

4–8 rest on the analytical and spectral data (Table I). All of these products had a common base ion peak at  $m/e$  110 as one of the characteristic mass spectral fragmentations.

In order to examine the photochemical behavior, **3** was irradiated in cyclohexane with a 100-W high-pressure mercury lamp at room temperature for 50 hr until **3** completely disappeared on glpc. The identified main product was the isocyanate **2** (20% yield),<sup>6</sup> while under similar conditions **2** remained mostly unchanged.<sup>7</sup> These results indicate that a photolytic conversion of **3** to **2** is possible which is different from that of known photovallence isomerization of **11** to **12**,<sup>3a</sup> but is quite similar to the homoelectrocyclic reaction reported recently for several bicyclic dienones such as **13**,<sup>8</sup> where the formation of cyclopropylketene **14** is photochemically favored, while that of **13** is thermally favored.

It should be mentioned here that considerable steric repulsion between a *flagpole* methyl group and one of the methyl groups on the cyclopropyl ring might be involved in the boatlike transition state <sup>9</sup> due to the geometrical constraint of **2** and **3** prohibiting [3,3] sigmatropic rearrangements, and, therefore, the **2** → **3** conversion proceeds only under energetic conditions (144°) compared to the mild ones (even room temperature) for the **9** → **10** → **11** conversion.<sup>3a,b,10</sup>

(6) Several other products were produced, but they have not been identified yet.

(7) **3** in cyclohexane was stable in dark at room temperature.

(8) (a) O. L. Chapman, M. Kane, J. D. Lassile, R. L. Loeschen, and H. E. Wright, *J. Amer. Chem. Soc.*, **91**, 6856 (1969), and references therein; (b) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *ibid.*, **91**, 6858 (1969), in which photochemistry of homocyclohexadienone (ii) has been described.

(9) For a recent review on the Cope rearrangement, see H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 111 (1969); see also M. Simonetta, G. Favini, C. Mariani, and P. Gramaccioni, *J. Amer. Chem. Soc.*, **90**, 1280 (1968), and references therein.

(10) For the facile valence isomerization of *cis*-2-vinylcyclopropane-carboxaldehyde, see S. J. Rhoads and R. D. Cockroft, *ibid.*, **91**, 2815 (1969).

Tadashi Sasaki, Shoji Eguchi, Masatomi Ohno

Institute of Applied Organic Chemistry, Faculty of Engineering  
Nagoya University, Chikusa-ku, Nagoya, Japan

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## Novel Chelated Biscarborane Transition Metal Complexes Formed through Carbon–Metal $\sigma$ Bonds

Sir:

Numerous  $\pi$ -bonded transition metal complexes with  $B_9C_2H_{11}^{2-}$ ,  $B_7C_2H_9^{2-}$ , and  $B_6C_2H_8^{2-}$  ligands have recently been reported.<sup>1–8</sup> In addition, a few examples of neutral  $\sigma$ -bonded transition metal complexes involving single carbon–transition metal bonds have been described.<sup>9,10</sup> We now wish to report the first example

(1) M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

(2) M. F. Hawthorne and T. A. George, *ibid.*, **89**, 7114 (1967).

(3) M. F. Hawthorne and A. D. Pitts, *ibid.*, **89**, 7115 (1967).

(4) T. A. George and M. F. Hawthorne, *ibid.*, **90**, 1661 (1968).

(5) J. N. Francis and M. F. Hawthorne, *ibid.*, **90**, 6553 (1968).

(6) M. F. Hawthorne and H. R. Rühle, *Inorg. Chem.*, **8**, 176 (1969).

(7) T. A. George and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 5475 (1969).

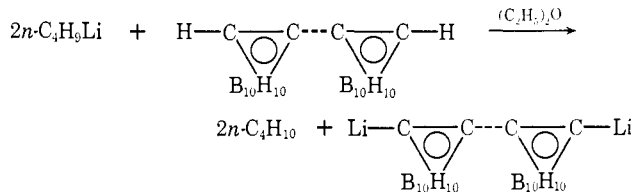
(8) M. F. Hawthorne, *Accounts Chem. Res.*, **1**, 281 (1968).

(9) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, **20**, 1205 (1968).

(10) J. C. Smart, P. M. Garrett, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **91**, 1031 (1969).

of anionic transition metal complexes which contain a novel chelating carborane group and unusually stable carbon–metal  $\sigma$  bonds.

Reaction of biscarborane [1-(1',2'-dicarba-*closo*-dodecaborano(12))-1,2-dicarba-*closo*-dodecaborane(12)] with 2 equiv of *n*-butyllithium in ethyl ether affords *n*-butane and a slurry of 2,2'-dilithio-biscarborane.<sup>11</sup> Treatment of this ether slurry with



1 equiv of anhydrous  $\text{CuCl}_2$  at reflux for 3 hr, followed by cation exchange with 0.5 mol equiv of  $(\text{C}_2\text{H}_5)_4\text{NBr}$  in  $\text{CH}_2\text{Cl}_2$ , elution of the product from a short silica gel column with 50:50  $(\text{C}_2\text{H}_5)_2\text{O}-\text{CH}_2\text{Cl}_2$ , and recrystallization from  $\text{CH}_2\text{Cl}_2-\text{C}_6\text{H}_{14}$  yields 52% of a diamagnetic yellow crystalline solid,  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Cu}^{\text{III}}\text{-}[(\text{B}_{10}\text{C}_2\text{H}_{10})_2]_2$ , mp 210–212° (I). Elemental analyses and molecular weights were satisfactory for I and all other complexes. The 32.1-MHz  $^{11}\text{B}$  nmr spectrum of I consisted of two sets of overlapping resonances centered at +3.9 and –0.5 ppm, respectively, relative to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ . The 60-MHz  $^1\text{H}$  nmr spectrum of I in deuterioacetone exhibited cation resonances centered at  $\tau$  8.60 (triplets of triplets, intensity 3) and 6.52 (quartet, intensity 2). The infrared spectrum of I as a Nujol mull contained absorptions at 2500 (s), 1170 (s), 1072 (s), 1030 (m), 999 (m), 928 (w), 782 (m), 735 (sh), and 725  $\text{cm}^{-1}$  (s). The electronic spectrum of I in  $\text{CH}_3\text{CN}$  exhibited maxima at 374 ( $\epsilon$  28,400), 272 ( $\epsilon$  14,000), and 200  $\text{m}\mu$  (sh,  $\epsilon$  9000).

Reduction of I with lithium in acetone containing  $(\text{C}_2\text{H}_5)_4\text{NBr}$ , followed by fractional crystallization of the product, gave blue needles of  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Cu}^{\text{II}}\text{-}[(\text{B}_{10}\text{C}_2\text{H}_{10})_2]_2$ , mp 221–223° (II), in 55% yield. The magnetic moment of solid II was 1.8 BM. The infrared spectrum of II as a Nujol mull showed absorptions at 2520 (s), 1185 (s), 1052 (sh), 1030 (m), 1000 (s), 956 (w), 851 (w), 785 (s), 732 (s), and 725  $\text{cm}^{-1}$  (sh). The electronic spectrum of II in  $\text{CH}_3\text{CN}$  exhibited maxima at 552 ( $\epsilon$  1030), 334 ( $\epsilon$  13,000), and 271  $\text{m}\mu$  ( $\epsilon$  40,000). Cyclic voltammetry of I or II in  $\text{CH}_3\text{CN}$  with  $(\text{C}_2\text{H}_5)_4\text{NClO}_4$  as the supporting electrolyte gave a reversible wave at +0.15 V vs. sce for the  $\text{Cu}^{3+}|\text{Cu}^{2+}$  couple and an irreversible wave at –1.36 V for an apparent  $\text{Cu}^{2+}|\text{Cu}^+$  couple.

Treatment of 2,2'-dilithio-biscarborane with 0.5 mol equiv of anhydrous  $\text{NiBr}_2$ <sup>12</sup> as an ether slurry for 3 hr gave a red-brown oil, which dissolved in dry  $\text{CH}_2\text{Cl}_2$  containing 1 mol equiv of  $(\text{C}_2\text{H}_5)_4\text{NBr}$ . Addition of ether precipitated an orange-brown solid which was recrystallized twice from  $\text{CH}_2\text{Cl}_2$ . Bright orange plates of diamagnetic  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Ni}^{\text{II}}\text{-}[(\text{B}_{10}\text{C}_2\text{H}_{10})_2]_2$ , mp 259–262° (III), were obtained in 58% yield. The 32.1-MHz  $^{11}\text{B}$  nmr spectrum of III contained overlapping resonances centered at +7.2 ppm. The 60-MHz  $^1\text{H}$  nmr spectrum of III in deuterio-

(11) J. A. Dupont and M. F. Hawthorne, *ibid.*, **86**, 1643 (1964).

(12) R. B. King, Ed., "Organometallic Syntheses," Vol. I, Academic Press, New York, N. Y., 1965, p 72.

acetone exhibited cation resonances centered at  $\tau$  8.63 (triplet, intensity 3) and 6.51 (quartet, intensity 2). The infrared spectrum of III as a Nujol mull contained absorptions at 2520 (s), 1300 (w), 1185 (s), 1170 (s), 1030 (m), 1003 (m), 928 (w), 796 (s), 783 (sh), 733 (s), and 724  $\text{cm}^{-1}$  (sh). The electronic spectrum of III in  $\text{CH}_3\text{CN}$  exhibited maxima at 448 ( $\epsilon$  575) and 219  $\text{m}\mu$  ( $\epsilon$  18,200).

Reaction of III with a large excess of anhydrous  $\text{CuCl}_2$  in dry  $\text{CH}_2\text{Cl}_2$  for 4 hr followed by filtration and fractional recrystallization of the filtrate from  $\text{CH}_2\text{Cl}_2$ - $\text{C}_6\text{H}_{14}$  gave, in 73% yield, bright green crystals of  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Ni}^{\text{III}}[(\text{B}_{10}\text{C}_2\text{H}_{10}^-)_2]_2$ , mp 178–181° (IV). The magnetic moment of solid IV was 1.7 BM. The 32.1-MHz  $^{11}\text{B}$  spectrum of IV consisted of three broad paramagnetic resonances. The infrared spectrum of IV as a Nujol mull exhibited absorptions at 2550 (s), 1300 (w), 1172 (s), 1071 (s), 1059 (sh), 1053 (sh), 1035 (sh), 1001 (m), 928 (w), 781 (m), 735 (sh), and 726  $\text{cm}^{-1}$  (s). The electronic spectrum of IV in  $\text{CH}_3\text{CN}$  exhibited maxima at 375 ( $\epsilon$  4600), 265 ( $\epsilon$  25,200), and 223  $\text{m}\mu$  ( $\epsilon$  24,000). Cyclic voltammetry of III or IV in  $\text{CH}_3\text{CN}$  gave only a reversible wave at +0.86 V *vs.* sce for the  $\text{Ni}^{\text{III}}|\text{Ni}^{\text{II}}$  couple.

Treatment of 2,2'-dilithiobiscarborane with 0.5 mol equiv of anhydrous  $\text{CoCl}_2$  as an ether slurry for 3 hr gave an oily purple solid which was stirred with 1 mol equiv of  $(\text{C}_2\text{H}_5)_4\text{NBr}$  in  $\text{CH}_2\text{Cl}_2$ , and the purple crystalline precipitate obtained was twice recrystallized from hot  $\text{CH}_2\text{Cl}_2$  containing 1–2% acetone. Bright violet air-stable needles of  $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{Co}^{\text{II}}[(\text{B}_{10}\text{C}_2\text{H}_{10}^-)_2]_2$ , mp 275–277° dec (V), were obtained in 76% yield. The magnetic moment of solid V was 4.1 BM. The infrared spectrum of V contained absorptions at 2550 (s), 1299 (w), 1186 (s), 1170 (s), 1070 (s), 1051 (w), 1031 (m), 1003 (m), 958 (w), 851 (w), 810 (sh), 793 (sh), 730 (sh), and 719  $\text{cm}^{-1}$  (s). The electronic spectrum of V in  $\text{CH}_3\text{CN}$  exhibited maxima at 584 ( $\epsilon$  890), 563 (sh), 254 ( $\epsilon$  14,000), and 229  $\text{m}\mu$  ( $\epsilon$  15,500). Reflux in water for 24 hr left V unchanged. Reaction of V with lithium amalgam in acetone yielded a red-brown solution, which was reconverted to V upon exposure to air, and presumably contained formal  $\text{Co}^{\text{I}}$ . Reaction of this red-brown acetone solution with 1 equiv of benzyl bromide gave 1,2-diphenylethane and V in good yield.

Reaction of V with large excess of anhydrous  $\text{CuCl}_2$  in dry  $\text{CH}_2\text{Cl}_2$  for 4 hr yielded a brown solution which was filtered. Careful recrystallization of the filtrate from  $\text{CH}_2\text{Cl}_2$  gave black needles of diamagnetic  $[(\text{C}_2\text{H}_5)_4\text{N}]\text{Co}^{\text{III}}[(\text{B}_{10}\text{C}_2\text{H}_{10}^-)_2]_2$ , mp 195–196° dec (VI), in 83% yield. The 60-MHz  $^1\text{H}$  nmr spectrum of VI in deuterioacetone consisted of cation resonances centered at  $\tau$  8.56 (triplet, intensity 3) and 6.47 (quartet, intensity 2). The 77-MHz  $^{11}\text{B}$  nmr spectrum of VI exhibited six discrete doublets at +15.9 ( $J = 114$ ), +8.7 ( $J = 129$ ), -2.5 ( $J = 136$ ), -8.6 ( $J = 121$ ), -15.7 ( $J = 128$ ), and -93.8 ( $J = 110$ ); their intensities were 2:1:2:1:2:2, respectively. The infrared spectrum of VI as a Nujol mull contained absorptions at 2530 (s), 1400 (sh), 1295 (m), 1180 (s), 1062 (s), 1025 (m), 1005 (sh), 926 (w), 833 (m), 790 (s), 740 (sh), and 719  $\text{cm}^{-1}$  (s). The electronic spectrum of VI in  $\text{CH}_3\text{CN}$  exhibited maxima at 548 (sh), 330 ( $\epsilon$  13,000), 274 ( $\epsilon$  5400), and 241  $\text{m}\mu$  ( $\epsilon$  8200). Cyclic voltammetry of either V or VI in  $\text{CH}_3\text{CN}$  gave a reversible wave at +0.62 V

*vs.* sce for the  $\text{Co}^{\text{3+}}|\text{Co}^{\text{2+}}$  couple. The  $\text{Co}^{\text{2+}}|\text{Co}^{\text{+}}$  couple was observed at -2.35 V.

Since the infrared spectra of complexes I–VI contained no sharp biscarborane C–H stretching absorption at 3040  $\text{cm}^{-1}$ ,<sup>11</sup> and since  $^1\text{H}$  nmr spectra of complexes of I, IV, and VI failed to show any carborane C–H resonances, we propose that the metal atom in each complex is  $\sigma$  bonded to four carbons of two biscarborane units (Figure 1). The color and magnetic moment of V suggest it to have a tetrahedral configuration (Figure 1, upper), while the colors and low spin of complexes I, III, IV, and VI suggest a planar configuration for these species (Figure 1, lower). The

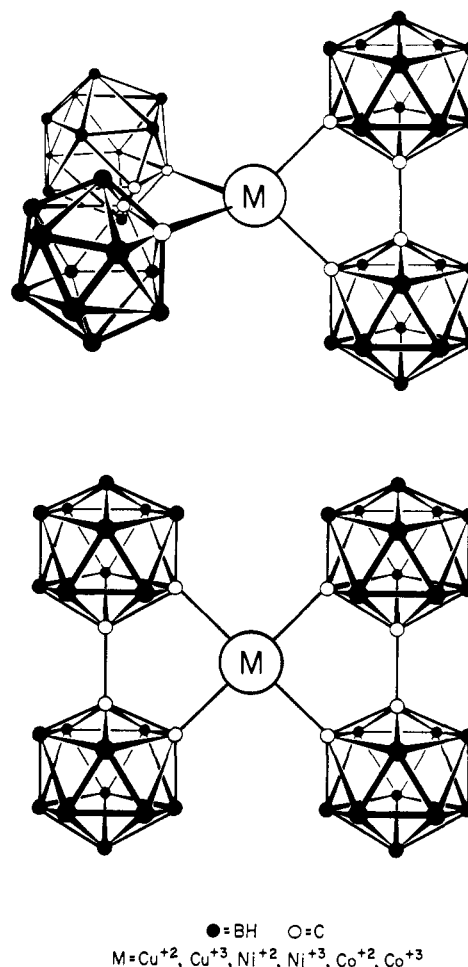


Figure 1. Proposed tetrahedral and planar structures for the  $\text{M}^{(4-n)+}[(\text{B}_{10}\text{C}_2\text{H}_{10}^-)_2]_2^{n-}$  ( $n = 1, 2$ ) ions.

$^{11}\text{B}$  nmr spectrum of VI, which contained a low-field doublet of relative intensity 2, indicates that two boron atoms of each icosahedron experience a drastic electron withdrawing effect not felt by the other boron atoms of the complex. This doublet may be assigned to the pair of boron atoms in each icosahedron bound to both carbon atoms and within bonding distance of the central metal atom. Additional bonding through these boron atoms to the metal may explain, in part, the unusual chemical stability of these novel complexes.

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David A. Owen, M. Frederick Hawthorne  
Contribution No. 2543, Department of Chemistry  
University of California  
Los Angeles, California 90024  
Received January 30, 1970

### Energy Transfer between Hexacyanochromate and Reineckate Ions

Sir:

Although energy transfer from excited organic molecules to chromium(III) complexes has been studied,<sup>1,2</sup> there is some ambiguity about the state of the inorganic acceptor molecule reached. Schläfer, *et al.*,<sup>3</sup> have observed energy transfer from a series of Cr(III) double salts. However, there is evidence<sup>4</sup> that the observed

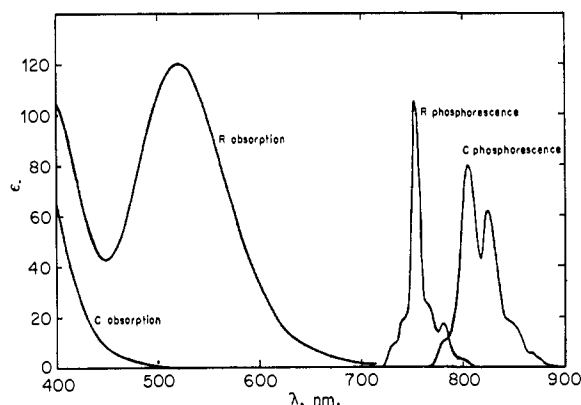


Figure 1. Absorption (25°) and phosphorescence (-65°) spectra of the donor,  $[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ , and acceptor,  $[\text{Cr}(\text{CN})_6]^{3-}$ , in methanol, water, and ethylene glycol (2:1:1) solvent.

effect is not caused by energy transfer but by a crystal perturbation. It is important to be able to populate and depopulate selectively at least one excited state of an inorganic complex in order to elucidate the pathways of the photophysical and photochemical primary processes. We describe here measurements of the energy transfer between the potassium salts of the reineckate ion (R),  $\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$ , and the hexacyanochromate(III) ion (C),  $[\text{Cr}(\text{CN})_6]^{3-}$ , by the quenching and sensitization, respectively, of the phosphorescence of the two complexes, and by lifetime measurements of the emission.

The absorption spectra of R and C are sufficiently different (see Figure 1) that exciting light of wavelength 546 nm is absorbed only by R in solutions containing both ions. At 546 nm the  $^4\text{T}_{2g}$  state<sup>5</sup> of R is populated directly, followed by intersystem crossing to the  $^2\text{E}_g$  state which emits phosphorescence,  $^2\text{E}_g \rightarrow ^4\text{A}_{2g}$ .<sup>6</sup> We

(1) D. J. Binet, E. L. Goldberg, and L. S. Forster, *J. Phys. Chem.*, **72**, 2016 (1968).

(2) A. W. Adamson, J. E. Martin, and F. D. Camessei, *J. Amer. Chem. Soc.*, **91**, 7530 (1969).

(3) H. Gausmann and H. L. Schläfer, *J. Chem. Phys.*, **48**, 4056 (1968); H. L. Schläfer, H. Gausmann, and C. H. Mobius, *Inorg. Chem.*, **8**, 1137 (1969).

(4) A. D. Kirk and H. L. Schläfer, *J. Chem. Phys.*, **52**, 2411 (1970).

(5) We use the  $O_h$  symmetry designations for simplicity, although R is quadrate complex with  $D_{4h}$  microsymmetry.

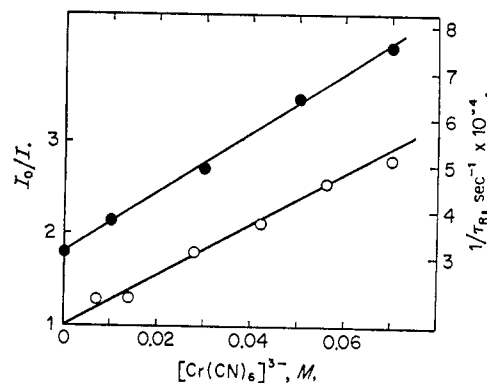


Figure 2. Stern-Volmer quenching of donor phosphorescence at -65° from steady-state intensity measurements (O) and from lifetimes (●) at 751 nm,  $[\text{R}] = 0.05 \text{ M}$ .

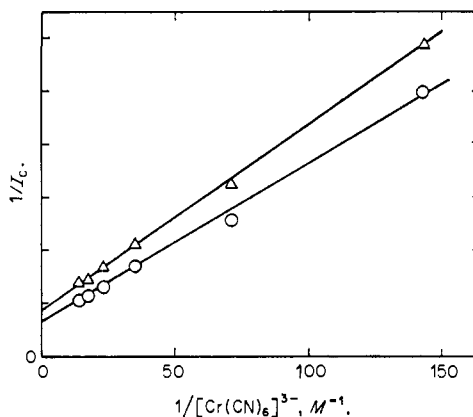


Figure 3. Sensitization of acceptor phosphorescence monitored at 806 nm (O) and at 825 nm ( $\Delta$ ),  $[\text{R}] = 0.05 \text{ M}$  at -65°.

find that in mixtures of the two ions phosphorescence of C also occurs and that the intensity of the phosphorescence of R is decreased correspondingly in the presence of C. The two phosphorescence spectra are easily separable, as shown in Figure 1. All measurements reported here were made with deoxygenated solutions<sup>7</sup> at -65° in the solvent methanol, water, and ethylene glycol in the ratio 2:1:1. Quenching and sensitization were studied at several concentrations of the acceptor, C, and at 0.05 M R with the results shown in Figures 2 and 3. For the donor (R) emission, Figure 2 shows a linear Stern-Volmer relationship between the ratio of the intensities of the unquenched to quenched emission and the concentration of C. The slope of the line,  $24.3 \text{ M}^{-1}$ , represents the product of the energy transfer rate constant (which includes possible quenching),  $k_{et}$ , and the lifetime of the phosphorescence decay of R,  $\tau_{\text{R}}^0$ , in the absence of C. For the acceptor emission, the Stern-Volmer mechanism requires a plot of reciprocal intensity against reciprocal concentration of acceptor (Figure 3). In this case the Stern-Volmer constant,  $k_{et}\tau_{\text{R}}^0$ , is the ratio of the intercept of the line to its slope. The values so obtained at two peaks in the C phosphorescence spectrum, at 806 and 825 nm, are 20.7 and 21.8  $\text{M}^{-1}$ , respectively.

Lifetime measurements of the luminescence from solutions containing both ions were made using a flash

(6) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964).

(7) Deoxygenation is necessary because oxygen quenches the emission at this temperature: A. Pfeil, submitted for publication.