Inorganica Chimica Acta, *126* (1987) 147–149

Racemization and Isomerization of $\Lambda[Co(en)_2(OH_2)OH]S_2O_6 \cdot H_2O$

W. G. JACKSON

Department of Chemistry, University College, University of N.S.W., Australian Defence Force Academy, Canberra, A.C.T. 2600, Australia

(Received July 18, 1986)

Abstract

The synthesis of Λ-*cis*$[Co(en)_2(OH_2)OH]S_2O_6 \cdot H_2O$ is described. Its specific rate of racemization ($k_r = (2.20 \pm 0.06) \times 10^{-3}$ s^{-1}) and isomerization ($k_{ct} = (2.2 \pm 0.17) \times 10^{-3}$ s^{-1}) have been determined for CO_2-free water at 25 °C, and the finding of identical rate constants removes an anomaly from the literature.

Introduction

Several studies have demonstrated the lability of the $Co(en)_2(OH_2)OH^{2+}$ ions [1–6]. The *trans* and *cis* forms interconvert with a half-life of *ca.* 130 s at 25 °C, and there is 59% *cis* isomer at equilibrium [1–2, 4]. It also appears from ^{18}O-exchange results [3] that each act of isomerization proceeds with the exchange of one water molecule, *i.e.*, it is a substitution rather than an intramolecular process. A salt of the resolved Λ-*cis*-$Co(en)_2(OH_2)OH^{2+}$ ion does not appear to have been crystallized, but it is readily generated in solution by acid cleavage of Λ-*cis*-$Co(en)_2OCO_2^{+}$ followed by pH adjustment. Following qualitative work [7, 8], its racemization has been studied [6] and the rate is reported to be 2- to 3-fold faster than *cis* to *trans* rearrangement [6a]. This contrasts sharply with the general result [9]* for water substitution in Λ-$Co(en)_2(A)OH_2^{n+}$ ($A = OH_2$, Cl^-, Br^-, N_3^-). For all these ions the specific rates for racemization and *cis* to *trans* isomerization are identical, consistent with full optical activity for the *cis* product of water exchange. This general result is also consistent with the stereochemistries for aquation of Λ-*cis*-$Co(en)_2(A)X^{n+}$ [9]. Since $Co(en)_2(OH_2)OH^{2+}$ can exchange water via an internal conjugate base and such a reaction would likely lead to appreciable racemic *cis* product [9], it became especially important to establish whether this was a genuine anomaly.

One [6a] of the publications [6] dealing with the rate of racemization of Λ-*cis*-$Co(en)_2(OH_2)OH^{2+}$ conceded that it was difficult to obtain accurate racemization and isomerization rate data pertaining to the individual Λ-*cis*- and *trans*-$Co(en)_2(OH_2)OH^{2+}$ ions because of uncertainties in the pH-dependence of the diaqua/hydroxoaqua/dihydroxo ion distributions; since this was not the main issue, the problem was not pursued. Earlier it was suggested that these difficulties did not arise if a solid hydroxoaqua salt was used directly as the reactant, and the solvent was unbuffered CO_2-free water [4]. However, only isomerization of the *trans* ion has been studied by this method (0, 10.2 °C). We have now obtained the first crystalline salt of optically pure Λ-*cis*-$Co(en)_2(OH_2)OH^{2+}$, which allows reasonably precise measurements of racemization and isomerization by this technique, and herein report the relevant data (25 °C) which resolve the apparent anomaly.

Results

The racemization and isomerization rate data (Tables I and II) were obtained for unbuffered CO_2-

TABLE I. Specific Rates for Λ-$Co(en)_2(OH_2)OH^{2+}$ Racemization in H_2O, 25 °C

10^3 $[Co]_0$ (M)	λ (nm)	10^3 k_r (s^{-1})
2.7	546	2.20
4.4	546	2.12
1.0[a]	546	2.20
7.4	546	2.25
2.7	546	2.27
7.4	520	2.18
5.4[b]	520	2.17
		2.20 ± 0.05[c]

[a] Added *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$, 5.0×10^{-4} M. [b] Added *trans* salt, 1.8×10^{-3} M. [c] Mean and standard deviation.

---

*Ref. 10 gives $k_r \simeq 1.2 \times 10^{-7}$ s^{-1} for *cis*-$Co(en)_2(OH_2)_2^{3+}$, and from ref. 5, $K_e = k_{tc}/k_{ct} \simeq 50$; using the value $k_i = k_{tc} = 6.8 \times 10^{-6}$ (ref. 3), k_{ct} can be evaluated, 1.3×10^{-7} s^{-1}. Thus for the *cis*-diaquo ion, $k_r \simeq k_{ct}$, although the experimental error in K_e precludes the improved definition of k_{ct}.

0020-1693/87/$3.50

TABLE II. Specific Rates and Equilibrium Position for $Co(en)_2(OH_2)OH^{2+}$ Isomerization in H_2O, 25 °C

λ (nm)	Reactant[a]	k_i (10^3 s^{-1})	ϵ_∞^{492} [b]	cis_∞ [c] (%)
510	*cis*	4.83	54.1	59
510		5.13	53.4	58
310		4.73		
510		5.37		
490		5.27		
310		5.00		
		5.06 ± 0.25[d]		
510	*trans*	4.93	52.9	57
510		5.17	52.8	57
510		5.30	53.0	57
490		5.33	52.5	56.5
310		5.67		
		5.28 ± 0.27[d]		
		5.16 ± 0.27[e]	53.1 ± 0.6[e]	57.5 ± 1.0[e]

[a] [Co], 10^{-3} to 10^{-2} M. [b] Quenched with 0.1 M $HClO_4$ after 10 $t_{1/2}$; products are $Co(en)_2(OH_2)_2{}^{3+}$. [c] % cis_∞ = 10^2 $(\epsilon_\infty^{492} - \epsilon_\mathrm{trans}^{492})/(\epsilon_\mathrm{cis}^{492} - \epsilon_\mathrm{trans}^{492})$; $\epsilon_\mathrm{cis}^{492} = 79.1$, $\epsilon_\mathrm{trans}^{492} = 18.0$ (this work). [d] Mean and standard deviation. [e] As d but for all data in the column.

free aqueous solutions at 25.0 °C. Good first-order racemization kinetics were observed over at least $3t_{1/2}$, and the derived rate constant was independent of the wavelength for the study (546, 520 nm), and also independent of [Co] in the range $(1-8) \times 10^{-3}$ M. These results indicate that Λ-$Co(en)_2(OH_2)OH^{2+}$ is not significantly transformed into $Co(en)_2(OH)_2{}^+$ and/or $Co(en)_2(OH_2)_2{}^{3+}$, a fact confirmed by the negligible effect on k_r of the presence of *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$, purposely added (up to 50%) to the Λ$[Co(en)_2(OH_2)OH]S_2O_6 \cdot H_2O$ starting material. Final optical rotations were zero, confirming the absence of CO_2 (which converts the substrate to the strongly rotating Λ-$Co(en)_2OCO_2{}^+$ ion [11]). Similarly, the *cis*/*trans* isomerization reaction gave excellent first-order kinetics over at least $3t_{1/2}$, and the result was independent of wavelength (310, 490 and 510 nm), [Co] in the range 10^{-3} to 10^{-2} M, and whether the starting isomer was *cis* or *trans* (Table II). The (same) sharp isosbestic points were observed for both *cis* to *trans* and *trans* to *cis* isomerization (580, 404 and 340 nm), confirming simple reversible isomerization of $Co(en)_2(OH_2)OH^{2+}$ uncomplicated by the formation of any $Co(en)_2(OH)_2{}^+$ or $Co(en)_2(OH_2)_2{}^{3+}$. The final isomer distribution was 57.5 ± 1.0% *cis* for all experiments (25 °C), in close agreement with reported values (H_2O, 59% *cis* [4]; 1 M $NaNO_3$, 58.6% *cis* [1]) in the range 0–25 °C. Moreover, the published rate data [4] extrapolated to 25 °C gave $k_\mathrm{i} = 5.0 \times 10^{-3}$ s^{-1}, identical to our value $(5.16 \pm 0.27)10^{-3}$ s^{-1}. The combined k_i, T data yielded $\Delta H = 115.2 \pm 1.2$ kJ mol^{-1} and $\Delta S = 97.5 \pm 4.4$ J mol^{-1} K^{-1} (from a weighted non-linear least squares analysis).

Discussion

Separating isomerically pure *cis*- or *trans*-$Co(en)_2(OH_2)OH^{2+}$ salts from mixtures has in the past proved troublesome [5], and this has also been true of the corresponding diaqua ions [1–3]. However, it is now clear that the $ClO_4{}^-$ ion is highly selective for the *trans* isomer [5, 6, 9] and $S_2O_6{}^{2-}$ for the *cis* isomer [12] in the hydroxo-aqua series, and this fact coupled with rapid isomer interconversion at ambient temperature affords a high yield and high purity synthesis of the desired form without regard to the configuration of the starting material, usually $[Co(en)_2OCO_2] \cdot ClO_4$ for convenience.

To our knowledge, no salts of optically pure *cis*-$Co(en)_2(OH_2)OH^{2+}$ have been described. This substance was required as a source of Λ-$Co(en)_2(OH_2)OH^{2+}$ in >99% abundance, by dissolution in CO_2-free aqueous solution, since the alternative procedure of adjusting the pH of a solution of Λ-$Co(en)_2(OH_2)_2{}^{3+}$ presupposes a very precise knowledge of the relevant pK_a values at the existing ionic strength and temperature. We have found that $S_2O_6{}^{2-}$ selectively crystallizes the Λ-*cis*-hydroxo-aqua isomer, as it does the racemate, from a solution of Λ-$Co(en)_2OCO_2{}^+$ treated with $HClO_4$ followed by pyridine to reduce the pH to *ca.* 7 where appreciable *cis*-$Co(en)_2(OH_2)OH^{2+}$ exists. At 0 °C, racemization and *cis* to *trans* isomerization are insignificant in the time required for the resolved *cis* salt to crystallize. The isolated Λ$[Co(en)_2(OH_2)OH]S_2O_6 \cdot H_2O$ salt on treatment with excess $HCO_3{}^-$ showed molar rotations within 1% of optically pure Λ-$Co(en)_2OCO_2{}^+$. Moreover, the electronic absorption spectra in 0.1 M $HClO_4$, 0.1 M OH^- and 0.01 M $NaHCO_3$ were identical to those [9, 12, 13] for authentic *cis*-$Co(en)_2(OH_2)_2{}^{3+}$, *cis*-$Co(en)_2(OH)_2{}^+$ and $Co(en)_2OCO_2{}^+$ respectively. The kinetic results confirm that disproportionation of Λ-*cis*- or *trans*-$Co(en)_2(OH)_2OH^{2+}$ is insignificant in CO_2-free water at the cobalt concentrations employed, as earlier suggested [4]. Also, in this respect, the presence of one isomer does not affect the other. The specific isomerization rate k_i $(5.16 \pm 0.27)10^{-3}$ s^{-1} leads to $k_\mathrm{ct} = (2.20 \pm 0.17)10^{-3}$ s^{-1}, using $k_\mathrm{i} = k_\mathrm{tc} + k_\mathrm{ct}$ and $K_\mathrm{e} = [cis_\infty]/[trans_\infty] = k_\mathrm{tc}/k_\mathrm{ct} = (57.5 \pm 1.0)/(42.5 \pm 1.0) = 1.35 \pm 0.06$. The values for k_ct and k_r $(2.20 \pm 0.06)10^{-3}$ s^{-1} provide the key comparison, and clearly these are identical within a relatively small experimental error. Thus Λ-$Co(en)_2(OH_2)OH^{2+}$ racemizes exclusively by isomerization to the achiral *trans* form. There is no significant contribution from a direct $\Lambda \rightarrow \Delta$ inversion path, in keeping with results for other Λ-$Co(en)_2A(OH_2)^{n+}$ ions [9, 10]. Thus the anomaly suggested by the results of Buckingham *et al.* [6] dissolves, and it appears that the errors in the k_r and k_{ct} numbers they extracted from k(obs.) data using an expression involving several parameters, were greater than they estimated.

Experimental

A Perkin-Elmer model 241 spectropolarimeter and Kontron model 810 spectrophotometer were used for measurements of optical rotation and electronic absorption spectra, respectively. Temperature control (±0.1 °C) was maintained by circulating water from a Lauda bath. First-order rate constants were obtained in the usual way from absorbance *vs.* time and optical rotation *vs.* time traces at selected wavelengths, for reactions studies *in situ* [9] using CO_2-free water (N_2, 10 min).

The complexes *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ [6, 9], *cis*-$[Co(en)_2(OH_2)OH]S_2O_6$ [13] and *cis*-$[Co(en)_2(OH_2)Cl]Br_2 \cdot H_2O$ [12] were prepared as described previously. The latter was resolved with NH_4(+)BCS [14] to provide a convenient source of Λ-$Co(en)_2OCO_2^+$, by treatment of a concentrated solution of Λ-*cis*$[Co(en)_2(OH_2)Cl]Br_2$ in aqueous $NaHCO_3$ (1 M) with $LiClO_4$ which crystallized $\Lambda[Co(en)_2OCO_2]ClO_4 \cdot 0.5H_2O$ in good yield. The spectroscopic data were in excellent agreement with accepted values [15] for the fully resolved hemihydrate. Λ-*cis*$[Co(en)_2(OH_2)OH]S_2O_6 \cdot H_2O$ was obtained as follows. Λ-*cis*$[Co(en)_2OCO_2]ClO_4 \cdot 0.5H_2O$ (0.5 g) was carefully dissolved (portionwise) in 1.0 M $HClO_4$ (10 ml), warmed if necessary, and then residual CO_2 was expelled (N_2, 10 min). A saturated aqueous solution of $Na_2S_2O_6 \cdot 2H_2O$ (3 ml) was then added, and the filtered mixture cooled to *ca.* 0 °C in ice/salt. The addition of pyridine (1.5 ml) under rapid stirring resulted in crystallization of a fine granular pink product within 30 s. This was quickly removed by filtration, and washed successively with ice water (2 × 3 ml), ethanol and ether, and air-dried (0.45 g; 80%). Recrystallization is unnecessary; the complex is isomerically and optically pure (0.1 M $HClO_4$ then excess $NaHCO_3$, 15 min: ϵ_{511}^{max} 133.0; $[M]_{589}$ 4602, $[M]_{578}$ 5463, $[M]_{546}$ −5675, $[M]_{365}$ −6266; these values correspond to those of authentic Λ-$Co(en)_2$-OCO_2^+ [15]; 0.1 M $HClO_4$, ϵ_{492}^{max} 79.1; 0.1 M NaOH, ϵ_{516}^{max} 95.4; these values agree well with those for authentic *cis*-$Co(en)_2(OH_2)_2^{3+}$ [13, 15] and *cis*-$Co(en)_2(OH)_2^+$ respectively).

Acknowledgements

The author is indebted to Prof. W. Marty and the Institute of Chemistry, University of Neuchâtel, Switzerland for their gracious hospitality. Part of this work was carried out there, and assistance from Mr. R. Fahrer at that time is gratefully acknowledged.

References

1 J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand., 6,* 1265 (1952).

2 J. Y. Long and P. E. Yankwich, *J. Am. Chem. Soc., 80,* 2664 (1958).

3 W. Kruse and H. Taube, *J. Am. Chem. Soc., 83,* 1280 (1961).

4 R. C. Henney, *Inorg. Chem., 8,* 389 (1969).

5 M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.,* 4637 (1961).

6 (a) D. A. Buckingham, J. MacB. Harrowfield and A. M. Sargeson, *J. Am. Chem. Soc., 95,* 7281 (1973); (b) D. A. Buckingham, J. Dekkers, A. M. Sargeson and L. G. Marzilli, *Inorg. Chem., 12,* 1207 (1973).

7 K. Garbett and R. D. Gillard, *J. Chem. Soc.,* 6084 (1965).

8 R. D. Gillard, *J. Chem. Soc. A,* 1945 (1968).

9 W. G. Jackson and A. M. Sargeson, *Inorg. Chem., 17,* 1348 (1978).

10 J. P. Mathieu, *Compt. Rend., 199,* 278 (1934); *201,* 1183 (1935); *Bull. Soc. Chim. France* [5] *3,* 476 (1936); [5] *4,* 687 (1937).

11 F. P. Dwyer, A. M. Sargeson and I. K. Reid, *J. Am. Chem. Soc., 85,* 1215 (1963).

12 J. Springborg and C. E. Schäffer, *Inorg. Synth., 14,* 63 (1973).

13 W. G. Jackson, *Inorg. Chim. Acta, 10,* 51 (1974).

14 A. Werner, *Helv. Chim. Acta, 4,* 113 (1921); *Justus Liebigs Ann. Chem., 386,* 122 (1911).

15 W. G. Jackson and C. M. Begbie, *Inorg. Chem., 22,* 1190 (1983).