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Factors Affecting Chelation of Carboxylates to *cis*-Diaqua Co(III) Complexes: Implications on the Reactivity of the Metal Complexes for Hydrolyzing Esters, Amides, Nitriles, and Phosphates

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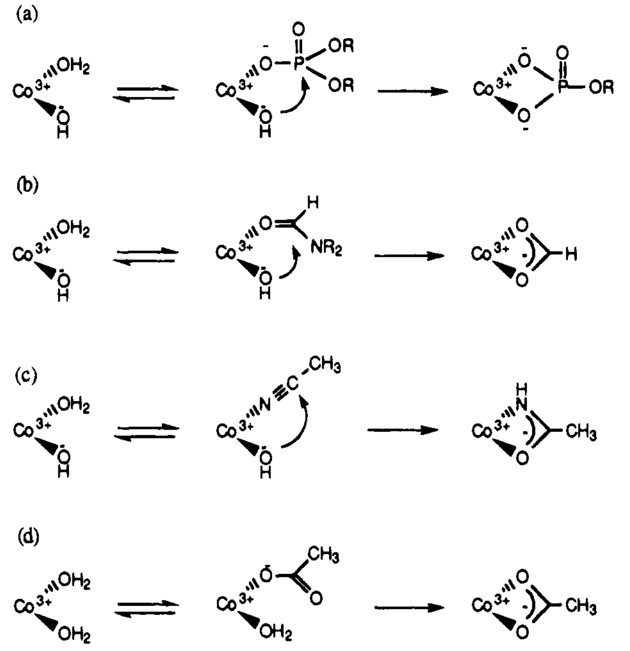
The equilibrium constant for chelation of carboxylates to *cis*-diaqua tetraamine Co(III) complexes is highly sensitive to the tetraamine ligand structure, basicity of the chelating carboxylate, and solvent polarity. *cis*-Diaqua tetraamine Co(III) complexes that easily accommodate chelation of carboxylates are also highly reactive for hydrolyzing carboxyl esters, amides, nitriles, and phosphate esters. The X-ray crystal strcuture of $[(\mathrm{trpn})\mathrm{Co}(\eta^2\text{-}\mathrm{O_2CC(CH_3)_3})](\mathrm{ClO_4})_2$ has been determined: trpn = tris(3-aminopropyl)amine, $\mathrm{C_{14}H_{33}N_4O_{10}Cl_2Co}$, orthorhombic, $P2_12_12_1$, $a = 8.7822(3)$ Å, $b = 14.9959(6)$ Å, $c = 17.5277(5)$ Å, $V = 2308.35(14)$ Å^3, $Z = 4$.

Carboxylates can coordinate to metal complexes as monodentate or bidentate ligands. They can form four-membered ring chelates or bridge two metal centers. Over the years, numerous crystal structures of all three types of coordinated carboxylates have been reported. *cis*-Diaqua Co(III) and Cu(II) metal complexes that allow chelation of carboxylates have been shown to be particularly reactive for hydrolyzing carboxyl esters,[1] amides,[2] and nitriles[3] as well as phosphate esters.[4] We proposed[5] that the *cis*-diaqua metal complexes hydrolyze the substrates by a combination of Lewis acid activation[6] and intramolecular metal–hydroxide activation,[7] resulting in the formation of four-membered ring intermediates or transition states (Scheme 1a–c). *cis*-Diaqua metal complexes that easily form four-membered rings with carboxylates (Scheme 1d) should also stabilize four-membered ring intermediates or transition states in the hydrolysis reactions. Therefore it is fundamentally important to understand factors affecting chelation of carboxylates to metal complexes. Although carboxylates can chelate to various metal centers, including transition metals and lanthanides, Co(III) complexes are ideal for studying the chelation reaction. Co(III) complexes are not only diamagnetic but also substitutionally inert making it possible to distinguish by NMR methods the chelated carboxylate from the monodentate carboxylate.[1] Furthermore, Co(III) complexes are generally labile enough to allow equilibration to occur between the chelated and the monodentate carboxylate within minutes to hours. Here we report factors affecting chelation of carboxylates to *cis*-diaqua Co(III) complexes.

Scheme 1



Tetraamine Ligand Effect

cis-Diaqua tetraamine Co(III) complexes (*cis*-$[\mathrm{N_4Co(OH_2)_2}]^{3+}$) efficiently hydrolyze phosphate diesters by a combination of Lewis acid activation and intramolecular metal–hydroxide activation, resulting in formation of four-membered ring intermediates or transition states (Scheme 1a). The reactivity of the metal complexes is highly sensitive to the tetraamine ligand structure. For example, the relative reactivities of **1**–**3** for hydrolyzing bis(*p*-nitrophenyl) phosphate (**BNPP**) are approximately 1 to 50 to 300.[8] It has been suggested that the difference in the reactivity of the metal complexes may be due

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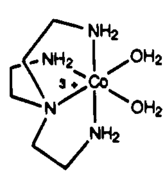

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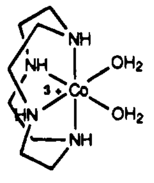

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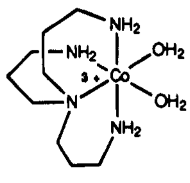

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to the difference in the rates of anation of the phosphate to the metal complexes.[9] However, we showed that anation is not the rate-determining step in the hydrolysis reaction.[10] If anation were the rate-determining step, the Co(III) complexes would hydrolyze **BNPP** and bis(2,4-dintrophenyl) phosphate (**BDNPP**) at comparable rates, which they do not.

The equilibrium constants for coordination of phosphate diesters to *cis*-diaqua Co(III) complexes can be determined by ^{31}P NMR methods.[4f,8a] Monodentate coordination of dimethyl phosphate to **1**, **2**, or **3** gives two new ^{31}P NMR signals (about 5–10 ppm downfield shifted relative to the free phosphate) since the two coordinated water molecules in each **1**–**3** are not equivalent (Figure 1). The equilibrium constants for coordination of dimethyl phosphate to **1**–**3** as determined by ^{31}P NMR are approximately 4, 3, and 5 M^{-1}, respectively. The difference in the reactivities of the metal complexes for hydrolyzing **BNPP** may be explained in terms of the ligand effect on stabilizing the four-membered-ring intermediates or transition states in the hydrolysis reaction (Scheme 1a) since anation is not the rate-determining step and the equilibrium constants for the anation step are comparable for **1**–**3**.

One might expect the relative reactivities of **1**–**3** for hydrolyzing **BNPP** to parallel the relative stabilities of acetate chelated to **1**–**3** since both processes involve the formation of four-membered rings. Chelation and monodentate coordination of acetate to *cis*-diaqua Co(III) complexes can be detected by ^{13}C NMR methods (Figure 2).[11] The carboxyl carbon signal due to acetate chelated to Co(III) is about 20 ppm downfield shifted compared to that for the free acetate. As in monodentate coordination of dimethyl phosphate to **1**–**3**, monodentate coordination of acetate to each of the cobalt complexes gives two new signals for the carboxyl carbon about 10 ppm downfield of the free acetate. Figure 2 shows that acetate coordinates to **3** predominantly as a chelate while it coordinates to **1** as a monodentate ligand. In contrast, significant amounts of monodentate and bidentate coordination of acetate to **2** can be observed. Hence there is excellent agreement between relative reactivities of **1**–**3** for hydrolyzing **BNPP** and relative stabilities of acetate chelated to **1**–**3**.

Why should acetate chelate to **2** and **3** but not to **1**? Chelation of acetate to *cis*-diaqua Co(III) complexes should become more favorable as the value of the O–Co–O bond angle is decreased.[12] In a strain-free system, the O–Co–O, Co–O–C, O–C–O, and C–O–Co bond angles should add up to 429° (90 + 109.5 + 120 + 109.5°). However, in any four-membered ring, the sum of the internal angles should be less than or equal to 360°. Therefore, each of the angles in the four-membered-ring acetate chelate must be compressed compared to the strain-free bond angles. One way to decrease the O–Co–O bond angle would be to increase the N–Co–N bond angle opposite the O–Co–O bond angle.[13] The N–Co–N bond angles in **2** and **3** should be greater than that in **1** since the bond angle in the latter case is locked into a five-membered ring. It follows that acetate should chelate more easily to **2** and **3** than to **1**.

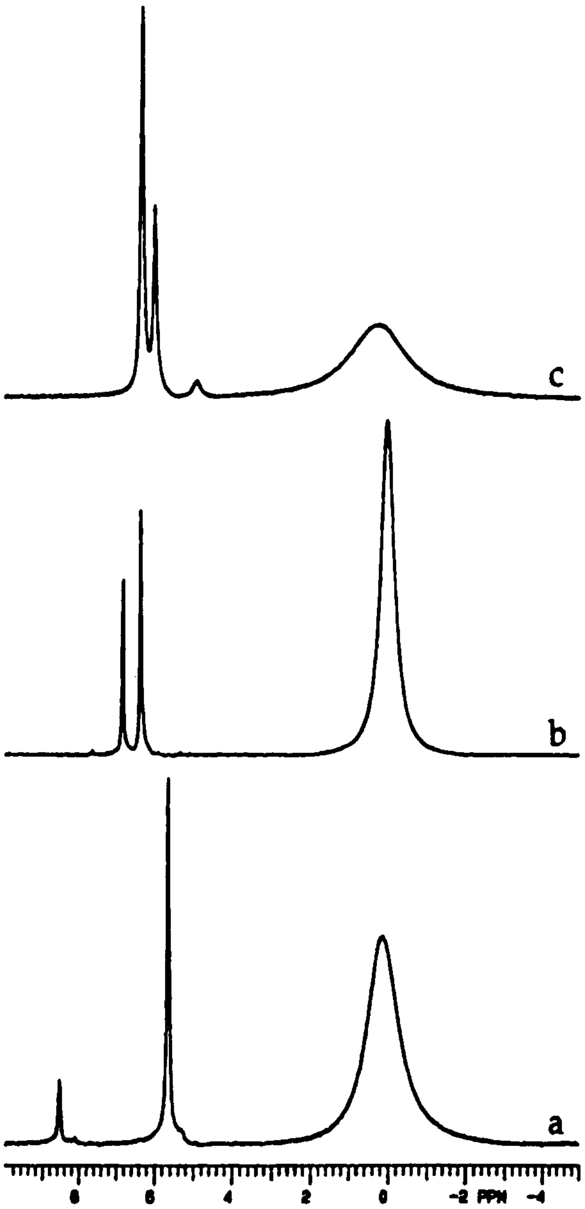

Figure 1. ^{31}P NMR spectra showing the complexation of dimethyl phosphate (0.10 M) to (a) **1** (0.10 M), (b) **2** (0.10 M), and (c) **3** (0.10 M) at pD 3.0 and 25 °C.

We have determined the structure of the perchlorate salt of pivalate chelated to **3** (**3a** in Figure 3). It is interesting to compare the structure of **3a** to the structures of carbonate chelated to **1** (**1a**)[14] and **2** (**2a**).[15] The O–Co–O bond angle in **3a** (67.1°) is considerably smaller than 90° and is comparable to the O–Co–O bond angles in **1a** (68.5°) and **2a** (68.4°). It is not surprising that the O–Co–O bond angle in **3a** is comparable to those in **1a** and **2a** since the four-membered rings should be highly strained and lack flexibility. As expected from theory,[13] the N–Co–N bond angle (97.5°) opposite the compressed O–Co–O bond angle in **3a** is significantly expanded from 90°. The corresponding N–Co–N bond angles in **1a** and **2a** are 88.0 and 103.0°, respectively. Strictly on the basis of values of the N–Co–N bond angle values, acetate is expected to chelate best to **2** followed by **3** and **1**. It is apparent from the above

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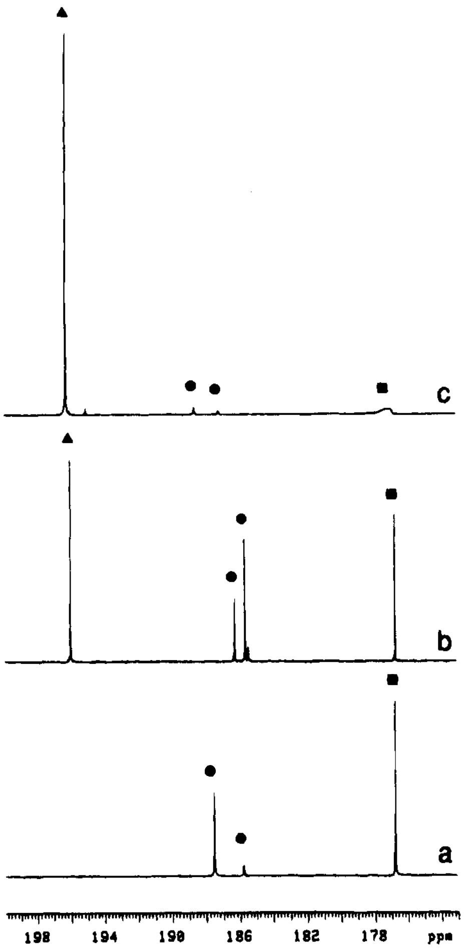


Figure 2. ^{13}C NMR spectra showing the complexation of sodium acetate-1-^{13}C (0.10 M) to (a) **1** (0.10 M), (b) **2** (0.10 M), and (c) **3** (0.10 M) at pD 2.5 and 25 °C. Peak assignments:[11] ▲, $[(N_4)Co(OAc)]^{2+}$; ●, $[(N_4)Co(H_2O)(OAc)]^{2+}$; ■, free AcOD.

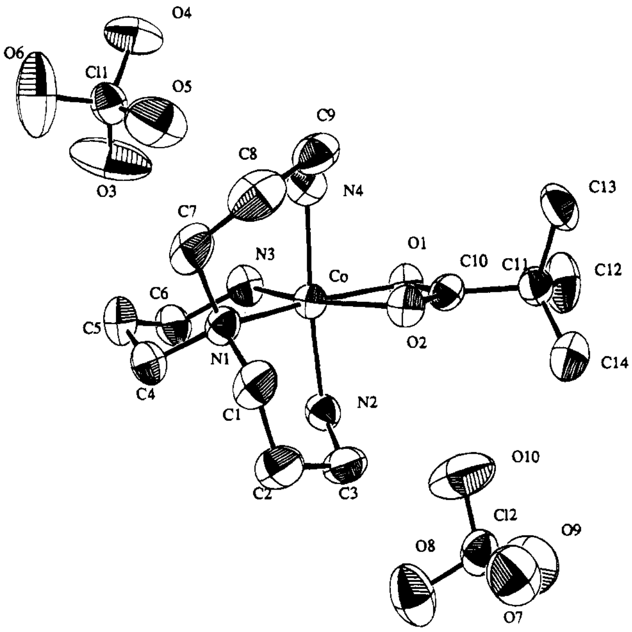


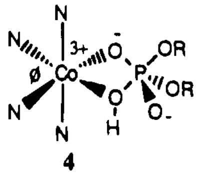
Figure 3. ORTEP[20b] plot of the carboxylate chelate structure **3a**. Thermal ellipsoids are shown at 50% probability.

Table 1. Ratio of Chelate to Monodentate Binding ([**3c**]/[**3b**]) of Monosubstituted Acetic Acids As Determined by ^{13}C and ^{1}H NMR

Subsituent	pK_a	K_{eq} (^{13}C)	K_{eq} (^{1}H)
Cl	2.86		1.7×10^{-1}
Br	2.86	3.2×10^{-1}	3.2×10^{-1}
MeO	3.58		4.6×10^{-1}
Ph	4.31	2.2×10^{0}	
H	4.76	1.3×10^{1}	

structural comparisons that although the N−Co−N bond angle is an important factor in determining the stability of the four-membered ring chelate, it is not the only factor. Another factor that should play an important role in stabilizing the four-membered-ring chelate is the Lewis acidity of the metal center. The first and second p*K*a values of the two metal-coordinated water molecules in **3** (4.8 and 7.6) are significantly lower than those of **1** (5.5 and 8.0) or **2** (5.6 and 8.0), indicating that the cobalt center in **3** is the most Lewis acidic and the cobalt centers in **1** and **2** are comparable.[8a] The more Lewis acidic cobalt center should be able to better stabilize the chelate.

It is interesting to note that the relative reactivities of **1**−**3** for hydrolyzing BNPP parallel the relative rates of anation of phosphate to the same cobalt complexes.[8,9] The parallel reactivities may be understandable in terms of the structural requirements of the two reactions. The phosphate diester hydrolysis reaction requires the formation of a four-membered-ring transition state with concomitant increase in the N−Co−N bond angle (ø) opposite the four-membered ring (**4**). The anation reaction requires the formation of a trigonal bipyramid intermediate (**5**) that also results in increasing the same N−Co−N bond angle. *cis*-Diaqua Co(III) complexes with tetraamine ligands that stabilize the large N−Co−N bond angle should undergo rapid anation as well as hydrolyze phosphate diesters rapidly.



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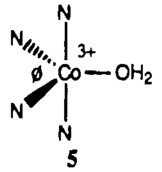

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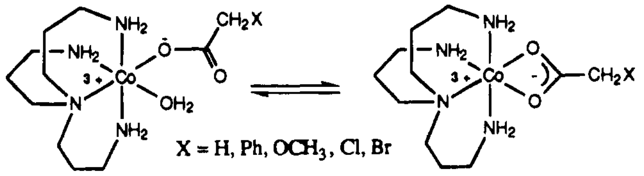
Electronic and Steric Effects of Carboxylates

Monodentate coordination and chelation of acetate and other carboxylates to *cis*-diaqua Co(III) complexes can be monitored not only by ^{13}C NMR but also by ^{1}H NMR. We examined monodentate coordination and chelation of acetate and monosubstituted (chloro, bromo, phenyl, methoxy) acetates to **3**. Coordination of bromoacetate to **3** was monitored by both ^{1}H NMR and ^{13}C NMR while coordination of chloroacetate and methoxy acetate was monitored only by ^{1}H NMR and coordination of acetate and phenylacetate was monitored only by ^{13}C NMR. There is excellent agreement between the ^{1}H NMR result and the ^{13}C NMR result for coordination of bromoacetate to **3** (Table 1). The values of the equilibrium constants for chelation increase with increase in the basicity of the carboxylates. The Brønsted plot of log([**3c**]/[**3b**]) vs the p*K*a of the monosubstituted acetic acids (eq 1) gives a surprisingly large slope (β_{chel}) of



3b **3c**

$$\log([\mathbf{3c}]/[\mathbf{3b}]) = (0.81)\mathrm{p}K_a - 3.0 \qquad (1)$$

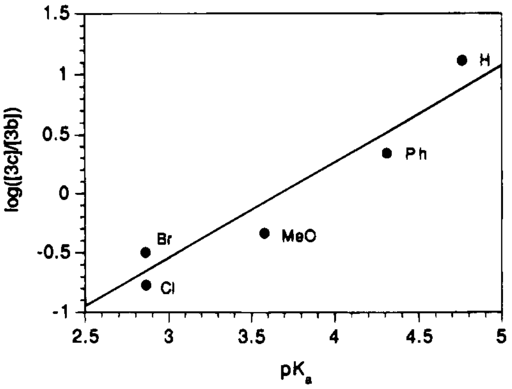


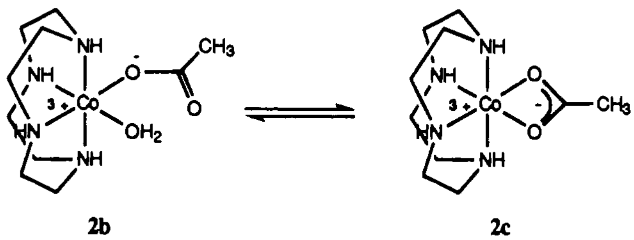
Figure 4. Plot of the ratio of chelate to monodentate binding ([**3c**]/[**3b**]) of various substituted acetic acids *vs* the pK_a of the acids at 25 °C (R = 0.95).

0.81 (Figure 4). It seems that strongly basic carboxylates can better withstand the four-membered-ring strain than weakly basic carboxylates.

The ratio of bidentate to monodentate coordination of benzoate to **3** as determined by ^{13}C NMR (11) is significantly greater than that calculated (2.5) from eq 1 using a p*K*a value of 4.20 for benzoic acid. In contrast, the ratio of bidentate to monodentate coordination of formate to **3** as determined by ^{13}C NMR (1.5×10^{-1}) or ^{1}H NMR (1.7×10^{-1}) is significantly less than that calculated (1.1) from eq 1 using a p*K*a value of 3.77 for formic acid. The O−C−O bond angle in a sterically bulky carboxylate should be smaller than that in acetate while the O−C−O bond angle in formate should be larger than that in acetate.[16] Chelation of carboxylates to *cis*-diaqua Co(III) complexes should become more favorable as the value of the O−C−O bond angle is decreased since the O−C−O bond angle in the four-membered ring should be compressed as that in **3a** (Figure 3).

Solvent Effect

The acidity of carboxylic acids decreases with decrease in solvent polarity.[17] Therefore, on the basis of the above electronic effect of carboxylates on the chelation reaction, one would expect chelation to increase in methanol compared to that in water. In methanolic water the ratio of [**2c**]/[**2b**] increases dramatically with the increase in the percentage of methanol in the mixed solvent (Figure 5).



2b **2c**

The solvent effect for chelation of acetate can also be observed for **1**. Although there is no detectable amount of chelation of acetate (0.05 M) to **1** (0.05 M) in water, ^{13}C NMR indicates that there is more than 5% chelation of acetate to **1** in 90% methanolic water. Chelation of bromoacetate (0.01 M) to **3** (0.01 M) increases dramatically with increase in the methanolic content of the solvent.

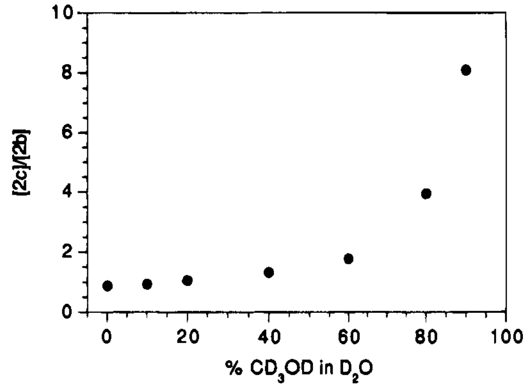


Figure 5. Plot of the ratio of chelate to monodentate binding ([**3c**]/[**3b**]) of sodium acetate-1-^{13}C to **2** *vs* the volume percent composition of deuterated methanol in D_2O at 25 °C.

Table 2. Crystallographic Data for $[(\text{trpn})\text{Co}(\eta^2\text{-O}_2\text{CC(CH}_3)_3](\text{ClO}_4)_2$

mol formula	$C_{14}H_{33}N_4O_{10}Cl_2Co$
mol wt	547.28
crystal dimens, mm	0.20 × 0.20 × 0.23
temp, °C	20 ± 1
D_{calcd}, g/cm^3	1.575
linear abs coeff, mm^{-1}	8.80
h, *k*, *l* limits	0−10, 0−17, 0−21
2θ range, deg	2−144
F(000)	1141
no. of unique data	2723
no. of data with $I > 2.5\sigma(I)$	2112
no. of variables	413
R^a	0.037
$R_w{}^b$	0.033
w	$[\sigma^2(F_o) + (1.25 \times 10^{-4})(F_o{}^2)]^{-1}$
goodness of fit^c	1.42

[a] $R = \Sigma(F_o - F_c)/\Sigma F_o$. [b] $R_w = [\Sigma[w(F_o - F_c)^2]/\Sigma w F_o{}^2]^{1/2}$. [c] GoF = $[\Sigma[w(F_o - F_c)^2]/(\text{no. of reflns} - \text{no. of params})]^{1/2}$.

Other Four-Membered Ring Chelates

Ligands other than carboxylates are known to chelate to *cis*-diaqua Co(III) complexes. Carbonate forms stable chelates with **1**, **2**, or **3**.[14,15] Carbonate chelates are more stable than carboxylate chelates since carbonate has two negative charges and is more basic than carboxylates. Similarly, inorganic phosphate[18] or phosphate monoesters[19] form stable chelates with *cis*-diaqua Co(III) complexes. However phosphate diesters do not form chelates with **1**, **2**, or **3** to any observable extent presumably because phosphate diesters have only one negative charge and are much less basic than dianionic phosphate monoesters. There is considerable interest in synthesizing phosphate diesters chelated to a metal center since such doubly coordinated phosphate diesters should hydrolyze more rapidly than singly coordinated phosphate diesters. To date, chelated phosphate diesters have not been detected, let alone synthesized.[20] Fundamental factors affecting chelation of carboxylates to metal centers should also play important roles in chelation of phosphate diesters to metal centers. Our present study indicates that several factors should be taken into consideration in synthesizing phosphate diesters that are chelated to Co(III) or other metal centers. First, the N−Co−N bond angle opposite

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Table 3. Final Coordinates and Equivalent Isotropic Thermal Parameters of the Non-Hydrogen Atoms[a]

atom	x	y	z	U_{eq}, Å^2
Co	0.77457(8)	0.42370(4)	0.13720(3)	0.0323(2)
O(1)	0.7879(4)	0.50824(17)	0.05323(13)	0.0373(9)
O(2)	0.7278(4)	0.54493(17)	0.16775(14)	0.0405(9)
N(1)	0.7428(5)	0.3600(2)	0.23526(17)	0.0396(13)
N(2)	0.5587(5)	0.4065(2)	0.11056(19)	0.0417(14)
N(3)	0.8388(5)	0.3214(2)	0.0770(2)	0.0460(14)
N(4)	0.9897(5)	0.4499(3)	0.1593(2)	0.0460(14)
C(1)	0.6191(7)	0.4063(4)	0.2779(2)	0.056(2)
C(2)	0.4615(7)	0.4030(4)	0.2429(3)	0.062(2)
C(3)	0.4461(6)	0.4450(3)	0.1658(3)	0.0523(19)
C(4)	0.6987(7)	0.2612(3)	0.2269(3)	0.0573(19)
C(5)	0.7981(7)	0.2064(3)	0.1747(3)	0.0613(19)
C(6)	0.7832(7)	0.2298(3)	0.0923(3)	0.0537(19)
C(7)	0.8844(7)	0.3610(3)	0.2842(3)	0.059(2)
C(8)	0.9529(7)	0.4508(4)	0.2988(3)	0.069(2)
C(9)	1.0254(7)	0.4959(3)	0.2323(3)	0.057(2)
C(10)	0.7500(5)	0.5700(3)	0.0990(2)	0.0374(14)
C(11)	0.7336(6)	0.6669(3)	0.0766(2)	0.0427(14)
C(12)	0.7428(8)	0.6736(3)	−0.0106(3)	0.072(2)
C(13)	0.8667(7)	0.7179(3)	0.1118(3)	0.063(2)
C(14)	0.5859(7)	0.7008(3)	0.1083(3)	0.072(2)
Cl(1)	0.24434(15)	0.20711(7)	0.12607(6)	0.0498(4)
O(3)	0.1508(5)	0.1693(4)	0.0700(2)	0.123(2)
O(4)	0.3831(5)	0.2347(3)	0.0925(2)	0.0763(14)
O(5)	0.1730(5)	0.2808(3)	0.1608(3)	0.112(2)
O(6)	0.2713(8)	0.1470(3)	0.1827(2)	0.145(3)
Cl(2)	0.77517(18)	0.02134(8)	0.51021(7)	0.0614(5)
O(7)	0.8223(6)	0.0783(3)	0.4497(2)	0.1033(19)
O(8)	0.8417(6)	−0.0618(2)	0.4923(3)	0.101(2)
O(9)	0.8236(6)	0.0551(3)	0.5791(2)	0.126(3)
O(10)	0.6137(5)	0.0149(3)	0.5110(3)	0.114(2)

[a] Esd's refer to the last significant digits. U_{eq} = one-third of the trace of the orthogonalized **U**.

Table 4. Bond Distances (Å)

Co−O(1)	1.946(2)	C(4)−C(5)	1.508(8)
Co−O(2)	1.939(3)	C(5)−C(6)	1.492(7)
Co−N(1)	1.986(3)	C(7)−C(8)	1.497(8)
Co−N(2)	1.969(4)	C(8)−C(9)	1.490(8)
Co−N(3)	1.946(3)	C(10)−C(11)	1.512(6)
Co−N(4)	1.968(4)	C(11)−C(12)	1.534(6)
Co−C(10)	2.304(4)	C(11)−C(13)	1.527(7)
O(1)−C(10)	1.270(5)	C(11)−C(14)	1.500(8)
O(2)−C(10)	1.277(4)	Cl(1)−O(3)	1.401(4)
N(1)−C(1)	1.490(7)	Cl(1)−O(4)	1.415(4)
N(1)−C(4)	1.538(6)	Cl(1)−O(5)	1.409(5)
N(1)−C(7)	1.511(7)	Cl(1)−O(6)	1.362(4)
N(2)−C(3)	1.500(6)	Cl(2)−O(7)	1.423(4)
N(3)−C(6)	1.482(6)	Cl(2)−O(8)	1.412(4)
N(4)−C(9)	1.487(6)	Cl(2)−O(9)	1.377(4)
C(1)−C(2)	1.515(8)	Cl(2)−O(10)	1.421(5)
C(2)−C(3)	1.497(7)		

Table 5. Bond Angles (deg)

O(1)−Co−O(2)	67.10(11)	Co−N(2)−C(3)	115.5(3)
O(1)−Co−N(1)	167.50(13)	Co−N(3)−C(6)	122.5(3)
O(1)−Co−N(2)	87.93(14)	Co−N(4)−C(9)	117.7(3)
O(1)−Co−N(3)	94.94(13)	N(1)−C(1)−C(2)	116.6(4)
O(1)−Co−N(4)	87.77(16)	C(1)−C(2)−C(3)	115.7(5)
O(1)−Co−C(10)	33.44(12)	N(2)−C(3)−C(2)	111.2(4)
O(2)−Co−N(1)	100.50(12)	N(1)−C(4)−C(5)	115.9(4)
O(2)−Co−N(2)	89.10(14)	C(4)−C(5)−C(6)	114.1(4)
O(2)−Co−N(3)	161.88(13)	N(3)−C(6)−C(5)	111.4(4)
O(2)−Co−N(4)	87.81(17)	N(1)−C(7)−C(8)	115.9(4)
O(2)−Co−C(10)	33.66(12)	C(7)−C(8)−C(9)	116.5(4)
N(1)−Co−N(2)	90.40(16)	N(4)−C(9)−C(8)	111.9(4)
N(1)−Co−N(3)	97.52(14)	Co−C(10)−O(1)	57.6(2)
N(1)−Co−N(4)	93.47(17)	Co−C(10)−O(2)	57.3(2)
N(1)−Co−C(10)	134.13(13)	Co−C(10)−C(11)	178.2(3)
N(2)−Co−N(3)	92.71(16)	O(1)−C(10)−O(2)	114.9(4)
N(2)−Co−N(4)	175.44(16)	O(1)−C(10)−C(11)	124.2(3)
N(2)−Co−C(10)	88.03(14)	O(2)−C(10)−C(11)	120.9(3)
N(3)−Co−N(4)	89.19(18)	C(10)−C(11)−C(12)	108.5(3)
N(3)−Co−C(10)	128.35(14)	C(10)−C(11)−C(13)	107.7(4)
N(4)−Co−C(10)	87.54(17)	C(10)−C(11)−C(14)	108.2(4)
Co−O(1)−C(10)	88.9(2)	C(12)−C(11)−C(13)	109.2(4)
Co−O(2)−C(10)	89.0(2)	C(12)−C(11)−C(14)	113.1(4)
Co−N(1)−C(1)	108.2(3)	C(13)−C(11)−C(14)	110.0(4)
Co−N(1)−C(4)	114.6(3)	O(3)−Cl(1)−O(4)	109.4(2)
Co−N(1)−C(7)	111.8(3)	O(3)−Cl(1)−O(5)	111.1(3)
C(1)−N(1)−C(4)	108.2(4)	O(3)−Cl(1)−O(6)	110.2(3)
C(1)−N(1)−C(7)	108.1(3)	O(4)−Cl(1)−O(5)	109.5(3)
C(4)−N(1)−C(7)	105.7(3)	O(4)−Cl(1)−O(6)	110.3(3)
O(5)−Cl(1)−O(6)	106.4(3)	O(8)−Cl(2)−O(9)	113.1(3)
O(7)−Cl(2)−O(8)	104.1(3)	O(8)−Cl(2)−O(10)	110.8(3)
O(7)−Cl(2)−O(9)	110.1(3)	O(9)−Cl(2)−O(10)	108.9(3)
O(7)−Cl(2)−O(10)	109.8(3)		

the O−Co−O bond angle should be as large as possible. Second, electron-donating groups on the phosphate diester group should stabilize the chelate. This implies that electron-withdrawing groups on the tetraamine ligand of the Co(III) complex should also stabilize the chelate. Finally, less polar solvents should be used to stabilize the chelate.

In conclusion *cis*-diaqua Co(III) complexes that efficiently hydrolyze esters, amides, nitriles, and phosphates also easily form four-membered ring complexes with carboxylates. Hence it is important to understand factors affecting chelation of carboxylates to *cis*-diaqua Co(III) complexes. We find that steric, electronic, and solvent effects all play important roles in the chelation reaction.

Experimental Section

Instruments. ^{1}H NMR (299.3 MHz), ^{31}P NMR (121.4 MHz), and ^{13}C NMR (75.4 MHz) were obtained with a Varian XL-300 FT spectrometer, and ^{1}H NMR (499.8 MHz) and ^{13}C NMR (125.7 MHz) were obtained with a Varian Unity-500 FT spectrometer. Unless otherwise stated, spectra were recorded in D_2O with chemical shifts reported in ppm with 3-(trimethylsilyl)-1-propanesulfonic acid (0 ppm), trimethyl phosphate (0 ppm), and dioxane (66.66 ppm) used as references for ^{1}H, ^{31}P, and ^{13}C NMR, respectively.

Materials. Acetic-*1*-^{13}C acid, sodium salt [23424-28-4]; benzoic-*carboxy*-^{13}C acid [3880-99-7], bromoacetic acid [79-08-3], bromoacetic-*1*-^{13}C acid [57858-24-9], chloroacetic acid [79-11-8], formic acid, sodium salt [141-53-7], formic-^{13}C acid, sodium salt [23102-86-5], methoxyacetic acid [625-45-6], benzeneacetic-*carboxy*-^{13}C acid [57825-33−9]; 1,4,7,10-tetraazacyclododecane (cyclen) [294-90-6]; trimethylacetic acid (pivalic acid) [75-98-9], and tris(2-aminoethyl)amine (tren) [4097-89-6] were purchased from Aldrich. Sodium dimethyl phosphate was prepared by the reaction of trimethyl phosphate with sodium iodide in acetone. The complexes $[(tren)Co(OH_2)_2](ClO_4)_3$ (**1**), $[(cyclen)Co(OH_2)_2](ClO_4)_3$ (**2**), and $[(trpn)Co(OH_2)_2](ClO_4)_3$ (**3**) were prepared according to published procedures.[19b]

$[(trpn)Co(\eta^2\text{-}O_2C(CH_3)_3](ClO_4)_2$ (3a). To a freshly prepared solution of **3** (2 mmol) in water (50 mL) was added pivalic acid, sodium salt (4 mmol). The volume of the solution was reduced *in vacuo*, and solid $NaClO_4$ was added to induce crystallization. The resulting violet needles were recrystallized from aqueous $NaClO_4$ at low temperature. Yield: 65%. UV−vis: 526.5 nm (ϵ 68.8), 359 (163.2). ^{13}C NMR, δ CO 214.44, DEPT CH_2 58.25, 55.85, 38.49, 37.99, 25.71, 24.01, CH_3 25.71, C 41.09. FAB MS: 349 *m/e* ($M^+ - 2ClO_4$). Anal. Calcd for $C_{14}H_{33}N_4Cl_2CoO_{10}P$: C, 30.73; H, 6.08; N, 10.24; Cl, 12.96; Co, 10.77. Found: C, 30.74; H, 6.20; N, 10.26; Cl, 12.80; Co, 10.72.

X-ray Diffraction Studies of 3a. All measurements were carried out on an Enraf-Nonius CAD-4 diffractometer using Cu Kα radiation (1.540 56 Å) with a graphite crystal, incident beam monochromator. The $\omega/2\theta$ scan mode was used. Lattice parameters for **3a** were determined by least-squares refinement using the setting angles of 30 reflections in the range $50.00 < 2\theta < 100.00°$. Data were collected to a maximum 2θ of 144°. The cell is orthorhombic, space group $P2_12_12_1$, with dimensions a = 8.7822(3)Å, b = 14.9959(6) Å, c = 17.5277(5) Å, V = 2308.35(14) Å^3, and Z = 4. An empirical absorption correction was applied with transmission factors ranging from 0.160 to 0.252. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically; hydrogen atoms, isotropically. The crystal structure consists of one cation and two perchlorate ions per asymmetric unit. The final cycle of full-matrix least-squares refinement was based on 2112 observed reflections ($I > 2.5\sigma(I)$) and 413 variable parameters and converged with agreement factors of $R = 0.037$ and $R_w = 0.033$. The deepest hole in the final difference map was -0.25 e Å^{-3} and the largest peak was 0.31 e Å^{-3}. All calculations were performed using the NRCVAX[21a] crystallographic software. Results are summarized in Tables 2–5 and Figure 3.

Equilibrium. Complexation of sodium dimethyl phosphate (100 mM) to **1**–**3** (100 mM) in D_2O at pD 3.0 and 25 °C was monitored by ^{31}P NMR (121.4 MHz) after 336, 168, and 6 h, respectively, by which times the equilibria were established. An acquisition time of 240 min was used (Figure 1).

Complexation of acetic-*1*-^{13}C acid, sodium salt (100 mM), to **1**–**3** (100 mM) in D_2O at 25 °C was monitored by ^{13}C NMR (75.4 MHz) with an acquisition time of 240 min after equilibrating 168, 24, and 6 h, respectively, at pD 2.5 and 25 °C (Figure 2).

Complexation of the carboxylic acid sodium and/or potassium salts to the diaqua species **3** was monitored by NMR at the following concentrations of metal complex to carboxylate: acetic acid ^{13}C (50:50, 50:25, 20:20, 5:5 mM) free (*f*) δ 180, monodentate (*m*) δ 187, δ 188, chelate (*c*) δ 196; benzoic acid ^{13}C (50:50 mM) *f* δ 176, *m* δ 180, δ 181, *c* δ 188; bromoacetic acid ^{1}H (50:50, 20:10, 10:10, 5:5 mM) *f* δ 3.90, *m* δ 3.95, δ 4.14, *c* δ 3.97, ^{13}C (50:50, 10:10 mM) *f* δ 173, *m* δ 180, δ 181, *c* δ 190; chloroacetic acid ^{1}H (50:50, 20:10, 10:10, 5:5 mM) *f* δ 4.05, *m* δ 4.14, δ 4.34, *c* δ 4.18; formic acid ^{1}H (50:50, 20:10, 5:5 mM) *f* δ 8.44, *m* δ 7.60, δ 8.00, *c* δ 7.74, ^{13}C (50:50 mM) *f* δ 171, *m* δ 176, δ 177, *c* δ 186; methoxyacetic acid ^{1}H (50:50, 20:10, 10:10, 5:5 mM) *f* δ 3.88, *m* δ 4.03, δ 4.27, *c* δ 4.16; phenyl acetic acid ^{13}C (50:50, 50:25, 10:10 mM) *f* δ 182, *m* δ 186, δ 187, *c* δ 196. The relative concentrations of mondentate and chelate species was calculated using the NMR integrals (Figure 4).

Complexation of sodium acetate-*1*-^{3}C (50 mM) to **2** (50 mM) in CD_3OD-D_2O at 25 °C was monitored by ^{13}C NMR (125.7 MHz) with an acquisition time of 90 min after equilibrating approximately 6 h at 25 °C. The pD of the 500 mM D_2O stock solution was 4.0 before dilution with CD_3OD-D_2O (Figure 5).

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, bond distances, and bond angles and a packing diagram for $[(trpn)Co(\eta^2\text{-}O_2CC(CH_3)_3](ClO_4)_2$ (4 pages). Ordering information is given on any current masthead page.

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(21) (a) NRCVAX: Gabe, E. J.; LePage, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, 22, 384. (b) ORTEP: Johnson, C. K. ORTEP: A Fortran Thermal Ellipsoid Plot Program. Technical Report ORNL-5138; Oak Ridge National Laboratory; Oak Ridge, TN, 1976.