1952 *Inorg. Chem.* **1986**, *25*, 1952-1956

Contribution from the Research School of Chemistry, The Australian National University, Canberra, ACT, Australia,
and Department of Chemistry, University of Otago, Dunedin, New Zealand

Opening of the β-Alaninate Chelate $[Co(en)_2(\beta\text{-alaO})]^{2+}$ in Alkali and the Properties of *cis*- and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$

Eveline Baraniak, David A. Buckingham,* Charles R. Clark, and Alan M. Sargeson

Received October 28, 1985

In strong alkali (ca. 1 mol dm^{-3}) the six-membered β-alaninate chelate in $[Co(en)_2(\beta\text{-alaO})]^{2+}$ opens via Co–O bond fission to form a mixture of *cis*- (70%) and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ (30%). The cis product retains ~70% chirality, and a first-order in $[OH^-]$ dependence is indicated for the process. Subsequently, both the *cis*- and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ ions hydrolyze to predominantly *cis*-$[Co(en)_2(OH)_2]^+$, which then isomerizes to an equilibrium mixture of *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$. Slow isomerization of *cis*- to *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ and chelation of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ occur in dilute alkali.

Introduction

Previously, we examined O exchange and ring opening of the five-membered glycinate chelate in $[Co(en)_2(glyO)]^{2+}$.[1] Two exchange rates were found in both acidic (pH 0–2) and alkaline (1.0–0.002 mol dm^{-3} NaOH) solution, but only in alkali did the chelate ring cleave. The latter process followed a first-order in $[OH^-]$ dependence to form a mixture of *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ and $Co^{2+}{}_{aq}$. No intermediate monodentate glycinate species was detected. In the present study, opening of the six-membered chelate is somewhat faster and the cis and trans monodentate intermediates have been detected and characterized. Since this involves hydrolysis of carboxylate oxygen coordinated to Co(III) the results have some relevance to ring opening of phosphato,[2] oxalato,[3] carbonato,[4,5] and malonato[6] chelates.

Experimental Section

Visible spectra were recorded with a Cary 14 spectrophotometer, infrared spectra with a Perkin-Elmer Model 459 Spectrophotometer, and ^1H NMR spectra with JEOL JNM-100-MHz Minimar or a Varian HA-100-MHz instrument using Me_4Si as external or NaTPS as internal reference. Co estimations were made from visible spectra or by AA analysis with a Techtron AA4 instrument and $[Co(NH_3)_6]Cl_3$ standards. Radiometer pH stat equipment was used to follow OH^- consumption against time by using a Teflon cell (3.2 cm) fitted to a Cary 16 K spectrophotometer. The ^{18}O content of β-alanine in $[Co(en)_2(\beta\text{-alaO})]HgI_4$ and in the ligand released following hydrolysis was analyzed as CO_2 by using an Atlas M-86 mass spectrometer and standard methods.[7] Bio-Rad Analytical Dowex 50W-X2 (200–400 mesh, Na^+ form) cation-exchange resin was used for the separation of reaction products.

Complexes. $[Co(en)_2(\beta\text{-alaO})](ClO_4)_2 \cdot H_2O$ was prepared by hydrolyzing $[Co(en)_2(\beta\text{-alaO-}i\text{-Pr})](ClO_4)_3$[8] in acid and alkaline aqueous solutions. The complex (3 g) was either heated on a steam bath for 3 h in 0.1 mol dm^{-3} $HClO_4$ or hydrolyzed for 1 h at pH ~9 at room temperature. The product crystallized on adding $NaClO_4$ and cooling the solution in an ice bath. It was washed with a little aqueous ethanol and ether and dried in a vacuum desiccator. Anal. Calcd for $[Co(en)_2(\beta\text{-alaO})](ClO_4)_2 \cdot H_2O$: Co, 12.17; C, 17.36; H, 5.00; N, 14.47. Found: Co, 11.9; C, 17.2; H, 5.0; N, 14.3. The chloride salt was obtained by elution from H^+-form Dowex 50W-X2 cation-exchange resin using 3 mol dm^{-3} HCl, evaporation of the eluant to dryness, trituration with acetone to remove excess acid, and crystallization from water by adding MeOH. The product was washed with a little ethanol and ether and dried as before. Anal. Calcd for $[Co(en)_2(\beta\text{-alaO})]Cl_2 \cdot H_2O$: C, 23.61; H, 6.79; N, 19.67. Found: C, 23.7; H, 6.7; N, 19.7. $\epsilon_{max} = 128$ mol^{-1} dm^3 cm^{-1} at 495 nm, $\epsilon_{max} = 88$ mol^{-1} dm^3 cm^{-1} at 351 nm for both salts in water, 0–3 mol dm^{-3} $NaClO_4$, 0.01–1.0 mol dm^{-3} $HClO_4$, and tris buffer pH ~8.5.

$(-)_{589}$-$[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$. Resolution into enantiomers was achieved as follows. To racemic $[Co(en)_2(\beta\text{-alaO})]Cl_2 \cdot H_2O$ (7.1 g) in 35 cm^3 of H_2O (40 °C) was added $(+)_{589}$-$Na[Co(en)(C_2O_4)_2]$ (6.35 g, $[\alpha]_{589}$ 490°, 1 molar equiv). When the mixture was cooled to room temperature and the walls of the reaction vessel were scratched, the diastereoisomer separated and after 1 h it was collected and washed with a little aqueous methanol and ether (5.4 g); a second fraction was obtained when the remaining mixture was allowed to stand overnight in a refrigerator (3.75 g). The initial product was recrystallized into three fractions from hot water (80 cm^3), and the two most soluble fractions were combined with the second fraction and again fractionated. Products of similar rotation were combined, and the resolving agent was removed by using Dowex anion-exchange resin (AGI-X8; 200–400 mesh, Cl^- form). The aqueous eluant was reduced to a small volume, and $(-)_{589}$-$[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$ crystallized on adding $NaClO_4$ and cooling. One recrystallization from hot water gave optically pure product. Anal. Calcd for $[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$: C, 18.03; H, 4.76; N, 15.03. Found: C, 18.0; H, 4.8; N, 14.7. [M] (deg mol^{-1} dm^2): −900 (589 nm), −1260 (546 nm), +1280 (436 nm) in 2.0 mol dm^{-3} $NaClO_4$.

Alkaline Hydrolysis. Visible spectra were recorded at specific time intervals for solutions of $[Co(en)_2(\beta\text{-alaO})](ClO_4)_2 \cdot H_2O$ in 1.0 mol dm^{-3} NaOH and in 0.5 mol dm^{-3} NaOH–0.5 mol dm^{-3} $NaClO_4$ over the 600–300 nm range, at 25.0 °C in a 1-cm cuvette.

Isolation and Characterization of Reaction Products. $[Co(en)_2(\beta\text{-alaO})](ClO_4)_2 \cdot H_2O$ was dissolved in 1.0 mol dm^{-3} NaOH or 0.5 mol dm^{-3} NaOH–0.5 mol dm^{-3} $NaClO_4$ at 25.0 °C to give a solution 10–40 mmol dm^{-3} in Co. Samples (ca. 0.1 g of complex) were withdrawn at specific time intervals, quenched to pH 4 (HOAc), diluted with water, sorbed as a narrow band on a short column of Na^+-form resin (1 × 7 cm), which was then converted to the basic form with 0.1 mol dm^{-3} NaOH. This resin was transferred to a longer Na^+-form column and the products were eluted with 0.5 mol dm^{-3} $NaClO_4$ (pH ~9) for the 1+ ions, and with 1.0–2.0 mol dm^{-3} $NaClO_4$ for unreacted $[Co(en)_2(\beta\text{-alaO})]^{2+}$. Products were eluted in the order *trans*-$[Co(en)_2(OH)_2]^+$, *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$, *cis*-$[Co(en)_2(OH)_2]^+$, and *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$. The first two were often collected together although they could be separated by using a very long column. Visible spectra of the eluates were recorded, and samples were retained for [Co] determination. $(-)_{589}$-$[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$ (0.1 g) was treated similarly in 1.0 mol dm^{-3} NaOH and quenched after 3 h, 25.0 °C.

Samples of *trans*- and *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ recovered as above were adjusted to $I = 1.0$ ($NaClO_4$) and then mixed with an equal volume of 1.0 mol dm^{-3} NaOH, and visible spectra were recorded at specific time intervals, 25 °C. For the cis isomer samples were quenched (pH ~4) and the products separated and analyzed as before.

Uptake of OH^- was followed over 106 min at pH 12.0, 25.0 °C, by using 0.1 g of $[Co(en)_2(\beta\text{-alaO})](ClO_4)_2 \cdot H_2O$ dissolved in 8 cm^3 of 1.0 mol dm^{-3} $NaClO_4$ by titration under a N_2 atmosphere with 0.1 mol dm^{-3} NaOH. Correction was made for a blank run, and the product was analyzed as above.

^{18}O-Tracer Study. ^{18}O-Labeled β-alanine HCl was prepared by refluxing overnight 5 g of the unlabeled material in 20 cm^3 of 2.0 atom % ^{18}O-labeled water and removing the solvent. Carbonyl-^{18}O-labeled isopropyl ester hydrochloride was prepared as for the unenriched ester[9] and labeled *cis*-$[Co(en)_2Br(\beta\text{-alaO-}i\text{-Pr})]Br_2$ and chelated ester $[Co(en)_2(\beta\text{-alaO-}i\text{-Pr})](ClO_4)_3$ were prepared as given elsewhere.[8,9] The latter complex (1.5 g) was hydrolyzed at pH 9.0 (pH stat) and recovered as

---

* To whom correspondence should be addressed at the University of Otago.

(1) Boreham, C. J.; Buckingham, D. A. *Aust. J. Chem.* **1980**, *33*, 27.
(2) Jones, D. R.; Lindoy, L. F.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7327.
(3) Andrade, C.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1328.
(4) Francis, D. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1969**, *91*, 6626.
(5) Scheidegger, H.; Schwarzenbach, G. *Chimia* **1965**, *19*, 166.
(6) Farago, M. E.; Smith, M. A. R.; Keefe, I. M. *Coord. Chem. Rev.* **1972**, *8*, 95.
(7) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6032; **1969**, *91*, 4102.
(8) Baraniak, E.; Buckingham, D. A.; Clark, C. R.; Sargeson, A. M., submitted for publication in *Inorg. Chem.*
(9) Baraniak, E.; Buckingham, D. A.; Clark, C. R.; Sargeson, A. M. *Inorg. Chem.*, following paper in this issue.

0020-1669/86/1325-1952$01.50/0

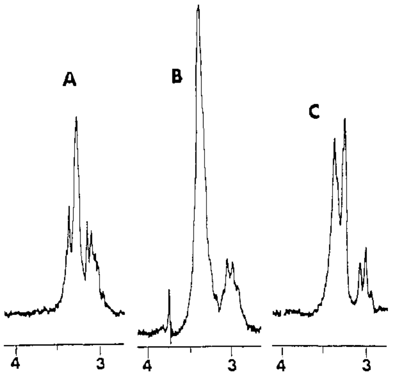
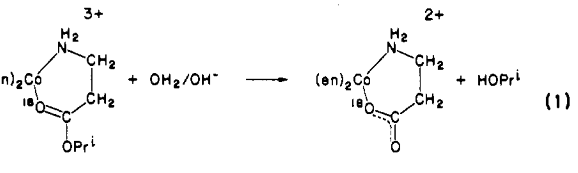


Figure 1. 90-MHz ^1H NMR spectra of (a) $[Co(en)_2(\beta\text{-alaO})]^{2+}$, (b) $[Co(en)_2(\beta\text{-alaO-}i\text{-Pr})]^{3+}$ and (c) $[Co(en)_2(OH)(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ in the CH_2 region.

$[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$. This material (0.5 g) was then hydrolyzed for 3 h in 1.0 mol dm^{-3} NaOH, and *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ and unreacted $[Co(en)_2(\beta\text{-alaO})]^{2+}$ were recovered as described above by using 0.5 and 1.0 mol dm^{-3} NaCl eluants. $[Co(en)_2(\beta\text{-alaO})]^{2+}$ was precipitated as the insoluble yellow HgI_4^{2-} salt from a concentrated solution, and the product was dried at 10^{-4} mmHg on a vacuum line. β-Alanine was recovered from this complex by sublimation at 215 °C (10^{-4} mmHg) and recrystallized from water (1 cm^3) by addition of acetone and cooling overnight. β-Alanine was recovered from *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ by electrolyzing a concentrated solution at −1.0 V (vs. SCE) and pH 2 for 3 h, taking the residue to dryness and extracting the β-alanine as its pink Co(II) complex into methanol. Addition of sodium oxalate (0.3 g) removed Co(II), and the aqueous residue was chromatographed on Dowex cation-exchange resin to separate β-alanine from remaining ethylenediamine (HCl eluant). This was recovered and recrystallized as the hydrochloride salt as described above.

Results and Discussion

The $[Co(en)_2(\beta\text{-alaO})]^{2+}$ ion has been prepared via hydrolysis of the isopropyl ester complex, eq 1, and isolated and characterized as its ClO_4^- and Cl^- salts.



I II

Figure 1 gives the ^1H NMR spectrum in the CH_2 region with the multiplet at ~3.0 ppm resulting from the β-alaninate chelate. Resolution into enantiomers was achieved via the $(+)_{589}$-$[Co(en)(C_2O_4)_2]^-$ salt. $(-)_{589}$-$[Co(en)_2(\beta\text{-alaO})]^{2+}$ is stable over very long periods of time in acidic (1–2 mol dm^{-3} HCl or $HClO_4$), neutral, or slightly alkaline (pH <11) solutions, contrary to a previous report.[10] Details of hydrolysis reaction 1 will be dealt with elsewhere,[8] but hydrolysis at pH 9 of specifically carbonyl-^{18}O-labeled ester I gave full retention of label in product II (Table II) consistent with solvent attack at the activated carbonyl center. Such hydrolyses have been explored for the related five-membered chelated glycine esters[7] and it is sufficient to note here that the chelate remains intact during, and subsequent to, hydrolysis.

The main topic of this paper concerns hydrolysis of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ in strongly alkaline solution. This occurs in three stages: first, the opening of the β-alaninate chelate to form *cis*- and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$; then, hydrolysis of these two complex ions to *cis*-$[Co(en)_2(OH)_2]^+$; last, equilibration of the latter to a mixture of *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$, Scheme I. Product data as a function of time are given in Table III for the reaction in 1.0 and 0.5 mol dm^{-3} NaOH. Identification was by spectral comparisons of eluted bands with known *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ ions,[11]

Table I. Extinction Coefficients for Complexes Produced during the Alkaline Hydrolysis of $[Co(en)_2(\beta\text{-alaO})]^{2+\,a}$

complex	λ_{max}, nm^b	ϵ_{max},^{c} mol^{-1} dm^3 cm^{-1}	ref
$[Co(en)_2(\beta\text{-alaO})]^{2+}$	495	128	this work
	350	90	
trans-$[Co(en)_2(OH)_2]^+$	518	54	this work
	375		
	520	53	*e*
	380	55	
cis-$[Co(en)_2(OH)_2]^+$	518	91	this work
	~370		
	520	93	*e*
	370	104	
trans-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$	500	76	this work
	~360		
trans-$[Co(en)_2(H_2O)(\beta\text{-alaOH})]^{3+\,d}$	495	55	this work
	350	60	
cis-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$	500	91	
	360		
cis-$[Co(en)_2(H_2O)(\beta\text{-alaOH})]^{3+\,d}$	490	72	this work
	350	65	

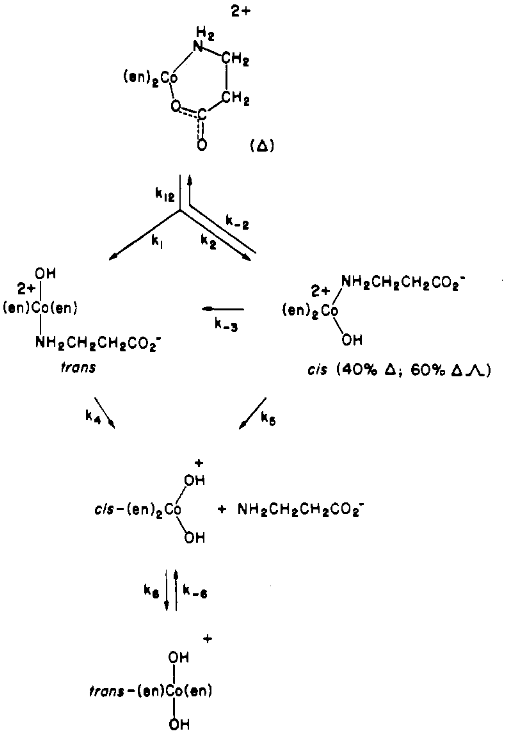
[a] At 25.0 °C in $NaClO_4$ (0.5–2.0 mol dm^{-3}). [b] λ is ±2 nm; average of 3 experiments. [c] ε is ±2 mol^{-1} dm^3 cm^{-1}; average of 3 experiments. Positions of maxima in the near-UV region are only approximate for eluted complexes, but see Figure 2. [d] Acidifying hydroxo complexes to pH ~2 ($HClO_4$). [e] Reference 12.

Table II. ^{18}O-Tracer Results

complex/compound	*R*	% $^{18}O^a$
β-ala·HCl	0.04032	1.976
β-ala-*i*-OPr·HCl	0.01656	0.821
$[Co(en)_2(\beta\text{-alaO})]HgI_4{}^c$	0.01633	0.810
β-ala·HCl^b	0.01589	0.788
$[Co(en)_2(\beta\text{-alaO})]HgI_4{}^d$	0.01627	0.807
CO_2 (unenriched)	0.00403	0.201

[a] Calculated as % = $(100R)/(2 + R)$ where $R = [46]/([45] + [44])$. [b] Recovered from *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ following hydrolysis of labeled $[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$ for 3 h in 1.0 mol dm^{-3} NaOH. [c] Reactant prepared by hydrolysis of $[Co(en)_2(\beta\text{-alaO-}i\text{-Pr})](ClO_4)_3$ at pH 9.0 for 2 h. [d] Recovered $[Co(en)_2(\beta\text{-alaO})]^{2+}$ from hydrolysis in 1.0 mol dm^{-3} NaOH.

Scheme I



---

[10] Hay, R. W.; Basak, A. K. *Inorg. Chim. Acta* **1983**, *69*, 1.

Table III. Products during Hydrolysis of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ in Strongly Alkaline Solution (25.0 °C, μ = 1.0, $NaClO_4$)[a]

run	time	% *trans*-$[Co(en)_2(OH)_2]^+$	% *trans*-$[Co(en)_2OH(\beta\text{-alaO})]^+$	% *cis*-$[Co(en)_2(OH)_2]^+$	% *cis*-$[Co(en)_2OH(\beta\text{-alaO})]^{+}$[d]	% $[Co(en)_2(\beta\text{-alaO})]^{2+}$
1	44 min[b]	0	7	0	14	77
2	1 h 20 min[b]	0	12	0	30	57
3	4 h 40 min[b]	0	17	3	44	36
4	15 h[b]	5	15	30	48	7
5	28 h[b]	23	0	50	23	4
6	170 h[b]	52	0	45	0	0
7	6 h 20 min[c]	0	25	~0	38	37
8	28 h 40 min[c]	17	0	39	39	5

[a] Duplicate experiments agreed within 5–10%; averaged values given. [b] $[OH^-]$ = 1.0 mol dm^{-3}. [c] $[OH^-]$ = 0.5 mol dm^{-3}. [d] Hydrolysis of $(-)_{589}$-$[Co(en)_2(\beta\text{-alaO})](ClO_4)_2$ for 3 h gave *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ (M_λ = −109° (589 nm) and −273° (546 nm)) and unreacted complex (M_λ = −910° (589 nm) and −1310° (546 nm)).

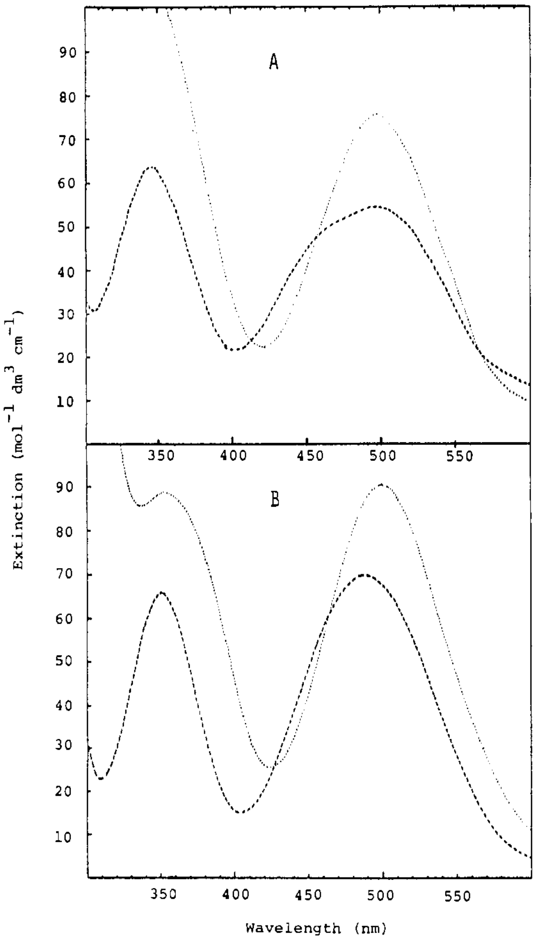


Figure 2. Absorption spectra (in 0.5 mol dm^{-3} $NaClO_4$): (A) *trans*-$[Co(en)_2(H_2O)(\beta\text{-alaOH})]^{3+}$ (--) and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ (···); (B) *cis*-$[Co(en)_2(H_2O)(\beta\text{-alaOH})]^{3+}$ (--) and *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ (···).

Figure 2, and *cis*- and *trans*-$[Co(en)_2(OH)_2]^{+}$[12] and product amounts were obtained from the extinctions listed in Table I and by direct AA analysis for Co. ^1H NMR of isolated *cis*- and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ showed the presence of β-alanine (multiplet, 3–4 ppm).

At early times only *cis*- and *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ result, with the cis product retaining ~40% chirality when compared with optically pure $(+)_{589}$-$[Co(en)_2(OH)(\beta\text{-alaO-}i\text{-Pr})]^{2+}$ ([M] (deg mol^{-1} dm^2): 295 (589 nm), 720 (546 nm), −1170 (436 nm)).[9] From entries 2 and 3, in Table III, [cis]/[trans] = 2.5. Rates calculated from these product data and from the spectral traces given in Figure 3a assuming $\epsilon_{500}{}^{\infty}$ = 87 mol^{-1} dm^3 cm^{-1} for the mixture cis + *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$, gives k_{obsd} = k_{12} (Scheme I) = (1.0 ± 0.2) × 10^{-4} s^{-1} in1.0 mol dm^{-3} NaOH. The slower formation in 0.5 mol dm^{-3} NaOH (0.5 mol dm^{-3} $NaClO_4$), and the 15% hydrolysis over 100 min at pH 12 (pH stat titration) support a first-order in $[OH^-]$ dependence, whence k_1(trans) = 3 × 10^{-5} mol^{-1} dm^3 s^{-1} and k_2(cis) = 7 × 10^{-5} mol^{-1} dm^3 s^{-1}. This latter experiment consumed 0.15 equiv of OH^-, consistent with the required stoichiometry.

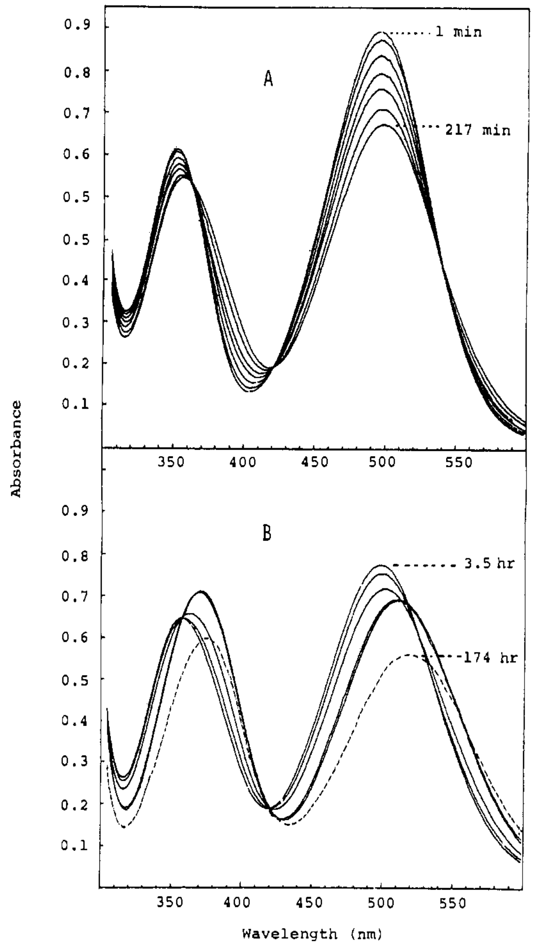


Figure 3. Spectra during alkaline hydrolysis of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ (8.0 × 10^{-3} mol dm^{-3}) in 1.0 mol dm^{-3} NaOH to give (A) a mixture of *cis*- + *trans* $[Co(en)_2(OH)(\beta\text{-alaO})]^+$ and subsequently (B) a mixture of *cis*- + *trans*-$[Co(en)_2(OH)_2]^+$ at 25.0 °C.

At longer times (>3 h, 1.0 mol dm^{-3} NaOH) the initial isosbestic points shown in Figure 3a (540, 421, 363 nm), are lost, and absorptions generally move to longer wavelengths, Figure 3b. The final spectrum ($\epsilon_{518}{}^{\infty}$ = 71.6 ± 0.5 mol^{-1} dm^3 cm^{-1}) is consistent with 55% *trans*- + 45% *cis*-$[Co(en)_2(OH)_2]^+$, and this ratio is found by ion-exchange analysis of the products. The identical equilibrium ratio has been demonstrated in alkaline solution by Bjerrum and Rasmussen.[12] However, the change involves two

---

(11) Baraniak, E. Ph.D. Thesis, Australian National University, 1972.
(12) Bjerrum, J.; Rasmussen, S. E. *Acta Chem. Scand.* **1952**, *6*, 1265.

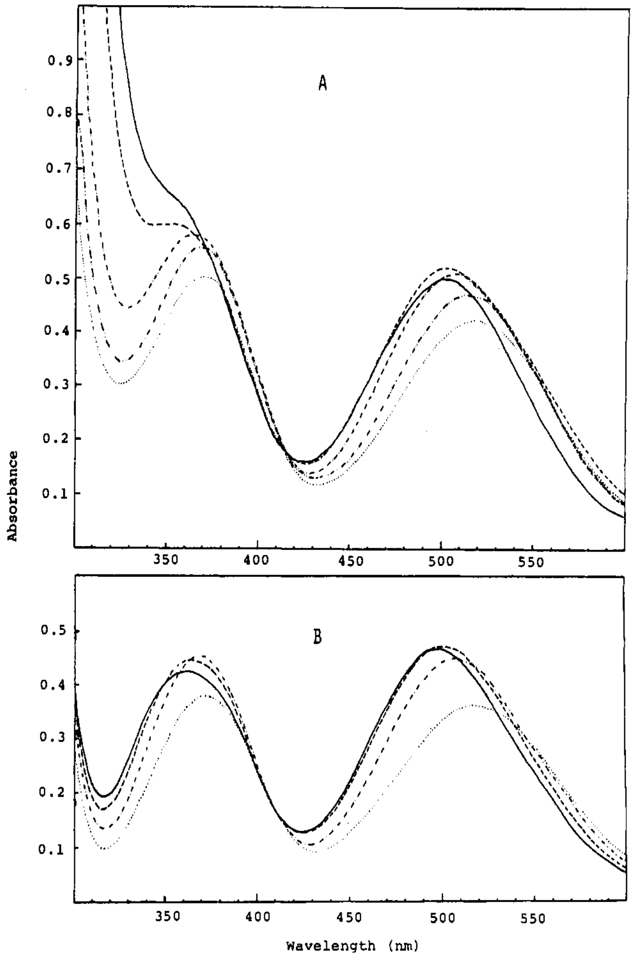


Figure 4. Spectra during the hydrolysis of (A) *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ (6.7×10^{-3} mol dm^{-3}) for (—) 1 min, (--) 3.2 h, (-·-) 17.4 h, (-··-) 54 h, and (···) 264 h and (B) *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ (5.0×10^{-3} mol dm^{-3}) for (—) 7 min, (--) 6.5 h, (-··-) 24.3 h, and (···) 392 h.

consecutive processes, and this is most obvious by consideration of the 358-nm absorption of the *cis*- + *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ + unreacted $[Co(en)_2(\beta\text{-alaO})]^{2+}$ mixture (Figure 3b). Initially the absorption increases in intensity and moves to longer wavelengths (isosbestic at 358 nm), followed by a decrease to conclude the reaction. Furthermore, the products over the same time period (Table III, entries 3 and 4) show only 5% *trans*-$[Co(en)_2(OH)_2]^+$ during the buildup of 30% *cis*-$[Co(en)_2(OH)_2]^+$. Clearly the latter arises at the expense of both *trans*- and *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ with *trans*-$[Co(en)_2(OH)_2]^+$ being largely (or only) a result of subsequent isomerization of *cis*-$[Co(en)_2(OH)_2]^+$ (Scheme I). The formation of substantial amounts of *cis*-$[Co(en)_2(OH)_2]^+$ from hydrolysis of *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ is supported by Figure 4a. Here the 500-nm absorption ($\epsilon = 76$) initially shows a slight increase as it moves to longer wavelengths consistent with the formation of *cis*-$[Co(en)_2(OH)_2]^+$ ($\epsilon = 91$) but not *trans*-$[Co(en)_2(OH)_2]^+$ ($\epsilon = 54$).

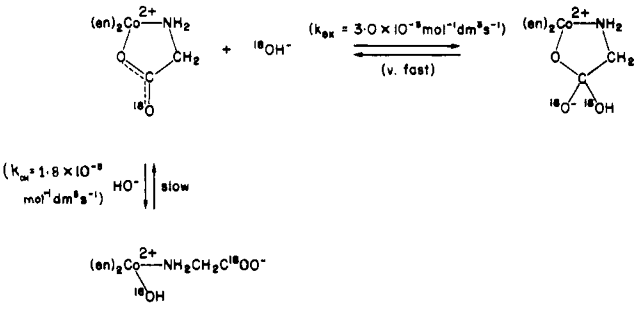
Finally, by the use of a solution of the separated species *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$, a return to the chelate (k_{-2}, Scheme I) was demonstrated as well as isomerization to *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$. After 4 h in 0.5 mol dm^{-3} NaOH, ion-exchange analysis of the products gave 22% reaction consisting of 4% $[Co(en)_2(\beta\text{-alaO})]^{2+}$, 13% *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$, and 5% *cis*-$[Co(en)_2(OH)_2]^+$; after 24 h 60% reaction gave 3% $[Co(en)_2(\beta\text{-alaO})]^{2+}$, 45% *cis*- and 12% *trans*-$[Co(en)_2(OH)_2]^+$. At an early stage the k_{-3} path appears to compete favorably for k_5. However the experiment was carried out by using a sample that had been stored at pH ~9 for several hours, and it is likely that the isomerization process (and possibly chelation) are pH independent, whereas the k_5 path appears to be first order in $[OH^-]$. Thus isomerization (and chelation) had probably occurred prior to carrying out the experiment in 0.5 mol dm^{-3} NaOH. However it does establish isomerization of *cis*- to *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$, and the formation of some chelate, in alkaline solution. No similar indication of reverse *trans*- to *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ isomerization was found with isolated *trans*--$[Co(en)_2(OH)(\beta\text{-alaO})]^+$. Also, after 2 months at pH 10, an 80% recovery of $[Co(en)_2(\beta\text{-alaO})]^{2+}$ from *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$ was achieved, so return via the k_{-2} path is slow. Table IV gives some approximate rate constants.

Table IV. Rate Constants for Alkaline Hydrolysis of Various β-Alanine Complexes (1.0 mol dm^{-3} NaOH, 25.0 °C)

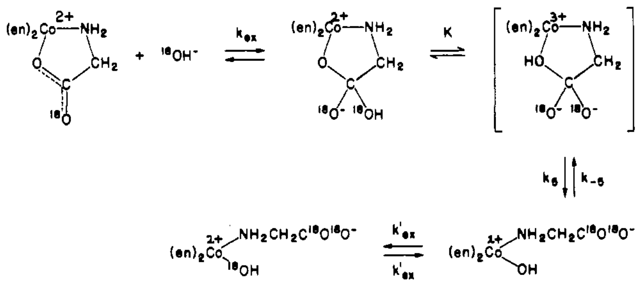
reacn	k, s^{-1}
opening of β-alaninate ring, $[Co(en)_2(\beta\text{-alaO})]^{2+}$	1.0×10^{-4} [a]
ring closure, *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$	$<1 \times 10^{-5}$
cis to trans isomerization, *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$	1×10^{-5}
loss of β-alanine, *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$	$\sim 2 \times 10^{-5}$ [a]
loss of β-alanine, *trans*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$	$<2 \times 10^{-5}$ [a]
cis to trans isomerization, *cis*-$[Co(en)_2(OH)_2]^+$	3.7×10^{-6} [b]

[a] Follows first-order in $[OH^-]$ kinetics. [b] Kruse, W.; Taube, H. *J. Am. Chem. Soc.* **1961**, *83*, 1280.

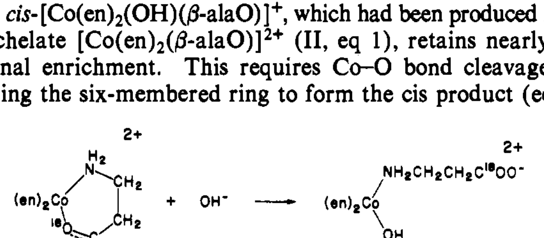
Scheme II



Scheme III



^{18}O data given in Table II establish that β-alanine recovered from *cis*-$[Co(en)_2(OH)(\beta\text{-alaO})]^+$, which had been produced from the chelate $[Co(en)_2(\beta\text{-alaO})]^{2+}$ (II, eq 1), retains nearly the original enrichment. This requires Co–O bond cleavage for opening the six-membered ring to form the cis product (eq 2).


(2)

A similar result is expected for the trans monodentate, but the small amount of material available prevented this determination. An S_N1 (CB) mechanism is likely for this reaction with deprotonation of a coordinated amine residue leading to a reactive species which loses carboxylate to form racemic (43% ΔΛ) and optically active (29% Δ) cis and trans (28%) products.

The k_{12} path for opening the six-membered β-alaninate chelate is some five times faster than that for opening the five-membered glycinate chelate ($k = 1.0 \times 10^{-4}$ vs. 1.8×10^{-5} mol^{-1} dm^3 s^{-1}).[1] The cleavage pattern for the latter complex has not been established, but a process similar to the above would provide an alternative for the slow exchange found for the Co–O oxygen in the chelate (k_{ex} = 1.7 × 10^{-6} s^{-1} in 1.0 mol dm^{-3} NaOH).[1] Scheme II outlines this proposal. Previously[1], it was assumed that this occurred via hydroxide exchange in *cis*-[Co(en)$_2$(OH)(glyO)]$^+$ with hydrolysis and cyclization occurring via C–O rather than Co–O bond cleavage and formation (Scheme III). Clearly only a tracer study similar to that described here could resolve this uncertainty.

Registry No. (−)$_{589}$-[Co(en)$_2$(β-alaO)](ClO$_4$)$_2$, 101758-90-1; [Co(en)$_2$(β-alaO)]Cl$_2$, 60866-21-9; OH$^-$, 14280-30-9.

Contribution from the Research School of Chemistry, The Australian National University, Canberra, ACT, Australia, and Department of Chemistry, University of Otago, Dunedin, New Zealand

Hg^{2+}- and OH$^-$-Induced Reactions of *cis*-[Co(en)$_2$X(β-alaOR)]$^{2+}$ and *cis*-[Co(en)$_2$Br(β-alaO)]$^+$ (X = Cl, Br; R = H, Me, *i*-Pr)

Eveline Baraniak, David A. Buckingham,* Charles R. Clark, and Alan M. Sargeson

Received October 28, 1985

cis-[Co(en)$_2$X(β-alaOR)]X$_2$ (X = Cl, Br; R = H, Me, *i*-Pr) complexes have been prepared and *cis*-[Co(en)$_2$Br(β-alaO-*i*-Pr)]$^{3+}$ has been resolved into its enantiomers. For R = H, pK_a values for the dangling carboxylic acid function are 3.85 ± 0.05 (X = Br) and 3.9 ± 0.1 (X = H$_2$O). Hg^{2+}-catalyzed removal of coordinated X (Cl, Br) occurs with retention of configuration about the metal, giving 80% *cis*-[Co(en)$_2$(H$_2$O)(β-alaOR)]$^{3+}$ and 20% [Co(en)$_2$(β-alaOR)]$^{3+}$ for R = H (k_{Hg} = 2.9 ± 0.1 mol^{-1} dm^3 s^{-1}, 25.0 °C, I = 1.0), and 90% and 10%, respectively, for R = Me and *i*-Pr (k_{Hg} = 2.4 mol^{-1} dm^3 s^{-1}). Alkaline hydrolysis occurs with ~60% racemization for R = *i*-Pr, X = Br$^-$ and forms 90% *cis*-[Co(en)$_2$(OH)(β-alaO/R)]$^{+/2+}$ and 10% [Co(en)$_2$(β-alaO)]$^{2+}$ for R = carboxylate (k_{OH} = 46 ± 2 mol^{-1} dm^3 s^{-1}, 25.0 °C, I = 1.0) and 32% and 68%, respectively, for R = *i*-Pr (k_{OH} = 68 ± 2 mol^{-1} dm^3 s^{-1}). Competitive entry by N$_3^-$ results in a greater decrease in the amount of chelated ester (R = *i*-Pr) compared to that of the hydroxo ester.

Introduction

The current work was undertaken to explore the consequences of expanding ring size on the capture of a competing intramolecular nucleophile (ester and carboxylate oxygen) by intermediates of reduced coordination number. This paper reports the preparation and resolution into enantiomers of *cis*-[Co(en)$_2$X(β-alaOR)]$^{2+}$ (X = Cl, Br; R = H, Me, *i*-Pr) and the consequences of the Hg^{2+}- and OH$^-$-induced removal of halide to form the six-membered β-alanine chelate in competition with entry by H$_2$O and N$_3^-$.

Previously it was shown that the related reaction of *cis*-[Co(en)$_2$X(glyOR)]$^{2+}$ with Hg^{2+} gives exclusive entry of ester oxygen to form the five-membered chelate [Co(en)$_2$(glyOR)]$^{3+}$.[1,2] This subsequently hydrolyzes rather rapidly to [Co(en)$_2$(glyO)]$^{2+}$ without ring opening. Alkaline hydrolysis of the same complex however results in substantial water entry for R = H (45–49% *cis*- and 7–10% *trans*-[Co(en)$_2$(OH)(glyO)]$^+$ are formed in addition to capture of carboxylate oxygen),[3] but for R = Me, Et, and *i*-Pr water entry could only be demonstrated by ^{18}O-tracer studies since the hydroxo ester rapidly cyclizes and hydrolyzes intramolecularly to [Co(en)$_2$(glyO)]$^{2+}$ under the reaction conditions.[4] In the present system the monodentate species [Co(en)$_2$(OH$_2$)(β-alaOR)]$^{3+}$, [Co(en)$_2$(OH)(β-alaOR)]$^{2+}$, and [Co(en)$_2$(N$_3$)(β-alaOR)]$^{2+}$ can be directly identified as being distinct from the chelate [Co(en)$_2$(β-alaOR)]$^{3+}$.

Experimental Section

Visible spectra were recorded on a Cary 14 spectrophotometer, and cobalt estimations were made by using a Techtron AA4 spectrophotometer.

A stock solution of Hg^{2+} in HClO$_4$ (I = 1.0 mol dm^{-3}) was prepared by dissolving HgO in HClO$_4$, diluting to [Hg^{2+}] = 0.2 mol dm^{-3} and [H$^+$] = 0.3 mol dm^{-3}, and adding NaClO$_4$. For reactions at pH ~4 Hg(OAc)$_2$ was dissolved in H$_2$O (0.025 mol dm^{-3}), and the ionic strength adjusted to 1.0 with NaClO$_4$.

Rate data were obtained by using a Cary 16K spectrophotometer and flow reactor assembly, or by pH stat titration with 1.0 mol dm^{-3} NaOH in a cell (3.2 cm) housed in the spectrophotometer. Optical rotations were measured at 25.0 °C with a Perkin-Elmer P22 spectropolarimeter (10-cm cell). Bio-Rad Analytical Dowex 50W-X2 (200–400 mesh, Na$^+$ form) and CM Sephadex C25 (Na$^+$–form) cation-exchange resins were used in separating reaction products.

Preparations. AnalaR reagents were used throughout.

[Co(en)$_2$CO$_3$]Cl was prepared by the method of Springborg and Schaffer.[5] [Co(en)$_2$CO$_3$]Br was crystallized from warm water with NaBr. *trans*-[Co(en)$_2$X$_2$]X (X = Cl, Br) was prepared by dissolution of [Co(en)$_2$CO$_3$]X in concentrated HX (50 g in 200 cm^3) at 70 °C followed by 1 h of cooling in an ice bath. The product was washed with ethanol and acetone until free of acid and dried at 100 °C for 3 h.

β-Alanine isopropyl ester hydrochloride was prepared by adding β-alanine (22.3 g) to cold 2-propanol (260 cm^3, 0 °C) to which had been slowly added thionyl chloride (20 cm^3). After 3 h of reflux (steam bath), the solution was evaporated to 50 cm^3 and cooled in ice and excess ether was added. The white opalescent crystals were washed with ether and recrystallized from 2-propanol by adding ether. Anal. Calcd for β-alaOCH(CH$_3$)$_2$·HCl: C, 42.99; H, 8.42; N, 8.35; Cl, 21.15. Found: C, 43.3; H, 8.3; N, 8.4; Cl, 21.1. β-Alanine methyl ester hydrochloride was prepared in a similar manner. Anal. Calcd for β-alaOCH$_3$·HCl: C, 34.40; H, 7.22; N, 10.04. Found: C, 33.9; H, 7.0; N, 9.5. β-Alaninamide hydrobromide was prepared via its dimedone derivative.[6,7] To β-alanine ethyl ester hydrochloride (0.2 mol) was added a solution of dimedone (0.2 mol) in chloroform (600 cm^3), and the suspension was neutralized with anhydrous triethylamine (0.2 mol). After 12 h at room temperature the filtrate was taken to dryness (steam bath), the residue dissolved in benzene, and NEt$_3$·HCl removed. The dimedone ethyl ester hydrochloride crystallized on cooling the filtrate overnight in a refrigerator. The amide was formed by adding concentrated ammonia and allowing the mixture to stand for 1 h. This was collected as a solid following removal of excess ammonia. An aqueous solution (400 cm^3, 70 °C) was treated dropwise with Br$_2$ until a yellow color remained and crystals of β-alaninamide hydrobromide deposited on cooling to 0 °C. These were washed with acetone and dried in an evacuated desiccator. Anal. Calcd for β-alaNH$_2$·HBr: C, 21.31; H, 5.36; N, 16.57. Found: C, 20.4; H, 5.1; N, 15.7.

***cis*-[Co(en)$_2$X(β-alaOR)]X$_2$ (X = Br, Cl; R = Me, *i*-Pr).** These complexes were prepared by modifying a conventional method.[1] To a finely ground mixture of *trans*-[Co(en)$_2$X$_2$]X (1.0 molar equiv), β-alanine ester hydrochloride (1.1 molar equiv), and a crystal of CoX$_2$·6H$_2$O was added sufficient water to make a thick paste, and then diethylamine (1.0

---

* To whom correspondence should be addressed at the University of Otago.

(1) Alexander, M. D.; Busch, D. A. *Inorg. Chem.* **1966**, *5*, 602.

(2) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6032.

(3) Boreham, C. J.; Buckingham, D. A.; Clark, C. R. *Inorg. Chem.* **1979**, *18*, 1990.

(4) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 4102.

(5) Springborg, J.; Schaffer, C. E. *Inorg. Synth.* **1973**, *14*, 64.

(6) Halpern, B. *Aust. J. Chem.* **1965**, *18*, 417.

(7) Halpern, B.; James, L. B. *Aust. J. Chem.* **1964**, *17*, 1282.

0020-1669/86/1325-1956$01.50/0