158. Reactions of Oxygenated Cobalt(II) Complexes. XIII¹). Diastereoisomeric Forms of μ-Peroxo-μ-hydroxo-bis[bis(ethylenediamine) Cobalt(III)]. Preparation, X-ray Structure Determination and Reactivity

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Summary

Oxygenation of solutions containing bis(ethylenediamine) cobalt(II) ions leads to a mixture of diastereomeric forms of μ-peroxo-μ-hydroxo-bis[bis(ethylenediamine) cobalt(III)] cations. The existence of a meso-isomer has now been proved by its isolation as perchlorate and by an X-ray structure determination. The crystals are monoclinic with space group $P2_1/n$ and lattice constants: $a = 19.280$, $b = 11.984$, $c = 11.654$ Å, $\beta = 99.190°$.

The UV./VIS. spectra of the isomers are practically identical but show different kinetic behaviour. In acidic solution the meso-isomer decomposes 4 times faster than the racemic form. In alkaline solution the meso-isomer isomerizes to the racemic form. A mechanism which explains all the kinetic observations has been devised.

Introduction. - Oxygenation of weakly alkaline cobalt(II) solutions containing ethylenediamine yields the binuclear species $[(en)_2Co(O_2,OH)Co(en)_2]^{3+}$. As *McLendon & Martell* have shown [2], its formation constant as determined by equilibrium titration methods places the complex cation among the most stable of this doubly bridged type [3]. Crystalline μ-peroxo-μ-hydroxo-dicobalt(III) complexes can easily be obtained [4]. X-ray analysis of a racemic $[(en)_2Co(O_2,OH)Co(en)_2](S_2O_6)(NO_3)$ showed the binuclear cation to have configuration **a** [5] and

Fig. 1. *Schematic drawing of the diastereomeric cations* $[(en)_2Co(O_2,OH)Co(en)_2]^{3+}$

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[1]) Part XII of this series: s. [1].

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enantiomorph. An indication that a second isomer, presumably **b**, also forms in solution, was given by kinetic experiments. Freshly oxygenated solutions of $Co(en)_2^{2+}$ when acidified decompose to give cobalt(II) and molecular oxygen [6]. This decomposition reaction monitored by UV./VIS. spectroscopy or a *Clark*-type oxygen sensor shows two phases. Analysis of the kinetic data (pH 2, 25°, 0.2 M KCl) yields pseudo-first order rate constants of $8.5 \cdot 10^{-3}$ s^{-1} and $3.9 \cdot 10^{-2}$ s^{-1}. The lower value is identical with the rate constant for decomposition of racemic **a**, and the higher value compares well with the rate constant for decomposition of another compound of the composition $[(en)_2Co(O_2,OH)Co(en)_2](ClO_4)_3 \cdot H_2O$, that could be isolated from concentrated oxygenation mixtures. This compound is now shown by X-ray analysis to be the mesoform **b**. The present communication reports our crystallographic results as well as a comparison of the solution properties of the two isomers.

Preparation. - A solution of 50 ml 50% aqueous ethanol containing 3.6 g $Co(ClO_4)_2 \cdot 6\,H_2O$ and 1.5 g ethylenediamine free base (*Merck*, *purum*) was stirred for 30 min with oxygen bubbled through the mixture. The dark brown solution was then filtered and set aside in an ice bath to give black crystals after 1-2 h. In order to get the pure meso-isomer the crystallisation period must be kept as short as possible. Adding further perchlorate results in precipitation of the racemate.

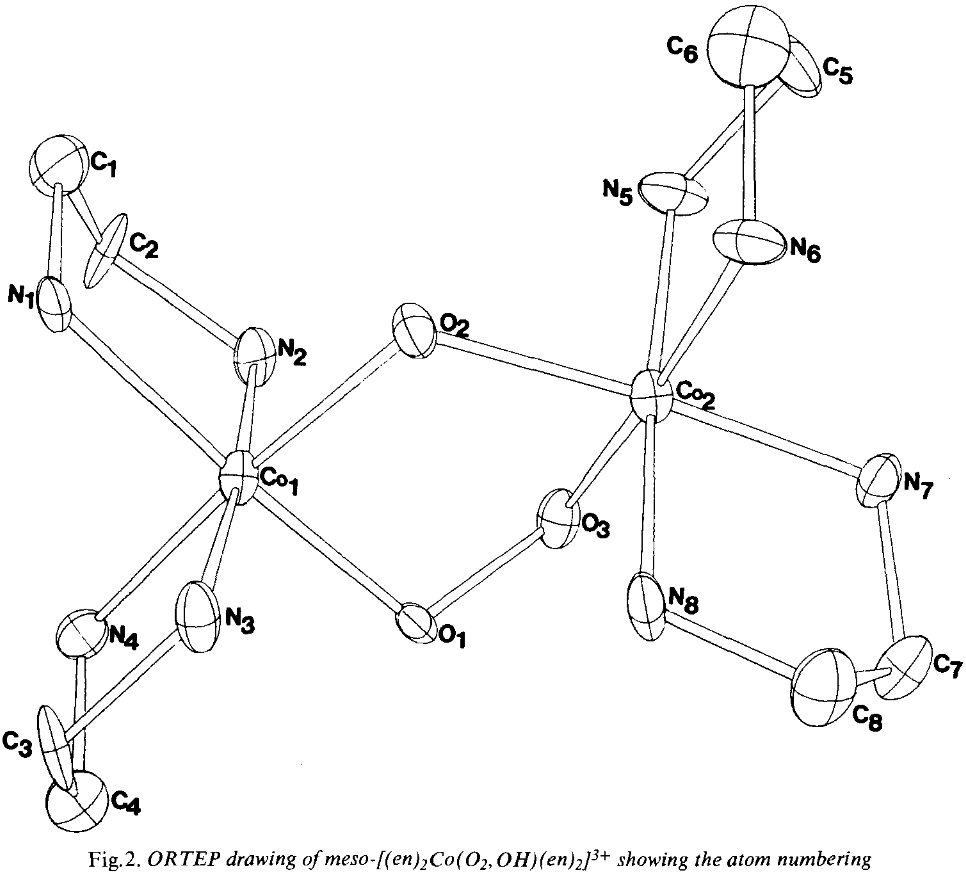


Fig. 2. *ORTEP drawing of meso-*$[(en)_2Co(O_2,OH)(en)_2]^{3+}$ *showing the atom numbering*

Table 1. *Positional and thermal parameters of the nonhydrogen atoms and their standard deviations.* The temperature factors are of the form $T = \exp\{-2\pi^2(U_{11}h^2a*^2 + \cdots + 2U_{12}hka*b*)\}$

	Atom[a])	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cation	Co(1)	0.5868 (1)	0.3527 (2)	0.6069 (2)	0.0297 (1)	0.0242 (1)	0.0162 (1)	−0.0005 (1)	0.0001 (1)	0.0028 (1)
	O(1)	0.5137 (4)	0.3498 (8)	0.4791 (7)	0.0183 (5)	0.0368 (6)	0.0181 (5)	0.0032 (5)	0.0085 (4)	0.0008 (5)
	N(1)	0.6682 (6)	0.3635 (12)	0.7371 (9)	0.0321 (7)	0.0607 (9)	0.0114 (6)	0.0040 (6)	0.0064 (5)	0.0001 (7)
	N(2)	0.6097(6)	0.5034 (10)	0.5718 (10)	0.0408 (7)	0.0188 (7)	0.0241 (6)	−0.0095 (6)	0.0073 (6)	0.0012 (6)
	N(3)	0.5609 (7)	0.2027 (10)	0.6571 (10)	0.0574 (8)	0.0208 (7)	0.0213 (6)	−0.0028 (6)	0.0100 (6)	−0.0027 (6)
	N(4)	0.5193 (6)	0.4072 (10)	0.7015 (10)	0.0246 (7)	0.0337 (7)	0.0286 (7)	0.0032 (6)	−0.0009 (6)	0.0049 (6)
	C(1)	0.7085 (9)	0.4696 (15)	0.7216 (14)	0.0440 (9)	0.0458 (9)	0.0371 (9)	0.0089 (8)	0.0021 (8)	−0.0090 (8)
	C(2)	0.6569 (9)	0.5541 (14)	0.6735 (13)	0.0575 (9)	0.0474 (9)	0.0220 (8)	−0.0086 (8)	−0.0243 (8)	−0.0042 (8)
	C(3)	0.5143 (9)	0.2124 (13)	0.7465 (12)	0.0762 (9)	0.0243 (8)	0.0128 (7)	0.0035 (7)	0.0209 (7)	0.0124 (8)
	C(4)	0.4680 (8)	0.3127 (13)	0.7152 (14)	0.0472 (9)	0.0240 (9)	0.0441 (9)	−0.0058 (7)	0.0099 (8)	−0.0049 (7)
	Co(2)	0.6083 (1)	0.2774 (2)	0.3435 (2)	0.0304 (1)	0.0250 (1)	0.0190 (1)	−0.0002 (1)	0.0046 (1)	0.0016 (1)
	O(2)	0.6472 (5)	0.2922 (8)	0.5049 (7)	0.0277 (5)	0.0346 (6)	0.0197 (5)	0.0009 (5)	0.0068 (4)	0.0093 (5)
	O(3)	0.5426 (5)	0.3824 (8)	0.3756 (7)	0.0395 (6)	0.0305 (6)	0.0179 (5)	0.0038 (4)	−0.0002 (4)	0.0015 (5)
	N(5)	0.6713 (6)	0.3943 (11)	0.3069 (11)	0.0264 (6)	0.0393 (8)	0.0557 (8)	0.0002 (6)	0.0180 (6)	−0.0068 (6)
	N(6)	0.6834 (6)	0.1711 (11)	0.3143 (11)	0.0225 (6)	0.0457 (8)	0.0473 (7)	0.0140 (6)	0.0107 (6)	−0.0038 (6)
	N(7)	0.5595 (6)	0.2732 (10)	0.1812 (9)	0.0318 (7)	0.0293 (7)	0.0240 (6)	−0.0067 (6)	−0.0016 (6)	−0.0055 (6)
	N(8)	0.5462 (6)	0.1569 (11)	0.3695 (9)	0.0513 (7)	0.0356 (7)	0.0174 (6)	−0.0054 (6)	0.0127 (6)	−0.0117 (6)
	C(5)	0.7252 (9)	0.3455 (16)	0.2428 (14)	0.0568 (9)	0.0704 (9)	0.0374 (9)	−0.0065 (9)	0.0329 (8)	−0.0094 (9)
	C(6)	0.7498 (10)	0.2404 (16)	0.3049 (16)	0.0622 (9)	0.0493 (9)	0.0654 (9)	0.0066 (9)	0.0044 (9)	0.0148 (9)
	C(7)	0.4943 (9)	0.1998 (16)	0.1771 (14)	0.0415 (9)	0.0666 (9)	0.0373 (9)	−0.0111 (9)	−0.0088 (8)	−0.0087 (8)
	C(8)	0.5136 (9)	0.1011 (14)	0.2627 (15)	0.0680 (9)	0.0316 (9)	0.0444 (9)	−0.0033 (9)	0.0045 (9)	−0.0092 (9)
Anions	Cl(1)	0.3876 (2)	0.4852 (4)	0.9954 (3)	0.0556 (3)	0.0447 (3)	0.0239 (2)	0.0037 (2)	0.0027 (2)	0.0029 (2)
	O(10)	0.4124 (8)	0.4809 (11)	0.8884 (10)	0.1392 (9)	0.0602 (8)	0.0380 (6)	−0.0045 (6)	0.0366 (7)	0.0135 (8)
	O(11)	0.3953 (7)	0.5979 (10)	1.0378 (10)	0.1107 (9)	0.0465 (8)	0.0485 (7)	−0.0188 (6)	0.0283 (7)	−0.0126 (7)
	O(12)	0.4252 (8)	0.4130 (13)	1.0760 (13)	0.1080 (9)	0.1016 (9)	0.0832 (9)	0.0414 (8)	0.0027 (8)	0.0375 (8)
	O(13)	0.3158 (7)	0.4576 (13)	0.9785 (14)	0.0548 (8)	0.1013 (9)	0.1338 (9)	−0.0106 (9)	−0.0029 (8)	−0.0315 (8)
	Cl(2)	0.1666 (3)	0.4437 (5)	0.4855 (5)	0.0903 (4)	0.0807 (4)	0.0555 (4)	0.0194 (3)	0.0014 (3)	−0.0372 (3)
	O(20)	0.1266 (11)	0.3990 (21)	0.5532 (17)	0.1768 (9)	0.1686 (9)	0.1327 (9)	0.0541 (9)	0.0691 (9)	−0.0939 (9)
	O(21)	0.1528 (13)	0.5526 (19)	0.4597 (22)	0.1233 (9)	0.1284 (9)	0.1571 (9)	0.0989 (9)	0.1191 (9)	0.0546 (9)
	O(22)	0.2389 (9)	0.4419 (18)	0.5372 (15)	0.1016 (9)	0.2020 (9)	0.1026 (9)	−0.0460 (9)	−0.0102 (9)	−0.0633 (9)
	O(23)	0.1636 (11)	0.3848 (22)	0.3801 (15)	0.1800 (9)	0.1792 (9)	0.0763 (9)	−0.0646 (9)	0.0015 (9)	−0.1221 (9)
	Cl(3)	0.8620 (2)	0.4126 (4)	−0.0141 (4)	0.0453 (3)	0.0553 (3)	0.0589 (3)	−0.0013 (2)	−0.0044 (2)	0.0011 (2)
	O(30)	0.9339 (8)	0.4106 (18)	0.0063 (15)	0.0709 (9)	0.1043 (9)	0.1373 (9)	0.0352 (9)	0.0366 (9)	0.0667 (9)
	O(31)	0.8399 (8)	0.5202 (12)	−0.0489 (13)	0.0985 (9)	0.0568 (9)	0.1087 (9)	−0.0011 (8)	−0.0377 (8)	0.0064 (8)
	O(32)	0.8099 (16)	0.3363 (20)	−0.0418 (26)	0.1837 (9)	0.1240 (9)	0.1736 (9)	0.0015 (9)	−0.0364 (9)	−0.0676 (9)
	O(33)	0.8496 (12)	0.4004 (24)	0.0964 (19)	0.1991 (9)	0.1961 (9)	0.1471 (9)	0.1348 (9)	0.1142 (9)	0.0621 (9)
	O(34)	0.8333 (16)	0.3404 (17)	−0.7940 (21)	0.2437 (9)					
	O(34′)	0.8552 (18)	0.3527 (21)	−0.1262 (21)	0.1291 (9)					
	W	0.7824 (8)	0.2381 (15)	0.6210 (13)	0.1058 (9)	0.1369 (9)	0.0923 (9)	−0.0098 (9)	−0.0067 (8)	0.0370 (9)

[a]) The numbering is that of the ORTEP-Plot.

Table 2. *Selected bond distances and bond angles in the cation*

Bonds	Distance [Å]	Bonds	Angle [°]
Co(1)–Co(2)	3.289	Co(1)–μO(2)–Co(2)	117.2 (4)
Co(1)–μO(1)	1.880 (8)	Co(1)–μO(1)–μO(3)	108.3 (6)
Co(1)–μO(2)	1.934 (10)	Co(2)–μO(3)–μO(1)	110.2 (6)
Co(1)–N(1)	2.005 (11)	μO(1)–Co(1)–μO(2)	87.4 (4)
Co(1)–N(2)	1.920 (12)	μO(2)–Co(2)–μO(3)	85.0 (4)
Co(1)–N(3)	1.979 (12)		
Co(1)–N(4)	1.947 (13)	N(1)–Co(1)–N(2)	85.5 (5)
		N(1)–Co(1)–N(3)	92.2 (5)
Co(2)–μO(2)	1.919 (8)	N(1)–Co(1)–N(4)	93.6 (5)
Co(2)–μO(3)	1.866 (10)		
Co(2)–N(5)	1.946 (13)	N(6)–Co(2)–N(5)	85.8 (5)
Co(2)–N(6)	1.999 (13)	N(6)–Co(2)–N(7)	93.9 (5)
Co(2)–N(7)	1.974 (10)	N(6)–Co(2)–N(8)	91.9 (5)
Co(2)–N(8)	1.930 (13)	Co(1)–μO(1)–μO(3)–Co(2)	64.5 (5)
μO(1)–μO(3)	1.460 (13)		

X-ray Structure Determination. - Crystallographic data are: $a = 19.280(5)$, $b = 11.984(3)$, $c = 11.654(3)$ Å, $\beta = 99.190(4)$, $D_{obs.} = 1.810$, $D_{calc.} = 1.809$ g/cm^3 for Z = 4, space group $P2_1/n$. Intensities of 2482 independent reflexions were collected ($\theta/2\theta$ scan) in the range $2 < \theta < 27°$ with a *Philips*-PW-1100 diffractometer equipped with a fine focus molybdenum tube and a graphite monochromator (MoK_a, $\lambda = 0.71069$ Å). No correction for absorption was applied. The structure was solved by direct methods. Programs used were developed by *G.M. Sheldrick* (Shelx-76) [7] and by ourselves. Scattering factors for neutral atoms including anomalous dispersion were taken from *Cromer et al.* [8]. The 1584 reflexions with $F_0 > 2\sigma(F_0)$ were used in the anisotropic refinement. All protons of the cation are localized. A final difference *Fourier* map showed no electron-density peak higher than 0.7 e/Å^3. The final R-index was 0.0639 $(R = \sum \| F_0 | - | F_c \| / | F_0 |)$. Atomic positional and thermal parameters are given in *Table 1,* while selected interatomic distances and bond angles of the cation are listed in *Table 2.* One of the perchlorate anions is disordered, O(34) being split into two half-populated positions.

Spectrophotometric Experiments. - Absorption spectra were taken on a *Beckman* model 24 on line with a *Hewlett Packard* 9825 desk calculator using a special interface *Kontron* WP 3800. Kinetic measurements and numerical analysis were performed as described in earlier publications [9].

Structure of meso-[(en)$_2$Co(O$_2$,OH)Co(en)$_2$]$^{3+}$. - *Figure 2* shows an ORTEP drawing of the cation **b**. The O–O distance of 1.46 Å marks it as a true peroxo complex. The bimetallic bridging ring is of the same type as in isomer **a** [5] and in [(tren)Co(O$_2$,OH)(tren)]$^{3+}$ [10], the group CoOOCo being nonplanar with torsion angle of 64° about the O–O bond (60° in **a**). As usual the octahedra are somewhat distorted [9] with bond angles N–Co–N between 85 and 94°. Comparison of the structural parameters of **a** and **b** does not furnish a clue to the observed differences in reactivity discussed below.

Results and Discussion of Solution Experiments. - The UV./VIS. spectra of freshly prepared solutions of complexes **a** and **b** in 0.01 M borate buffer are very similar. *Figure 3* shows the spectrum of **b** in 0.02 M borate buffer solution. The absorption maxima of **a** are shifted towards lower wavelengths by about 3 nm. The molar extinctions of the lower energy band ($\varepsilon \approx 5.5 \cdot 10^3$) are equal for **a** and **b** within experimental error. **a** exhibits a somewhat smaller ratio $\varepsilon(279)/\varepsilon(358)$ than **b**. Two strong bands in the near UV. range seem to be typical for the

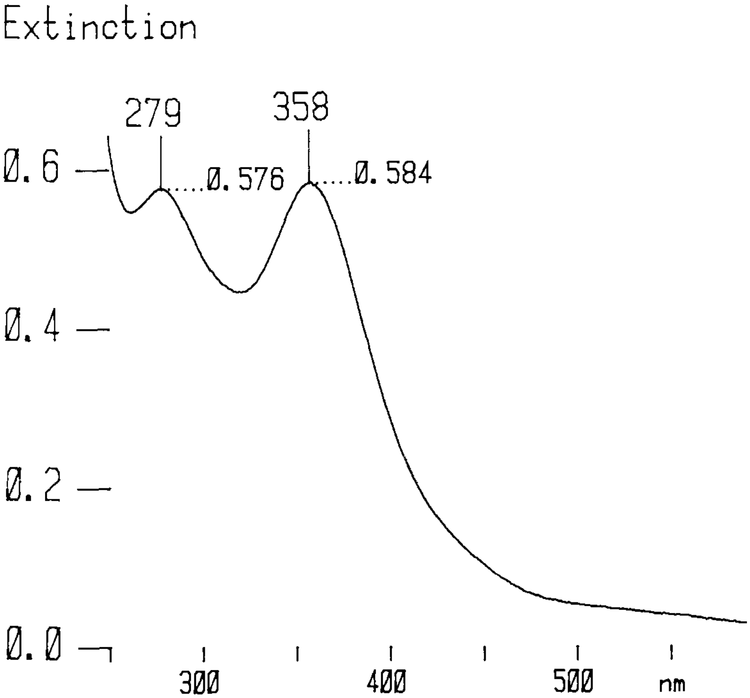


Fig. 3. *UV./VIS. spectrum* (Extinction *vs.* wavelength) *of a 1.105*M solution of **b** in 0.02M borate buffer solution of pH 9

nonplanar bridging system Co(O_2,OH)Co [11] (see stereoplot *Fig. 4*). Similar spectra have been observed for other μ-peroxo-μ-hydroxo complexes with quadridentate nitrogen donor ligands [9].

The same type of absorption is also obtained with freshly oxygenated solutions of Co(en)$_2^{2+}$. However, the full development of the two-band spectrum shown in *Figure 3* demands at least a 6-fold excess of ligand en at pH 10. A further

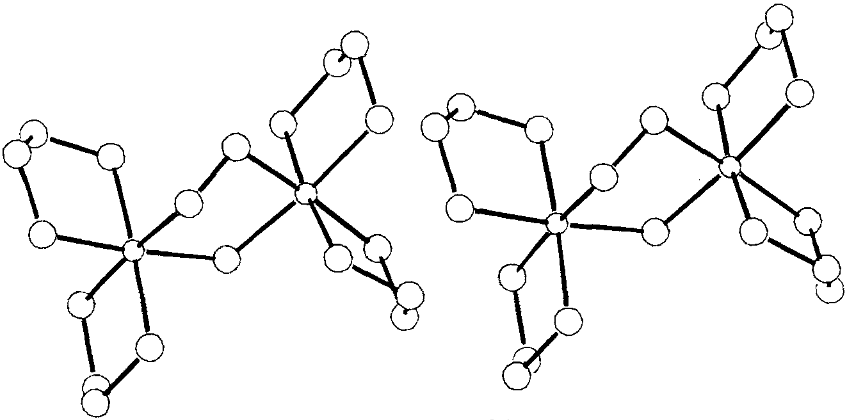


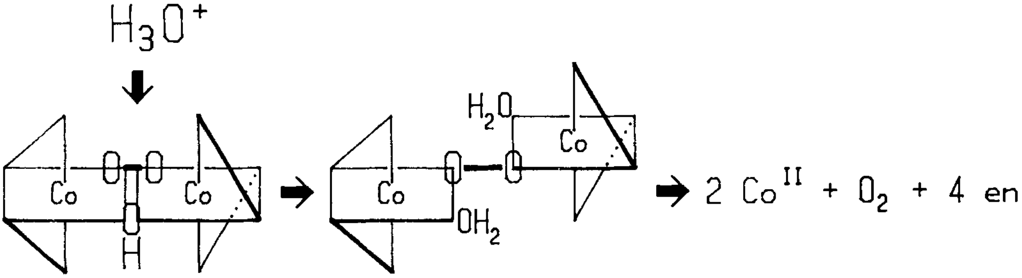
Fig. 4. *Stereopair view of the cation* **b**

increase of [en] does not lead to any significant spectral changes, in contrast to findings of *Nakon et al.* [12] who reported formation of an ethylenediamine bridged complex in solutions of high [en].

In acid both isomers decompose to cobalt(II) and dioxygen [6]. The reaction is H^+-catalyzed and the rate data can be fitted to an equation of type (1) and interpreted in terms of *Scheme 1*, involving a fast protonation step, a rate determining structural change of the protonated species, and a fast decay to mononuclear fragments. The meso-isomer **b** turns out to be the more labile. Differences in decomposition rate are due mainly to differences in reactivity of the protonated species but partly also to a different protonation constant, the precise determination of which is difficult. The decomposition rates also depend on other factors: increase in halide concentration increases the observed rate constants. This effect can be explained by assuming a shift of the protonation equilibrium due to ion pairing of the higher charged protonated species. An apparent pK_a of about 1.1 (25°) in 0.2 M KCl solution can be estimated from parameter c_2 in (1). Since the existence of a μ-hydronium group seems unlikely, the site of protonation is probably at the peroxo group. The rate determining step is assumed to be opening of the bridging ring *(Scheme 1)* to give a singly bridged bis(aquo)-μ-peroxo complex. Since no intermediate of this type can be isolated or detected spectrophotometrically it must decompose to mononuclear fragments significantly faster as it is formed.

$$k = c_1[H^+]/(c_2 + [H^+]) \tag{1}$$

Scheme 1



As mentioned earlier, decomposition of a freshly oxygenated dilute solution of $Co(en)_2^{2+}$ takes place in two phases with the same two rate constants as for the pure crystalline samples. The oxygenated solution must therefore contain a mixture of the isomers **a** and **b**. No other species can be present in appreciable (>5%) amounts. From the amplitudes of the two reaction phases an isomer ratio **a**:**b** = 55:45 can be computed.

In neutral or slightly basic solution both isomeric μ-peroxo-μ-hydroxo complexes slowly decompose. The intense charge transfer absorption decreases, and the well known d-d bands of mononuclear bis(ethylenediamine)cobalt(III) species appear. Numerical analysis of the observed spectral changes with respect to time reveals a multistep process. The reaction is first order to about 85% but there must be at least one intermediate before, by slower steps, the final product $[Co(en)_2(OH)_2]^+$ is formed. Following E(358), in this first phase of decomposition of isomer **a** a rate constant $k_a \approx 4.1 \cdot 10^{-6}\ s^{-1}$ (25°) was determined in 0.02 M borate at pH 10.

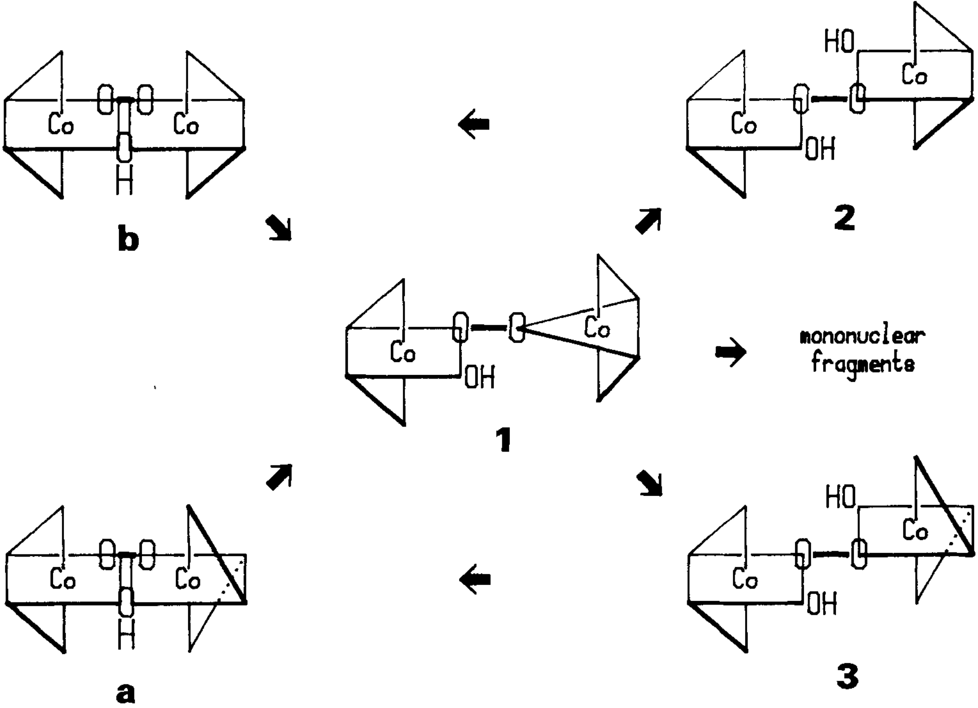
The decomposition of isomer **b** is faster and within the period of time producing an 85% extinction change two rate constants can be computed: $k_b \approx 3.6(\pm 0.5) \cdot 10^{-5}$, $k_b' \approx 4.6(\pm 0.7) \cdot 10^{-6}\ s^{-1}$ (25°). Since k_b', within normal experimental error, is identical with k_a, partial formation of isomer **a** is strongly suspected during decomposition of **b**.

As outlined above, the kinetic analysis of the decomposition experiments in acidic medium furnishes a convenient and accurate method for the determination of the isomer ratio. Starting with a fresh solution of **b** at pH 10, the isomer purity of which was checked to be within ±5%, at different stages of the comparatively slow decomposition process the actual ratio [**a**]/[**b**] was calculated by acidifying and determining the two reaction phases as indicated above. The relative amount of **a** was found to increase with $k \approx 4.2(\pm 0.2) \cdot 10^{-5}\ s^{-1}$ (25°).

This result explains why the decomposition of isomer **b** at pH 10 apparently takes place in two phases: An appreciable amount of isomerization **b**→**a** must be assumed in this medium. The fact that isomer **b** decomposes with a rate which is identical with the isomerization rate can be accounted for by reaction *Scheme 2*.

Opening of the bimetallic bridging ring in **b** leads first to a pentacoordinated intermediate (**1**) which, by nucleophilic attack of OH^-, forms the singly bridged

Scheme 2



bis(hydroxo) complexes with *ΛΛ*- (**2**) and *ΛΔ*-configuration (**3**). Both isomers can decompose to mononuclear fragments but they predominantly revert to **b** and **a** respectively. Since step **a**→**1** has been found to be 10 times slower than **b**→**1**, [**a**] must increase in relation to [**b**].

From an investigation of the kinetics of oxygenation of cobalt(II)amine complexes [13] the bridging steps **2**→**b** and **3**→**a** were estimated to have rate constants $\approx 1\ s^{-1}$. Since steps **1**→**2** and **1**→**3** can also be reasonably expected to be fast, the overall rate must be determined by the rates of **b**→**1** and **a**→**1** and by the amount of pentacoordinated intermediate which decomposes. Because **b**→**1** is appreciably faster than **a**→**1**, ring opening in **b** is also rate determining for the change of the isomer ratio.

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