was isolated as the white tetramethylammonium salt in 84% yield and identified by its infrared spectrum. *Anal.* Calcd for $BeB_9C_8H_{21}O$: Be, 4.18; B, 45.16; C, 33.42; H, 9.82. Found: Be, 3.87; B, 44.74; C, 33.26; H, 9.97.

Reaction of Diethylberyllium with $B_9C_2H_{13}$. Preparation of II.—The reaction vessel was a 100-ml three-necked round-bottomed flask, equipped with a pressure-equalized 10-ml addition funnel, a magnetic stirring bar, and a reflux condenser bearing a gas buret.

The round-bottomed flask contained a solution of 7.72 g (57 mmol) of (3)-1,2-$B_9C_2H_{13}$ in 50 ml of dry, oxygen-free benzene. In the addition funnel was 7 ml of diethylberyllium etherate which contained 57.8 mmol of diethylberyllium and 21.2 mmol of diethyl ether. The solution was maintained at room temperature and the diethylberyllium was added dropwise with stirring. Gas evolution occurred immediately and after about 1 ml of diethylberyllium was added a white solid precipitated. The evolved gas was identified as ethane by its characteristic vpc retention time; its volume was 2500 ml after the addition was completed (2800 ml expected).

The white precipitate was separated by filtration, washed three times with 10 ml of benzene, and dried under high vacuum at 50°. The yield was 2.15 g. From the filtrate $B_9C_2H_{11}Be \cdot O(C_2H_5)_2$ (I) was obtained as described earlier. The white solid did not melt below 350° and was not soluble in common organic solvents such as benzene, pentane, dichloromethane, acetone, tetrahydrofuran, or chloroform.

If treated for about 5 hr with liquid trimethylamine, $B_9C_2H_{11}Be \cdot N(CH_3)_3$ could be isolated in a 67% yield.

The infrared spectrum in a Nujol mull exhibits five distinct absorptions in the B–H region: 2550 (sh), 2850 (sh) 2590, 2610, and 2640 cm^{-1} (sh). It possesses a bridge-type hydrogen which absorbs at 2150 cm^{-1}. The absorptions between 700 and 1200 cm^{-1} which can be ascribed to cage absorptions have the same pattern as those of $B_9C_2H_{11}Be \cdot O(C_2H_5)_2$ and $B_9C_2H_{11}Be \cdot N(CH_3)_3$ but are shifted about 15 cm^{-1} to lower frequencies.

Preparation of (3)-$BeN(CH_3)_3$-1,2-$B_9C_2H_{11}$ (III).—The reaction vessel was a 100-ml three-necked round-bottomed flask, equipped with a pressure-equalized addition funnel, a magnetic stirring bar, and a reflux condenser. The round-bottomed flask contained a solution of 6.44 g (48 mmol) of (3)-1,2-$B_9C_2H_{13}$, dissolved in 50 ml of dry oxygen-free benzene. In the addition funnel was 1.87 g (48 mmol) of dimethylberyllium, dissolved in 8 ml of dry diethyl ether. The solution was maintained at room temperature and the dimethylberyllium solution was added dropwise with stirring. Gas evolution occurred immediately which stopped when the addition of dimethylberyllium was completed. The evolved gas was identified as methane from its characteristic vpc retention time.

After the reaction was completed, a yellow oil layer had separated on the bottom of the flask. The upper colorless benzene layer was decanted, and the remaining oil was washed three times with 40 ml of dry benzene and dried under high vacuum at room temperature. The remaining semisolid was dissolved in 30 ml of dry dichloromethane and filtered, and dry trimethylamine was passed through the solution. A white material precipitated which was separated by filtration, washed with benzene, and dried under high vacuum. This white solid was recrystallized from a dichloromethane–hexane mixture by passing dry oxygen-free nitrogen over the surface of the solution. The white solid product (mp 221–223° dec) was obtained in a 51% overall yield. The product was less air sensitive than the analogous etherate and was decomposed by water.

Degradation with ethanolic KOH gave (3)-1,2-$B_9C_2H_{12}^-$ which was isolated as the white tetramethylammonium salt in 79% yield and identified by its infrared spectrum. *Anal.* Calcd for $BeB_9C_5H_{20}N$: Be, 4.50; B, 48.54; C, 29.93; H, 10.05; N, 6.98. Found: Be, 3.79; B, 47.45; C, 28.46; H, 9.67; N, 7.19.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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The Photochemistry of $(en)_2Co(NH_2)(O_2)Co(en)_2^{4+}$

BY JOAN S. VALENTINE AND DONALD VALENTINE, JR.*

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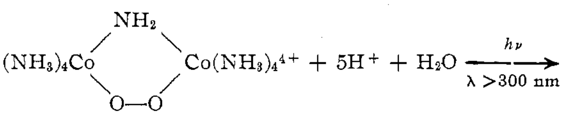
Irradiation of the O_2^- to Co^{III} electron absorption bands of **1** and **2** led in acidic, aqueous solutions to reactions 1 and 2.[1] These reactions were found to be molecular processes in which the photoreactive excited states of the μ-superoxo complexes collapsed to give fragments such as $Co(NH_3)_5(O_2)^{3+}$ and a short-lived cobalt(II)–ammine which decayed subsequently to Co^{2+}.[1] The apparent simplicity of this mechanism and the absence of side reactions led us to believe that reactions such as (1) and (2) might prove general for μ-superoxo-dicobalt ammines. We have now studied the photochemistry of **3** and **4** which are, respectively, analogs of **2** and **1** with coordinated ammonia replaced by chelating organic amines.

$$\underset{\mathbf{1}}{(NH_3)_5CoO_2Co(NH_3)_5^{5+}} + 5H^+ + H_2O \xrightarrow[\lambda > 300\ nm]{h\nu}$$

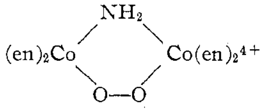
$$Co(NH_3)_5(H_2O)^{3+} + Co^{2+} + 5NH_4^+ + O_2 \quad (1)$$



2

$$(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4^{4+} + 5H^+ + H_2O \xrightarrow[\lambda > 300\ nm]{h\nu}$$

$$Co(NH_3)_5(H_2O)^{3+} + Co^{2+} + 5NH_4^+ + O_2 \quad (2)$$



3

$(en)_2Co(NH_2)(O_2)Co(en)_2^{4+}$

$(tetren)CoO_2Co(tetren)^{5+}$
4

Results and Discussion

Samples of **3** prepared following Werner[2] (reaction 3a) were found to be contaminated with as much as 20% of $(en)_2Co(NH_2)(NO_2)Co(en)_2^{4+}$, **5**, which could be isolated by destroying **3** photochemically and separating **5** from the photochemical decomposition products (*vide infra*) by ion-exchange chromatography. Elution of the fraction containing **5** with 4 *M* HCl gave a solution which upon flash evaporation afforded the chloride salt of **5**, identical with an authentic sample.[3] Formation

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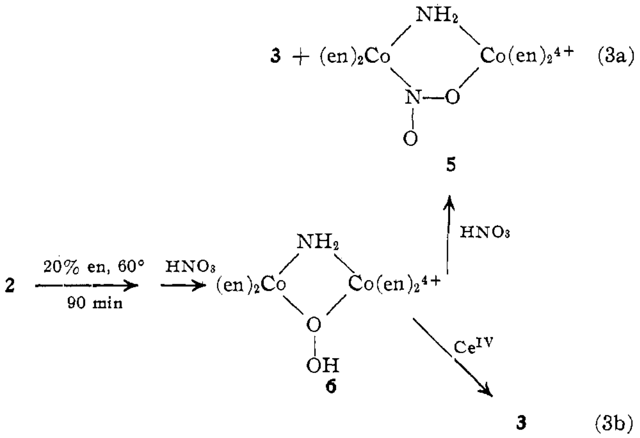
[1] J. S. Valentine and D. Valentine, Jr., *J. Amer. Chem. Soc.*, in press. Preliminary reports of this work appeared in: (a) D. Valentine, Jr., and J. Valentine, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. L-19; (b) J. Valentine and D. Valentine, Jr., in "Progress in Coordination Chemistry," M. Cais, Ed., Elsevier, Amsterdam, 1968, pp 72–74; (c) D. Valentine, Jr., J. Valentine, and B. Sarver, "Proceedings of the Symposium on Electronically Excited States," Los Angeles, Calif., Oct 1969, in press.

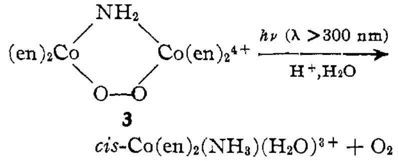
[2] A. Werner, *Justus Liebig's Ann. Chem.*, **375**, 1 (1910).

[3] A. Werner, *Chem. Ber.*, **46**, 3674 (1913). Complex **5** forms a nitrate salt isostructural with the nitrate of **3**: *cf.* G. L. Goodman, H. G. Hecht, and J. A. Weil, *Advan. Chem. Ser.*, **36**, 90 (1962), and references therein. We had no success in purifying **3** contaminated with **5**. Recent work with **3** and the related $(pn)_2Co(NH_2)(O_2)Co(pn)_2^{4+}$ (pn = 1,2-diaminopropane), including both circular dichroism studies and the products of reaction of **3** with iodide ion, should probably be reexamined. See ref 4 and also Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **42**, 146 (1969).

of **5** occurs during oxidation of solutions of $(en)_2Co(NH_2)(OOH)Co(en)_2^{4+}$, **6**,[4] by HNO_3, probably through attack of NO_2 on **6**.[5] Pure samples of **3** may be obtained by oxidation of acidic solutions of **6** with ceric ion (reaction 3b) or chlorine.[4] Samples of pure **3** in 0.1 M $HClO_4$ solutions gave λ_{max} 688 nm (ϵ 500) and λ_{max} 466 nm (ϵ 537). Complex **4**, whose synthesis has been described elsewhere,[6] gave under the same conditions λ_{max} 703 nm (ϵ 1.35 × 10^3) and λ_{max} 468 nm (ϵ 545). Complex **3** was almost indefinitely stable in 0.1 M $HClO_4$ solution at 25° if protected from light. Samples of **4** were surprisingly unstable under similar conditions, decomposing with apparently first-order kinetics about 10 times faster than **1** under the same conditions. Thermal decomposition of **4** gave α-$Co(tetren)(H_2O)^{3+}$ [7] and Co^{2+} in about a 9:11 ratio.



Stoichiometries for photochemical decompositions of **3** in acidic aqueous solutions were determined by irradiating solutions with near-ultraviolet light (*i.e.*, light of wavelengths longer than 300 nm) until there was no remaining absorption near 700 nm. Irradiated solutions were analyzed by spectrophotometry and by ion-exchange chromatography. It was found that (1) from irradiations of **3** in degassed 0.1 M $HClO_4$ solutions, a quantitative yield (0.98–1.02 mol/mol of **3**) of O_2 based on reaction **4** was obtained, (2) the yield of Co^{2+} based on reaction 4 was quantitative within experimental uncertainty, and (3) the Co^{III} product obtained by ion-exchange chromatography on irradiated solutions was *cis*-$Co(en)_2(NH_3)(H_2O)^{3+}$.[8] Accordingly, we conclude that reaction 4 describes the stoichiometry for photochemical decomposition of **3** under our conditions. The ratio of Co^{2+} to Co^{III} products was unity under a wide variety of irradiation conditions: (1) in 0.005–2.00 M $HClO_4$; (2) in 0.10 M $HClO_4$ containing H_2O_2 or $Na_2S_2O_8$ in concentrations up to 0.1 M; (3) in 0.10 M $HClO_4$ containing 0.5 M NaCl. In the last case formation of $Co(en)_2(NH_3)(Cl)^{2+}$ in addition to $Co(en)_2(NH_3)(H_2O)^{3+}$ was detected. The stoichiometry observed in photochemical decompositions of **3** was thus exactly analogous to that observed with **2**.



$$\text{cis-}Co(en)_2(NH_3)(H_2O)^{3+} + O_2 + Co^{2+} + 2enH_2^{2+} \quad (4)$$

Irradiations of acidic solutions of **3** with 254-nm light gave rise to complicated reactions which eventually led to 2 mol of Co^{2+} for each mole of **3** decomposed.[9]

Quantum yields for the photochemical decomposition of **3** in 0.1 M $HClO_4$ according to reaction 4 were found to be 0.005 ± 0.001 for 405-nm exciting light, 0.040 ± 0.005 for 350-nm exciting light, and 0.065 ± 0.005 for 320-nm exciting light. The quantum yield for decomposition of **3** with 320 nm exciting light was independent of solution acidity in the range $[H^+] = 0.001$–1.00 M (as $HClO_4$), of complex concentration in the range [**3**] = 0.001–0.050 M, and of dose rate (*ca.* 2 × 10^{16}–*ca.* 4 × 10^{16} photons/sec) absorbed by the solution. Spectrophotometric analyses of solutions of **3** in 0.1 M $HClO_4$, which had been irradiated only long enough to produce fractional decomposition (about 20–50%) as measured by loss of absorption near 700 nm, had absorption spectra in the region 290–700 nm consistent with the exclusive presence of a 1:1 mixture of Co^{2+} and $Co(en)_2(NH_3)(H_2O)^{3+}$ and unreacted **3**. The observed products of photochemical decomposition of **3** can thus be attributed to the primary photochemistry of that cation and not to secondary photolyses of initial photochemical products.

Since the kinetic and stoichiometric aspects of photochemical decompositions of **3** are so similar to those reported earlier for **2** it is reasonable to conclude that similar photochemical mechanisms operate in the two systems. It is noteworthy that such a dramatic reduction in quantum yield for photochemical decomposition of the $A_4Co(NH_2)(O_2)CoA_4^{4+}$ chromophore occurs upon replacement of ammonia by the chelating organic amine ethylenediamine. With 320-nm exciting light, for instance, the quantum efficiency observed for reaction 2 was 0.48, while for reaction 4 it was 0.06. Photochemical decomposition of **4** induced by (λ >320 nm) irradiation provided an even more dramatic illustration of the same effect. The quantum yield for reaction 1 upon 320-nm irradiation was found to be 0.30; the quantum yield for decomposition of **4** under the same conditions was less than 0.005. Stoichiometric studies for this reaction were difficult to carry out because of the long irradiation times required and the pronounced affinity of tetraethylenepentamine for cobaltous ion in even strongly acidic solutions. Somewhat erratic results were obtained but the complete photochemical decomposition of **4** appeared to give 1.1 ± 0.1 mol of Co^{2+} and 0.9 ± 0.1 mol of α-$Co(tetren)(H_2O)^{3+}$ for each

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[4] M. B. Stevenson and A. G. Sykes, *J. Chem. Soc. A*, 2293 (1969), reported that in their hands preparation of $(en)_2Co(NH_2)(OOH)Co(en)_2^{4+}$ by Werner's method gives material contaminated with **5**. We find this not to be the case provided pure HNO_3 is used in the acidification step (*cf.* ref 3).

[5] K. Garbett and R. D. Gillard, *J. Chem. Soc. A*, 1725 (1968).

[6] D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem.*, **31**, 2053 (1969).

[7] D. A. House and C. S. Garner, *Inorg. Chem.*, **6**, 272 (1967).

[8] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

[9] This reaction was first studied by G. Bredig, P. Mangold, and T. G. Williams, *Angew. Chem.*, **36**, 456 (1923).

mole of **4** decomposed. This reaction was not studied further.

Other examples of reduced quantum yields for photoreduction of Co^{III} in systems where ammonia has been replaced by chelating organic amines have been reported,[10] but the present example is the only one of which we are aware in which the ligands being substituted are not chemically changed (except for being released from the cobalt coordination sphere and subsequently protonated) during the reaction. It is conceivable that the chelated organic amine offers mechanical hindrance to reorganization of the cobalt coordination sphere necessary to proceed from photoexcited complex to products. On the other hand, organic amines are somewhat better donors than ammonia. This is reflected in the ground state of **3**, in which the O–O bond distance is 1.36 Å,[11] compared to 1.32 Å in **2**, and might result in the excited states of **3** having more electron density on the bridging superoxide than the corresponding excited state of **2** and a consequently lower tendency to complete electron transfer from O_2^- to Co^{III}.

Experimental Section

Sodium perchlorate was prepared following Olin.[12] Mononuclear cobalt(III) ammines were prepared by standard methods. A sample of the perchlorate of **4** was kindly supplied by Professor W. K. Wilmarth. Analyses for Co^{2+} were made by the method of Gould and Taube.[13] Ion-exchange chromatography was done with a Dowex 50W-X8 resin. Divalent fractions were eluted with 1.00 *M* $NaClO_4$ containing 10^{-3} *M* $HClO_4$ and trivalent fractions were eluted with 3 *M* HCl.

Stoichiometric determinations were made using as light source a 450-W Hanovia medium-pressure mercury arc whose output was filtered through a 2-mm thickness of Pyrex to remove light of wavelengths shorter than 300 nm. Solutions were not deaerated before or during photolyses because preliminary comparison experiments showed that this made no difference in the observed results. All irradiations were terminated when the 700-nm absorbance had been reduced to zero.

Quantum yield measurements were made using the same monochromator and approximate light intensities employed in our previous work.[1] All solutions for kinetic experiments were optically dense at the irradiating wavelength. Because of the geometry of our apparatus it was not possible to stir solutions during photolyses for kinetic measurements. All quantum yields were determined using less than 10% conversion to products so as to minimize local bleaching and for these low conversions the observed quantum yields did not depend on the amount of conversion to products. Reaction 2 was used as the actinometric system.[1] Spectrophotometric analyses were made with a Cary 14 spectrometer.

μ-Amido-μ-superoxo-bis[bis(ethylenediamine)cobalt](4+), 3.—A concentrated solution of the nitrate of **6**, prepared following Werner,[2] in 0.1 *M* $HClO_4$ was treated with 100-mg portions of ceric ammonium nitrate until the solution color was deep green. Excess ammonium nitrate was added and the solution was refrigerated for several hours. The green precipitate of the nitrate of **3** was recovered by filtration, washed with ethanol and ether, and air dried. *Anal.* Calcd for $C_8H_{34}N_{13}O_{14}Co_2$: Co, 18.1. Found: Co, 18.1.

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[10] J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, **87**, 3348 (1965).

[11] U. Thewalt and R. E. Marsh, *ibid.*, **89**, 6364 (1967); R. E. Marsh private communication.

[12] A. Olin, *Acta Chem. Scand.*, **11**, 1445 (1957).

[13] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

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CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT,
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Behavior of Silver(I)–Olefin Complexes in Organic Media[1]

BY JOHN SOLODAR* AND JOHN P. PETROVICH

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A series of papers[2] has recently appeared in which the nature of the bonding in silver(I)–olefin complexes is examined by nmr techniques; *i.e.*, conclusions have been drawn concerning the structure of the silver–olefin bond from differences in chemical shifts and coupling constants between free and complexed olefins.

The most severe restriction to the use of this technique is that the ligands may be so labile that one records time-averaged spectra of rapidly equilibrating free and complexed ligands which renders the intended conclusions useless. Nmr detection of ligand lability is well established for many transition metal complexes[3] but is virtually unreported for silver(I)–olefin compounds.[4]

Our nmr investigation of solutions of silver(I)–olefin complexes in organic solvents shows that these systems do involve time-averaged equilibria and suggests that the work in the papers cited above be reconsidered in the light of our results. Especially interesting is the fact that the equilibrium constants are very much solvent dependent and may vary over a wide range.

Experimental Section

Nmr Studies.—All nmr spectra were recorded on a Varian A-60 proton resonance spectrometer at a probe temperature of 33° and at a sweep width of 500 Hz. Cyclohexane[5] (1% by volume) was used as an internal standard except in those cases in which cyclohexane could not be seen under a solvent peak. In these cases, a solvent peak was used as the standard. All chemical shifts were tabulated in hertz relative to the standard.

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* To whom correspondence should be addressed.

[1] Presented in part at the 25th Southwest Regional Meeting of the American Chemical Society, Tulsa, Okla., Dec. 5, 1969.

[2] (a) G. Bressan, R. Broggi, M. P. Lachi, and A. L. Segre, *J. Organometal. Chem.*, **9**, 355 (1967); (b) H. W. Quinn, J. S. McIntyre, and D. J. Peterson, *Can. J. Chem.*, **43**, 2896 (1965); (c) J. C. Schug and R. J. Martin, *J. Phys. Chem.*, **66**, 1554 (1962); (d) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960); (e) H. W. Quinn and R. L. Van Gilder, *Can. J. Chem.*, **47**, 4691 (1969).

[3] For example, M. Orchin and P. J. Schmidt, *Inorg. Chim. Acta*, **2**, 123 (1968); R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964).

[4] In ref 2b Quinn noted a change of $\Delta\delta$ with temperature for the *trans*-2-butene–$AgBF_4$ system only and correctly concluded that a rapid equilibrium is involved in this particular case. This is the only mention we could find of any prior hint of the extent of the equilibria involved.

[5] We have found that an external standard is unsatisfactory due to the fact that the changes in bulk magnetic susceptibility which occur with silver salt addition are normally quite significant with respect to the size of $\Delta\delta$. Internal TMS was also unsatisfactory as it was attacked by silver ion in some solvents.