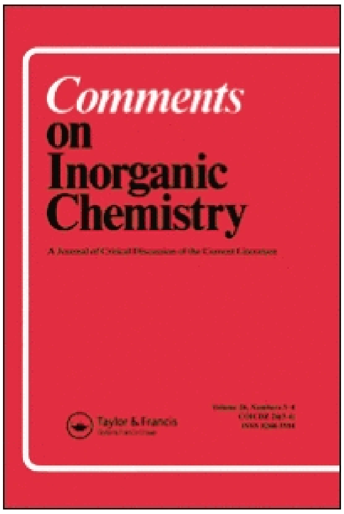

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Oxyanion Chelates of Cobalt(III). Oxygen Exchange, Chelate Ring Opening and Closing, and Hydrolysis of Monodentates

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To cite this Article Buckingham, David A. , Clark, Charles R. and Miskelly, Gordon M.(1988) 'Oxyanion Chelates of Cobalt(III). Oxygen Exchange, Chelate Ring Opening and Closing, and Hydrolysis of Monodentates', Comments on Inorganic Chemistry, 7: 4, 171 — 193

To link to this Article: DOI: 10.1080/02603598808072307

URL: http://dx.doi.org/10.1080/02603598808072307

Oxyanion Chelates of Cobalt(III). Oxygen Exchange, Chelate Ring Opening and Closing, and Hydrolysis of Monodentates

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This Comment summarizes present understanding of the rates and mechanisms of O-exchange and chelate ring opening and closing in oxyanion chelates of Co(III); oxalate and glycinate (5 membered), β-alaninate and malonate (6 membered), and phosphate, carbonate, and sulfate (4 membered). Under some conditions the product monodentate species isomerize between *cis* and *trans* configurations about the metal and these isomers differ in their ability to recyclize. Also complete hydrolysis from the metal may occur in competition with, or instead of, recyclization. Thus complete hydrolysis, as well as recyclization, of the monodentates needs to be considered.

1. INTRODUCTION

Two fundamentally different mechanisms exist for cyclization and its reverse, ring opening. These are (1) substitution at the metal with displacement of coordinated solvent or (2) attack by coordinated solvent at the oxyanion, or protonated oxyanion, of the dangling monodentate. Both mechanisms occur ((1), (2) below),

Comments Inorg. Chem.
1988, Vol. 7, No. 4, pp. 171–193
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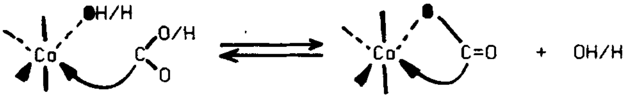
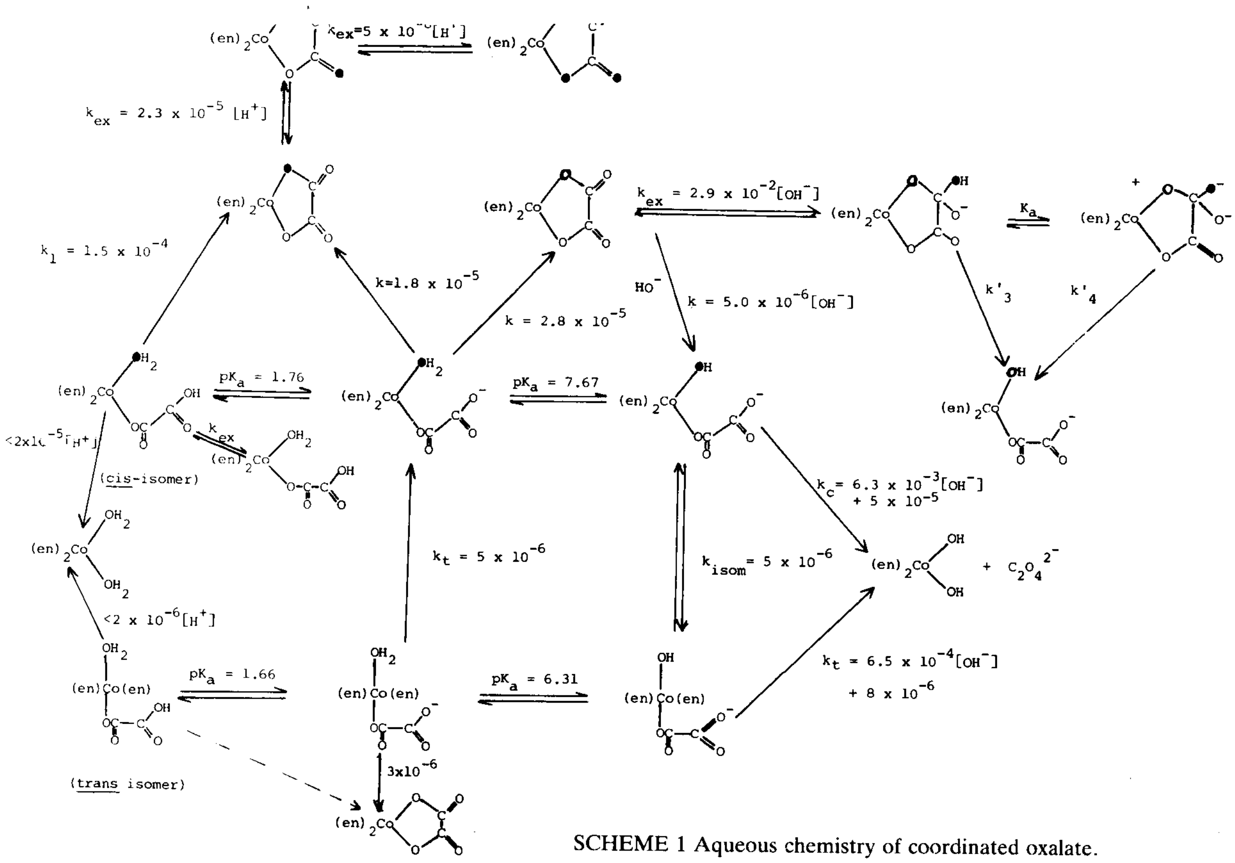
(1)



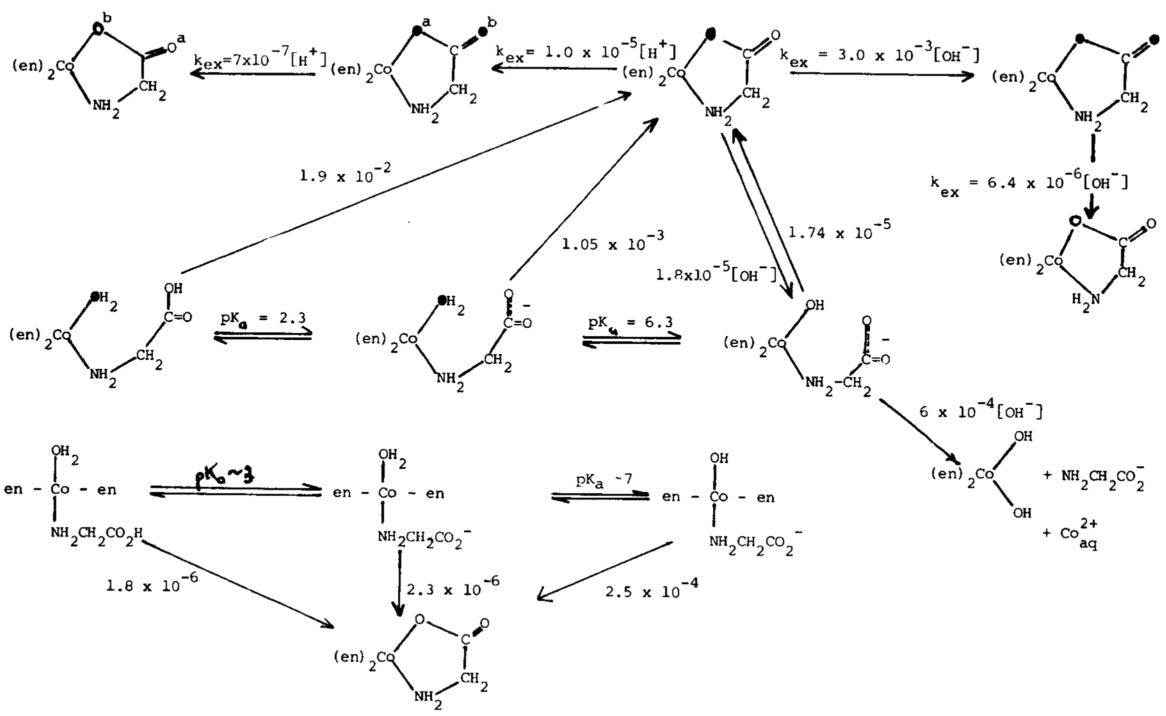
(2)

with the former identifying itself with the more "inorganic" process of solvent exchange at the metal and the latter with the more "organic" process of lactonization. Surprisingly little is known about the "chelate effect" as it relates to substitution at metal centers[1]; however four-, five-, and six-membered rings are certainly favored. Different metal ions enjoy wide variations in donor atom acceptance, and the relation between this and bond angle/bond length distortions at the metal and donor atom has yet to receive systematic experimental evaluation for each ligand type; some theoretical treatments are, however, available, especially for nontransition metals.[2] Much, however, is known about lactonization in organic systems,[3] and since the metal is not directly involved in the corresponding metal chelate (reaction (2) above) there might be expected to be some parallel between this process and its organic equivalent. Thus with Co(III) systems five- and six-membered rings form most readily, and their rates of formation are much facilitated if the leaving group on the dangling monodentate ligand is improved such as it is with anhydrides and esters of carboxylic acids. These more favorable cyclizations have recently received attention elsewhere[4] and we concentrate here on the parent oxyanion species.

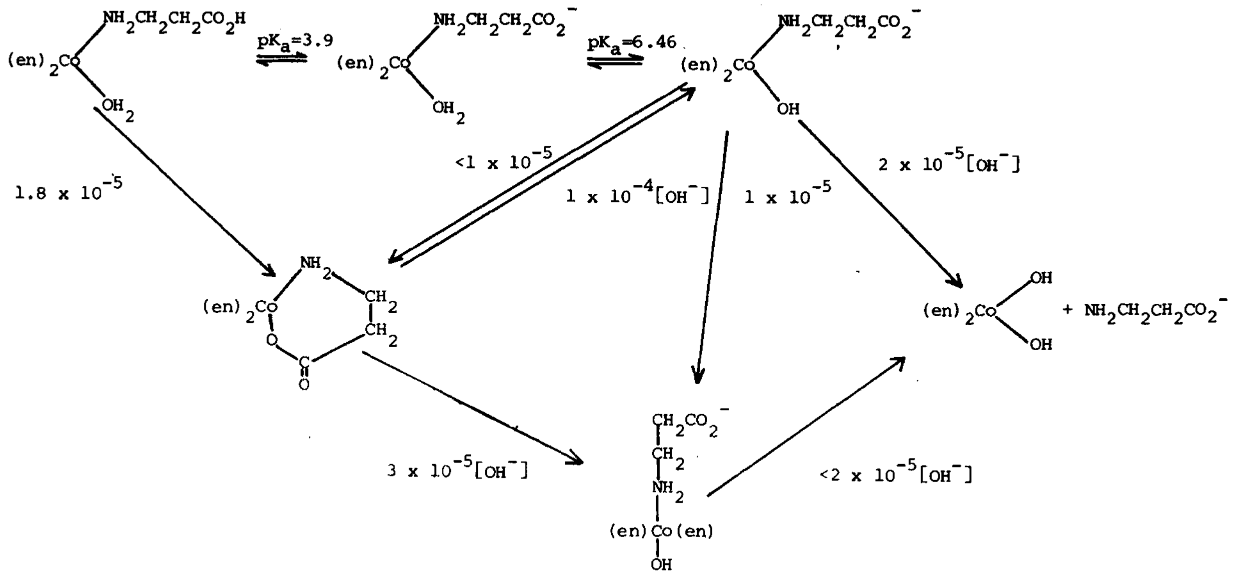
Our own work in this area using bis(ethylenediamine) complexes, together with earlier studies by others, gives a reasonably clear picture of the relative importance of the two mechanisms given above, and particularly with the changes that occur as a function of solution pH. Schemes 1–6 summarize the overall reactions of $[Co(en)_2(O-X)]^{n+}$ chelates where O–X represents oxalate, glycinate, β-alaninate, malonate, phosphate and carbonate, respectively. Rate constants in these schemes are all expressed as first-order values (s^{-1}, 25°C), which for reactions with a first-order $[H^+]$ or $[OH^-]$ dependence relate to reaction at 1 mol dm^{-3}, H^+



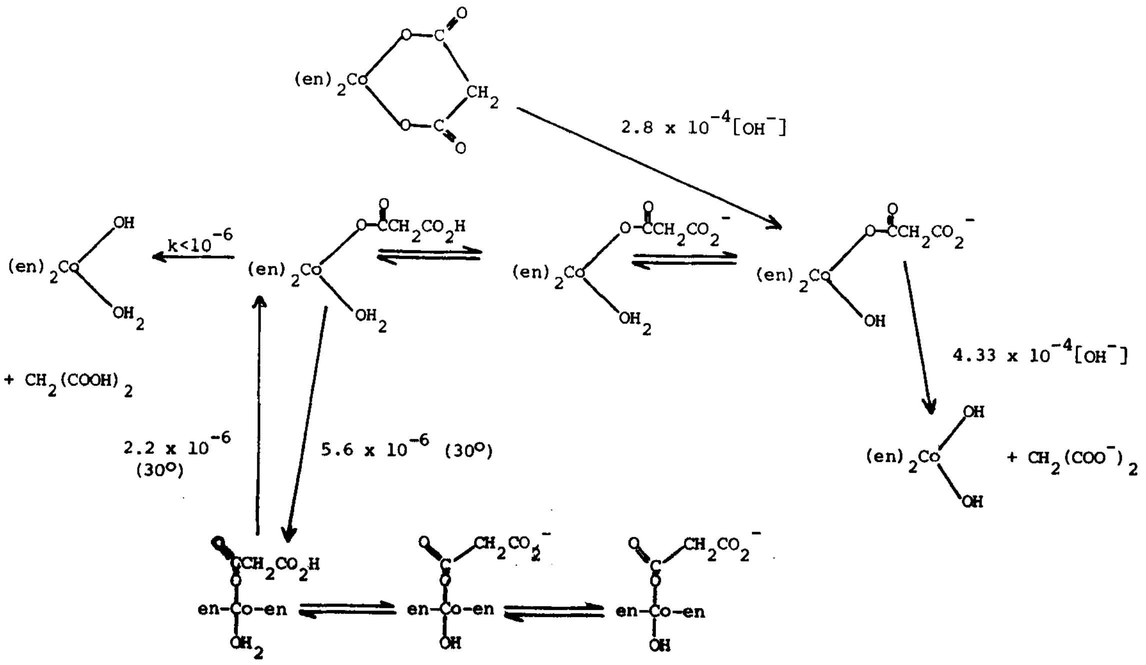
SCHEME 1 Aqueous chemistry of coordinated oxalate.



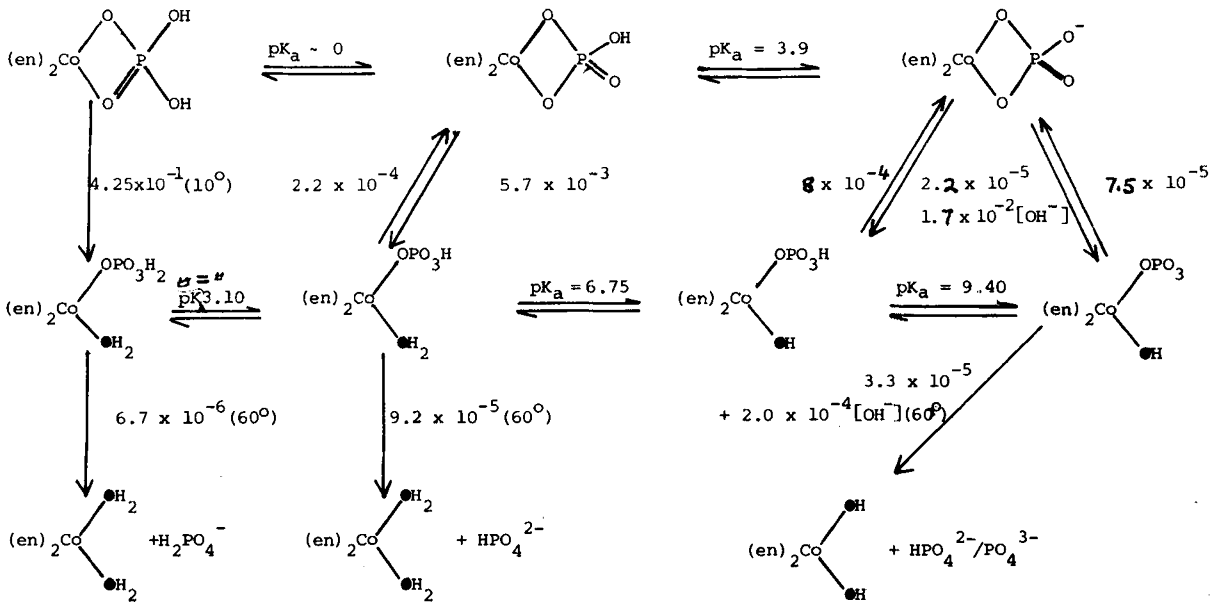
SCHEME 2 Aqueous chemistry of coordinated glycinate.



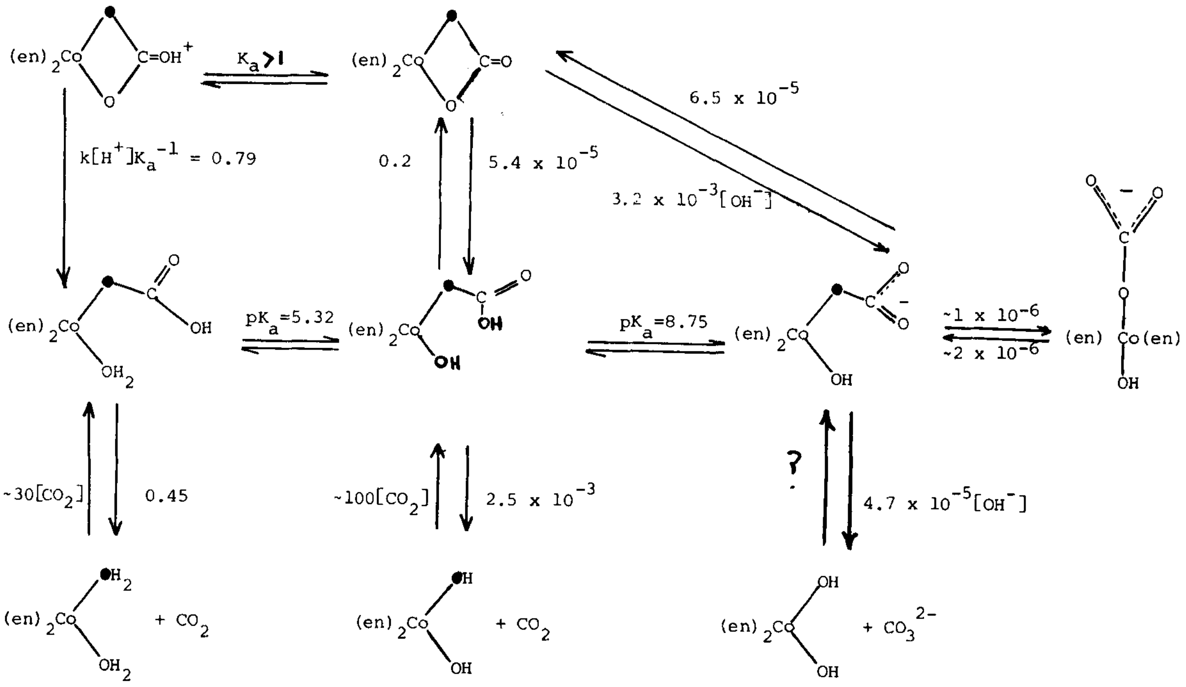
SCHEME 3 Aqueous chemistry of coordinated β-alaninate.



SCHEME 4 Aqueous chemistry of coordinated malonate.



SCHEME 5 Aqueous chemistry of coordinated phosphate.



SCHEME 6 Aqueous chemistry of coordinated carbonate.

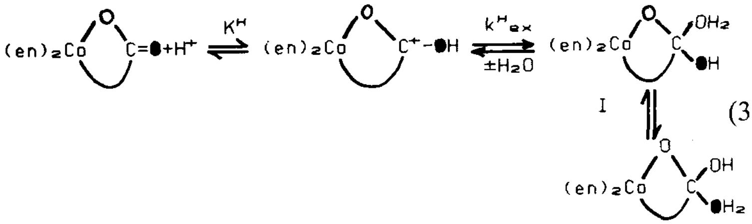
or OH^- concentration. Filled in O atoms identify positions of O-exchange, or cleavage. Tables I–V tabulate rate data (first- or second-order constants, 25°C).

2. OXYGEN EXCHANGE IN THE INTACT CHELATE (TABLE I)

This is a fundamental property since it relates the ability of the chelated oxyanion to interact chemically with its environment.

2.1. Acid-Catalyzed Exchange

The exocyclic oxygens in the five-membered chelates $[Co(en)_2(NH_2CH_2CO_2)]^{2+}$ and $[Co(en)_2(O_2C_2O_2)]^+$ undergo H^+-catalyzed exchange much more rapidly than do the coordinated (endo) oxygens. Such behavior is also found with monodentate carboxylate species, e.g., $[(NH_3)_5CoOC(O)R]^{2+}$ ions (R═H, CF_3, CO_2H).[5] Undoubtedly exchange occurs via protonation at oxygen and reversible addition of water at carbon, (3),

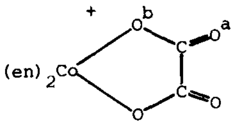
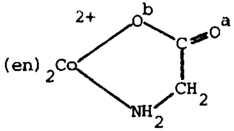


(3)

(k^H_{ex}(obs) = $k^H_{ex}K^H[H^+]/2$) and it will undoubtedly be a property of all Co(III) carboxylates which do not first aquate at the metal. This latter possibility becomes important with less stable ligand systems (e.g., it is likely for β-trien, cyclen and tren complexes) where one or both of the remaining coordination sites holding the oxyanion chelate is susceptible to bond rupture at the metal. The exchange mechanism given by reaction (3) is somewhat facilitated by the metal, but not overly so. Uncomplexed carboxylic acids are normally refluxed in acidic solution to assist exchange. Coordi-

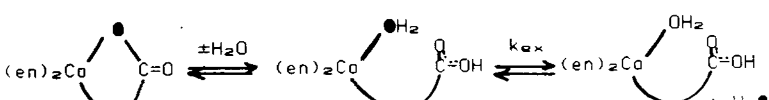
TABLE I

Oxygen exchange in chelate rings

Complex	H⁺-Catalyzed Exchange $k^{H}_{cx(a)}$ (mol⁻¹dm³s⁻¹)	$k^{H}_{cx(b)}$	OH⁻-Catalyzed Exchange $k^{OH}_{cx(a)}$ (mol⁻¹dm³s⁻¹)	$k^{OH}_{cx(b)}$
	2.3×10^{-5}	5×10^{-8}	2.9×10^{-2}	4×10
	1.0×10^{-5}	7×10^{-7}	3.0×10^{-3}	6.4×10

nated carboxylate is poorly basic and protonation has never been directly observed, $pK^{H} < 0$. Thus k_{ex}^{H} of reaction (3) remains undetermined.

Acid-catalyzed exchange into the endo position has also been observed with both the above complexes, but is very slow compared to exocyclic exchange. Endo exchange could occur via interchange in intermediate I of reaction (3) (or in its deprotonated diol form) and it probably does not occur with complete Co–O bond fission; rather a rolling about the now saturated carbon center is envisaged. Alternatively, ring oxygen exchange could occur via acid-catalyzed C–O cleavage in the chelate followed by exchange of coordinated water in the monodentate, and reverse ring closure, reaction (4).



(4)

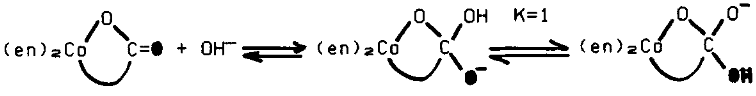
(The possibility of Co–O cleavage in acid and recapture of carboxylate, with exchange, in the resulting monodentate species is unlikely in view of the lower energy C–O bond formation process found for the reverse cyclization under the same condition; see below). However, no evidence has been found for chelate ring opening in acid solution so that the interchange mechanism is favored. No acid-independent switching of oxygen atoms in these chelates has been observed, such as is found with the monodentate $[(NH_3)_5CoOC(O)CH_3]^{2+}$.[6]

^{18}O-tracer results show that O-exchange into the exo or endo positions of the chelates $[Co(en)_2O_2PO_2]$ or $[Co(en)_2O_2CO]^+$ does not occur in acid solution (i.e., in the protonated complexes $[Co(en)_2O_2PO_2H]^+$, $[Co(en)_2O_2PO_2H_2]^{2+}$ or $[Co(en)_2O_2COH]^{2+}$); Co–O bond fission with formation of monodentate aqua complexes occurs instead (see below).

2.2. Exchange in Neutral and Alkaline Solution

In neutral solution no exchange into the chelated oxyanion occurs even though an equilibrium sometimes exists between the chelate and monodentate (i.e., with carbonate and phosphate). Ring opening without O-exchange occurs in $[Co(en)_2O_2PO_2]$,[7] but McKenzie, O'Connor and Odell[8] report substantial exchange into $[Co(NH_3)_4O_2CO]^+$ at pH 9.5 which they attribute to exchange into the ring opened monodentate species. Such a result should be re-examined since O-exchange into carbonate is normally viewed in terms of equilibration with CO_2, which in this case would imply some existence for a Co–OCO intermediate, or to complete hydrolysis to $[Co(NH_3)_4(OH)_2]^+$ plus CO_2.[9] Alternatively, OH^- might add to the chelated or monodentate carbonate (such as it does with most other carbonyl substrates); this pathway has apparently never been contemplated for carbonate species.[10] No OH^--catalyzed pathway for exchange of either oxygen in $[Co(en)_2O_2PO_2]$ or $[Co(en)_2O_2CO]^+$ has been observed in more alkaline solution. Co–O bond fission to hydroxo intermediates is preferred (see below).

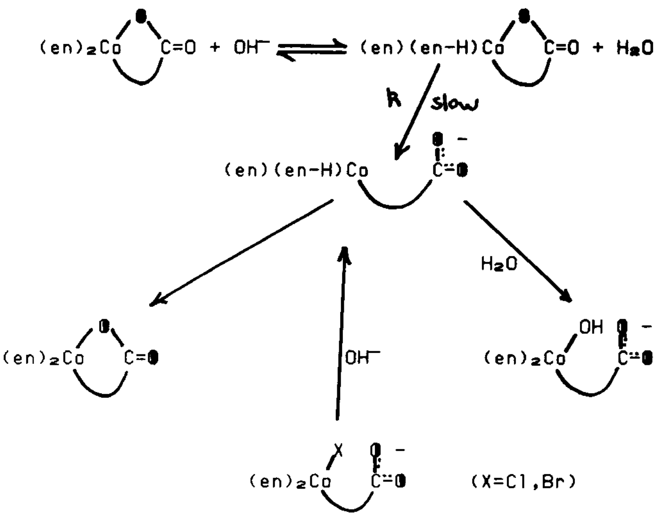
In mildly alkaline solution the exo-cyclic oxygens in $[Co(en)_2NH_2CH_2CO_2]^{2+}$ and $[Co(en)_2O_2C_2O_2]^+$ exchange by a specific OH^--catalyzed route, and much more rapidly than the endo oxygens (Table I). This presumably occurs via OH^- addition to the chelate (5).



(5)

Opening up of the chelate does not occur under these conditions. The slower exchange into the endo positions (Table I) is also specifically OH^--catalyzed and is only observed under very alkaline conditions (~1M OH^-) where hydrolysis to monodentate hydroxo complexes is also observed. Such internal exchange probably occurs via Co–O bond fission in an S_N1 (CB) process, with scrambling of oxygens resulting from re-entry of carboxylate into the five-coordinate intermediate (6).

For $[Co(en)_2NH_2CH_2CO_2]^{2+}$ there is a 50:50 division between exchange and water entry into this intermediate and the same



(6)

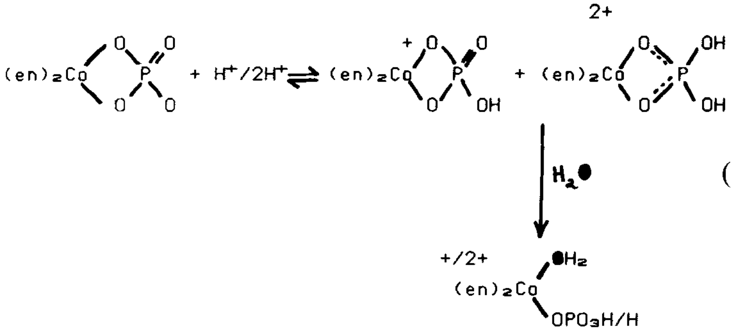
division has also been observed in the base hydrolysis of *cis*-$[Co(en)_2X(NH_2CH_2CO_2)]^+$ (X = Cl, Br) where the carboxylate is not coordinated.[11] This is good evidence for a mechanism which involves competition between the solvent and adjacent carboxylate for the vacated coordination site. However, such exchange of internal oxygens also occurs in competition with C–O bond fission in the OH^--addition intermediate (II of Eq. (5)), and this complicates matters (see below).

3. CHELATE RING OPENING (TABLE II)

3.1. Acidic and Neutral Solution

In acidic solution (pH < 7) the glycinate, oxalate, and β-alaninate chelates $[Co(en)_2(O{-}X)]^{k+}$ appear to be indefinitely stable. The properties of the corresponding aqua–monodentate complexes are known and none have been detected as products under such conditions. This does not prohibit ring opening, but requires the equilibrium to very much favor the chelate. Some further facts are known: if ring opening does occur it must be very slow since the rates of ring closure are not overly fast (Table II); also C–O bond fission will be preferred since C–O bond formation is the favored process for ring closure in acidic media.

In contrast the four-membered chelates $[Co(en)_2O_2PO_2]$ and $[Co(en)_2O_2CO]^+$ rapidly cleave via Co–O bond fission in acid solution, e.g., (7).



(7)

In the case of $[Co(en)_2O_2CO]^+$ the $[Co(en)_2(OH_2)OCO_3H]^{2+}$ intermediate subsequently loses CO_2 rapidly, probably via C–O cleavage as is found for $[Co(NH_3)_4O_2CO]^+$.

In neutral solution $[Co(en)_2O_2PO_2]$ and $[Co(en)_2O_2CO]^+$ undergo slow ring opening (Table II) but with the chelate being the stable product at equilibrium. The early report by Stranks and Lincoln[12] of substantial P–O cleavage at pH 6.8 for $[Co(en)_2O_2PO_2]$ is almost certainly incorrect since the reverse ring closure reaction at pH 8.0 occurs entirely by incorporation of phosphate oxygen at the metal.[7] Similar Co–O cleavage is likely with $[Co(en)_2O_2CO]^+$; the H^+ and OH^- catalyzed reactions occur in this manner.

The four-membered sulfato chelate $[Co(en)_2O_2SO_2]^+$ is at present unknown since the complex previously described by Tobe and Barraclough and Barraclough and Murray[13] has recently been shown to be the *cis*, bis-μ-bridged dimer $[(en)_2Co(OS(O)_2O)_2Co(en)_2]^{2+}$.[14] This species undergoes uncatalyzed and OH^--catalyzed hydrolysis for which rate data are included in Table II.

3.2. Alkaline Solution

All oxyanion chelates appear to open under alkaline conditions to give hydroxo-monodentates. The rate and the equilibrium posi-

TABLE II

Rates of chelate ring opening[a]

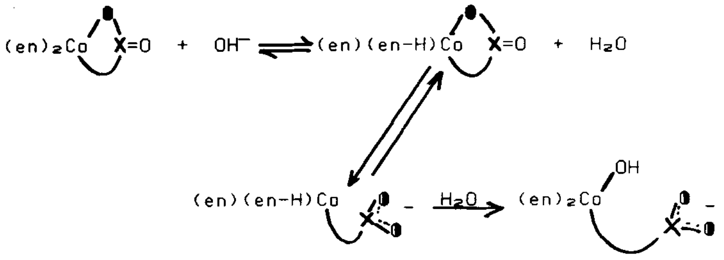
Complex	k_H/mol^{-1}dm^{3}s^{-1}	k_0/s^1	k_{OH}/mol^{-1}dm^{3}s^{-1}	k^2_{OH}/mol^{-2}dm^{6}s^{-1}
$[Co(en)_2(O_2CO)]^+$	0.79	5.4×10^{-5}	3.2×10^{-3}	–
$[Co(en)_2(O_2PO_2H_2)]^{2+}$	–	0.42(10°)	–	–
$[Co(en)_2(O_2PO_2H)]^+$	–	5.7×10^{-3}	–	–
$[Co(en)_2(O_2PO_2)]$	–	2.2×10^{-5}	1.7×10^{-2} [b]	–
$[Co(en)_2(O_2SO_2)]^+$ (μ-bridged dimer)	–	8×10^{-5}	1.85×10^{-2} [b]	–
$[Co(en)_2(NH_2CH_2CO_2)]^{2+}$	–	–	1.8×10^{-5}	–
$[Co(en)_2(O_2C_2O_2)]^+$	–	–	8.3×10^{-6}	6.3×10^{-5}
$[Co(en)_2(NH_2CH_2CH_2CO_2]^{2+}$	–	–	1.0×10^{-4}	–
$[Co(en)_2(O_2CCH_2CO_2)]^+$	[c]	–	2.81×10^{-4}	–
$[Co(en)_2(maleato)]^+$	–	–	0.36	–

[a] k_H, k_0, k_{OH} are the acid-catalyzed, pH-independent, $[OH^-]$-dependent and $[OH^-]^2$-dependent rate constants, respectively.

[b] Lincoln and Stranks[12] report a value of 1.75 mol^{-1}dm^{3}s^{-1} for this rate constant, but this is incorrect.

[c] $[Co(NH_3)_4(O_2CCH_2CO_2)]^+$ is reported to be hydrolyzed in acid with $k_H = 3.15 \times 10^{-2}$ mol^{-1}dm^{3}s^{-1}. However, the $(en)_2$ analogue appears to be stable in acid solution.

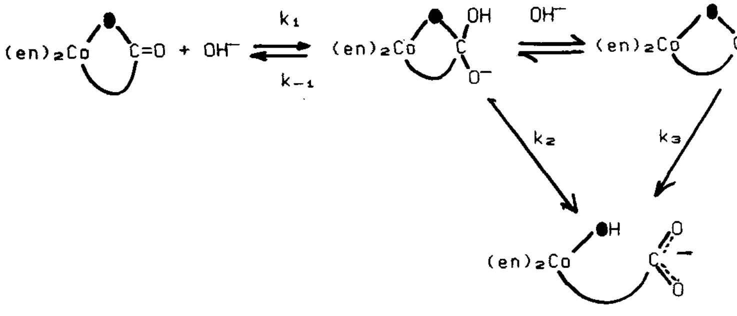
tion depends on ring size as well as on the nature of the chelate, with the rate decreasing in the order seven > four > six > five membered (Table II). This emphasizes the stability of five-membered chelates. Specific first-order in OH^- kinetics with Co–O cleavage is found for $[Co(en)_2O_2PO_2]$, $[Co(en)_2O_2CO]^+$ and $[Co(en)_2(NH_2CH_2CH_2CO_2)]^{2+}$, and a S_N1 (CB) mechanism seems appropriate (8).



III

(8)

The five-coordinate intermediate III either recaptures the oxyanion (leading to endo O-exchange; see above), or solvent (giving rise to largely *cis* hydroxo-monodentate product). Little or no *trans* product appears to be directly formed in these reactions. With the more stable five-membered chelates $[Co(en)_2(NH_2CH_2CO_2]^{2+}$ and $[Co(en)_2O_2C_2O_2]^+$ the first-order in OH^- process is accompanied by C–O cleavage resulting from addition of OH^- to the carboxylate center, k_2 (9).



(9)

For $[Co(en)_2NH_2CH_2CO_2]^{2+}$ this is a relatively minor pathway (~16%), but for $[Co(en)_2O_2C_2O_2]^+$ it is more important with ~40% of the first-order in OH^- reaction occurring in this manner, and 100% of the second-order in OH^- pathway. This latter pathway arises through further deprotonation of the addition intermediate and is the predominant process (88%) for $[Co(en)_2O_2C_2O_2]^+$ in 1M OH^-. Such paths for chelate ring cleavage (k_2,k_3) are considerably slower than return to the chelate (k_{-1}), with the latter being the process leading to exo-oxygen exchange ((5) above). These addition intermediates have not been directly observed, however, so that values for k_{-1}, k_2 and k_3 remain unknown. Paths like this involving chelate cleavage in a non-metal position will be favored by ring atoms which readily add nucleophiles, (e.g., carbonyl C, P, S), and where the Co–O bond is strong, such as is found with five- and six-membered rings. They are unlikely to be encountered with more labile metal–oxyanion systems.

4. CYCLIZATION OF MONODENTATES (TABLE III)

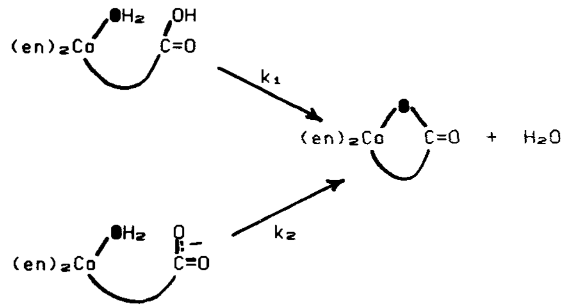
Cyclizations involving phosphate, carbonate or sulfate monodentates have not been observed in acidic solution; the ring opening reaction is preferred (see above). For five-membered chelates acid catalyzed cyclization is found with glycinate and oxalate monodentates (Table III), with the limiting rates at pH < 2 being at-

TABLE III

Cyclization of monodentates

Complex	$k_{cyc}(cis)/s^{-1}$	$k_{cyc}(trans)/s^{-1}$
$[Co(en)_2(OCO_2)OH_2]^+$	0.2	
$[Co(en)_2(OCO_2)OH]$	6.5×10^{-5}	
$[Co(en)_2(OPO_3H)OH_2]^+$	2.2×10^{-4}	
$[Co(en)_2(OPO_3H)OH]$	8×10^{-4}	
$[Co(en)_2(OPO_3)OH]^-$	7.5×10^{-5}	
$[Co(en)_2(NH_2CH_2CO_2H)OH_2]^{3+}$	1.9×10^{-2}	1.8×10^{-6}
$[Co(en)_2(NH_2CH_2CO_2)OH_2]^{2+}$	1.05×10^{-3}	2.3×10^{-6}
$[Co(en)_2(NH_2CH_2CO_2)OH]^+$	1.74×10^{-5}	2.5×10^{-4}
$[Co(en)_2(OC_2O_3H)OH_2]^{2+}$	1.5×10^{-4}	
$[Co(en)_2(OC_2O_3)OH_2]^+$	4.6×10^{-5}	3×10^{-6} (isom)
$[Co(en)_2(OC_2O_3)OH]$		$<2 \times 10^{-6}$
$[Co(en)_2(NH_2CH_2CH_2CO_2H)OH_2]^{3+}$	1.8×10^{-5}	
$[Co(en)_2(NH_2CH_2CH_2CO_2)OH]^+$	$<1 \times 10^{-5}$	

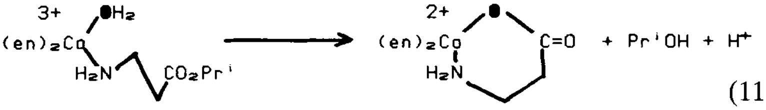
tributed to reaction of the aqua-carboxylic acid species. This occurs without displacement of coordinated water and requires attack by coordinated water at the carboxylic acid carbon (10).



(10)

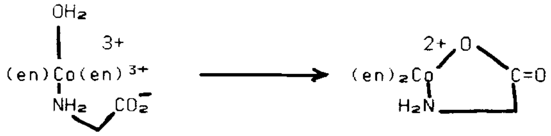
Presumably a concerted mechanism involving proton transfer and loss of H_2O from carbon is involved. At pH ~ 4 the deprotonated monodentate carboxylate complexes also cyclize in this manner; 100% for *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CO_2)]^{2+}$ and 40% for *cis*-$[Co(en)_2(OH_2)(OC(O)CO_2)]^+$. In the former case k_2 is some 20 times smaller than k_1, implying that proton transfer and loss of OH_2 from carbon is less facile for the carboxylate reactant. The remainder (60%) of the uncatalyzed reaction with *cis*-$[Co(en)_2(OH_2)(OC(O)CO_2)]^+$ involves displacement of metal-bound water by the "dangling" carboxylate, but that part proceeding via attack by coordinated water is catalyzed by CH_3CO_2H and $HC_2O_4^-$ at pH ~ 4. Presumably such catalysts provide the necessary proton for loss of OH_2 from the carboxylate center.

Cyclization of *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CH_2CO_2H)]^{3+}$ to give the six-membered chelate is some 10^3 times slower than cyclization in *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CO_2H)]^{3+}$ to give the corresponding five-membered system (Table III). The former reaction probably occurs by displacement of coordinated water even though hydrolysis and cyclization of the related isopropyl ester derivative occurs by attack of coordinated water at carbon (11).[4]



(11)

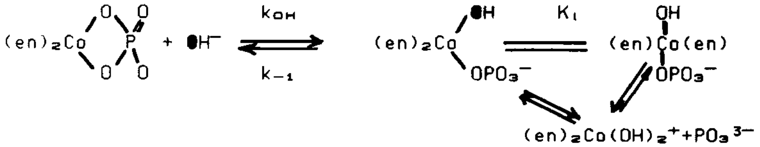
Cyclization in the stereochemically different *trans* aquamonodentates depends on whether cyclization or isomerization to the *cis* isomer is the faster process. For *trans*-$[Co(en)_2(OH_2)(NH_2CH_2CO_2)]^{2+}$ the former occurs, presumably by backside expulsion of coordinated water (12).



(12)

With *trans*-$[Co(en)_2(OH_2)(OC(O)CO_2)]^+$, however, isomerization to the *cis* isomer is the faster process, with the *cis* isomer then cyclizing by attack of *cis*-coordinated water (10). Clearly a balance between water exchange at the metal and direct substitution by the carboxylate anion at the metal is involved. In general *cis*-aqua isomers appear to be favored over *trans*-aqua isomers at equilibrium in acid solution, but the reverse appears to be true for the hydroxo isomers in alkali.

In alkaline solution (pH > 8) a balance between displacement of coordinated hydroxide with chelation, attack by coordinated hydroxide with chelation, and complete loss of the oxyanion ligand appears to be involved. For $[Co(en)_2(OH)OPO_3]^-$ recent ^{31}P NMR data from our laboratory suggests equilibria such as (13)



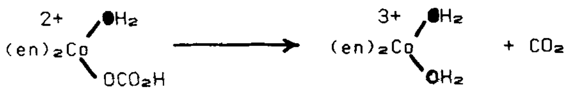
(13)

($K_{Ch} = k_{-1}/k_{OH} = \sim 4 \times 10^{-3}\,mol\,dm^{-3}, 25°C, I = 1.0\,(NaNO_3)$) with Co–O bond fission in the chelate resulting in a *cis*-hydroxo product. Subsequent equilibria are then set up with the *trans*-hydroxo isomer ($K_i \approx 10$) and also with free phosphate. With the *cis*-hydroxo oxalato complex complete hydrolysis to *cis*-$[Co(en)_2(OH)_2]^+ + C_2O_4^{2-}$ is favored, and a similar situation exists with cis-$[Co(en)_2(OH)OSO_3]$; return to the chelate is not observed under very alkaline conditions, and the chelate $[Co(en)_2O_2SO_2]^+$ is unknown (see above).[14] However, *cis*-$[Co(en)_2(OH)(NH_2CH_2CO_2)]^+$ slowly cyclizes between pH 8 and 10 (Table III) probably via the reverse of (8) for the uncatalyzed reaction. The reverse of (9) involving attack by coordinated hydroxide at carboxylate carbon appears to be favored in the presence of buffers; thus the phosphate catalyzed reaction at pH 8.82 results in exchange of one carboxylate oxygen on forming the chelate under these conditions. The significant overall conclusion is that attack by coordinated hydroxide on monodentate oxyanions to form chelates is not generally favored. This is in keeping with the reluctance of carboxylates to undergo O-exchange under alkaline conditions; acid-catalyzed exchange processes (including chelation) are, however, more favored.

5. HYDROLYSIS OF MONODENTATES (TABLE IV)

5.1. Acidic and Neutral Conditions

Monodentate phosphate and sulfate complexes hydrolyze very slowly in neutral solution. Protonation of the phosphate ligand produces little rate enhancement, and no evidence has been found for protonation of monodentate sulfate. Hydrolysis of *cis* and *trans*-$[Co(en)_2(OH_2)(OC_2O_3H)]^{2+}$ occurs slowly in strongly acidic solution, probably via a mechanism featuring protonation of the coordinated oxygen. Monodentate malonate in $[Co(en)_2(OH_2)(OC(O)CH_2CO_2H)]^{2+}$ is hydrolyzed even more slowly under such conditions. This contrasts with $[Co(en)_2(OH_2)(OCO_2H)]$ which is rapidly hydrolyzed in acidic solution. However, this process involves C–O bond fission with release of CO_2 (14), and thus is not readily comparable with the other systems.



$$[(en)_2Co(\overset{\bullet}{O}H_2)(OCO_2H)]^{2+} \longrightarrow [(en)_2Co(\overset{\bullet}{O}H_2)(\overset{\bullet}{O}H_2)]^{3+} + CO_2 \qquad (14)$$

TABLE IV

Hydrolysis of monodentates[a]

Complex	k_H/mol^{-1}dm^{3}s^{-1}	k_0/s^{-1}	k_{OH}/mol^{-1}dm^{3}s^{-1}
$[Co(en)_2(OCO_2H)OH_2]^{2+}$	–	0.45	–
$[Co(en)(NH_3)_2(OCO_2)OH_2]^+$	–	2.5×10^{-3}	–
$[Co(en)_2(OCO_2)OH]$	–	–	4.7×10^{-5}
$[Co(en)_2(OPO_3H_2)OH_2]^{2+}$	–	6.7×10^{-6} (60°)	–
$[Co(en)_2(OPO_3H)OH_2]^+$	–	9.2×10^{-5} (60°)	–
$[Co(en)_2(OPO_3)OH]^-$	–	3.3×10^{-5} (60°)	2.0×10^{-4} (60°)
$[Co(en)_2(OSO_3)OH_2]^+$	–	6.8×10^{-5} (46°)	–
$[Co(en)_2(OSO_3)(OH)]$	–	4.1×10^{-3}	0.22
cis-$[Co(en)_2(OC_2O_3H)OH_2]^{2+}$	$<1.05 \times 10^{-5}$	–	–
trans-$[Co(en)_2(OC_2O_3H)OH_2]^{2+}$	$<2 \times 10^{-6}$	—	—
cis-$[Co(en)_2(OC_2O_3)OH]$	—	5×10^{-5}	6.3×10^{-3}
trans-$[Co(en)_2(OC_2O_3)OH]$	—	8×10^{-6}	6.5×10^{-4}
cis-$[Co(en)_2(OC(O)CH_3)OH]^+$	—	—	8.15×10^{-3}
trans-$[Co(en)_2(OC(O)CH_3)OH]^+$	—	—	1.26×10^{-3}
cis-$[Co(en)_2(OC(O)CH_2CO_2H)OH_2]^{2+}$	$<10^{-6}$	—	—
cis-$[Co(en)_2(OC(O)CH_2CO_2)OH]$	—	—	4.33×10^{-4}
cis-$[Co(en)_2(NH_2CH_2CH_2CO_2)OH]^+$	—	—	2×10^{-5}

[a] k_H, k_0 and k_{OH} are rate constants for H^+-catalyzed, H^+-independent, and OH^--catalyzed hydrolysis, respectively.

TABLE V

Isomerization of monodentates

	$k_{c \to t}/s^{-1}$	$k_{t \to c}/s^{-1}$
$[Co(en)_2(OC_2O_3)OH_2]^+$	–	5×10^{-6}
$[Co(en)_2(OC_2O_3)OH]$	5×10^{-6}	–
$[Co(en)_2(OC(O)CH_2CO_2H)OH_2]^{2+}$	5.6×10^{-6}	2.2×10^{-6} (30°)
$[Co(en)_2(NH_2CH_2CH_2CO_2)OH]^+$	1×10^{-5}	–
$[Co(en)_2(OPO_3)OH]^-$	1×10^{-5}	1×10^{-6}

The glycinate and β-alaninate monodentates are bound through the amine group and do not hydrolyze in acidic or neutral solution.

5.2. Alkaline Conditions

All monodentate oxyanion complexes hydrolyze with rates first-order in $[OH^-]$. ^{18}O-tracer studies show that the process occurs with Co–O bond fission for *cis* and *trans*-$[Co(en)_2(OH)OC_2O_3]$ and this is a likely general result. Amine-bound glycinate in *cis*-$[Co(en)_2(OH)NH_2CH_2CO_2]^+$ also undergoes OH^--induced hydrolysis in strong alkali, but the products include radical Co(II) species as well as $[Co(en)_2(OH)_2]^+$[11].

6. ISOMERIZATION OF MONODENTATES (TABLE V)

Isomerization rates are all of a similar magnitude. This probably means that they are controlled by water, or hydroxide, exchange at the metal center. It is most unlikely that isomerization occurs without solvent exchange. The $[Co(en)_2(OH)(NH_2CH_2CH_2CO_2)]^+$, $[Co(en)_2(OH)OC_2O_3]$, $[Co(en)_2(OH)(OC(O)CH_2CO_2)]$, and $[Co(en)_2(OH)OPO_3]^-$ species favor the *trans* isomer at equilibrium, whereas for $[Co(en)_2(OH)OCO_2]$ a *cis*:*trans* ratio of 2:1 has been found.[15] *Cis* isomers appear to be favored in acid solution.

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