

# Long-Range Electron Transfer in Photoexcited Cobalt(III)-Copper(I) Binuclear Ions

Kenneth A. Norton, Jr., and James K. Hurst\*

Contribution from the Department of Chemistry and Biochemical Sciences, Oregon Graduate Center, Beaverton, Oregon 97006. Received December 21, 1981

**Abstract:** We report the photoredox behavior of cobalt(III)-copper(I) binuclear ions containing aminoalkene, alkenylpyridine, and alkenoic acid bridging ligands, for which  $\text{Cu(d)} \rightarrow \text{L}(\pi^*)$  excitation gives rise to intramolecular electron transfer between the metal ions. For the ligand series  $\text{NH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$  and  $\text{NC}_3\text{H}_4(\text{CH}_2)_n\text{CH}=\text{CH}_2$ , quantum yields are sensitive to the length of the bridging chain, decreasing regularly with increasing numbers ( $n$ ) of methylene units. The reactivities of binuclear ions with polyisoprenylamine bridging ligands exhibit exceptionally high efficiencies ( $\Phi \approx 0.9$ ) and no apparent dependence upon chain length. Cobalt(III) photoreduction also occurs in ions that are sterically constrained by rigid bicyclocotene rings to prevent close approach of the redox centers. Lower limits for electron transfer in selected ions were established by pulse laser spectroscopy to be  $k \geq 10^7\text{--}10^8 \text{ s}^{-1}$ . We infer from the data that the initially excited singlet state is photoreactive and that electron transfer is facile at intermetallic separation distances of up to 7–8 Å.

Ion association is generally thought to precede electron transfer between complex ions in solution.<sup>1</sup> Close approach of reactant ions is definitely established in inner-sphere mechanisms where direct evidence of ligand bridging exists, and the bulk of data from extensive investigations of outer-sphere reactions is consistent with kinetic models in which charge transfer occurs by way of reactant ion pairs. Relatively efficient electron transfer also occurs in inner-sphere reactions over a distance comprising several molecular bonds when bridging ligands contain  $\pi$ -delocalized orbitals. In all of these reactions, precursor complex formation is thought to be essential to obtaining the strong overlap of donor and acceptor orbitals necessary for facile charge transfer.

In sharp contrast to these studies, a considerable body of experimental evidence has accumulated<sup>2–16</sup> to indicate that electron transfer between metal-centered redox sites in biological systems often occurs over relatively large distances ( $\geq 10$  Å) without any apparent indirect coupling that might be provided by  $\pi$ -delocalized structures within the protein matrix.<sup>17</sup> This capacity for long-

range transfer in biomolecules has been rationalized to be a consequence of relatively small nuclear reorganizational energies attending charge redistribution. Accordingly, nuclear activation barriers are low, so that rapid electron-transfer rates can be attained despite relatively weak coupling of donor and acceptor sites. Some structural evidence consistent with these suggestions has been presented,<sup>4,18</sup> but optical spectroscopic measurements indicate that the Franck-Condon barriers for biological redox molecules may not be unusually small. Thus, energies for intervalence transfer excitation appear to be comparable in biomolecules containing well-separated redox sites<sup>5,8,12</sup> and mixed-valent ruthenium bridged binuclear ions<sup>19,20</sup> ( $\sim 1$  eV) and approach the values for mixed-valent solids<sup>21</sup> (0.3–2.0 eV) and for inorganic aquo ions<sup>21</sup> (1.5–2.3 eV), the latter estimated from activation energies for thermal electron exchange. It may be, therefore, that the capacity for charge transfer over relatively large distances is underestimated in simple inorganic ions, especially in instances where the electronic charge is delocalized onto ligand atoms, e.g., as occurs in  $\pi$ -back-bonding interactions and metal-to-ligand charge-transfer photoexcitation.

Intramolecular electron transfer to cobalt(III) from ruthenium(II)<sup>19,22–24</sup> and nitrophenyl radicals<sup>25</sup> bridged by ligands containing coordinatively saturated chain segments has been observed. Similarly, we have found<sup>26</sup> quantum yields for photoinitiated electron transfer in cobalt(III)-copper(I) binuclear ions bridged by aminoalkene and alkenoic acid ligands to be insensitive to chain length, at least for ligands containing up to four carbon atoms in the bridge. Although the results suggest the possibility of electron tunneling through these barriers, the great flexibility that introduction of alkyl groups imparts to the chains renders attempts at gauging electron-transfer distances extremely difficult. The data have generally been interpreted in terms of chain folding to allow close approach of the redox centers leading either to direct overlap of donor and acceptor orbitals or to pseudo- $\pi$ -conjugative interaction of ligating functional groups; in instances where electron-transfer rates increase with increasing chain length,<sup>25</sup> it

(1) Recent reviews include: Haim, A. *Acc. Chem. Res.* **1975**, *8*, 264–272. Sutin, N. "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; Vol. 2, Chapter 19, pp 611–653. Linck, R. G. *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One* **1971**, *9*, 303–352. Taube, H.; Gould, E. S. *Acc. Chem. Res.* **1969**, *2*, 321–329.

(2) Devault, D.; Chance, B. *Biophys. J.* **1966**, *6*, 825–847.

(3) Gupta, R. K.; Yonetani, T. *Biochim. Biophys. Acta* **1973**, *292*, 502–508.

(4) Carter, C. W., Jr.; Kraut, J.; Freer, S. T.; Alden, R. A. *J. Biol. Chem.* **1974**, *249*, 6339–6346. Carter, C. W., Jr.; Kraut, J.; Freer, S. T.; Xuong, Ng. H.; Alden, R. A.; Bartsch, R. G. *Ibid.* **1974**, *249*, 4212–4225.

(5) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640–3644.

(6) Leonard, J. J.; Yonetani, T. *Biochemistry* **1974**, *13*, 1465–1468.

(7) Mizrahi, I. A.; Wood, F. E.; Cusanovich, M. A. *Biochemistry* **1976**, *15*, 343–348.

(8) Potasek, M. J.; Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3817–3820.

(9) Vanderkooi, J. M.; Landesberg, R.; Hayden, G. W.; Owen, C. S. *Eur. J. Biochem.* **1977**, *81*, 339–347.

(10) Dockter, M. E.; Steinemann, A.; Schatz, G. *J. Biol. Chem.* **1978**, *253*, 311–317.

(11) Peters, K.; Avouris, Ph.; Rentzepis, P. M. *Biophys. J.* **1978**, *23*, 207–217.

(12) Potasek, M. J. *Science (Washington, D.C.)* **1978**, *201*, 151–153.

(13) Tiede, D. M.; Leigh, J. S.; Dutton, P. L. *Biochim. Biophys. Acta* **1978**, *503*, 524–544.

(14) Ballard, S. G.; Mauzerall, D. "Tunneling in Biological Systems"; Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds. Academic Press: New York, 1979; pp 581–587.

(15) Babcock, L. M.; Bradić, Z.; Harrington, P. C.; Wilkins, R. G.; Yoneda, G. S. *J. Am. Chem. Soc.* **1980**, *102*, 2849–2850.

(16) Mauk, A. G.; Scott, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 4360–4363.

(17) Hurst, J. K. *Biochemistry* **1979**, *18*, 1504–1510 and references therein.

(18) Freeman, H. C. "Coordination Chemistry"; Laurent, J. P., Ed.; Pergamon Press: Oxford, 1981; Vol. 21, pp 29–51.

(19) Fischer, H.; Tom, G. M.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 5512–5517.

(20) Curtis, J. C.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 6284–6286 and references therein.

(21) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391–444.

(22) Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 8198–8200.

(23) Rieder, K.; Taube, H. *J. Am. Chem. Soc.* **1977**, *99*, 7891–7894.

(24) Zawacky, S. K. S.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 3379–3387.

(25) Whitburn, K. D.; Hoffman, M. Z.; Simic, M. G.; Brezniak, N. V. *Inorg. Chem.* **1980**, *19*, 3180–3181.

(26) Farr, J. K.; Hulett, L. G.; Lane, R. H.; Hurst, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 2654–2660.

Table I. Visible Absorption Spectra of A<sub>3</sub>Co<sup>III</sup>L Ions

L <sup>a</sup>	λ (ε <sub>λ</sub> )	L <sup>b</sup>	λ (ε <sub>λ</sub> )
4-vinylpyridine	344 (77), 477 (68)	1-amino-4-pentene	340 (64), 477 (63)
4-(3-butenyl)pyridine	340 (69), 473 (70)	1-amino-5-hexene	340 (64), 477 (65)
4-(4-pentenyl)pyridine	340 (71), 472 (64)	1-amino-7-octene	340 (64), 477 (66)
4-(5-hexenyl)pyridine	340 (68), 473 (73)	1-amino-9-decene	340 (64), 477 (66)
4-(6-heptenyl)pyridine	340 (71), 473 (69)	geranylamine <sup>44</sup>	478 (65) <sup>c</sup>
4-(8-nonenyl)pyridine	473 (67)	farnesylamine <sup>44</sup>	478 (65) <sup>c</sup>
4-(10-undecenyl)pyridine	474 (70)		
geranylpicoline <sup>44</sup>	472 (71) <sup>c</sup>	<i>endo</i> -carboxylate <sup>44</sup>	351 (76), 503 (86)
farnesylpicoline <sup>44</sup>	470 (73) <sup>c</sup>	<i>exo</i> -carboxylate <sup>44</sup>	351 (77), 503 (78)

<sup>a</sup> In 0.1 M HTFA unless otherwise noted. <sup>b</sup> In 0.1 M HClO<sub>4</sub> unless otherwise noted. <sup>c</sup> In 0.1 M HClO<sub>4</sub>, 75% ethanol.

seems particularly clear that reaction occurs from folded conformational states.

Good evidence exists for long-range electron transfer in reactions involving organic radical ions and redox dyes. Photoinitiated electron transfer between surfactant derivatives of Ru(bpy)<sub>3</sub><sup>2+</sup> and viologen acceptor ions in juxtaposed monolayer films is effective up to only ~10 Å average distance of separation but up to 75 Å when photoexcited cyanine dyes are used as donors;<sup>27</sup> in the latter case, charge transfer has also been demonstrated to occur across fatty acid membrane monolayers of thickness up to 30 Å.<sup>28</sup> Electron transfer between aromatic molecules immobilized in glass matrices is reported to occur over comparable distances.<sup>29</sup> Calculated distances in each of these studies are based upon the random distribution of molecules; experimental data are quantitatively accounted for by simple quantum tunneling models. Rapid intramolecular electron exchange was measured by ESR analysis between the α-naphthyl group and its radical anion when linked by a rigid cyclohexane-based bridge;<sup>30</sup> in this molecule, the distance of closest approach of aromatic groups is constrained to be greater than ~4 Å.<sup>31</sup>

A report<sup>33</sup> of photosensitized oxidation of viologen dyes by EDTA across lecithin bilayers that contain bound surfactant derivatives of Ru(bpy)<sub>3</sub><sup>2+</sup> has been interpreted in terms of a mechanism in which transmembrane charge transfer occurs by electron exchange between ruthenium(II) and ruthenium(III) at the opposite interfaces; electron transfer from photoexcited Ru(bpy)<sub>3</sub><sup>2+</sup> to methylviologen across dicetyl phosphate vesicle bilayers has also been claimed.<sup>34,35</sup> The mechanistic proposals that electron tunneling from Ru(bpy)<sub>3</sub><sup>2+</sup> occurs over a distance comprising the bilayer widths (40–50 Å) are clearly at odds with the other results discussed above and point to the need for clarification of factors that admit long-range site-to-site charge transfer.

## Experimental Procedures

**Reagents.** Alkylpyridine compounds were synthesized by reaction of alkyl bromides with 4-methylpyridine,<sup>36</sup> when commercially unavailable,

(27) Seefeld, K.-P.; Möbius, D.; Kuhn, H. *Helv. Chim. Acta* **1977**, *60*, 2608–2632.

(28) Kuhn, H. *Pure Appl. Chem.* **1979**, *51*, 341–352.

(29) Miller, J. R. *Science (Washington, D.C.)* **1975**, *189*, 221–222; *J. Chem. Phys.* **1972**, *56*, 5173–5183.

(30) Shimada, K.; Szwarc, M. *Chem. Phys. Lett.* **1974**, *28*, 540–545.

(31) The authors have suggested a minimum separation distance of ~9 Å,<sup>30,32</sup> although when examined with Fisher–Hirshfelder–Taylor space-filling structural models, it is apparent that the aromatic rings can be placed in mutually parallel alignment at a distance comprising about three carbon-carbon single bonds.

(32) Shimada, K.; Szwarc, M. *Chem. Phys. Lett.* **1975**, *34*, 503–507.

(33) Ford, W. E.; Otvos, J. W.; Calvin, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 3590–3593.

(34) Tunuli, M. S.; Fendler, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 2507–2513.

(35) More recent evidence suggests that the redox mechanism involves photoinduced transmembrane diffusion of methyl viologen dication followed by its reaction with photosensitizer on the same vesicular surface (Lee, L. Y.-C.; Hurst, J. K.; Fendler, J. H. *J. Am. Chem. Soc.*, in press). We have observed kinetic behavior consistent with net transmembrane electron transfer in reactions of lecithin-bound (4-alkylpyridine)pentaammineruthenium<sup>III</sup> ions with several reducing agents, however (Lee, L. Y.-C.; Hurst, J. K., unpublished experiments).

(36) Brown, H. C.; Murphey, W. A. *J. Am. Chem. Soc.* **1951**, *73*, 3308–3312.

the alkyl bromides were synthesized from the corresponding alcohols.<sup>37</sup> Aminoalkenes were prepared by reaction of alkyl bromides with potassium phthalimide, followed by hydrolysis of the isolated *N*-alkylphthalimides.<sup>38</sup> Isomeric 5-methylbicyclo[2.2.2]oct-2-ene-5-carboxylic acids were prepared by Diels–Alder condensation of 1,3-cyclohexadiene with methacrylic acid;<sup>39</sup> the geometrical isomers were separated by converting the *endo*-carboxylic acid to its iodo lactone.<sup>39,40</sup> Attempts to convert the carboxylic acids to amines<sup>41,42</sup> were unsuccessful. The organic compounds were characterized by <sup>1</sup>H NMR analysis in CDCl<sub>3</sub> or CCl<sub>4</sub>. A detailed procedural description of their syntheses, isolation, and proton magnetic resonance spectra has been published.<sup>43</sup>

Pentaamminecobalt(III) complexes of 4-vinylpyridine and the various 4-alkylpyridine and aminoalkene compounds were synthesized by heating (dimethyl sulfoxide)pentaamminecobalt(III) ion (A<sub>3</sub>Co(Me<sub>2</sub>SO))<sup>44</sup> with excess ligand in dry dimethyl sulfoxide (Me<sub>2</sub>SO) or dimethylformamide (DMF).<sup>43</sup> Molecular sieve (4 Å) was added to exclude moisture, and the solution was stirred continuously under nitrogen to minimize oxidation of the organic ligand. Bicyclo[2.2.2]oct-2-ene-5-carboxylate complexes were similarly prepared by reaction of A<sub>3</sub>CoDMF ions with excess lithium salt of the isomerically pure acids in refluxing methanol. The coordination complexes were isolated by partitioning product solutions between water and diethyl ether, then precipitating from the aqueous phase with added salt, generally sodium perchlorate. The A<sub>3</sub>Co-4-vinylpyridine ion was initially isolated as the iodide salt and converted to the perchlorate by precipitation of iodide with a stoichiometric equivalent of silver perchlorate. Complexes were characterized by their electronic absorption and <sup>1</sup>H NMR spectra in Me<sub>2</sub>SO-*d*<sub>6</sub> or D<sub>2</sub>O. These measurements, taken together, provide good indication of complex purity.<sup>45</sup> General features of the <sup>1</sup>H NMR spectra are the appearance of broad new bands in the δ 3.0–4.0 region ascribable to *cis*- and *trans*-ammines and relatively large downfield shifts in the organic spectral peaks from protons adjacent to the cobalt(III) coordination sites, with chemical shifts and spin–spin splitting patterns at other positions remaining largely unaffected. Pyridine ring proton resonances shift δ 0.1–0.6 downfield, peaks associated with free base amine and α-methylene protons shift underneath the broad ammine bands, and 5-methyl and 2-olefin peaks for bicyclooctenecarboxylic acids shift downfield δ 0.06–0.1 and 0.24–0.28, respectively, upon binding the A<sub>3</sub>Co(III) moiety. Free and Co(III)-complexed organic compounds are thereby clearly distinguished. Because the A<sub>3</sub>CoMe<sub>2</sub>SO and A<sub>3</sub>CoDMF ions also give strong characteristic <sup>1</sup>H NMR spectra, the presence of even minute amounts (~5%) of unconverted reactant complexes is also detectable. Comparison of electronic absorption spectra in acidic and basic solutions gives a sensitive test for the presence of A<sub>3</sub>CoOH<sub>2</sub> ion impurities.<sup>45</sup> Complexes were recrystallized repeatedly, generally from dilute aqueous perchloric

(37) Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964–965.

(38) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509–2520.

(39) Boehme, W. S.; Schipper, E.; Scharpf, W. G.; Nichols, J. *J. Am. Chem. Soc.* **1958**, *80*, 5488–5495.

(40) VerNooy, C. D.; Rondstedt, J. R. *J. Am. Chem. Soc.* **1955**, *77*, 3583–3586.

(41) Krow, G.; Damodaran, K. M.; Michener, E.; Miller, S. I.; Dalton, D. R. *Synth. Commun.* **1976**, *6*, 261–267.

(42) Kaiser, C.; Weinstock, J. *Org. Synth.* **1971**, *51*, 48–50.

(43) Norton, K. A., Jr. Ph.D. Dissertation, Oregon Graduate Center, 1982.

(44) Abbreviations used: A<sub>3</sub>Co, pentaamminecobalt(III) moiety; HTFA, trifluoroacetic acid; geranylamine, 1-amino-3,7-dimethyl-2(*E*),6-octadiene; geranylpicoline, 4-(4,8-dimethyl-3(*E*),7-nonadienyl)pyridine; farnesylamine, 1-amino-3,7,11-trimethyl-2(*E*),6(*E*),10-dodecatriene; farnesylpicoline, 4-(4,8,12-trimethyl-3(*E*),7(*E*),11-tridecatrienyl)pyridine; *endo*-carboxylate, 5-*exo*-methylbicyclo[2.2.2]oct-2-ene-5-*endo*-carboxylate; *exo*-carboxylate, 5-*endo*-methylbicyclo[2.2.2]oct-2-ene-5-*exo*-carboxylate.

(45) Hurst, J. K.; Lane, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 1703–1709.

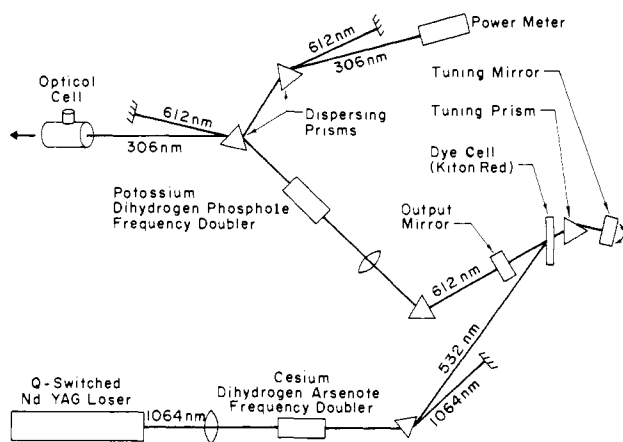


Figure 1. Near-ultraviolet laser energy source.

acid, until no trace of impurities was detectable; for the ligands with long alkyl chains, recrystallization was made from 50% aqueous ethanol. The isomeric purity of the (carboxylato)pentaamminecobalt(III) ions was confirmed by their  $^1\text{H}$  NMR spectra. The 5-methyl peak appears at  $\delta$  1.34 in the  $\text{A}_5\text{Co-5-endo-methylbicyclo[2.2.2]oct-2-ene-5-exo-carboxylate}$  ion and at  $\delta$  1.61 in the  $\text{A}_5\text{Co-5-exo-methylbicyclo[2.2.2]oct-2-ene-5-endo-carboxylate}$  ion in  $\text{D}_2\text{O}$  relative to external  $\text{Me}_4\text{Si}$ ; only single methyl peaks were found in the spectra of isolated complex ions, indicating isomeric scrambling had not occurred during their synthesis. Electronic absorption spectra are recorded in Table I; values are consistent with structures assigned from the proton magnetic resonance spectra. Electronic spectra were taken on Cary Model 15 or 16 spectrophotometers;  $^1\text{H}$  NMR spectra were taken on Varian HA-100 or JEOL FX 90Q FT spectrometers.

Solvents employed were reagent grade or better and used as received. Commercially available ligands were distilled immediately before use. Aqueous solutions were prepared with reverse osmosis deionized water. Cupric perchlorate solutions were made by dissolving cupric oxide in perchloric acid; Cu(II) ion concentrations were determined by spectrophotometric analysis as the  $\text{Cu}(\text{SCN})_4^{2-}$  ions.<sup>46</sup> Chromic perchlorate solutions were prepared by reduction of primary standard potassium dichromate with hydrogen peroxide after addition of perchloric acid to precipitate potassium ion; Cr(III) ion concentrations were determined by oxidation to chromate ion with alkaline peroxide.<sup>47</sup> Chromous solutions were obtained by Cr(III) ion reduction with zinc-mercury amalgam in an argon atmosphere. Cuprous ion was formed by anaerobic reduction of cupric ion with chromous ion.<sup>48</sup>

**Photochemical Methods.** Methods for continuous sample illumination, quantum yield calculations, and product determination followed, with slight modification, the general procedures previously outlined.<sup>26</sup> Reactants were anaerobically introduced by syringe through septa into 2-cm pathlength cylindrical optical cells; solution concentrations were adjusted to absorb at least 90% of the incident light. Samples were illuminated with either of two light sources: (1) a mercury-xenon arc lamp and monochromator assembly<sup>26</sup> or (2) Q-switched Nd:YAG pulsed laser that was frequency quadrupled and dye shifted (Kriton Red) to give excitation at 306 nm<sup>49</sup> (Figure 1). Light intensities were determined either by ferrioxalate actinometry<sup>50</sup> or with a bolometer<sup>51</sup> whose signal output was monitored over the course of the experiment and the intensity averaged. Light intensities from the mercury-xenon lamp were adjusted with variable-width slits over the range of values  $I_0 = (0.5-2.5) \times 10^{-9}$  einstein  $\text{s}^{-1}$ ; intensities of the laser line were  $0.5-1.9 \times 10^{-8}$  einstein  $\text{s}^{-1}$ . The extent of photoredox decomposition of illuminated samples were determined from losses in absorbancy in the Co(III) visible bands and/or by measurement of Co(II) produced as the  $\text{Co}(\text{SCN})_4^{2-}$  ion.<sup>46</sup>

Quantum yields were generally calculated from

$$\Phi_{\text{Cu} \rightarrow \text{L}} = \text{mol of Co(III) reacted} / (I_a \bar{t}) \quad (1)$$

where  $I_a$  is the average number of einsteins absorbed by the solution in unit time,  $t$  is the illumination time, and  $\bar{f}$  is the average fraction of light

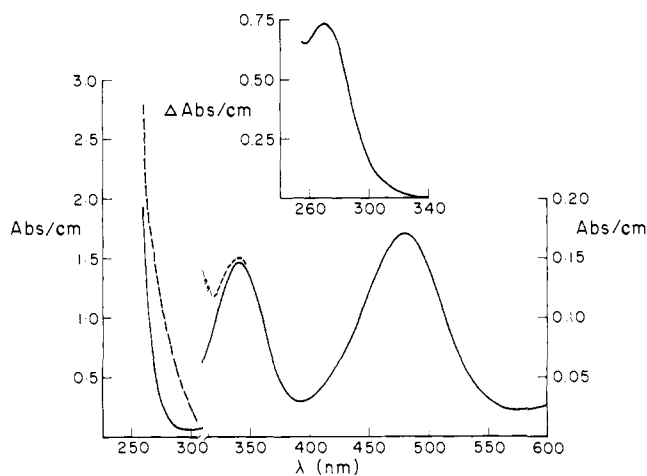


Figure 2. Electronic absorption spectra of  $\text{A}_5\text{Co-1-amino-5-hexene}$  ions. Conditions: dashed line, 3.1 mM  $\text{A}_5\text{CoL}$ , 0.51 mM Cu(I), 15 mM Cu(II), 0.1 M  $\text{HClO}_4$ , 23 °C; solid line, after oxygenation. The absorption difference is plotted in the inset.

absorbed by the  $\text{Cu}(d) \rightarrow \text{L}(\pi^*)$  transition.<sup>26</sup> The electronic absorption spectrum of  $\text{A}_5\text{Co-1-amino-5-hexene}$  and its binuclear ion formed by Cu(I)-olefin coordination is shown in Figure 2. Because ultraviolet absorption attributable to other charge-transfer excitation, i.e., ammine-to-cobalt LMCT, does not occur above 280 nm, the copper-to-olefin MLCT band is well resolved. For cobalt(III) complexes that contain coordinated carboxylate or pyridine and amine groups attached to long alkyl chains, ligand-to-cobalt LMCT absorption strongly overlaps the copper-to-olefin MLCT band. The choice of illumination at 306 nm in most of the experiments was made on the basis that absorption into the MLCT band is optimized; i.e.,  $I_a \bar{f}$  is maximized. In two instances, the reactions of  $\text{A}_5\text{Co-carboxylate-Cu(I)}$  and  $\text{A}_5\text{Co-isoprenylamine-Cu(I)}$  binuclear ions, quantum yield measurements are further complicated by photoredox decomposition producing Co(II) that results from direct excitation of the LMCT bands. Similar photoredox decomposition of other  $\text{A}_5\text{Co-carboxylates}$  has been reported.<sup>52,53</sup> Calculations of apparent quantum yields ( $\Phi_{\text{app}}$ ) from eq 1 were corrected for photolysis of  $\text{A}_5\text{CoL}$  by means of<sup>26</sup>

$$\Phi_{\text{Cu} \rightarrow \text{L}} = \Phi_{\text{app}} - \Phi_{\text{Co} \rightarrow \text{L}}(1 - \bar{f}) / \bar{f} \quad (2)$$

where  $\Phi_{\text{Co} \rightarrow \text{L}}$ , the quantum yield for LMCT decomposition, was determined by illumination of solutions of binuclear ions that had been oxygenated and then purged of  $\text{O}_2$  with argon. Except for oxidation of Cu(I) to Cu(II), the solutions were identical with those containing the binuclear ions. For the other Co(III) ions studied, LMCT excitation gave no evidence of photoredox decomposition over the illumination time of the experiments.

Large quantities of photolabilized bridging ligands were obtained for analysis by illumination of 250-mL solutions containing binuclear ions at millimolar concentration levels; the photolysis cell has been previously described.<sup>26</sup> Reactions were allowed to proceed until about 25% loss of binuclear ions had occurred; for minimization of ligand aquation during the lengthy illumination times required (10–30 h), the cell was cooled to 7 °C by partial immersion in a thermostated water bath. Ligands were recovered by neutralizing reaction solutions and extracting with diethyl ether, either in batchwise fashion or by continuous liquid-liquid extraction. Isolated ligands were taken up in water or ethanol and identified by gas chromatographic analysis on 4% Carbowax 20 M or 0.8% KOH on Carbowax B (Supelco, Inc.). Chromatograms were taken on a Varian Model 1200 Aerograph in the isothermal mode equipped with either a Spectra Physics SP4100 computing integrator or Linear chart recorder.

Flash kinetic studies were made in the laboratory of Dr. Michael Grätzel (EPFL, Lausanne) with a frequency-quadrupled pulse (266 nm, 15-ns width) from a JK 2000 Nd:YAG laser. Optical detection was essentially as previously described;<sup>54</sup> transient curves were recorded with a Tektronix WP-2221 data acquisition system equipped with R-7912 transient digitizers.

(46) Kitson, R. E. *Anal. Chem.* **1950**, *22*, 664–667.

(47) Baltisberger, R. J.; King, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 796–801.

(48) Shaw, K.; Espenson, J. H. *Inorg. Chem.* **1968**, *7*, 1619–1622.

(49) Massey, G. A.; Johnson, J. C. *J. Quant. Electron.* **1976**, *QE-12*, 721–727.

(50) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518–536.

(51) Johnson, J. C.; Massey, G. A. *Appl. Opt.* **1978**, *17*, 2268–2269.

(52) Kantrowitz, E. R.; Endicott, J. F.; Hoffman, M. Z. *J. Am. Chem. Soc.* **1970**, *92*, 1776–1777.

(53) Balzani, V.; Carassiti, V. "Photochemistry of Coordination Compounds"; Academic Press: New York, 1970.

(54) McNeil, R.; Richards, J. T.; Thomas, J. K. *J. Phys. Chem.* **1970**, *74*, 2290–2294.

Table II. Quantum Yields for Photoinitiated Electron Transfer in A<sub>5</sub>CoL-Cu(I) Binuclear Ions<sup>a</sup>

ligand (L)	irradiation wavelength, nm	$\Phi_{\text{Cu} \rightarrow \text{L}}^b$
A. Aminoalkenes <sup>c</sup>		
NH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	300	0.65 ± 0.06 (4) <sup>d</sup>
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	290	0.57 ± 0.09 (8) <sup>d</sup>
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	306	0.34 ± 0.03 (7)
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CH <sub>2</sub>	306	0.24 ± 0.04 (8)
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH=CH <sub>2</sub>	306	0.03 ± 0.01 (8)
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>8</sub> CH=CH <sub>2</sub>	306	<0.005
NH <sub>2</sub> (CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> ) <sub>2</sub> H	306	0.80 ± 0.10 (10)
		0.67 ± 0.04 (6)
		(25% ethanol)
		0.50 ± 0.02 (3)
		(83% ethanol)
NH <sub>2</sub> (CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> ) <sub>3</sub> H	306	0.91 ± 0.06 (5)
		0.51 ± 0.05 (4)
		(50% ethanol)
		0.33 ± 0.05 (3)
		(90% ethanol)
B. 4-Alkylpyridines <sup>e</sup>		
NC <sub>5</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	306	0.15 ± 0.04 (8)
NC <sub>5</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	306	0.10 ± 0.04 (8)
NC <sub>5</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CH <sub>2</sub>	306	0.05 ± 0.07 (6)
NC <sub>4</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>5</sub> CH=CH <sub>2</sub>	306	<0.005 (6)
NC <sub>5</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>7</sub> CH=CH <sub>2</sub>	306	<0.005 (6)
NC <sub>5</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>9</sub> CH=CH <sub>2</sub>	306	<0.005 (6)
NC <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> (CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> ) <sub>2</sub> H	306	<0.005 (6)
NC <sub>5</sub> H <sub>4</sub> CH <sub>2</sub> (CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> ) <sub>3</sub> H	306	<0.005 (6)
C. Carboxylates <sup>c</sup>		
<i>exo</i> -carboxylate <sup>44</sup>	290	0.62 ± 0.006 (5)
<i>endo</i> -carboxylate <sup>44</sup>	290	1.0 ± 0.15 (4)

<sup>a</sup> In 0.1 M acid (HClO<sub>4</sub> or HTFA), 0.015 M Cu(II), at 23 °C, with [Cr(III)] = [Cu(I)]; other conditions given in text. <sup>b</sup> Error limits are average deviations from mean value; number of individual runs given in parentheses. <sup>c</sup> HClO<sub>4</sub>. <sup>d</sup> Reference 26. <sup>e</sup> HTFA.

## Results

**Binuclear Ion Formation.** Copper(I) coordinates strongly to olefin bonds,<sup>55</sup> giving rise to broad Cu(d) → olefin(π\*) bands in the near-ultraviolet region.<sup>17,45,56</sup> When the olefin is not conjugated to electron-withdrawing substituent groups, the peak maximum for the lowest energy band is found at 260–270 nm.<sup>17,45</sup> With the single exception of the A<sub>5</sub>Co-4-vinylpyridine ions, Cu(I) addition to solutions of the cobalt(III) complex ions used in this study gave these characteristic spectral features (Figure 2); consistent with expectations,<sup>17,56</sup> the first band maximum for A<sub>5</sub>Co-4-vinylpyridine-Cu(I)<sup>44</sup> appears at 340 nm. Association constants for copper(I) binding to simple olefins are generally large<sup>55</sup> ( $K \approx 10^4 \text{ M}^{-1}$  in aqueous solution) are not appreciably altered by metal ion coordination at other nucleophilic sites on the ligand.<sup>17,56</sup> For most A<sub>5</sub>CoL ions used in this study, binuclear ion formation under the experimental conditions is therefore nearly (>90%) complete. Copper(I) π bonding is sensitive to steric effects arising from organic substituent groups adjacent to the olefin.<sup>55</sup> Weaker binding to the [2.2.2]bicyclooctenecarboxylates might therefore be anticipated as a consequence of steric repulsion from the bridging methylene groups or substituents located at the 5-ring position. Formation constants for the A<sub>5</sub>Co-*exo*-carboxylate-Cu(I) and A<sub>5</sub>Co-*endo*-carboxylate-Cu(I) binuclear ions were determined<sup>17,45</sup> from the magnitudes of the copper-olefin MLCT bands [ $\lambda_{\text{max}}$  (nm) ( $\epsilon_{\lambda}$  (mM<sup>-1</sup> cm<sup>-1</sup>)) = 270 (1.5), 270 (1.3), respectively] to be  $K = (3-4) \times 10^3 \text{ M}^{-1}$  at 23 °C in 0.1 M HClO<sub>4</sub>. The magnitudes of these numbers are consistent with results from our studies on other Cu(I)-olefin complexes;<sup>17,45</sup> for example,  $K$

Table III. Ligand Recovery from A<sub>5</sub>CoL-Cu(I) Ion Photoinitiated Reactions<sup>a</sup>

ligand (L)	A <sub>5</sub> CoL reacted, mmol	ligand recovered, mmol	L/A <sub>5</sub> CoL
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	0.16	0.15	0.94
NH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CH <sub>2</sub>	0.21	0.19	0.90
NH <sub>2</sub> (CH <sub>2</sub> CH=C(CH <sub>3</sub> )CH <sub>2</sub> ) <sub>2</sub> H	0.24, 0.19	0.21, 0.17	0.88, 0.90
NC <sub>5</sub> H <sub>4</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	0.18	0.17	0.94

<sup>a</sup> Irradiation wavelength, 306 nm; other experimental conditions given in the text.

=  $3.0 \times 10^3 \text{ M}^{-1}$  for the A<sub>5</sub>Co-4-vinylpyridine-Cu(I) ion under comparable conditions.<sup>56</sup> Under the experimental conditions for illumination, Cu(I) coordination to the A<sub>5</sub>Co-carboxylates is about 70% complete. We have previously shown by optical and Raman spectroscopic measurements<sup>17</sup> that Cu(I) binds only to a single olefin group of geranyl and farnesyl compounds, even when the metal ion is in considerable excess. Cobalt coordination complexes containing ligands with the di- and triisoprenyl substituents therefore also likely bind only a single Cu(I), despite the presence of several potential coordination sites on the bridging ligands.

**Quantum Yields for Photoinitiated Electron Transfer.** Illumination of the binuclear ions with near-ultraviolet light causes net one-electron reduction of cobalt (III). Quantum yields vary with the nature of the bridging ligands; data are summarized in Table II, where the values listed are calculated from eq 1 or, where ligand-to-cobalt LMCT excitation causes detectable photoredox decomposition, from eq 2. Quantum yields for redox decomposition, measured in the absence of Cu(I), are as follows: for A<sub>5</sub>Co-geranylamine and A<sub>5</sub>Co-farnesylamine,  $\Phi_{\text{Co} \rightarrow \text{L}} = 0.10$ ; for A<sub>5</sub>Co-*exo*-carboxylate,  $\Phi_{\text{Co} \rightarrow \text{L}} = 0.14 \pm 0.03$ ; for A<sub>5</sub>Co-*endo*-carboxylate,  $\Phi_{\text{Co} \rightarrow \text{L}} = 0.17 \pm 0.02$ . Because the carboxylate-to-cobalt LMCT band strongly overlaps the copper-to-olefin MLCT band, correction for LMCT photoredox decomposition was especially large in the carboxylate-bridged binuclear ions; about 60–65% of the incident light was absorbed into the LMCT band at 290 nm, so that 30–45% of the total reaction was accountable by cobalt(III) photodecomposition.

Quantum yields were found to be independent of reactant ion concentrations, generally over the ranges [A<sub>5</sub>CoL] ≈ 0.5–5.0 mM, [Cu(I)] ≈ 0.3–3.0 mM, with [A<sub>5</sub>CoL]/[Cu(I)] ≈ 1–10. Poor solubilities in aqueous solution limited the concentrations for ions with long alkyl substituents to a slightly narrower range, and because the near-ultraviolet spectrum of the A<sub>5</sub>Co carboxylate-Cu(I) ions is dominated by LMCT absorption, the data for these ions were taken at a single concentration ([A<sub>5</sub>Co-carboxylate] = 0.6 mM, [Cu(I)] = 1.0 mM), which is optimal for absorption into the MLCT band.<sup>57</sup>

Illumination of Cu(I) π complexes of the organic ligands in the absence of bound A<sub>5</sub>Co, i.e., simple Cu(I) mononuclear ions, gave no evidence of net photoreaction. Similarly, as previously found for related reactants,<sup>17,45</sup> the A<sub>5</sub>CoL complex ions were not reduced by Cu(I) in the absence of light, indicating that the binuclear ions are stable to thermal electron transfer.

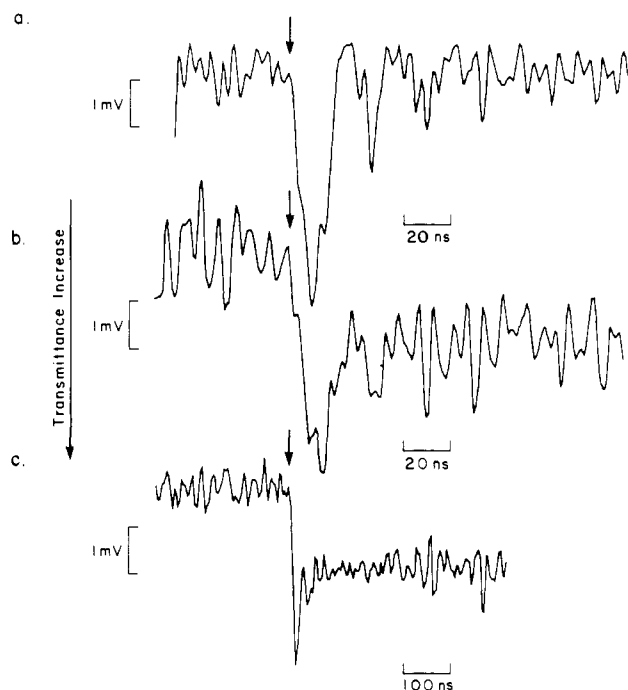
The A<sub>5</sub>Co-4-vinylpyridine-Cu(I) ion gave highly erratic photoredox behavior, with quantum yields varying from  $\Phi_{\text{Cu} \rightarrow \text{L}} = 1$  to 5; solutions turned opaque upon continued irradiation, suggesting polymerization of the organic material. Synthesis of the A<sub>5</sub>CoL complex ion was also rendered difficult by the tendency of 4-vinylpyridine to undergo polymerization. The cumulative results suggest that the reaction(s) involve organic radical formation, either in net redox transfer between the metals or as a prominent degradative side reaction.

**Ligand Stoichiometries.** Yields of ligands recovered from illuminated solutions of the binuclear ions are listed in Table III. The values reported are corrected for procedural losses encountered in extraction and gas chromatographic analysis of the products

(55) Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163–190.

(56) Norton, K. A., Jr.; Hurst, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 7237–7242.

(57) Metastable solutions containing Cu(I) in excess of 10<sup>-3</sup> M undergo rapid disproportionation to Cu(0) and Cu(II) when irradiated at 290 nm, thereby placing an upper limit on its accessible concentration range.



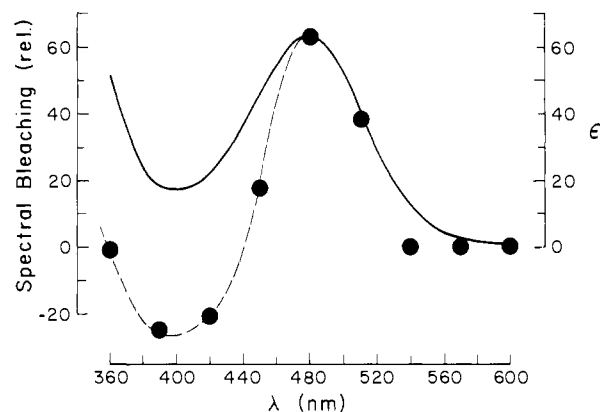
**Figure 3.** Optical traces from laser flash of the  $A_5Co$ -1-amino-4-pentene-Cu(I) ion. Conditions: 1.3 mM  $A_5CoL$ , 1.2 mM Cu(I), 14 mM Cu(II), 0.1 M  $HClO_4$ , ambient temperature, 266-nm excitation wavelength. Trace a, optical path blocked; traces b and c, 477-nm detection. Arrows indicate initiation of laser pulse.

and for small amounts of ligands labilized by hydrolysis over the course of the measurements;<sup>26</sup> in general, these corrections amounted to about 10% of the total isolated ligand. The value for geranylamine was also corrected for the amount of ligand photolabilized by LMCT excitation on cobalt(III). All recovered ligands co-chromatographed with samples of the organic compounds used in the  $A_5CoL$  syntheses.

**Kinetic Studies.** Electron-transfer rates of several binuclear ions were investigated with pulsed laser spectroscopy. For the  $A_5Co$ -1-amino-4-pentene-Cu(I) ion, excitation at 266 nm gave rise to irreversible photobleaching of Co(III) within the duration of the laser pulse (Figure 3); no further spectral changes were detected at 477 nm up to 0.5 s after the flash. The wavelength dependence of the amplitude changes corresponds closely to the absorption spectrum of the Cu(III) chromophore at longer wavelengths (Figure 4) but deviates somewhat in the near-ultraviolet region, presumably as a consequence of formation of absorbing impurities generated from the laser flash. Illumination of solutions of the  $A_5Co$ -1-amino-4-pentene ion in the absence of Cu(I) gave rise to the same ultraviolet absorption behavior but no detectable loss of Co(III) absorption. After 30–40 laser pulses, the absorption bands of the Co(III) ion had decreased about 5%, indicating some net photodecomposition. In these experiments the major fraction of the exciting light is absorbed into the amine-to-cobalt LMCT bands (Figure 2), whereas under conditions of the continuous photolysis experiments, illumination led primarily to copper-to-olefin MLCT excitation. These differences may account for our inability to detect photoredox decomposition of the cobalt(III) ion under continuous illumination. Because the Co(III) ligand field absorption bands are weak, formation of absorbing products arising from only a few percent of the total overall reaction can introduce large distortions in the visible photobleaching spectrum.

Flash illumination of the  $A_5Co$ -4-(3-butenyl)pyridine-Cu(I) and  $A_5Co$ -geranylamine-Cu(I) ions also gave net photobleaching of the Co(III) visible absorption bands. For these ions, a lower limit for reaction was established<sup>58</sup> at  $t_{1/2} \leq 100$  ns. Illumination

(58) Optical detection on submicrosecond time scales requires use of impedance-matched cables which, in this instance, caused loss of spectral resolution of below detectable levels.

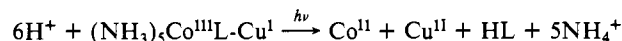


**Figure 4.** Wavelength dependence of  $A_5Co$ -1-amino-4-pentene-Cu(I) ion photobleaching. Conditions: 2.7 mM  $A_5CoL$ , 1.8 mM Cu(I), 14 mM Cu(II), 0.1 M  $HClO_4$ , ambient temperature, 266-nm excitation wavelength. Data points are amplitudinal changes measured 100 ns after laser pulse normalized to correspond to the visible peak maximum of the  $A_5CoL$  ion; the solid line gives the  $A_5CoL$  ion absorption spectrum.

of the  $A_5Co$ -4-(3-butenyl)pyridine ion in the absence of Cu(I) gave no permanent spectral changes, either in the transient response or as measured from the absorption spectrum after repetitive pulsing. Consistent with results from continuous photolysis studies, illumination of the  $A_5Co$ -geranylamine ion gave rise to Co(II) formation that was about half as great as occurred in the binuclear ion under comparable experimental conditions; net absorption below 400 nm was also observed in this system. The reduced bleaching efficiencies for these binuclear ions despite favorable electron-transfer quantum yields (Table III) is a consequence of relatively intense absorption at 266 nm into LMCT and ligand bands.

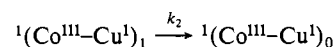
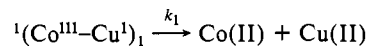
## Discussion

**Nature of the Photoinduced Reactions.** Our observations that the bridging ligands are photolabilized in stoichiometric equivalence with cobalt(II) formed and that there is negligible photooxidation of amines<sup>26</sup> indicate that the net redox reaction is Cu(I) reduction of cobalt(III):

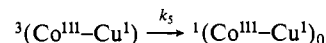
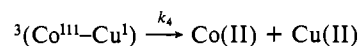
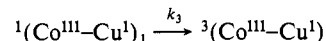


Quantum yields ( $\Phi_{Cu \rightarrow L}$ ) are independent of reagent concentrations, indicating intramolecular reaction pathways. Furthermore, the constancy of  $\Phi_{Cu \rightarrow L}$  for a given reaction calculated from eq 1 or 2 over widely varying solution absorbancies indicates that  $Cu(d) \rightarrow olefin(\pi^*)$  MLCT excitation is the redox-initiating process.

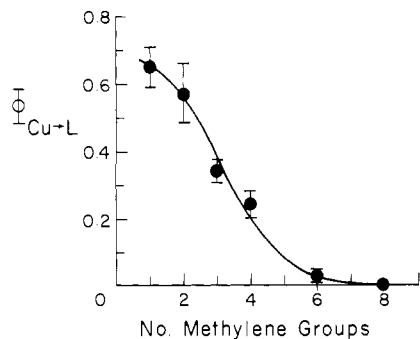
Electron transfer must occur either from this excited singlet state, which is the only energetically accessible one, or from the triplet manifold reached by intersystem crossing. Quantum yields are less than unity, indicating physical deactivation competes with electron transfer. Two mechanisms consistent with these constraints are direct competition between electron transfer and internal conversion in the singlet state:



with  $\Phi_{Cu \rightarrow L} = k_1/(k_1 + k_2)$ , and competition between internal conversion and intersystem crossing:



where  ${}^3(Co^{III}-Cu^I)$  can be any of the low-lying  $Cu \rightarrow L$ ,  $Cu \leftarrow L$  charge-transfer or ligand-field triplet states. Measured lifetimes



**Figure 5.** Chain length dependence of electron transfer quantum yields for the  $\text{A}_5\text{CoNH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2\text{Cu}^{\text{I}}$  ions. Data are taken from Table II.

for intersystem crossing to ground electronic states in transition-metal ions are substantially longer<sup>59</sup> than the upper limit for electron transfer in the binuclear ions ( $t_{1/2} < 10$  ns). Assuming similar triplet lifetimes for the  $\text{Co}^{\text{III}}\text{-Cu}^{\text{I}}$  ions,  $k_4 > k_5$ , so that  $\Phi_{\text{Cu} \rightarrow \text{L}} \approx k_3/(k_2 + k_3)$ .

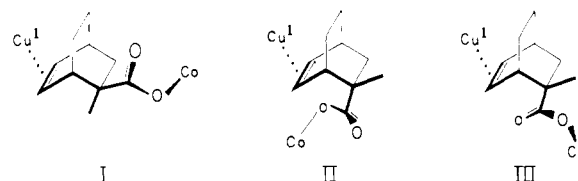
In the first mechanism, quantum yield variations should reflect principally changes in  $k_1$  since electron transfer is sensitive to the distance of separation between metal ions. Intersystem crossing rates ( $k_3$ ) might show a similar dependence upon bridging ligand if there exists appreciable spin-orbit interaction between the metals. However,  $\text{Ag}(\text{I})$   $\pi$  coordination to  $\text{A}_5\text{Co}(\text{III})\text{L}$  ions gives no evidence of altering photophysical or photochemical deactivation processes.<sup>26</sup> Furthermore, experiments designed to directly populate the  $\text{Co}^{\text{III}}\text{-Cu}^{\text{I}}$  binuclear triplet state manifold by energy transfer from the biacetyl triplet show biacetyl phosphorescence quenching, but no  $\text{Co}(\text{II})$  formation.<sup>26</sup> The first mechanism, which identifies the initially populated singlet state as photoreactive, is therefore more likely.

**Electron-Transfer Distances.** The present experiments differ in one important respect from most other studies<sup>19,22-25,60</sup> on electron transfer between redox pairs connected by flexible chains. Generally, measured electron-transfer rates have been much slower than diffusional motion of the chain ends,<sup>62,63</sup> making it impossible to distinguish kinetic models in which electron transfer occurs from a small number of conformationally equilibrated states with closely approaching redox sites from models that include long-range transfer between redox sites on substantially extended chains. However, photoinitiated electron transfer in the  $\text{Co}^{\text{III}}\text{-Cu}^{\text{I}}$  binuclear ions is more rapid ( $t_{1/2} < 10$  ns) than chain conformational dynamics, where changes occur on the 10–100-ns time scales.<sup>62,64</sup> Reaction must therefore occur from a distribution of states very near to that found at equilibrium.

Electron-transfer quantum yields for the  $\text{A}_5\text{Co}$ -aminoalkene- $\text{Cu}^{\text{I}}$  ions decrease with increasing chain length (Figure 5). Beyond four to five methylene groups, electron transfer is no longer competitive with physical deactivation of the excited state. Since the reactions are intramolecular, the distance between redox centers in fully extended chains, estimated to be 8.5–9.7 Å, sets an upper limit on the actual electron-transfer distance. For short chains, calculations based upon the rotational isomeric state model<sup>65,66</sup> that include excluded volume and cis-trans steric repulsion effects indicate that the trans rotamer is favored over cis orientations; the chains will therefore assume average end-to-end separation distances which approach the values for full extension. It is not presently possible to treat the problem quantitatively

because the tendency toward conformational extension in the cobalt(III)-copper(I) ions is enhanced by electrostatic repulsions of the like-charged metal ions but diminished by the hydrophobic effect of the aqueous medium to unknown extents.

Internuclear distances are relatively well-defined in the  $\text{A}_5\text{Co}$ -carboxylate- $\text{Cu}(\text{I})$  ions. The *exo*-carboxylate isomer is constrained by the bicyclooctene ring to geometries with a cobalt-copper distance of 7.1–7.9 Å (structure I), whereas rotation



about the carboxylate-ring carbon-carbon bond in the *endo*-carboxylate isomer allows internuclear separation to vary from 4 Å, the distance of collisional interactions for analogous intermolecular reactions (structure II), to about 8 Å at full extension (structure III). For both binuclear ions, photoinitiated electron transfer is efficient (Table II). The greater reactivity of the *endo*-carboxylate isomer may reflect either a predominance of folded conformations with corresponding shorter metal-metal distances or, because the carbonyl oxygen is rotated into a position immediately between the olefin bond and cobalt(III) in extended conformations (structure III), changes in barrier shapes that promote reactivity relative to simple hydrocarbon chains. The binuclear separation in the *exo*-carboxylate bridged ion is similar to the maximum possible distance in the  $\text{A}_5\text{Co}$ -1-amino-3-butene- $\text{Cu}(\text{I})$  ion (6.3 Å); the nearly identical electron-transfer quantum yields support our contention that the latter bridging ligand exists primarily in extended chain conformations.

Olefin substitution into the alkyl chains enhances electron transfer between metal centers, based upon results obtained with the geranylamine and farnesylamine ligands (Table II). These relatively long bridging ligands appear to be extensively folded in aqueous solution;<sup>17</sup> the five-carbon coplanarity imposed by the olefin bonds severely limits the number of conformational states accessible to the polyisoprenyl ligands, so that folding gives rise to an approximately parallel overlapping of olefins in a manner suitable for promoting delocalized interaction between metal-centered donor and acceptor orbitals.<sup>17,67</sup> Ethanol addition may increase randomization of the chains, leading to disruption of overlap and reduced photoredox quantum yields (Table II). Electron transfer in the photoexcited ions containing pyridine derivatives as bridging ligands is relatively inefficient despite the presence of  $\pi$  unsaturation in the heterocyclic ring, however, pointing to the need for information on physical deactivation rates to quantitatively interpret these effects.

In view of the recent results with biological redox particles<sup>2-16</sup> and other matrix-immobilized systems,<sup>28,29</sup> it is perhaps surprising that electron transfer was not found to occur beyond  $\sim 8$  Å in these studies. However, deactivation rates for the photoexcited states are extremely fast. It is evident that if physical deactivation were not competitive with the chemical reaction, electron transfer would be demonstrable over considerably longer distances. For example, electron tunneling calculations<sup>5,16</sup> using  $k \approx 10^9 \text{ s}^{-1}$  at 7.5 Å (approximately the conditions for electron transfer in the  $\text{A}_5\text{Co}$ -*exo*-carboxylate- $\text{Cu}(\text{I})$  ion) to evaluate the barrier-dependent parameters indicate that barrier penetration occurs with a rate constant of  $10^3 \text{ s}^{-1}$  over a distance of 17 Å.

**Other Factors Controlling Reactivity.** Rates of thermal oxidation-reduction in the  $\text{Co}^{\text{III}}\text{-Cu}^{\text{I}}$  ions are too slow to measure ( $t_{1/2} \geq 5$  years),<sup>45</sup> whereas reaction in photoexcited ions is too rapid to measure ( $t_{1/2} \leq 10$  ns) with conventional methods. This dra-

(59) Porter, G. B. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; pp 37-79.

(60) ESR measurements between organic free radicals may also be exceptional.<sup>61,62</sup>

(61) Harriman, J. E.; Maki, A. H. *J. Chem. Phys.* **1963**, *39*, 778-786.

(62) Shimada, K.; Shimozato, Y.; Szwarc, M. *J. Am. Chem. Soc.* **1975**, *97*, 5834-5841.

(63) Haas, E.; Katchalski, E.; Steinberg, I. Z. *Biopolymers* **1978**, *17*, 11-31.

(64) Winnik, M. A. *Acc. Chem. Res.* **1977**, *10*, 173-179.

(65) Smith, R. P. *J. Chem. Phys.* **1965**, *42*, 1162-1166.

(66) Saunders, D. S.; Winnik, M. A. *Macromolecules* **1978**, *11*, 18-24.

(67) Introduction of olefin unsaturation into monolayer films has recently been demonstrated to markedly increase transmembrane photoconduction from organic dyes; electron transfer is thought to occur by parallel pathways involving thermal activation and tunneling through the energy barrier.<sup>68</sup>

(68) Polymeropoulos, E. E.; Möbius, D.; Kuhn, H. *Thin Solid Films* **1980**, *68*, 173-190; *J. Chem. Phys.* **1978**, *68*, 3918-3931.

matic rate difference, greater than  $10^{16}$ , is primarily a consequence of the large differences in reaction free energies. The electron-transfer step for the thermal reaction is energetically unfavorable by  $\Delta G^\circ = 1-2$  kcal/mol;<sup>45</sup> photoexcitation increases reactant energies by 50-100 kcal/mol, which substantially diminishes nuclear activation barriers. Additionally, sufficient excess energy exists to form Co(II) in its  $t_{2g}^6e_g$  excited electronic state, thereby removing potential ligand field spin restrictions on Co(II) reduction, and charge transfer to olefin  $\pi^*$  orbitals in the photoexcited state may act to increase orbital overlap of the transferred electron with the acceptor.

Thermal electron transfer does occur in the  $A_5Ru^{II}$ -4-vinylpyridine-Cu<sup>I</sup> ion,<sup>56</sup> but not when  $\pi$  conjugation in the bridging ligand is disrupted by introduction of intervening methylene groups.<sup>17</sup> Unlike the  $Co^{III}$ -Cu<sup>I</sup> photochemistry, this behavior is conventional in the sense that long-range transfer is identified with the presence of  $\pi$ -delocalized structures. Because the driving forces for thermal reactions with  $A_5Co^{III}$  and  $A_5Ru^{III}$  oxidants are comparable, the reactivity differences are a clear manifestation of orbital symmetry requirements for electron transfer.<sup>1</sup>

**Acknowledgment.** Financial support was provided by the U. S. Public Health Service under Grant GM 20943. J.K.H. is grateful to Professor Michael Grätzel, Institut de Chimie Physique, EPFL, Lausanne, Switzerland, for his warm hospitality and use of his instrumentation facility to undertake the laser flash kinetic studies. We are also most grateful to Gail A. Massey and Joel

C. Johnson for their invaluable assistance in assembling and maintaining the laser used at OGC in the continuous photolysis experiments.

**Registry No.**  $A_5Co^{III}-NH_2CH_2CH=CH_2-Cu(I)$ , 82903-21-7;  $A_5Co^{III}-NH_2((H_2)_2CH=CH_2-Cu(I)$ , 82903-22-8;  $A_5Co^{III}-NH_2-(CH_2)_3CH=CH_2-Cu(I)$ , 82903-23-9;  $A_5Co^{III}-NH_2(CH_2)_4CH=CH_2-Cu(I)$ , 82903-24-0;  $A_5Co^{III}-NH_2(CH_2)_6CH=CH_2-Cu(I)$ , 82903-25-1;  $A_5Co^{III}-NH_2(CH_2)_8CH=CH_2-Cu(I)$ , 82903-26-2;  $A_5Co^{III}-NH_2-(CH_2CH=C(CH_3)CH_2)_2H-Cu(I)$ , 82917-46-2;  $A_5Co^{III}-NH_2-(CH_2CH=C(CH_3)CH_2)_3H-Cu(I)$ , 82903-27-3;  $A_5Co^{III}-NC_5H_4-(CH_2)_2CH=CH_2-Cu(I)$ , 82903-28-4;  $A_5Co^{III}-NC_5H_4(CH_2)_3CH=CH_2-Cu(I)$ , 82903-29-5;  $A_5Co^{III}-NC_5H_4(CH_2)_4CH=CH_2-Cu(I)$ , 82903-30-8;  $A_5Co^{III}-NC_5H_4(CH_2)_5CH=CH_2-Cu(I)$ , 82903-31-9;  $A_5Co^{III}-NC_5H_4(CH_2)_7CH=CH_2-Cu(I)$ , 82903-32-0;  $A_5Co^{III}-NC_5H_4-(CH_2)_3CH=CH_2-Cu(I)$ , 82903-33-1;  $A_5Co^{III}-NC_5H_4CH_2(CH_2CH=C(CH_3)CH_2)_2H-Cu(I)$ , 82903-34-2;  $A_5Co^{III}-NC_5H_4CH_2(CH_2CH=C(CH_3)CH_2)_3H-Cu(I)$ , 82950-35-4;  $A_5Co^{III}-exo$ -carboxylate-Cu(I), 82903-35-3;  $A_5Co^{III}-endo$ -carboxylate-Cu(I), 82949-89-1;  $A_5Co^{III}-NC_5H_4CH=CH_2$ , 68842-72-8;  $A_5Co^{III}-NC_5H_4(CH_2)_2CH=CH_2$ , 82903-36-4;  $A_5Co^{III}-NC_5H_4(CH_2)_3CH=CH_2$ , 82903-37-5;  $A_5Co^{III}-NC_5H_4(CH_2)_4CH=CH_2$ , 82903-38-6;  $A_5Co^{III}-NC_5H_4(CH_2)_5CH=CH_2$ , 82903-39-7;  $A_5Co^{III}-NC_5H_4(CH_2)_7CH=CH_2$ , 82903-40-0;  $A_5Co^{III}-NC_5H_4(CH_2)_9CH=CH_2$ , 82903-41-1;  $A_5Co^{III}$ -geranylpicoline, 82949-90-4;  $A_5Co^{III}$ -farnesylpicoline, 82903-42-2;  $A_5Co^{III}-NH_2-(CH_2)_3CH=CH_2$ , 82903-43-3;  $A_5Co^{III}-NH_2(CH_2)_4CH=CH_2$ , 82903-44-4;  $A_5Co^{III}-NH_2(CH_2)_6CH=CH_2$ , 82903-45-5;  $A_5Co^{III}-NH_2-(CH_2)_8CH=CH_2$ , 82903-46-6;  $A_5Co^{III}$ -geranylamine, 82903-47-7;  $A_5Co^{III}$ -farnesylamine, 82903-48-8;  $A_5Co^{III}-endo$ -carboxylate, 82903-49-9;  $A_5Co^{III}-exo$ -carboxylate, 82949-91-5.

## Thermodynamics of Molecular Metal Formation: Metallophthalocyanine and Tetrathiafulvalene Iodides

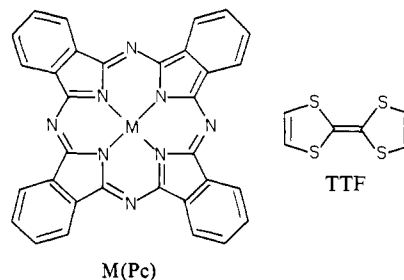
William B. Euler, Mary E. Melton, and Brian M. Hoffman\*

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. Received January 4, 1982

**Abstract:** Solid-state electrochemical cells are employed to investigate the formation reaction of several iodinated materials,  $DI_x$ , where D is a metallophthalocyanine (M(Pc), M = H<sub>2</sub>, Ni, Co, Cu) or tetrathiafulvalene (TTF). I<sub>2</sub> and  $[(CH_3)_4N]I_3$  cells were also studied as controls. The M(Pc)I constitute a set of isostructural and isoionic molecular conductors; in contrast, the  $TTFI_x$  ( $x = 0.7, 2, 3$ ) differ in structure, level of oxidation, and the state of the iodine. For none of the  $DI_x$  studied does the formation reaction of the parent D and molecular iodine have a free energy more favorable than -5.2 kcal/mol. This is so despite the highly favorable lattice stabilization energies,  $L$ , that are calculated from appropriate Born-Haber cycles:  $L$  ranges from -103 to -117 kcal/mol in the nonintegrally (partially) oxidized materials while  $L = -164 \pm 5$  kcal/mol in the integrally oxidized  $TTFI_3$ . Individual contributions to  $L$ , namely the nonbonded, ionic, and mixed-valence, or carrier-delocalization, contributions, are also discussed. The first two of these are large and contribute in different proportions for the M(Pc)I and  $(TTF)_I_x$ . The third, though small, can be of the same magnitude as or greater than the total free energy of formation.

The preparation and characterization of new highly conductive molecular crystals, the so-called molecular metals, has as yet been accompanied by only a limited understanding of the nature and strength of the interactions that govern the formation of such materials.<sup>1</sup> We report here the thermodynamics of crystal formation for two types of conductive molecular compounds, the iodide complexes of the metallophthalocyanines (M(Pc)I) and of tetrathiafulvalene ( $TTFI_x$ ), and use the results to calculate the lattice energies of these materials.

(1) (a) Metzger, R. M. *J. Chem. Phys.* **1977**, *66*, 2525-2533. (b) Torrance, J. B.; Silverman, B. D. *Phys. Rev. B: Solid State* **1977**, *15*, 788-801. (c) Aronson, S.; Mittelman, J. S. *J. Solid State Chem.* **1981**, *36*, 221-224. (d) Metzger, R. M. In "Crystal Cohesion and Confirmation Energies"; Metzger, R. M., Ed.; Springer-Verlag New York: New York, 1981.



The reaction of Ni(Pc) with I<sub>2</sub> results in a highly conducting compound, Ni(Pc)I, which consists of metal-over-metal stacks of planar Ni(Pc) macrocycles surrounded by parallel chains of