general usefulness of this type of relationship. From the NMR shifts obtained for the monobromo and monoiodo carboranes (Table I) appropriate additivity constants can be derived by comparing the chemical shifts of each boron position of the substituted carborane with the corresponding position of the parent $C_2B_5H_7$. These additivity parameters, along with those derived from the corresponding fluoro[2] and chloro[5] compounds, are given in Table VI and are graphically displayed in Figure 7. The trends seen in this figure can be summarized as follows: (a) a downfield shift is obbserved for the boron atom directly attached to the halogen, with greater shifts observed for borons with smaller halogens; (b) an upfield shift is noted for the boron atom antipodal (i.e. 7-position) to the substituted 1-position, with greater anti-podal-boron upfield shifts found when smaller halogens are attached to B(1); (c) as might be reasonably expected, smaller effects are observed for other borons in the cage. The general utility of the additivity parameters to predict the chemical shifts of the dibromo- and diiodocarboranes in the present work is demonstrated by a comparison of experimental with calculated values in Table I (cf. chemical shifts "out-of-brackets" with chemical shifts "in-brackets", respectively). The differences between the observed and calculated shifts average ca. 0.4 ppm, with a slightly better correspondence noted for the dibromo isomers than for the diiodo isomers.

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**Registry No.** 1-Br-2,4-$C_2B_5H_6$, 98821-51-3; 3-Br-2,4-$C_2B_5H_6$, 98821-52-4; 5-Br-2,4-$C_2B_5H_6$, 27733-74-0; 1,3-$Br_2$-2,4-$C_2B_5H_5$, 98821-53-5; 1,5-$Br_2$-2,4-$C_2B_5H_5$, 98821-54-6; 3,5-$Br_2$-2,4-$C_2B_5H$, 98821-55-7; 5,6-$Br_2$-2,4-$C_2B_5H_5$, 98821-56-8; 1-I-2,4-$C_2B_5H_6$, 98821-57-9; 3-I-2,4-$C_2B_5H_6$, 98821-58-0; 5-I-2,4-$C_2B_5H_6$, 98838-28-9; 1,3-$I_2$-2,4-$C_2B_5H_5$, 98821-59-1; 1,5-$I_2$-2,4-$C_2B_5H_5$, 98838-29-0; 3,5-$I_2$-2,4-$C_2B_5H_5$, 96343-25-8; 5,6-$I_2$-2,4-$C_2B_5H_5$, 98821-60-4; 1-F-2,4-$C_2B_5H_6$, 55124-16-8; 3-F-2,4-$C_2B_5H_6$, 55124-15-7; 5-F-2,4-$C_2B_5H_6$, 55124-17-9; 1-Cl-2,4-$C_2B_5H_6$, 28347-69-5; 3-Cl-2,4-$C_2B_5H_6$, 28347-93-5; 5-Cl-2,4-$C_2B_5H_6$, 28347-92-4; 2,4-$C_2B_5H_7$, 20693-69-0.

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# Photochemical and Thermal Decomposition of $(\Delta\Delta,\Lambda\Lambda)$-($\mu$-Hydroxo)($\mu$-peroxo)bis[bis(ethylenediamine)cobalt(III)] Ions in Basic Aqueous Solution

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The title ion in aqueous basic solution does not undergo deoxygenation in the dark, but it does on irradiation with ultraviolet light to give the photoinduced equilibration

$$[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2]^{3+} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} 2[Co^{II}(en)_2(H_2O)_2]^{2+} + O_2$$

The quantum yield determined in the presence of excess EDTA is ca. $2.2 \times 10^{-3}$ on irradiation at 366 nm at 5 °C and is virtually independent of pH (8.1–10.4). The yield on irradiation at 515 nm at ca. 25 °C is $<2 \times 10^{-6}$. The ligand($O_2$)-to-metal charge-transfer excited state is relevant to the deoxygenation reaction. Continuous irradiation leads to subsequent irreversible decomposition to give cobalt(III) species including $[Co^{III}(en)_2(H_2O)_2]^{3+}$. Such an irreversible decomposition is much slower in the dark (ca. $5 \times 10^{-7}$ s$^{-1}$ at 5 °C, pH 8.9, and $I$ = 0.1 M ($NaClO_4$); 1 M = 1 mol dm$^{-3}$).

Peroxo-bridged and superoxo-bridged dicobalt(III) complexes have been extensively studied to elucidate their chemical and physical properties with reference to the behavior of the coordinated dioxygen moiety.[2] There are several reports on the photochemical decomposition of ($\mu$-superoxo)dicobalt(III) complexes[3-6] but none on that of $\mu$-peroxo complexes.[7] We have recently found that continuous irradiation with ultraviolet light on basic aqueous solutions of $\mu$-peroxo complexes such as $[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2]^{3+}$ (**1**) (en = ethylenediamine) and $[(dien)(en)Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(en)(dien)]^{4+}$ (**2**) (dien = diethylenetriamine) caused reversible redox decomposition to cobalt(II) species and $O_2$.[8] Furthermore, both **1** and **2** undergo irreversible decomposition to give mononuclear cobalt(III) complexes on prolonged irradiation.

In the dark, ion **2** undergoes deoxygenation,[9] while **1** does not.[10] Both **1** and **2** decompose irreversibly and completely to mononuclear cobalt(III) species, after several days at 25 °C.[11-13] The

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decomposition of **1** to give $[Co^{III}(en)_2(H_2O)_2]^{3+}$ has been studied kinetically.[12,13]

We report here our results on the photochemical reversible and irreversible decomposition of **1** and its thermal irreversible decomposition in basic aqueous solution. Brief studies on the photoreactivities of **2** and (ΔΔ,ΛΛ)-$[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{2-})Co^{III}(en)_2]^{3+}$ (**3**) are also mentioned.

## Experimental Section

**1. Materials.** (ΔΔ,ΛΛ)-($\mu$-Hydroxo)($\mu$-peroxo)bis[bis(ethylenediamine)cobalt(III)] perchlorate trihydrate, (ΔΔ,ΛΛ)-$[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2](ClO_4)_3\cdot3H_2O$, was prepared as described previously.[14] The absorption peak of the complex at 25 °C in aqueous solution at 356 nm ($\epsilon$ = 5540 $M^{-1}$ $cm^{-1}$) (1 M = 1 mol $dm^{-3}$) shifts to 355 nm at 15 °C and to 354 nm at 5 °C without changing its intensity. ($\mu$-Peroxo)bis[(diethylenetriamine)(ethylenediamine)cobalt(III)] perchlorate, $[(dien)(en)Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(en)(dien)](ClO_4)_4$,[15] and (ΔΔ,ΛΛ)-($\mu$-amido)($\mu$-peroxo)bis[bis(ethylenediamine)cobalt(III)] nitrate–2.5-water, (ΔΔ,ΛΛ)-$[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{2-})Co^{III}(en)_2](NO_3)_3\cdot2.5H_2O$,[16] were prepared by the methods described previously.

Propylenediamine was resolved by Dwyer's method.[17] Special-grade reagents of ethylenediamine, disodium dihydrogen ethylenediaminetetraacetate, and sodium perchlorate were used as received. Ammonia ($NH_3$–$NH_4ClO_4$) and borate buffer were prepared from special-grade reagents.

**2. Photochemical Reactions.** All the experiments were carried out in air. A sample solution containing (ΔΔ,ΛΛ)-$[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2]^{3+}$ (**1r**) ($1.8 \times 10^{-4}$ M) and appropriate ingredients was irradiated continuously in a 1-cm quartz cell by a low-pressure mercury lamp (L-937-1 (5 W), Hamamatsu) or by a high-pressure mercury lamp (USH-102D (100 W), Ushio Electric Co.), mostly at 25 °C. Absorption spectra were recorded on a Hitachi 323 or a Hitachi 330 spectrophotometer by placing the cell in the spectrophotometer at appropriate time intervals.

For investigating the reaction products, 40–50 $cm^3$ of the solution ($[Co^{III}_2] = 3 \times 10^{-3}$ M) in a fused silica tube was irradiated by a high-pressure mercury lamp (UM-452 (350 W), Ushio Electric Co.) at 0 °C until the characteristic brown color of **1** disappeared. The pH was then made ca. 2 with 0.1 M $HClO_4$ at room temperature in order to decompose any remaining **1**. The products were passed through a cation-exchange column (SP-Sephadex C-25 or Dowex 50W-X8 in $Na^+$ form, approximately 1 cm in diameter and 30 cm in length). Cationic species held on the column were separately eluted with 0.2–0.5 M $NaClO_4$ solution and identified by visible absorption spectra. An anion-exchange column (QAE-Sephadex A-25 in $Cl^-$ form) was also used whenever necessary.

Similar experiments were carried out for the other $\mu$-peroxo complexes, **2** and **3**.

**3. Quantum Yield of the Deoxygenation of 1r.** Light of a high-pressure mercury lamp (USH-102D (100 W)) at 366 nm was filtered with a UV-D36A filter and a saturated aqueous copper sulfate solution (5-cm cell) and was incident continuously on the cell (1 cm) containing a sample solution across the light path of the spectrophotometer (Hitachi 323). Decrease in absorbance was followed at 354 nm, where the absorbance of reaction products can be ignored. The quantum yield ($\Phi$) was calculated by eq 1. Here $\Delta A$, $\epsilon$, $I_s$, and $T_{366}$ are the absorbance

$$\Phi = (\Delta A)\epsilon^{-1} \times 0.003/[I_s(\Delta t)(1 - T_{366})] \qquad (1)$$

change during the irradiation time $\Delta t$, the molar absorption coefficient of the dimer at 354 nm (5540 $M^{-1}$ $cm^{-1}$ at 5 °C), the light intensity (E/min; E = einstein), and the transmittance of the sample solution at 366 nm (1-cm cell), respectively. The incident-light intensity was measured by use of the tris(oxalato)ferrate(III) ion as the actinometer, before and after each experiment. The $T_{366}$ value was the average value during the measurement. The quantum yield was obtained from the measurement within a 10% decrease of the initial absorbance.

The light of an argon ion laser (Molectron 52 B at 515 nm) was used for the measurement of quantum yield on irradiation with visible light. The incident-light intensity was measured by use of a power meter (Scientific Model 36-0001). The sample solution ($[Co^{III}_2] \approx 2 \times 10^{-3}$ M) in a 1-cm cell was transferred to a 1-mm cell after irradiation for measuring the degree of photodecomposition by the change in absorbance at 354 nm.

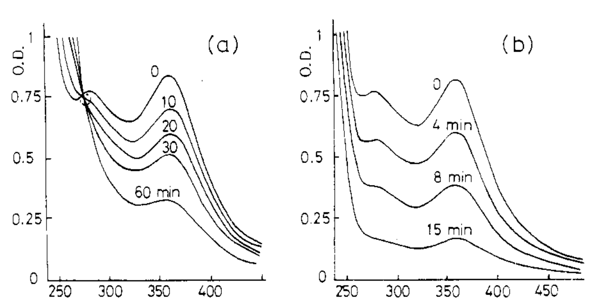
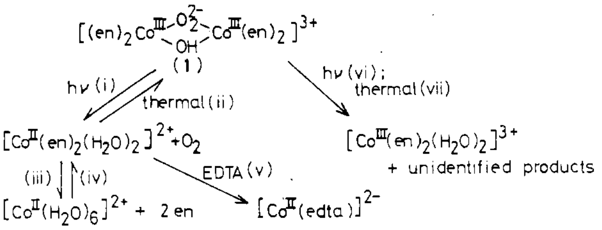


**Figure 1.** Changes in the absorption spectra of aqueous solutions of (ΔΔ,ΛΛ)-$[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2]^{3+}$ ($1.5 \times 10^{-4}$ M) on continuous irradiation with light at 366 nm of the high-pressure mercury lamp (USD-102D, 100 W) at 25 °C: (a) no ingredient added, pH changed from 8.5 (before irradiation) to ca. 9 (after irradiation); (b) [EDTA] = 0.0015 M, pH 8.5–9.0.

Scheme I. Reactions[a] of 1r



[a] Thermal reaction ii gives a mixture of racemic and meso forms.

**4. Thermal Reactions of 1r.** The change in the absorption spectrum of **1r** in aqueous solution was followed at 5–50 °C with a Hitachi 323 and a Hitachi 330 spectrophotometer. A solution of the complex ($[Co^{III}_2] = 1 \times 10^{-3}$ M) was kept in the dark in a constant-temperature bath, and small portions were taken at certain time intervals for measurement of the absorption spectra. For analyzing the products, solutions ($[Co^{III}_2] = (4\text{–}7) \times 10^{-3}$ M) were kept at 50 °C (in nitrogen atmosphere whenever necessary) until the absorption peak at 357 nm disappeared (7–20 h, depending on the pH and ingredients). The solution was made to pH ca. 2 and submitted to ion-exchange column chromatography, similar to the procedure for the products of the photochemical reaction.

Ligand replacement of **1r** by (*R*)-propylenediamine was investigated by observing the appearance of the circular dichroism (CD) spectrum with a JASCO J-40A automatic recording spectropolarimeter.

## Results

**1. Photochemical Reactions of 1r. (a) Changes in Absorption Spectra and the Reaction Products.** The absorption spectrum of **1r** in basic aqueous solution changed rapidly in at least two steps on continuous irradiation by the high-pressure mercury lamp at 25 °C (Figure 1a). The initial, rapid, and small decrease of the extinction in the region 260–500 nm was followed by a slower change with an isosbestic point at 273 nm, which disappeared toward the end of change. The extent of the initial rapid decrease was more marked when the low-pressure mercury lamp was used as the source of incident light. The location of the isosbestic point also shifted to shorter wavelength (271 nm). When irradiation by the low-pressure mercury lamp was interrupted immediately after the initial rapid decrease of extinction, the absorption in the range 260–500 nm recovered most, but not all, of the original intensity.

The final products, after irradiation by the high-pressure mercury lamp, were analyzed by ion-exchange column chromatography (SP-Sephadex C-25). The identified unique product was $[Co^{III}(en)_2(H_2O)_2]^{3+}$ with ca. 25% yield. At least three other bands were observed on the column, none of which was identified.

When a solution of **1r** containing free ethylenediamine (0.001 M) was irradiated by the high-pressure mercury lamp, the decrease (10% after 3 h of irradiation) of the extinction in the region 260–500 nm was much slower, and the rate is virtually the same as that observed in the dark (vide infra). Thus, the photochemical

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**Table I.** Quantum Yields of the Deoxygenation of $(\Delta\Delta,\Lambda\Lambda)$-$[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2]^{3+}$ in the Presence of Excessive EDTA in Aqueous Basic Solution[a]

| temp/°C | pH | $[Co^{III}_2]$/ $10^{-4}$ M | [EDTA]/ $10^{-4}$ M | quantum yield/$10^{-3}$ |
|---|---|---|---|---|
| 5 | 8.1[b] | 1.38 | 2.76 | 2.2 ± 0.3 |
| 5 | 8.3[c] | 1.44 | 2.88 | 2.2 ± 0.4 |
| 5 | 8.9[c] | 1.51 | 3.02 | 2.3 ± 0.2 |
| 5 | 8.9[c] | 1.57 | 3.14 | 2.2 ± 0.3 |
| 5 | 10.4[b] | 1.61 | 3.22 | 2.0 ± 0.2 |
| 5 | 10.4[b] | 1.54 | 3.08 | 1.5 ± 0.3 |
| 5 | 10.4[b] | 1.58 | 3.16 | 2.2 ± 0.4 |
| 5 | 9.1[c] | 1.64 | 16.4 | 2.0 ± 0.4 |
| 15 | 9.0[c] | 1.68 | 3.36 | 2.8 ± 0.3 |
| 25 | 9.0[c] | 1.57 | 3.14 | 4.7 ± 0.4 |

[a] Irradiated at 366 nm; $I = 0.1$ M ($NaClO_4$). [b] Borate buffer ($Na_2B_4O_7$–HCl) ($[Na_2B_4O_7] = 0.01$ M). [c] Ammonia buffer ($NH_4ClO_4$–$NH_3$) ($[NH_4ClO_4] = 0.01$ M).

reaction seems to be suppressed in the presence of free ethylenediamine.

When $Na_2H_2$edta (edta$^{4-}$ = ethylenediaminetetraacetate ion) was added to the initial solution of **1r** as a scavenger of cobalt(II),[9] the intensity of the absorption in the region 260–550 nm decreased in one step on irradiation (Figure 1b), the rate of which was close to the rapid stage of Figure 1a. The main product (>85% yield) was identified as $Co^{II}(edta)^{2-}$ by anion-exchange analysis.

**(b) Reaction Scheme.** These observations are consistent with Scheme I.

The initial rapid change of absorption in Figure 1a should correspond to the photoinduced equilibrium involving processes i–iv, and the slower change, to irreversible decomposition of **1** (process vi). The cobalt(II) species $[Co^{II}(en)_2(H_2O)_2]^{2+}$ should rapidly equilibrate with the aquated species $[Co^{II}(en)(H_2O)_4]^{2+}$ (omitted in the scheme for simplification) and $[Co^{II}(H_2O)_6]^{2+}$, which do not react with dioxygen.[18] It was confirmed that the aqueous solution containing $10^{-4}$ M of cobalt(II) and en gives a $\mu$-peroxo complex in the dark. Thus the thermal reaction (ii) should take place effectively under the present experimental conditions. When free ethylenediamine is added, the relative amount of $[Co^{II}(en)_2(H_2O)_2]^{2+}$ increases among other $Co^{II}$ species, and thus the photoinduced equilibrium should shift more to the dimer than in the absence of free ethylenediamine. The establishment of photoinduced equilibrium is also supported by the photocatalyzed substitution of $\mu$-propylenediamine for en in **1r** (vide infra).

EDTA[19] reacts rapidly with photochemically produced cobalt(II) species to give more stable $[Co^{II}(edta)]^{2-}$, the thermal back-reaction (ii) does not take place, and therefore the photoinduced reaction (vi) is not feasible.

The thermal reaction (vii) is slower by more than 1 order of magnitude than the photoinduced reaction (vi) under the given condition (vide infra).

**(c) Quantum Yield of the Deoxygenation of 1r.** The quantum yield of the process (i) was determined in the presence of EDTA at 5 °C on irradiation with light at 366 nm. It was independent of pH (8.1–10.4), the kind of buffer, and the concentration of EDTA ($0.3 \times 10^{-3}$ and $1.6 \times 10^{-3}$ M), and it increased slightly with an increase in temperature (Table I). Irradiation at 515 nm did not cause appreciable photoreaction (quantum yield $<2 \times 10^{-6}$) at ca. 25 °C.

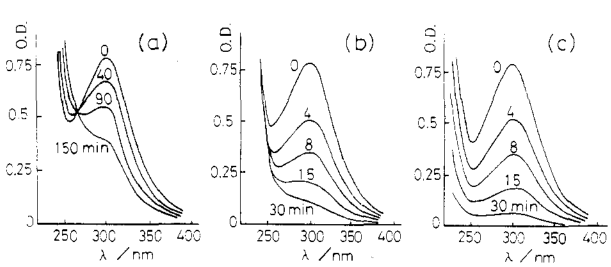

**Figure 2.** Changes in the absorption spectra of aqueous solutions of $[(dien)(en)Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(en)(dien)]^{4+}$ ($7.3 \times 10^{-5}$ M) on continuous irradiation with light at 366 nm of the high-pressure mercury lamp (USD-102D, 100 W) at 25 °C: (a) no ingredient added, pH ca. 8; (b) [EDTA] = 0.0015 M, pH 10.8; (c) pH 2.1.

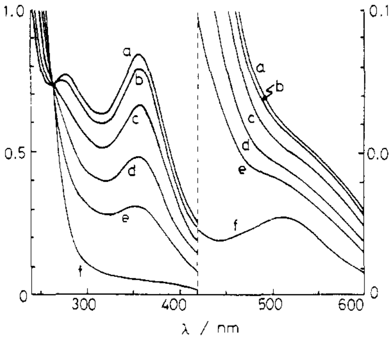

**Figure 3.** Changes in the absorption spectrum of $(\Delta\Delta,\Lambda\Lambda)$-$[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2]^{3+}$ ($9.1 \times 10^{-4}$ M) in aqueous solution (pH 8) at $I = 0.1$ M ($NaClO_4$) at 50 °C in the dark: (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min; (e) 40 min; (f) 1 h.

**2. Photochemical Reaction of 2.** The single-bridged $\mu$-peroxo complex, $[(dien)(en)Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(en)(dien)]^{4+}$ (**2**), shows an absorption maximum at 300 nm with $\epsilon = 11\,110$ $M^{-1}$ $cm^{-1}$ ($\epsilon$ at 366 nm, the wavelength of the intense light of the high-pressure mercury lamp, is ca. 1850 $M^{-1}$ $cm^{-1}$). The ion is known to undergo deoxygenation in the dark with the first-order rate constant $2.3 \times 10^{-5}$ $s^{-1}$ ($I = 0.1$ M) at 25 °C, which is independent of the pH of the solution over the range $2.0 < pH < 12.4$.[20]

The deoxygenation occurred much more rapidly on irradiation by the high-pressure mercury lamp than in the dark. The solution of **2** ($\sim 1 \times 10^{-4}$ M) containing EDTA ($1.5 \times 10^{-3}$ M) at pH 10.8 caused a photoinduced deoxygenation with the rate (half-life ca. 6 min under conditions similar to those for **1r**) almost identical with that without EDTA at pH 2.1 (Figure 3b,c). At pH 2.1, protons behave as scavengers for amines so that EDTA is not required as scavenger. The results clearly indicate that EDTA and protons are not involved in the photoinduced deoxygenation.[9,20-22]

In the absence of EDTA, the solution of **2** (ca. $7 \times 10^{-5}$ M) at pH ca. 8 shows much a slower change in absorption spectrum with a decrease in absorbance in the region >270 nm (Figure 3a). An isosbestic point was observed at 264 nm during the first half (ca. 1 h) of the decrease in absorbance. Addition of $1.2 \times 10^{-3}$ M free ethylenediamine and $1.2 \times 10^{-3}$ M free diethylenetriamine increased the rate of spectral change by ca. 2 times (the pattern of the change is similar). The major product was $[Co^{III}(dien)(en)(H_2O)]^{3+}$ (>70%), as found by ion-exchange chromatography.

The photoinduced reactions of **2** are summarized in a reaction scheme similar to that of **1** except that there is a thermal pathway toward deoxygenation of **2**.

**3. Photochemical Reactions of 3.** In the dark, the ion $(\Delta\Delta,\Lambda\Lambda)$-$[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^{2-})Co^{III}(en)_2]^{3+}$ (**3**) did not show any appreciable change in the absorption spectrum in basic aqueous solution (pH 8–11) after 5 h at room temperature both in the presence and in the absence of excessive EDTA. Neither did it show any change on continuous irradiation with light of the high-pressure mercury lamp for 3 h at pH 8.5 in the absence of EDTA ($[Co^{III}_2] = 1 \times 10^{-4}$ M). A decrease in absorption was observed, however, in the range >270 nm (half-life ca. 1 h) when the solution contained $1.0 \times 10^{-3}$ M EDTA. The reaction products

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Table II. Identified Products and Their Yields for the Thermal Decomposition of ($\Delta\Delta$,$\Lambda\Lambda$)-[(en)$_2$Co$^{III}$($\mu$-OH,O$_2$$^{2-}$)Co$^{III}$(en)$_2$]$^{3+}$ (1r) in Aqueous Solution

| $[1r]_i{}^a$/M | other ingredients$^b$ (concn/M) | reacn conditions | identified products | yield$^c$/% |
|---|---|---|---|---|
| $6.25 \times 10^{-3}$ | none | 50 °C, 6 h | [Co$^{III}$(en)$_2$(H$_2$O)$_2$]$^{3+}$ | 64 |
| $7.0 \times 10^{-3}$ | none | 55 °C, 4 h | | 78 |
| $7.0 \times 10^{-3}$ | none | 50 °C, 6 h | | 62 |
| $7.0 \times 10^{-3}$ | none | 55 °C, 5.5 h | | 69 |
| $6.3 \times 10^{-3}$ | en (0.125) | 60 °C, 13.5 h | [Co$^{III}$(en)$_2$(H$_2$O)$_2$]$^{3+}$<br>[Co$^{III}$(en)$_3$]$^{3+}$ | 61<br>25 |
| $6.3 \times 10^{-3}$ | en (0.13); Co$^{II}$ (0.013) | 65 °C, 21 h | [Co$^{III}$(en)$_2$(H$_2$O)$_2$]$^{3+}$<br>[Co$^{III}$(en)$_3$]$^{3+}$ | 126<br>64 |
| $6.3 \times 10^{-3}$ | en (0.13); Co$^{II}$ (0.013) | room temp, 1.5 months | [Co$^{III}$(en)$_2$(H$_2$O)$_2$]$^{3+}$<br>[Co$^{III}$(en)$_3$]$^{3+}$ | 166<br>30 |

$^a$ Initial concentration of 1r. $^b$ en = ethylenediamine. $^c$ Yield per cobalt ion of the dimer (Co$^{II}$ added is not included).

separated by anion-exchange chromatography included [Co$^{III}$(edta)]$^-$ as well as [Co$^{II}$(edta)]$^{2-}$.

The spectrum at pH 2.5 remained unchanged over a period of 5 h at room temperature in the dark. The solution showed a change (half-life ca. 5 h), however, on irradiation with light of the high-pressure mercury lamp. The products include [Co$^{III}$(en)$_2$(H$_2$O)$_2$]$^{3+}$ (ca. 10% yield) as well as [Co$^{II}$(H$_2$O)$_6$]$^{2+}$ (>67%). The change was accelerated by the presence of $1.0 \times 10^{-3}$ M EDTA (half-life 1.5 h).

Complex **3** is photochemically much less reactive than **1** and **2**, and the observed photochemical reactions of **3** appear to be complicated. No simple deoxygenation reaction (corresponding to process i of Scheme I) takes place. If the deoxygenation occurred in basic solution in the absence of EDTA, the reverse oxygenation process (cf. process ii in Scheme I) would produce **1** rather than **3**, and the photochemical irreversible decomposition of **1** would follow. Such a process was not observed.

**4. Thermal Reactions of 1r. (a) Change in the Absorption Spectrum in the Dark.** Complex **1r** undergoes rapid deoxygenation (studied by the stopped-flow technique) in acid solution (pH <3).[14] In basic aqueous solutions, however, the intensity of the absorption peak at 357 nm decreased by less than 5% after 1 h at room temperature.

Figure 3 shows the changes in the absorption spectrum of an aqueous solution of **1r** at 50 °C in the dark. The characteristic peak at 357 nm slowly disappeared while an isosbestic point was observed at 263 nm at least over ca. 50% of the change. The decrease in absorbance at 357 nm showed good first-order behavior over 2 half-lives to give a first-order rate constant $1.3 \times 10^{-4}$ s$^{-1}$ (50 °C, initial pH 8.0 (adjusted with NaOH solution), $I = 0.1$ M). Rate constants under various conditions are ca. $7 \times 10^{-6}$ s$^{-1}$ [25 °C, pH 8.5 (ammonia buffer NH$_3$–NH$_4$ClO$_4$)], ca. $5 \times 10^{-7}$ s$^{-1}$ [5 °C, pH 8.9 (adjusted with NaOH solution)], and ca. $7 \times 10^{-7}$ s$^{-1}$ (5 °C, pH 11.4 (adjusted with NaOH solution)] at $I = 0.1$ M. The pH dependence does not seem to be significant in the given pH range. Mitchell obtained rate constants of $5.9 \times 10^{-5}$ s$^{-1}$ at pH 8.4 and $8.9 \times 10^{-4}$ s$^{-1}$ at pH 13.6 and 50 °C,[13] and Fallab et al. reported a rate constant of $4.1 \times 10^{-6}$ s$^{-1}$ at 25 °C pH 10 (0.02 M borate buffer).[12] These values might have been obtained without precautions for possible influence by laboratory light. Our kinetic experiment under laboratory light indicated that the first-order rate constant was practically the same as that obtained in the dark, although the first-order plots deviated from the straight line more than those obtained in the dark. Addition of Na$_2$H$_2$edta to the solution of **1r** did not significantly affect the rate constant (EDTA is expected to scavenge cobalt(II) species, if formed[9]). Thus the equilibrium between **1r** and [cobalt(II) + O$_2$] cannot be involved in the decomposition process.[9] The conclusion was further supported by the following experiment. (*R*)-Propylenediamine added to the solution of **1r** does not replace ethylenediamine of **1r** at all in the dark, while it does slowly (but much faster than the decomposition of **1r**) under laboratory light, as indicated by the appearance of CD spectra of ($\Delta\Delta$)-[(*R*-pn)$_2$Co$^{III}$($\mu$-OH,O$_2$$^{2-}$)Co$^{III}$(*R*-pn)$_2$]$^{3+}$ (*R*-pn = (*R*)-propylenediamine).[15]

The change in absorbance was much slower (first-order rate constant $<3 \times 10^{-6}$ s$^{-1}$ at 50 °C) for the solution containing free ethylenediamine ([Co$^{III}$$_2$] = $9.10 \times 10^{-4}$ M; [en] = $1.2 \times 10^{-2}$ M; pH 11.2; $I = 0.1$ M), but laboratory light accelerated the change (ca. $7 \times 10^{-6}$ s$^{-1}$ at 50 °C).

**(b) Reaction Products.** Identified products and their yields determined by the chromatographic separation and absorption intensity are summarized in Table II, together with reaction conditions. When the solution contained no ingredient other than **1r**, the identified unique product was [Co$^{III}$(en)$_2$(H$_2$O)$_2$]$^{3+}$, of which the yield was 50–70%. An "orange species" was always detected, but no cobalt(II) species was found. The "orange species" should possess an ionic charge less than +3, since it was eluted at ca. pH 2 more easily than [Co$^{III}$(en)$_2$(H$_2$O)$_2$]$^{3+}$. This species had an absorption maximum at 505 nm when Dowex resin was used for the separation and at 495 nm when SP-Sephadex C-25 resin was used. Subsequent treatment of the Sephadex eluent with an SP-Sephadex column followed by elution with 0.05 M Na$_2$SO$_4$ solution revealed that it consists of at least two components. The "orange species" was not found when the initial solution contained some ingredients such as free ethylenediamine or cobalt(II) ions. A further attempt was not made to characterize it.

In the presence of free ethylenediamine, the decomposition products included [Co$^{III}$(en)$_3$]$^{3+}$ as well as [Co$^{II}$(en)$_2$(H$_2$O)$_2$]$^{3+}$. The total yield of the products was close to 90%. Some of the added ethylenediamine should have been picked up during the overall reaction of **1r**.

When the initial solution contained free ethylenediamine and cobalt(II) ions as well as **1r**, the total yield of the two mononuclear cobalt(III) complexes amounted to nearly 200% based on the cobalt(II) ions in the dimer. It is clear that 2 mol of added cobalt(II) ion is oxidized by 1 mol of **1r**. This is understood by considering that the bridging peroxide ion is reduced to two water molecules (or hydroxide ions).

## Discussion

**1. Photoinduced Deoxygenation.** The deoxygenation of the $\mu$-hydroxo–$\mu$-peroxo ion **1r** occurs only photochemically in basic aqueous solution. The $\mu$-peroxo single-bridged complex **2** undergoes thermal deoxygenation under a similar condition, but the corresponding photochemical reaction is much more rapid at room temperature. The photochemical deoxygenation of **1r** and **2** occurs in nearly 100% yield whenever the appropriate scavenger of Co$^{II}$ is added. Photochemical deoxygenation was not observed, however, for the $\mu$-amido–$\mu$-peroxo ion **3**.

The deoxygenation of ($\mu$-peroxo)dicobalt(III) complexes should occur in two consecutive steps expressed by eq 2 and 3 (ligand omitted). In the cases of thermal deoxygenation of some ($\mu$-peroxo)dicobalt(III) complexes, step 2 is considered to be rate-determining.[9,14] The changes in absorption spectra for deoxygenation (Figures 1b and 2b,c) clearly occur in a single step, and the accumulation of the intermediate species is not observed. The Co$^{III}$–O$_2$$^-$ species should rapidly decompose under the given conditions. This rapid second step (3) is very likely thermal unless

$$\mathrm{Co^{III}{-}O_2{}^{2-}{-}Co^{III}} \rightarrow \mathrm{Co^{III}{-}O_2{}^{-}} + \mathrm{Co^{II}} \qquad (2)$$

$$\mathrm{Co^{III}{-}O_2{}^{-}} \rightarrow \mathrm{Co^{II}} + \mathrm{O_2} \qquad (3)$$

the quantum yield for this step is very high as compared with that of the first step (2).

The absorption peak of **1r** at ca. 356 nm and that of **2** at ca. 300 nm are due to the charge transfer from the bridging peroxide to cobalt(III).[23] Such a charge-transfer excited state should be involved in the photodeoxygenation. The d–d excited state does not seem to lead to deoxygenation.

The quantum yield of **1r** on irradiation at 356 nm is relatively low as compared with those reported for the redox decomposition of some mononuclear cobalt(III) complexes upon irradiation of the ligand-to-metal charge-transfer band.[24] It is 1 or 2 orders of magnitude lower than those for the decomposition of ($\mu$-superoxo)dicobalt(III) complexes.[5,7]

Despite the low quantum yield, the photoinduced deoxygenation is interesting, since it indicates the photocontrolled reversible oxygen uptake. The reversibility is unfortunately not maintained in the present systems due to the slow irreversible photodecomposition of the binuclear species to mononuclear cobalt(III) complexes.

**2. Irreversible Decomposition of 1r to Mononuclear Cobalt(III) Complexes.** **1r** undergoes irreversible decomposition both thermally and photochemically, the thermal reaction being much slower and observed appreciably only at >50 °C. The mechanism of the thermal reaction is discussed first, since some relevant studies[11,25,26] permit more detailed discussion.

**(a) The Thermal Reaction.** A mononuclear (hydroperoxo)cobalt(III) complex was confirmed as an intermediate of the decomposition of $[(CN)_5Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(CN)_5]^{6-}$ in neutral solution[25] and of $[(NO_2)(en)_2Co^{III}(\mu\text{-}O_2^{2-})Co^{III}(en)_2(NO_2)]^{2+}$ in acid solution.[26] Thus reaction 4[27] is likely to be the initial step of the decomposition of **1r**.

$$[(en)_2Co^{III}(\mu\text{-}OH,O_2^{2-})Co^{III}(en)_2]^{3+} \rightarrow [Co^{III}(en)_2(H_2O)_2]^{3+} + [Co^{III}(en)_2(O_2H)(H_2O)]^{2+} \quad (4)$$

In the absence of other ingredients, initially produced $[Co^{III}(en)_2(O_2H)(H_2O)]^{2+}$ would slowly react with coordinated ligand or ion-exchange resin during product analysis to give "orange species". Free ethylenediamine added to the solution of **1r** would be oxidized by $[Co^{III}(en)_2(O_2H)(H_2O)]^{2+}$. The decrease in decomposition rate in the presence of free ethylenediamine is not clearly accounted for.[28]

In the presence of both free ethylenediamine and $Co^{II}$ ions, reaction 5[27] would take place.

$$[Co^{III}(en)_2(O_2H)(H_2O)]^{2+} + 2[Co^{II}(en)_n(H_2O)_{6-2n}]^{2+} \rightarrow [Co^{III}(en)_2(H_2O)_2]^{3+} + 2[Co^{III}(en)_n(H_2O)_{6-2n}]^{3+} \quad (5)$$

$$n = 2 \text{ or } 3$$

**(b) The Photochemical Decomposition.** The reaction products contain various unidentified species. The reaction may be initiated by homolytic cleavage of the $Co^{III}–(O_2Co^{III})$ bond as is the thermal reaction. The reactive intermediate, $Co^{III}–O_2^{2-}(H)$, would undergo further complicated reactions. It is also plausible that the photodecomposition may be initiated by the reaction of **1** with $Co^{II}$ species, which is produced by the initial photoequilibration. Addition of free ethylenediamine considerably decreases the amount of $Co^{II}$ species by shifting the equilibrium to the dimer side, and it would retard the photodecomposition.[28]

Finally, it should be pointed out that previous studies on ($\mu$-peroxo)dicobalt(III) complexes with amines might have been affected by possible photochemical reactions and might require reexamination.

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(27) The products of reactions 4 and 5 should be in equilibrium with their conjugate bases, hydroxo complexes, depending on the pH of the solution.

(28) One possible explanation for the effect of free ethylenediamine on the rate of decomposition is that the free ligand would replace the hydroxo bridge to give the $\mu$-ethylenediamine complex, $[(en)_2Co^{III}(\mu\text{-}O_2^{2-},en)Co^{III}(en)_2]^{4+}$, which has been claimed to exist (Crawford, M.; Bedell, S. A.; Patel, R. I.; Young, L. W.; Nakon, R. *Inorg. Chem.* **1979**, *18*, 2075–2079). The observed slow decomposition rate would be understood if the $\mu$-ethylenediamine complex were more stable toward a decomposition similar to reaction 4. Also the production of $[Co^{III}(en)_3]^{3+}$ is expected from the decomposition of the $\mu$-en complex. The failure to observe any photodecomposition of **1r** in the presence of free ethylenediamine would be explained if the postulated $\mu$-en complex were photostable. We are not fully convinced, however, of the existence of the $\mu$-en complex under our experimental conditions. No appreciable change in the absorption spectrum of **1r** was observed on addition of free ethylenediamine, and no CD spectrum appeared on addition of (*R*)-propylenediamine in the dark (the $\mu$-*R*-pn complex, if formed, would show some CD spectrum).

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# Hypervalent Tellurium in One-Dimensional Extended Structures Containing $Te_5^{n-}$ Units

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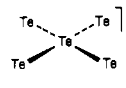
The electronic structure of three one-dimensional chains containing square-planar $Te_5^{n-}$ units is presented, with employment of both molecular and band calculations. Two chains containing only $Te_5^{2-}$ in different conformations and one in which they are modulated by Sn are treated. The $Rb_2Te_5$ or $Cs_2Te_5$ and $K_2SnTe_5$ structures are thus modeled. A three-center, four-electron model can be used to understand the elongation of the Te–Te bands within the $Te_5$ unit, whose inherent instability is overcome by the formation of the chains. It is suggested how oxidation of the chain, for instance, by suitable choice of synthetic conditions, would alter the geometric physical properties of these polymers.

The recent literature contains a number of examples of a square-planar tellurium structural unit which may formally be defined as $Te_5^{n-}$ (**1**). In some cases such as $Rb_2Te_5$[1] and $Cs_2Te_5$[2] the stoichiometry clearly defines the charge on the unit as 2–. In these instances the unit is the basic building block of a one-di-



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