molecular orbitals of the metallic complex which arise from back-bonding to have approximately 80% ligand character[18] one calculates a π bond order of 0.25 for C–S and −0.05 for C_4–C_4'. These results are compatible with our C–S distance and with the 1.48-A C_4–C_4' bond distance which is in good agreement with the expected value of 1.479 A for singly bonded sp^2C–sp^2C.[19] This is 0.07 A longer than the "ethylenic" bond distance found in any of the other dithiolate–metal systems (C–C = 1.407 A in $Co_2S_8C_8(CF_3)_8$[7]). A strong argument for the dithioketonic structure cannot be made on the basis of the C–S distance alone, since it is always found to lie within 1.69–1.75 A.[3–11] The C_4–C_5 distance is 1.51 A, as expected for a sp^2C–sp^3C single bond.[19] The average C–F bond length is 1.27 A. The C_5H_5 ring is planar to within 0.005 A and the average ring C–C bond length is 1.37 A. The intramolecular sulfur–sulfur distance is 3.00 A, which is close to the value found in the previously mentioned related complexes. The estimated standard deviations of the heavy atom distances, Co–S and S–S, are ~0.01 A and those for the light atom distances are ~0.05 A.

Intermolecular contacts are normal. The shortest cobalt–cobalt distance is 5.76 A and the closest intermolecular approach to the metal atom is made by fluorine atoms at 3.83 A.

The over-all molecular configuration and the bond distances thus suggest that the nature of the chelating ligand in this five-coordinated cobalt complex is best described in terms of a dithioketone. We believe that this type of coordination also will be found in the recently reported π-$C_5H_5CoS_2C_2(CN)_2$.[20] An X-ray study now underway in our laboratory has found the analogous nickel complex, $C_5H_5NiS_2C_4F_6$,[1] to be isomorphous with the cobalt compound (a = 9.22, b = 12.22, and c = 10.61 A), and a comparison of the $0kl$ and $1kl$ precession photographs of the two complexes also indicates that the molecules are indeed isostructural. A detailed correlation of the bond distances is of interest in order to further elucidate the nature of the bonding in these systems. A complete report will be published later.

Acknowledgment. The authors wish to thank Bell Telephone Laboratories at Winston-Salem for the use of their computing facilities, and we gratefully acknowledge financial support of this research from Research Corporation and from the Wake Forest College Research and Publication Fund.

[18] This seems not unreasonable since the metal character of the $3b_{2g}$ orbital in bis(dithioglyoxal)nickel was calculated to be 18.3%.[17]

[19] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **11**, 96 (1960).

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Received August 4, 1966

Chemiluminescence from Reduction Reactions

Sir:

Solution chemiluminescence reported to date generally falls into one of three categories: reactions involving molecular oxygen or peroxides,[1] oxidation of anion radicals,[2,3] and alternating current electrolysis of aromatic hydrocarbons.[4–6] It is unlikely that chemiluminescence from the oxidation of anion radicals results from a simple one-electron transfer process; a multistep reaction is probably involved.[3] Although chemiluminescence from the electrolysis of hydrocarbons probably is initiated by a one-electron transfer process, there are several subsequent reaction sequences that are consistent with the experimental data published to date.

Recent studies in this laboratory have shown that solution chemiluminescence can be produced by reaction of electron donors with the radical cation of rubrene.[7] These results prompted us to look at other possibilities for producing chemiluminescence by electron transfer *to* a potential emitter, *i.e.*, *via* reduction reactions. We wish to report two different types of systems producing chemiluminescence, both having over-all reactions that fit this category.

The over-all reaction for the first type of system studied can be written as

$$ML_x^{+(n+1)} + \text{reductant} \longrightarrow ML_x^{+n} + h\nu \qquad (1)$$

where M represents a metal ion and L a suitable ligand. The complexes used in the present study all had ruthenium as the central metal ion (n = 2). The ligands were 2,2′-bipyridyl, 5-methyl-*o*-phenanthroline, 5,6-dimethyl-*o*-phenanthroline, and 3,5,6,8-tetramethyl-*o*-phenanthroline (all having x = 3).[8]

Experimentally, an acidic, aqueous solution millimolar in the ruthenium(II) complex was treated with solid lead dioxide. The lead dioxide was subsequently separated by centrifugation from the resulting solution of the ruthenium(III) complex. (None of the ruthenium(III) complexes could be generated in nonaqueous solvents and none could be isolated in the solid form.) The ruthenium(III) solution was then added to aqueous base and light emission was observed. Subsequent spectroscopic examination of the reacted solution showed that the ruthenium complex had been reduced to its initial oxidation state. The intensity of the emitted light depended upon the strength of the acid and base used. When a solution of the tris(2,2′-bipyridyl)–ruthenium(III) complex in 9 N sulfuric acid was allowed to react with 9 N NaOH, the orange chemiluminescence was clearly visible in a dimly lighted room. The duration of light emission was very short, generally less than 1 sec.

Figure 1 shows a comparison between the chemiluminescence spectrum for reduction of the tris(2,2′-bipyridyl)–ruthenium(III) complex and the fluorescence spectrum of the corresponding ruthenium(II) complex. The chemiluminescence spectrum was obtained using a flow system in conjunction with a spectrofluorometer assembled from Aminco building blocks. The fluores-

[1] For a general review of this type of reaction, see K. D. Gundermann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 566 (1965).

[2] E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

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[4] R. E. Visco and E. A. Chandross, *ibid.*, **86**, 5350 (1964).

[5] K. S. V. Southanam and A. J. Bard, *ibid.*, **87**, 139 (1965).

[6] D. M. Hercules, *Science*, **145**, 808 (1964).

[7] D. M. Hercules, R. C. Lansbury, and D. K. Roe, *J. Am. Chem. Soc.*, **88**, 4578 (1966).

[8] Chemiluminescence from a ruthenium chelate has also been observed by J. P. Paris (unpublished studies, Juniata College, Huntingdon, Pa., 1962).

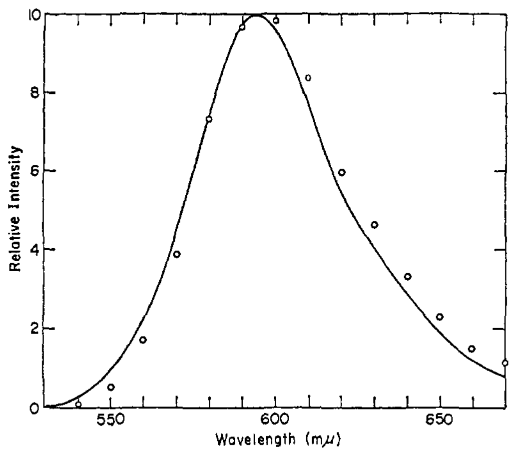

Figure 1. Comparison between chemiluminescence and fluorescence spectra of ruthenium chelates. (———) Fluorescence spectrum of the Ru(bipy)$_3^{+2}$ chelate in aqueous solution; (o-o-o-o) points taken from the chemiluminescence spectrum of the Ru(bipy)$_3^{+3}$ chelate.

cence spectrum was obtained on the same spectrofluorometer. Both spectra are unconnected for monochromator–photomultiplier response characteristics (RCA-1P21). It is evident from Figure 1 that the two spectra are identical.

The over-all reaction for the second type system studied can be written as

$$RNH_2^{+m} + \text{reductant} \longrightarrow RNH_2 + h\nu \qquad (2)$$

where RNH_2 represents an aromatic amine. The compound used in the present study was 1,6-diaminopyrene. Cyclic voltammetry indicated two reversible waves for 1,6-diaminopyrene, one corresponding to oxidation to the radical cation ($m = 1$) and the other to the dication ($m = 2$). The diamine is also capable of forming stable, solid, radical salts.[9] Electron spin resonance was used to prove the presence of radicals both in solid-state salt preparations and in dimethylformamide (DMF) solution.

Experimentally there are two procedures leading to light emissions for 1,6-diaminopyrene. The first was analogous to the ruthenium system. A DMF solution, millimolar in the diamine, was oxidized with solid lead dioxide or chlorine gas. The lead dioxide was separated by centrifugation or the chlorine was separated by bubbling with nitrogen gas. The resulting solution was added to a DMF solution 0.1 *M* in hydrazine hydrate and light emission was observed.[10] The second procedure involved preparing the radical bromide salt. The salt was added to a DMF solution, 0.1 *M* in hydrazine hydrate, and light was produced. In both cases the blue luminescence was visible in a darkened room to the non-dark-adapted eye. The duration of light emission was about 5–10 sec.

As can be seen from Figure 2, the chemiluminescence spectrum does not exactly match the fluorescence spectrum of 1,6-diaminopyrene. The difference cannot be attributed to self-absorption since the rising portions of the curves are identical. More experimental data are needed before the origin of this long-wavelength component can be completely explained. The chemiluminescence and fluorescence were obtained similarly to those for the ruthenium complexes except that an EMI-9558B photomultiplier tube was used.

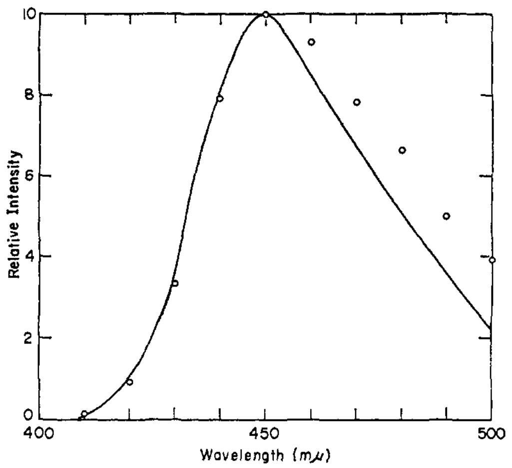

Figure 2. Comparison between the chemiluminescence and fluorescence spectra of 1,6-diaminopyrene. (———) Fluorescence spectrum of 1,6-diaminopyrene in DMF; (o-o-o-o) points taken from the chemiluminescence spectrum of the oxidized diamine.

We believe that these results, combined with earlier studies,[7] indicate that electron-transfer reactions involving a potentially fluorescent acceptor show great promise for discovering new chemiluminescent systems. A detailed investigation of the mechanism of both reactions reported in this communication is continuing. Experimental details will be published at a later date.

Acknowledgment. This work was supported in part through funds provided by the U. S. Atomic Energy Commission under Contract AT(30-1)-905.

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Five-Coordinate Complexes. II.[1] Trigonal Bipyramidal Copper(II) in a Metal Atom Cluster

Sir:

We wish to report the preparation, properties, and structure of an unusual triphenylphosphine oxide complex of copper(II); the structure, which has been definitely established by a single-crystal X-ray analysis, consists of a metal atom cluster. However, no metal–metal bonding, superexchange, or other interaction between the copper atoms is indicated by the structure nor by the properties of the compound.

When dichlorobis(triphenylphosphine oxide)copper(II) was refluxed in methyl isobutyl ketone, the initial yellow color gradually changed to orange; well-formed orange crystals of $Cu_4OCl_6(TPPO)_4$ (in formulas, TPPO represents triphenylphosphine oxide) were deposited over a period of several days. *Anal.* Calcd for $Cu_4Cl_6P_4O_5C_{72}H_{60}$: Cu, 15.92; Cl, 13.33; P, 7.76; C, 54.17; H, 3.80. Found: Cu, 16.21; Cl, 13.55; P, 7.41; C, 53.61; H, 3.64.

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