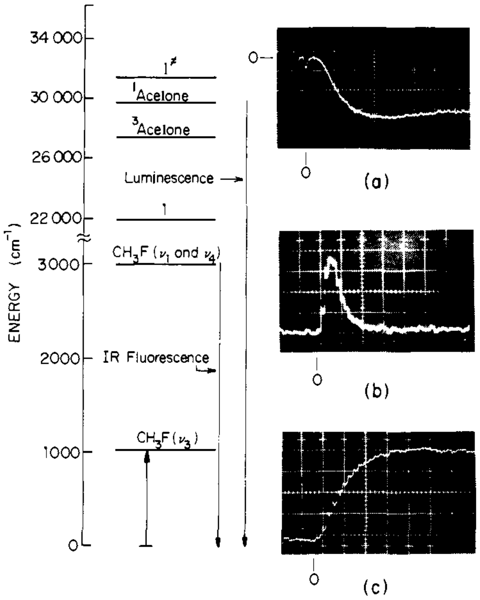

Figure 1. A partial energy level diagram for CH_3F, **1**, and acetone up to about 32 000 cm^{-1}. Energy scale referenced to CH_3F and acetone both in ground vibrational state. $1^{\ddagger}$ denotes the transition state for the decomposition of **1**. Also displayed are: (a) Time resolved visible luminescence ($\lambda_{max} \simeq 410$ nm). Signal is inverted with respect to (b) and (c). The small spike at short time is an instantaneous spark reflected off of the front of the reaction cell. Zero on the abscissa represents the initiation of the laser pulse. Zero on the ordinate represents the ambient signal level. (b) Time resolved 3 μ infrared fluorescence. Zero on the abscissa represents the initiation of the laser pulse. (c) Time resolved translation heating. Zero on the abscissa represents the initiation of the laser pulse. Time base is 5 μs per major division along the abscissa in (a), (b), and (c) measured with $P_{CH_3F} = 5$ Torr and $P_{C_6H_{12}O_2} \simeq 1$ Torr.

temperature (Figure 1c) in CH_3F–**1** mixtures indicates that on this same timescale, energy transfer is overall highly exothermic (translations heat). These results are consistent with and support the idea that eq 3, 5, and 6 rapidly drain laser energy into heat. The buildup rate of acetone luminescence should be governed both by these processes and eq 8. Based on Figures 1a and 1c, which show comparable risetimes for visible luminescence and translational heating, the rate of production of acetone is apparently limited only by the translational heating rate. This observation is indicative of a "laser temperature jump" mechanism; the rate of product formation occurs on a timescale comparable to (or slower than) the rate of ambient temperature rise.[14]

The millisecond long decay of luminescence mentioned previously is consistent with the transport of heat over a distance comparable to the reaction cell size.[15] The temperature rise due to laser heating was estimated to be 100–150 K based upon the measured laser pulse energy and percent absorption in pure CH_3F and an estimate of the heat capacity of the gas mixture.[16] Using this result and the known Arrhenius parameters[17] for the thermal decomposition of **1** yields a decomposition rate which is consistent with the observed decomposition rate measured as a function of successive laser shots. In addition, the quenching of the luminescence by added bath gases can be related to smaller translational temperature jumps as the heat capacity increases.

In summary, reaction 1 is the first example of an infrared photosensitized chemiluminescent organic reaction. A combination of measurements of infrared fluorescence from the photosensitizer, of visible luminescence from the primary product and of the translational temperature reequilibration are consistent with a predominant "temperature jump" mechanism (eq 2–7) wherein any contribution from $\mathbf{1}^{\dagger}$ in eq 7 is dominated by the contribution from **1**(T′). These studies are being extended to 1,2-dioxetanes which directly absorb the laser pulse and to other systems in which a high energy content reaction possesses the potential of infrared laser induced electronic excitation.

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References and Notes

(1) M. J. Berry, *Annu. Rev. Phys. Chem.*, **26**, 259 (1975), and references cited therein.
(2) See, for example, T. J. Odiorne, P. R. Brooks, and J. V. V. Kasper, *J. Chem. Phys.*, **55**, 1980 (1971); D. Arnoldi, K. Kaufmann, and J. Wolfrum, *Phys. Rev. Lett.*, **34**, 1597 (1975); Z. Karny, B. Katz, and A. Szoke, *Chem. Phys. Lett.*, **35**, 100 (1975).
(3) See, for example, H. R. Bachmann, H. Noth, R. Rinck, and K. L. Kompa, *Chem. Phys. Lett.*, **29**, 627 (1974); S. D. Rockwood and J. W. Hudson, *ibid.*, **34**, 542 (1975).
(4) N. J. Turro, P. Lechtken, N. E. Shore, G. Schuster, H.-C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).
(5) F. R. Grabiner, D. R. Siebert, and G. W. Flynn, *Chem. Phys. Lett.*, **17**, 189 (1972).
(6) D. R. Siebert, F. R. Grabiner, and G. W. Flynn, *J. Chem. Phys.*, **60**, 1564 (1974).
(7) (a) E. Weitz, G. W. Flynn, and A. M. Ronn, *J. Chem. Phys.*, **56**, 6060 (1972); (b) E. Weitz and G. W. Flynn, *ibid.*, **58**, 2679 (1973).
(8) F. R. Grabiner and G. W. Flynn, *J. Chem. Phys.*, **59**, 2330 (1973); E. Weitz and G. W. Flynn, *ibid.*, **58**, 2781 (1973).
(9) L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn and A. Javan, *Phys. Rev. Lett.*, 17, 233 (1966).
(10) R. D. Bates, Jr., G. W. Flynn, J. T. Knudtson, and A. M. Ronn, *J. Chem. Phys.*, **53**, 3621 (1970).
(11) CO_2 laser excited emission spectrum of reaction 1 was compared to an emission spectrum of a gas mixture of acetone, **1**, and CH_3F excited at 300 nm with a xenon lamp using the identical detection system in both cases. Approximately 10^6 CO_2 photons must be absorbed per visible photon emitted in the CO_2 laser initiated reaction.
(12) P. F. Zittel and C. B. Moore, *J. Chem. Phys.*, **58**, 2004 (1973); B. M. Hopkins, A. Baronavski, and H.-L. Chen, *ibid.*, **59**, 836 (1973); R. C. Slater and G. W. Flynn, *ibid.*, **65**, 425 (1976).
(13) I. Shamah and G. W. Flynn, submitted for publication in *J. Chem. Phys.*
(14) Similar processes can be found in W. M. Shaub and S. H. Bauer, *Int. J. Chem. Kinet.*, **7**, 509 (1975).
(15) R. C. L. Yuan and G. W. Flynn, *J. Chem. Phys.*, **56**, 1316 (1972).
(16) Molar heat capacities estimated using group additivity. See, for example, S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.
(17) H.-C. Steinmetzer, A. Yekta, and N. J. Turro, *J. Am. Chem. Soc.*, **96**, 282 (1974).
(18) Members, Columbia Radiation Laboratory.

William E. Farneth, George Flynn*[18]
Richard Slater,[18] **Nicholas J. Turro**
Chemistry Department, Columbia University
New York, New York 10027

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Salt-Type Complexes of Porphyrins: Monocation Octaethylporphinium Tri-μ-halogeno-hexacarbonyldirhenate(I)

Sir:

Porphyrins have been reported as the free base, the dicationic species, and, recently, as the monocationic species.[1] It has been suggested that in the biosynthesis of porphyrins the cationic species plays a role in the final stages of oxidation from porphyrinogen to porphyrins.[2] Recently out-of-plane bimetallic porphyrin complexes[3-6] have received considerable attention. However, bimetallic salt complexes[7,8] of porphyrin acids are rare.

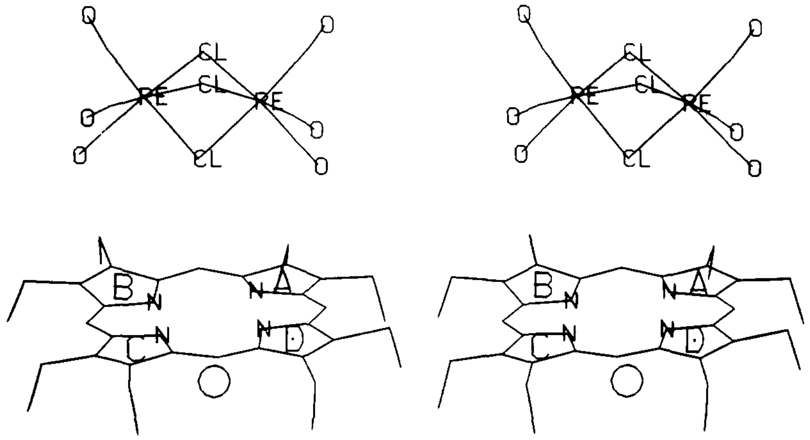

Figure 1. A stereoview of the asymmetric unit of $(H_3OEP)^+[Re_2(CO_6)Cl_3]^-H_2O$, as viewed along a pseudomirror plane passing through the structure. The water of solvation is illustrated by a circle. The notation of the pyrrole rings is shown, as is the tilt of ring B with respect to the macrocycle.

We wish to report the synthesis and characterization of a monocationic porphyrin species which includes a new anionic halogenocarbonyl rhenium(I) species as the counterion.

When a mixture of $Re(CO)_5Cl$ and H_2OEP in a 2:1 mole ratio was refluxed in decalin under argon for approximately 20 h and then allowed to stand at room temperature, a large quantity of burgundy colored substance crystallized out leaving a solution of dirhenium octaethylporphine complex,[9] $OEP[Re(CO)_3]_2$ (eq 1).

$$4Re(CO)_5Cl + 2H_2OEP \xrightarrow{\text{decalin}} (H_3OEP)^+[Re_2(CO)_6Cl_3]^- + OEP[Re(CO)_3]_2 + 8CO\uparrow + HCl\uparrow \quad (1)$$

The burgundy colored substance was collected by centrifugation, washed with decalin and *n*-pentane, and finally recrystallized from dichloromethane/cyclohexane as dark red crystals, 1, mp 215–220 °C. The structure of the new compound was formulated as $(H_3OEP)^+\cdot[Re_2(CO)_6Cl_3]^-$, monocation octaethylporphinium tri-μ-chloro-hexacarbonyldirhenate(I), based on elemental analysis, spectroscopic data, and a single-crystal x-ray diffraction analysis.

Rhenium forms a series of both monomeric and dimeric carbonyl halide complexes. The preparative,[10–16] mechanistic,[17–18] and spectroscopic properties[19–21] of these complexes have been extensively studied. Four series of anionic halogenocarbonylrhenate(I), i.e., $[Re(CO)_4X_2]^-$, $[Re(CO)_3X_3]^{2-}$, $[Re_2(CO)_7X_3]^-$, and $[Re_2(CO)_6X_4]^{2-}$ have been reported by Abel,[22] Hawkes,[23] and Colton,[24] respectively. All of the possible structures of anionic halogenocarbonylrhenates are deduced from infrared spectroscopic studies.

Compound I has visible absorptions in dichloromethane at 390 (Soret band), 530, 555, 570, and 602 nm. The visible spectrum is extremely similar to that of monocation octaethylporphinium triiodide, $(H_3OEP)^+\cdot I_3^-$ (the only previously known porphyrin monocation salt),[2] and is distinctly different from that of the dication salt, $(H_4OEP)^{2+}\cdot 2Cl^-$.[26] When ethanol is added to the dichloromethane solution of I, the visible spectrum reverts to that of metal free octaethylporphine, H_2OEP. The infrared spectrum of I in the solid state (KBr pellet) has two broad peaks at 3350 and 3375 cm^{-1} attributed to stretching vibrations of the two chemically independent N–H bonds, and three strong metal–carbonyl stretching bands at 1950, 2020, and 2050 cm^{-1}. The far-infrared spectrum of I (in Nujol) has two broad metal–halide stretching peaks at 200 and 250 cm^{-1}. The ^1H NMR solution of I in deuteriochloroform shows two sharp peaks at δ 1.90 (t) and 4.20 (q) for the ethyl substituents and two broad peaks at δ 10.70 and −3.50 for the bridged methine protons and the pyrrolic N–H protons, respectively. The new compound I is moisture sensitive and thermally unstable. It is fairly stable in dry methylene chloride, tetrahydrofuran, and ethyl acetate but decomposes immediately in alcohols, acetone, and water to free octaethylporphine, H_2OEP. It can be kept under argon for several days without decomposition in a vacuum desiccator stored in a refrigerator. However, it decomposes gradually to dirhenium octaethylporphine as indicated by its visible absorption spectrum. This behavior was confirmed by heating a purified sample of I in decalin under argon. Dirhenium octaethylporphine formed in the supernatant while the undecomposed burgundy colored solid of I remained at the bottom of the reaction flask. The amount of the dirhenium octaethylporphine varied with the heating time and temperature. Prolonged heating of I in refluxing decalin caused further decomposition to monorhenium octaethylporphine, $(H\text{-}OEP)Re(CO)_3$, as indicated by its visible absorption spectrum.[9]

By reaction of $H_2MPIXDME$ with stoichiometric quantities of $Re(CO)_5Br$ or $[Re(CO)_4Br]_2$ in refluxing decalin under argon, an analogous salt-like complex of I was prepared: $(H_3MPIXDME)^+[Re_2(CO)_6Br_3]^-$ (II), monocation mesoporphinium IX dimethyl ester tri-μ-bromo-hexacarbonyldirhenate(I). This complex has chemical and spectroscopic properties similar to that of I. Therefore, a structure identical with that of I is proposed for II.

Because of the instability of *meso*-tetraphenylporphine monocation, none of the corresponding monocation tetraphenylporphinium analogues can be prepared; possible reasons for this instability are outlined by Fleischer.[26]

Crystals mounted in capillaries have remained stable over a period of several months.[27] Crystal data for the x-ray structural determination of I: $[C_{36}H_{47}N_4]^+[Re_2Cl_3(CO)_6]^-\cdot H_2O$; M = 1200.6 daltons; space group $P2_1/a$; a = 18.140 (3), b = 19.847 (3), c = 13.625 (2) Å; β = 111.64 (2)°; V = 4559 $Å^3$; Z = 4; d_c = 1.750 g cm^{-3}; linear absorption coefficient, μ, for Cu Kα radiation is 119.5 cm^{-1}. Three-dimensional data were collected using pyrolitic graphite monochromatized Cu Kα radiation (λ 1.541 78 Å) on a Datex-Syntex automated diffractometer. A total of 2905 independent reflections were measured out to 2θ ca. 80°. Of these 2197 were considered observed and were used in the analysis. Absorption corrections were applied to the data.

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares techniques to the present discrepancy indices of R = 0.091 (based on F) and weighted R = 0.103. At the present stage of refinement the thermal motion for all atoms has been assumed to be isotropic. Hydrogen atoms have not been found and thus are omitted from the calculations.

A stereoview of the structure is given in Figure 1. This is the first anionic rhenium(I) halogenocarbonyl species having x-ray structural data reported. The two rhenium ions have octahedral coordination and are joined by three bridging chlorine atoms. Three carbonyl groups on each metal ion complete the coordination. The average Re–Cl distance is 2.51 Å while the average Re–C distance is 1.86 Å. The Re–Re distance is 3.37 Å, far too long to postulate any metal–metal bonding.

A brief note on the structure of the triiodide salt of the monocation octaethylporphinium species has appeared.[2] The porphyrin monocation in the present structure is in many ways very similar, even to the orientation of the terminal carbon atoms of the ethyl groups. In both compounds three rings are approximately coplanar, while the fourth is tilted with respect to the mean plane. In the present case the interplanar angles between the three approximately coplanar pyrrole rings from the mean plane of those rings range from 2.2 to 2.8°. The interplanar angle between this mean plane and the plane of the fourth ring (ring B) is 9.4°.

In the triiodide salt the pyrrolenine ring, which is the pyrrole ring not bearing a hydrogen atom was quite clearly indicated by a C–N–C angle of 102° as compared to angles of 109–110° in the other rings. In the present case the C–N–C angles in two adjacent rings (B and C) are 109.1 and 110.0°, while for the other two rings (A and D) the analogous angles are 106.5 and 104.3°. These two sets of angles are similar to those found in the neutral free bases[1] for pyrrole rings respectively bearing and lacking imino hydrogen atoms. It may be that one imino hydrogen atom position is disordered.

Within the relatively poor standard deviations, other bond lengths and angles in the pyrrole rings agree with those found for the free bases.[8] The distance between the pairs of diagonally situated nitrogen atoms is 4.11 Å for those in rings A and C and 4.06 Å for those in rings B and D.

There is a solvent molecule, most likely a water molecule, present. The oxygen atom is within hydrogen-bonding distance of three of the four pyrrole nitrogen atoms with N···O distances of 2.89–3.07 Å. The fourth N···O distance is 3.20 Å, probably too long to be considered a hydrogen bonding distance. There are no significant short intermolecular contacts between the anion and either the cation or the solvent molecule.

Further study is planned, including measuring a more extended data set to provide greater precision to positional and thermal parameters.

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References and Notes

(1) J. L. Hoard, "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, see especially p 337.

(2) N. Hirayama, A. Takenaka, Y. Sasada, E. Watanabe, H. Ogoshi, and Z. Yoshida, *J. Chem. Soc., Chem. Commun.*, 330 (1974).

(3) (a) D. Ostfeld, M. Tsutsui, C. P. Hrung, and D. C. Conway, *J. Am. Chem. Soc.*, **93**, 2548–2549 (1971); (b) D. Ostfeld and M. Tsutsui, *Acc. Chem. Res.*, **7**, 52 (1974); (c) M. Tsutsui, C. P. Hrung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **97**, 3952 (1975); (d) G. A. Taylor and M. Tsutsui, *J. Chem. Educ.*, **52**, 715 (1975); (e) ref 1, pp 279–313.

(4) M. F. Hudson and K. M. Smith, *Tetrahedron Lett.*, 2223 (1974).

(5) P. Clare and F. Glockling, *Inorg. Chim. Acta*, **14**, L12 (1975).

(6) H. Ogoshi, J. Setsune, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **97**, 6461 (1975), and references therein.

(7) Z. Yoshida, H. Ogoshi, T. Omura, E. Watanabe, and T. Kurosaki, *Tetrahedron Lett.*, 1077 (1972).

(8) E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. McLaughlin, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1236 (1974).

(9) C. P. Hrung, dissertation, Texas A&M University, 1975.

(10) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, *J. Chem. Soc.*, 3149 (1958).

(11) J. G. Dunn and D. A. Edwards, *J. Organomet. Chem.*, **27**, 73 (1971).

(12) B. N. Storhoff, *J. Organomet. Chem.*, **43**, 197 (1972).

(13) D. Vitali and F. Calderazzo, *Gazz. Chim. Ital.*, **102**, 587 (1972).

(14) F. Calderazzo and D. Vitali, *Coord. Chem. Rev.*, **16**, 13 (1975).

(15) R. Colton and J. E. Garrard, *Aust. J. Chem.*, **26**, 529 (1973).

(16) R. Colton and J. E. Garrard, *Aust. J. Chem.*, **26**, 1781 (1973).

(17) F. Zingales, U. Sartorelli, F. Canziani, and M. Ravegli, *Inorg. Chem.*, **6**, 154 (1967).

(18) F. Zingales, U. Sartorelli, and A. Trovati, *Inorg. Chem.*, **6**, 1246 (1967).

(19) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).

(20) W. A. McAllister and A. L. Marston, *Spectrochim Acta, Part A*, **27**, 523 (1971).

(21) M. S. Wrighton, D. L. Morse, and L. Pdungsap, *J. Am. Chem. Soc.*, **97**, 2073 (1975).

(22) E. W. Abel, I. S. Butler, M. C. Ganorkar, C. R. Jenkins, and M. H. B. Stiddard, *Inorg. Chem.*, **5**, 25 (1966).

(23) M. J. Hawkes and A. P. Ginsberg, *Inorg. Chem.*, **8**, 2189 (1969).

(24) R. Colton and J. E. Knapp, *Aust. J. Chem.*, **25**, 9 (1972).

(25) H. Ogoshi, E. Watanabe, and Z. Yoshida, *Tetrahedron*, **29**, 3241 (1973).

(26) A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, **90**, 2735 (1968).

(27) E. F. Meyer, Jr., *J. Appl. Crystallogr.*, **6**, 45 (1973).

C. P. Hrung, M. Tsutsui*
Department of Chemistry, Texas A&M University
College Station, Texas 77843

D. L. Cullen, E. F. Meyer, Jr.
Department of Biochemistry and Biophysics
Texas Agricultural Experiment Station
Texas A&M University
College Station, Texas 77843

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Excited State Acid–Base Reactions of Transition Metal Complexes: Dicyanobis(2,2′-bipyridine)ruthenium(II) in Aqueous Acid

Sir:

We wish to report the first direct observation of an excited state acid–base reaction of a transition metal complex. Excited state acid–base reactions and equilibria in organic systems routinely have been directly observed by emission.[1] In inorganic systems, however, the presence of such reactions has only been inferred from the variation of photochemical yield with pH,[2] or in Cr(III) systems by OH^- quenching of the d-d luminescence,[3] but most results can be explained by reactions subsequent to the primary excited state process.

$Ru(bpy)_2(CN)_2$ (D) is a luminescent donor[4–6] of considerable interest. It exhibits a long-lived charge-transfer (CT) emission in fluid solution, and its neutrality frees it of the electrostatic repulsion and ion pairing problems of the widely used $[Ru(bpy)_3{}^{2+}]$.[7–12] In addition to being a good diffusional donor, D also possesses two CN's which can function as bridging ligands to transition metal ions and which gives rise to static association quenching; the first equilibrium constant can be evaluated from intensity and decay time data.[4,5] The two CN's are both sufficiently basic to be protonated.[13] While attempting to study the static and dynamic quenching of D by H^+, we discovered that $K_{sv}{}^{\tau}$ $(=(\tau_0/\tau - 1)/[H^+])$ was strongly dependent on $[H^+]$. $K_{sv}{}^{\tau} \approx 0.2\ M^{-1}$ at $[H^+] = 1$ M and 0.6 M^{-1} at $[H^+] = 4$ M. This unusual result suggested an excited state acid-base equilibrium, and we reexamined by spectrofluorimetry our original assumption that $[Ru(bpy)_2(CN)(CNH)]^+$ (HD^+) and $[Ru(bpy)_2(CNH)_2]^{2+}$ (H_2D^{2+}) were nonluminescent, instantly quenched species.

Figure 1 shows absorption spectra of D with varying concentrations of $HClO_4$. Up to $[H^+] \sim 0.6$ M, there is a near isosbestic point, and the solution consists predominantly of D and HD^+. At higher $[H^+]$, H_2D^{2+} is also present, and at $[H^+] = 2.5$ M, the mono- and diprotonated forms predominate. In luminescence, however, the sole emission is the broad featureless *D one (λ_{max} 635 nm) regardless of $[H^+]$ or λ_{exc} (350–450 nm). Thus, the only significant emission arises from *D.

To determine the sources of *D in the different solutions,