by following the procedure described in the Experimental Section. ^e Estimation of Co(II) was hampered by the decomposition of the parent compound itself into Co(II) with concentrated HCl. ^f The yield of the Co(III) glyoxalato complex was about 65%.

Scheme I



Scheme II



The stoichiometric results indicate that for 1 mol of cobalt(III) complex, about 1.8 mol of Ce(IV) is consumed, whereas with the unbound ligands for 1 mol of α -amino acid about 2.2 mol of Ce(IV) is consumed (Table IV). The stoichiometric results, coupled with kinetic data and product analyses, can be accounted for by the following reaction schemes.

Scheme I proposes that Ce(IV) oxidizes the $-\text{NH}$ center and induces the formation of a radical which, in a synchronous step undergoes carbon-carbon bond fission, yielding Co(II). As the amount of HCHO or Co(II) formed is only 20% of $[\text{Co(III)}]_i$, the above reaction probably contributes only 20% of the total reaction.

Scheme II envisages the formation of a nitrogen radical that reacts with Ce(IV) in subsequent steps, yielding ultimately the Co(III) complex of glyoxalic acid. This probably forms the rest of the reaction (about 80%). In this case the amount of Ce(IV) consumed by 1 mol of Co(III) should be around 1.8 mol, which is in agreement with the observed stoichiometric results. In the case of unbound glycine and *N*-acetyl glycine, the consumption of Ce(IV) is around 2.2 mol, the yield of HCHO is about 20%, and that of glyoxalic acid is about 75%. In the case of the Co(III)

glycinato complex, the other product is the Co(III) glyoxalato complex.

Sethuram et al.¹¹ consider the breaking of the N-H bond a fast step. Still, such an amino acid radical formation has been invoked in the Ag⁺-catalyzed S₂O₈²⁻ oxidation of α -amino acids.¹²

Registry No. I (R = H), 93922-97-5; I (R = CH₃), 93895-26-2; I (R = H, *N*-acetyl), 93895-27-3; I (R = H, *N*-benzoyl), 93895-28-4; I (R = CH₃, *N*-benzoyl), 93895-29-5; (NH₃)₅Co^{III}L (L = glycine), 44982-38-9; (NH₃)₅Co^{III}L (L = alanine), 34371-90-9; (NH₃)₅Co^{III}L (L = *N*-acetyl glycine), 80327-72-6; (NH₃)₅Co^{III}L (L = *N*-benzoyl glycine), 93895-30-8; (NH₃)₅Co^{III}L (L = *N*-benzoyl alanine), 93895-31-9; (NH₃)₃Co(OH)₃Co(NH₃)₃³⁺, 45976-80-5; (NH₄)₂Ce(NO₃)₆, 10139-51-2; Ce, 7440-45-1; Co, 7440-48-4; glycine, 56-40-6; α -alanine, 56-41-7; *N*-acetyl glycine, 543-24-8; *N*-benzoyl glycine, 495-69-2; *N*-benzoyl alanine, 2198-64-3.

Supplementary Material Available: A table of kinetic data for Ce(IV) oxidation of Co^{III} complexes of α -amino acids (1 page). Ordering information is given on any current masthead page.

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Structural Approach to the Behavior of ClO₄⁻ as a Ligand in Transition-Metal Complexes Using EXAFS, IR, and Raman Spectroscopy. 2.^{1a} Crystal Structure of M(ClO₄)₂ (M = Co, Ni). A Novel Mode of Perchlorate Coordination

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Recently, new synthetic routes have allowed the preparation of a whole series of anhydrous metal perchlorates. Such compounds provide the unique opportunity of investigating the coordinating behavior of the perchlorate anion.^{2,3} A number of X-ray crystal studies have already demonstrated weak bonding between the perchlorate anion and metal atoms,⁴⁻⁹ but it was only recently that structural evidence of significantly strong metal

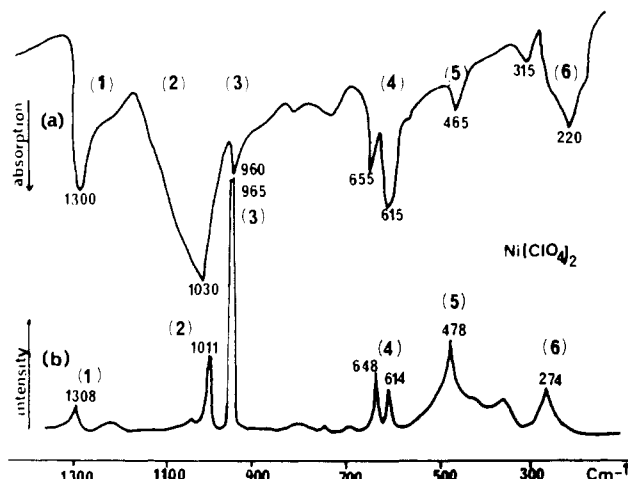


Figure 1. Vibrational spectra of Ni(ClO₄)₂: (a) infrared; (b) Raman. Peak assignments: (1) $\nu(\text{Cl}=\text{O})$; (2) $\nu_{\text{as}}(\text{ClO}_3)_{\text{coord}}$; (3) $\nu_{\text{s}}(\text{ClO}_3)_{\text{coord}}$; (4) δ_{as}^- and $\delta_{\text{s}}(\text{ClO}_3)_{\text{coord}}$; (5) $\delta(\text{Cl}=\text{O})$; (6) $\nu(\text{M}-\text{O})$.

perchlorate interactions has been obtained.^{10,11} Interest in the anhydrous metal perchlorate family arises in part from their possible practical use as catalysts in cationic polymerization reactions. The perchlorates of magnesium, aluminum, cobalt(II), nickel(II), and copper(II) and the triflates (trifluoromethanesulfonates) of gallium and aluminum have recently been shown to be very active initiators of polymerization reactions in heterogeneous¹² and in homogeneous reaction systems.¹³ Attempts to rationalize chemical reactivity in terms of atomic structure and intermolecular interactions require a detailed knowledge of the geometrical arrangement. However, the high reactivity of these complexes prevents the employment of the solvents usual in crystal growth, and solids are more often obtained in the form of microcrystalline powders. In the absence of single crystals suitable for complete radiocrystallographic investigation, structural information can be deduced by using spectroscopic techniques. Among these, extended X-ray absorption fine structure (EXAFS) spectroscopy is one of the most powerful, giving radial distances and information about the type and the number of scattering atoms.¹⁴

A previous paper in this series described the study of copper perchlorate using EXAFS, infrared, and Raman spectroscopies.¹⁵ The oxygen atoms of the perchlorate groups are strongly coordinated, with copper-oxygen distances of 1.96 Å, forming a square-planar arrangement around copper while two oxygen atoms at longer distances (2.67 Å) complete its coordination shell.

We present here an EXAFS study of cobalt and nickel perchlorates for which a regular octahedral MO₆ chromophore has been predicted,¹⁶ thus making the analysis of EXAFS data much easier than for the copper analogue.

Experimental Section

A. Synthesis. The preparation of nickel and cobalt perchlorates used the general method described elsewhere for the synthesis of anhydrous metal perchlorates.¹⁷ Anhydrous or hydrated metal chloride was allowed

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