7.4×10^4 dpm/mmole. This degradation thus established that essentially all the activity of the quinine was located at the position indicated with a heavy dot in formula **6**, a result which is consistent with the previously discussed hypothesis.

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The Molecular Configuration of π-Cyclopentadienyl-*cis*-1,2-bis(trifluoromethyl)ethanedithionecobalt

Sir:

In the recent report of the synthesis of a π-cyclopentadienylcobalt dithietenyl complex, $C_5H_5CoS_2C_4F_6$,[1] King proposed a sandwich-type structure of six-coordinate cobalt(III) with coordination to two sulfur atoms and the double bond of the ethylenic linkage and with the usual threefold coordination to the π-cyclopentadienyl ring. This structure reasonably accounts for the observed diamagnetism of the compound and for the shift of the C=C stretching frequency from 1621 cm^{-1} in bis(trifluoromethyl)dithietene, $(CF_3)_2C_2S_2$,[2] to 1480 cm^{-1}. However, a structure involving a dithioketone ligand and Co(I) could achieve the effective atomic number of 36 and leave the CoS_2C_4 fragment planar. The planar metal–S_2C_4 moieties have been found recently in several related metal–dithiolate complexes (*e.g.*, the square-planar[3–8] and the trigonal prismatic[9–11] dithiolate–metal systems). From the results of a three-dimensional X-ray analysis on $C_5H_5CoS_2C_4F_6$, we present here evidence for a transition metal–dithioketonic complex.

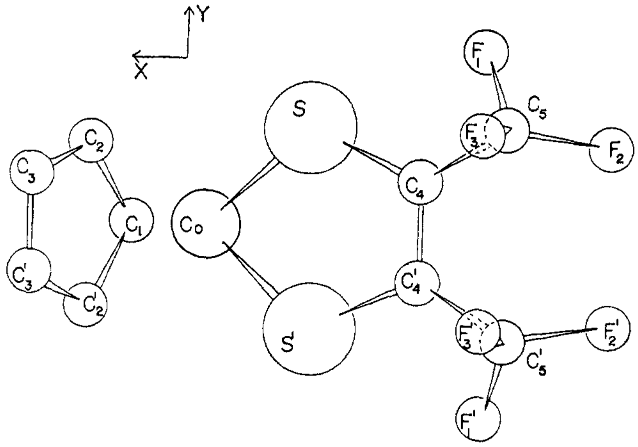

Figure 1. [001] molecular projection of $C_5H_5CoS_2C_4F_6$.

Purple crystals suitable for X-ray analysis were kindly supplied by Dr. R. B. King. Weissenberg and precession photographs taken with Zr-filtered Mo Kα radiation showed the crystals to be orthorhombic with lattice parameters $a = 9.24$, $b = 12.24$, $c = 10.62$ A. Systematic absences showed the probable space groups to be $Pn2_1a$ and Pnma. A piezoelectric test[12] gave negative results and the solution and refinement of the structure subsequently confirmed the choice of the centric space group. The calculated density of 1.92 g/cm^3 for four monomeric molecules per unit cell agrees well with the observed value of 1.93 g/cm^3 obtained by the flotation method. The centric space group thus demands that the molecule contain a crystallographic mirror plane.

X-Ray intensity data were collected by the Weissenberg multiple-film technique and were estimated visually. Proceeding through three-dimensional Patterson functions, three-dimensional electron density calculations, and least-squares refinement, the structure analysis has yielded the molecular configuration. The present reliability index, R_1, is 14.0% for 419 independent reflections. One fluorine atom has a large isotropic thermal parameter even though the atom clearly appears in the electron density maps at a reasonable distance from the methyl carbon. All other thermal parameters are reasonable. It is felt that anisotropic least-squares refinement is needed, and this will be carried out when more data are processed.

The centers of the seven atoms of the CoS_2C_4 moiety (Co, S, S′, C_4, C_4', C_5, C_5') are within 0.033 A of a plane which is perpendicular to the π-bonded cyclopentadienyl ring. The molecular geometry is shown in Figure 1. The bond distances of particular significance are 2.08 A for Co–S, 1.74 A for S–C_4, and 1.48 A for C_4–C_4'. The related bond angles are 92.2° for S–Co–S′, 108.0° for Co–S–C_4, 115.8° for S–C_4–C_4', and 120.6° for S–C_4–C_5. Comparison of the Co–S bond distance with the sum of the single bond radii (2.20 A)[13] and with the average Co–S distance of 2.16 A in $Co_2S_8C_8(CF_3)_8$[7] suggests that there is multiple Co–S bonding in $C_5H_5CoS_2C_4F_6$ as expected. Part of the Co–S π bonding will be due to back-donation of charge from the cobalt atom into antibonding orbitals of the dithione ligand leading to a carbon–sulfur bond of order less than 2. The C–S distance of 1.74 A is close to the value of 1.71 A which has been assigned as the distance for a C–S bond of order 1.22[14] and is to be compared with the values of 1.60 A for C=S[14,15] and 1.81 A[13,16] for singly bonded C–S. If one uses the π molecular orbitals reported for dithioglyoxal[17] and takes the

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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^{2}C–sp^{2}C.[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^{2}C–sp^{3}C 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.

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[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]

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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-

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