

Solar Chemistry of Metal Complexes

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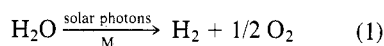
Solar chemistry may be defined as that area of photochemistry in which the excitation energies fall within the spectrum of solar radiation at the surface of the earth. The potential importance of solar chemistry in the generation of energy-rich molecules from cheap, energy-poor raw materials has been discussed by many authors, and the role transition metal complexes could play in such energy storage schemes has received special attention in recent years (*1*).

Summary. Electronic excited states of certain transition metal complexes undergo oxidation-reduction reactions that store chemical energy. Such reactions have been extensively explored for mononuclear complexes. Two classes of polynuclear species exhibit similar properties, and these complexes are now being studied as possible homogeneous sensitizer-catalysts for hydrogen production from aqueous solutions.

This article deals primarily with one area of transition metal solar chemistry, namely, that involving the photochemical properties of several types of polynuclear metal complexes in homogeneous solution. We will begin with some general considerations of photochemical processes and their previous application to photochemical energy storage reactions, and then discuss current research in our laboratory (*2*). We have emphasized polynuclear complexes in our own work because they are promising as robust, efficient absorbers of visible light and because they offer stability in a number of different oxidation states. The latter feature is attractive for the design of systems capable of multielectron oxidation-reduction (redox) reactions in homogeneous solution.

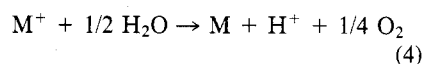
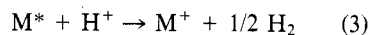
Photochemical Energy Storage Reactions

Of the energy storing reactions discussed for these photochemical systems, by far the most popular has been the splitting of water:



In reaction 1, which stores 2.46 electron volts of chemical energy, M represents a metal complex sensitizer. The reaction

could be accomplished by allowing the sensitizer in its electronically excited form (M^*) to reduce protons to hydrogen, followed by thermal oxidation of water by M^+ :

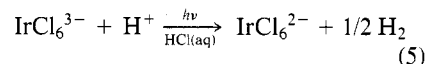


Bolton (*3*) suggests that a system such as that represented by reactions 2 to 4 could be driven by 611-nanometer (2.03-eV) excitation, with as much as 14 percent of the available solar energy stored in chemical form.

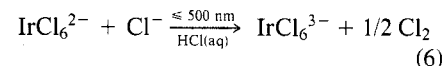
There are several examples of reaction 3 involving high-energy excited states of

simple aqueous complexes of metal ions (*4-7*) (Table 1). Although some of these photoreactions produce oxidants powerful enough to accomplish reaction 4, they involve excitation wavelengths shorter than those found in the solar spectrum. Thus the systems are of interest mainly as mechanistic models.

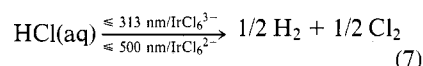
Irradiation of halogen complexes of certain transition metals leads to the production of hydrogen and the corresponding one-electron oxidized species. Recent work with hexachloroiridate (III) is a case in point (*8*):



Once again, relatively high excitation energies are involved, as the quantum yield data for reaction 5 show (Table 2). This system is of interest, however, as the oxidized product IrCl_6^{2-} may be converted photochemically back to IrCl_6^{3-} , producing chlorine:

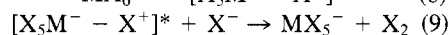
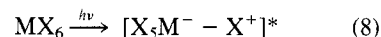


The net result is a photochemical cycle for splitting HCl to hydrogen and chlorine, which involves substantial energy storage:

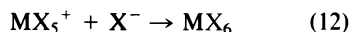
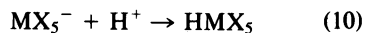


The hydrogen-producing half of this cycle appears restricted to radiation of relatively high energy. However, corresponding electronic transitions are found at lower energy in IrBr_6^{3-} and IrBr_6^{2-} ; thus we hope to demonstrate similar photochemical reactions with light of longer wavelengths in the $\text{IrBr}_6^{3-/2-}$ system.

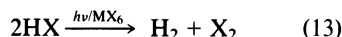
Another possibility is that the charge-transfer excited state of a halogen complex (MX_6) might undergo two-electron redox reactions, leading to the following scheme:



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with the net conversion

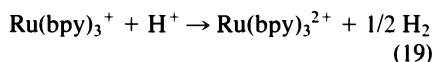
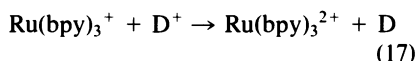
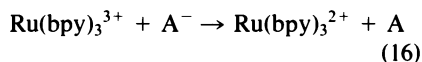
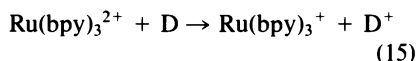
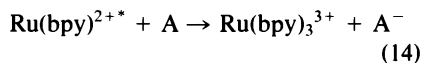


Although ligand dissociation is a well-known process for certain excited states of metal complexes, step 9 would represent a new type of reactivity based on a charge-transfer excited state. Good candidates for these reactions might be systems based on the favorable d^6 (MX_6) and d^8 (MX_5^-) electronic configurations. Again, the process would be more likely to occur with visible light for $\text{X} = \text{Br}$ and $\text{X} = \text{I}$.

Reactions of Long-Lived Excited Metal Complexes

One approach to systems for storage of solar energy has been to initiate a redox reaction by electron transfer quenching of a long-lived excited state of a suitable metal complex (9). A ruthenium complex, $\text{Ru}(\text{bpy})_3^{2+}$ ($\text{bpy} = 2,2'$ -bipyridine), has been extensively used in this manner. A modified Latimer dia-

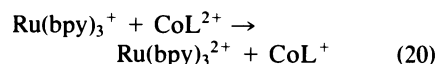
gram illustrating the redox properties of the ground and lowest excited states of $\text{Ru}(\text{bpy})_3^{2+}$ appears in Fig. 1. Energy storage systems based on $\text{Ru}(\text{bpy})_3^{2+}$ have involved electron transfer quenching by suitable acceptors A and donors D, reactions 14 and 15; the energy-wasting back electron transfer steps 16 and 17; and the reduction of protons to hydrogen, reactions 18 and 19:



Gafney and Adamson (10) were the first to observe reaction 14; since then, several strategies have been followed in order to incorporate these reactions into efficient systems for hydrogen production. The back electron transfer reactions 16 and 17 may be inhibited if A^- or D^+ decomposes; this was the case in the experiments of Gafney and Adamson with the acceptor $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, where

the $\text{Co}(\text{II})$ product complex (A^-) hydrolyzed before it could be reoxidized by $\text{Ru}(\text{bpy})_3^{3+}$. Amines are suitable as donors in this respect because their radical cations often decompose in solution. Micellar solutions have also been used to isolate A^- (11) or $\text{Ru}(\text{bpy})_3^+$ (12) physically and thereby to decrease the back electron transfer rate. Finally, the hydrogen-producing steps 18 and 19, which are very slow for $\text{Ru}(\text{bpy})_3^+$ and for most one-electron reductants A^- , can be accelerated by heterogeneous catalysts such as colloidal platinum (13). Grätzel and co-workers (14) showed that solid RuO_2 catalyzes the evolution of O_2 from oxidants such as $\text{Ru}(\text{bpy})_3^{3+}$. By adding both RuO_2 and Pt to the irradiated solution, they combined the two reactions, thereby achieving sensitization of the full water-splitting cycle with visible light.

The problem of conducting reactions 18 and 19 in homogeneous solution is a formidable one. Brown *et al.* (15) developed a system which accomplishes this with a cobalt-based macrocyclic catalyst, $\text{Co}(\text{Me}_6[14]\text{dieneN}_4)(\text{H}_2\text{O})_2^{2+}$ (CoL^{2+} , where L stands for the ligand), according to the following scheme:



Here $\text{Ru}(\text{bpy})_3^+$, produced in reaction 15, reduces the $\text{Co}(\text{II})$ complex by one electron; but the $\text{Co}(\text{I})$ species then acts as a two-electron donor, yielding a molecule of H_2 . The overall cycle is rendered catalytic in both $\text{Ru}(\text{bpy})_3^{2+}$ and CoL^{2+} by reaction 22, in which a second donor molecule is consumed. This system is a major step toward overcoming the limitations imposed by one-electron reactions such as 14 to 19.

Other transition metal complexes have been examined for their ability to undergo bimolecular excited state electron transfer reactions. A bipyridine complex of chromium, $\text{Cr}(\text{bpy})_3^{3+}$, like a number of other $\text{Cr}(\text{III})$ complexes, exhibits phosphorescence from a long-lived metal-centered excited state. In this case the $\text{Cr}(\text{II})$ complex is accessible by reductive quenching of the luminescent excited state (16); and it is reoxidized to $\text{Cr}(\text{III})$ by H^+ in the presence of a noble metal catalyst (17).

Polynuclear Complexes

In recent years photochemical studies in our laboratory have centered on reactions of polynuclear complexes. Our interest arose initially from studies of the

Table 1. Photochemical hydrogen production from simple metal ions (M) in aqueous solution: $\text{M} + \text{H}^+ \xrightarrow{h\nu} \text{M}^+ + 1/2 \text{H}_2$.

M	E° (V)	Solvent	Irradiation wavelength (nm)	Quantum yield of H_2	Reference
Eu^{2+}	-0.43	4.8M HCl	366	0.32	(4)
Cr^{2+}	-0.41	1.9M HCl	254	0.18	(5)
Fe^{2+}	0.77	2.0M H_2SO_4	254	0.20	(6)
Ce^{3+}	1.70	1.0M HClO_4	254	0.0006	(7)

*Standard electrode potential for the couple $\text{M}^+ + \text{e}^- \rightarrow \text{M}$ versus a normal hydrogen electrode.

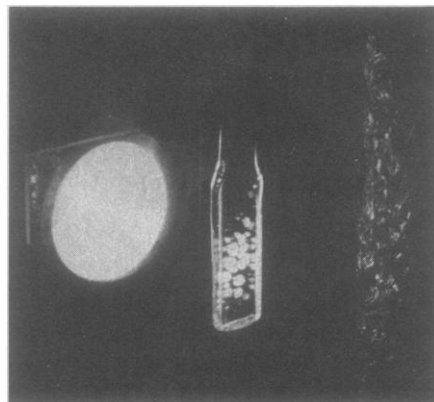
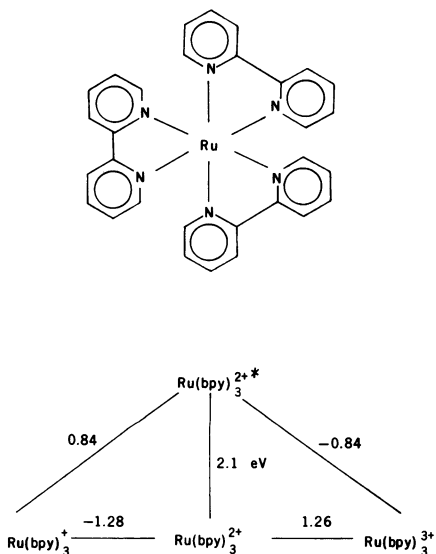
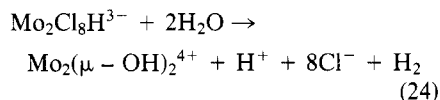
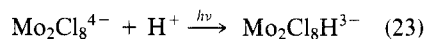


Fig. 1 (left). Structure and modified Latimer diagram (9) for $\text{Ru}(\text{bpy})_3^{2+}$. Electrode potentials versus a normal hydrogen electrode in aqueous solution. Fig. 2 (right). Hydrogen evolution from irradiated aqueous acidic (HBr) solution of $\text{Rh}_4\text{b}_8\text{Br}_2^{4+}$.

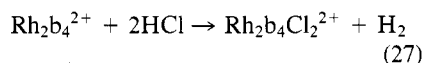
photochemistry of binuclear complexes with strong metal-metal bonds. The data presented in Table 3 (18–25) demonstrate that a number of quadruply bonded binuclear ions yield H₂ on ultraviolet irradiation in acidic solution. The example of Mo₂Cl₈⁴⁻ is of particular interest in that the details of its photochemical reactions may be useful in future studies of polynuclear species:



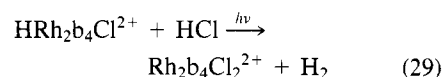
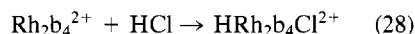
In this scheme Mo₂Cl₈⁴⁻ is protonated photochemically, and the "hydride" character of the Mo₂Cl₈H³⁻ intermediate is manifested in its reduction of water, according to reaction 24 (18). This is an example of one type of reaction we hope to conduct, using visible light, with a polynuclear species represented by M_n:



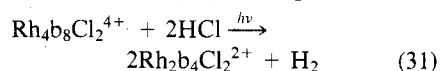
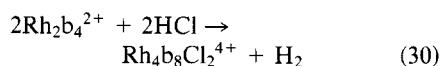
Most of the reactions outlined in Table 3 proceed only with ultraviolet light and therefore cannot form the basis for a solar energy storage system. However, with polynuclear isocyanide complexes, many of which have intense absorption bands in the visible region of the spectrum, we have been able to use light of considerably lower energy. Indeed, the deeply colored solutions that are formed when Rh₂b₄²⁺ (b = "bridge," or 1,3-diisocyanopropane) dissolves in aqueous acid produce H₂ on visible irradiation (22) (Fig. 2). In degassed concentrated HCl each Rh₂b₄²⁺ ultimately gives up two electrons:



We had originally thought that the blue solution formed from Rh₂b₄²⁺ in HCl contained a hydrogen chloride adduct. The evolution of H₂ could presumably be promoted in such a hydride species by irradiation:



We found (23–25), however, that hydrogen is evolved in two steps, the first thermal and the second photochemical:



The tetranuclear structure of the blue Rh₄b₈Cl₂⁴⁺ ion, produced according to reaction 30, was later confirmed by a crystallographic study (26). It is one of a number of polynuclear ions, some containing as many as 12 rhodium atoms, which have been identified in redox equi-

Table 2. Quantum yields for photooxidation of IrCl₆³⁻ by H⁺ in aqueous HCl solutions (254-nm irradiation) (8).

HCl (M)	Quantum yield of H ₂
12.0	0.14
9.0	0.064
6.0	0.012
4.0	0.0046
2.0	0.0043
1.0	0.0033

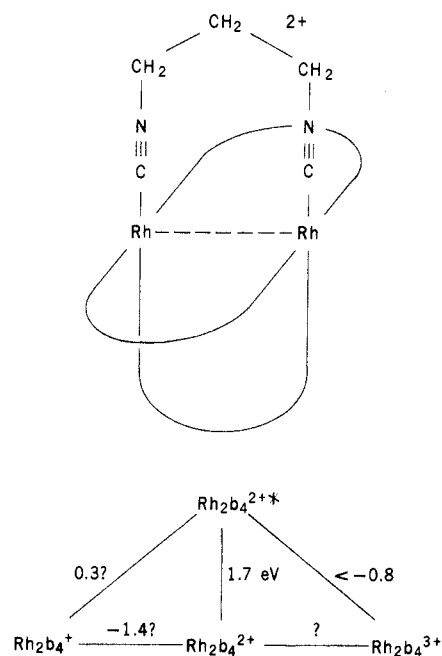


Fig. 3. Structure and modified Latimer diagram for Rh₂b₄²⁺ (30). Numbers are electrode potentials versus a standard calomel electrode in acetonitrile solution.

Table 3. Photochemical hydrogen production from polynuclear metal complexes in aqueous solution.

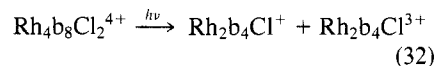
Species	Solvent	Irradiation wave-length (nm)	Products*	Quantum yield of H ₂	Reference
Mo ₂ Cl ₈ ⁴⁻	3M HCl	254	Mo ₂ (μ - OH) ₂ ⁴⁺	0.14	(18)
Mo ₂ Br ₈ ⁴⁻	3M HBr	254	Mo ₂ (μ - OH) ₂ ⁴⁺	0.043	(18)
Mo ₂ ⁴⁺ (aq)	1M CF ₃ SO ₃ H	254	Mo ₂ (μ - OH) ₂ ⁴⁺	0.035	(18)
Mo ₂ (SO ₄) ₄ ⁴⁻	2.5M H ₂ SO ₄	254	Mo ₂ (SO ₄) ₄ ³⁻	0.17	(18, 19)
Re ₂ Cl ₈ ²⁻	12M HCl	< 366†	Re ₂ Cl ₉ ²⁻	< 0.0001	(20)
Re ₂ Br ₈ ²⁻	9M HBr	< 366†	Re ₂ Br ₉ ²⁻	< 0.0001	(20)
Fe ₃ (CO) ₁₁ ²⁻	1M NaOH	254	Fe(OH) ₂ CO	0.011	(21)
Fe ₃ (CO) ₁₁ ²⁻	1M NaOH	313	Fe(OH) ₂ CO	0.0055	(21)
Rh ₄ b ₈ Cl ₂ ⁴⁺	12M HCl	546	Rh ₂ b ₄ Cl ₂ ²⁺	0.0018	(22–25)
Rh ₄ b ₈ Br ₂ ⁴⁺	9M HBr	546	Rh ₂ b ₄ Br ₂ ²⁺	0.022	(22–25)

*Hydrogen was produced in all cases.

†Principally 313 nm.

libria in acidic aqueous solution (27).

We now believe that hydrogen production in reaction 31 is triggered by photodisproportionation of Rh₄b₈Cl₂⁴⁺. One possibility is the direct production of binuclear Rh(I) and Rh(II) species:



This could be followed by hydrogen production from Rh₂b₄Cl⁺, as in reaction 30. The mechanism of reaction 30 itself is uncertain, but may involve the formation of short-lived hydrides such as HRh₂b₄Cl²⁺ (reaction 28). Such adducts have been identified by Smith and Gray (28) in reactions of Rh₂(TMB)₄²⁺ and Ir₂(TMB)₄²⁺ (TMB = 2,5-diisocyanopropane) with various protic acids. In addition to their possible intermediacy in the formation of H₂ from Rh₂b₄²⁺, the hydrides may themselves be photosensitive, as we had originally predicted in reaction 29.

Our studies of polynuclear isocyanide complexes centered originally on their spectroscopic features. Intense fluorescence was observed in early spectroscopic studies of the Rh(I) complexes (29), but more recently we have examined the corresponding triplet states and their phosphorescence (30). The ³A_{2u} excited states of Rh₂b₄²⁺ (Fig. 3) and Rh₂(TMB)₄²⁺ have lifetimes of 8.5 microseconds and 25 nanoseconds, respectively, in acetonitrile solution. Simple molecular orbital theory suggests that the excited states should be more strongly bound, in terms of metal-metal interactions, than the ground states. Recently, experimental evidence in favor of this interpretation has been obtained from low-temperature absorption and emission spectra (31) and from ground and excited state resonance Raman spectra (32).

The long-lived excited states of Rh₂b₄²⁺ and Rh₂(TMB)₄²⁺ undergo oxidative and reductive quenching (30). The use of

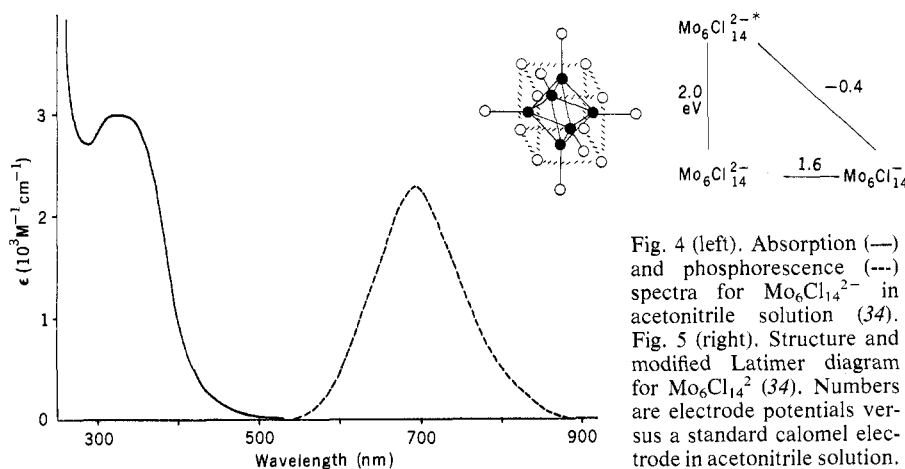
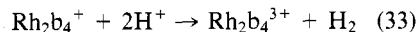


Fig. 4 (left). Absorption (—) and phosphorescence (---) spectra for $\text{Mo}_6\text{Cl}_{14}^{2-}$ in acetonitrile solution (34). Fig. 5 (right). Structure and modified Latimer diagram for $\text{Mo}_6\text{Cl}_{14}^{2-}$ (34). Numbers are electrode potentials versus a standard calomel electrode in acetonitrile solution.

these ions in solar energy storage reactions seemed attractive, because the partially oxidized tetranuclear species $\text{Rh}_4\text{b}_8^{6+}$ (described above as its chloride complex, $\text{Rh}_4\text{b}_8\text{Cl}_2^{4+}$) had already been shown to reduce protons to H_2 photochemically in strongly acidic solution. We hoped that one-electron redox reactions of the rhodium complexes could be utilized in schemes analogous to reactions 14 to 19 for $\text{Ru}(\text{bpy})_3^{2+}$. Indeed, electrochemical studies suggest (33) that the reducing power of Rh_2b_4^+ is sufficient to produce H_2 from aqueous solution. An additional possibility was that the availability of three oxidation states might, as with the cobalt-based cocatalyst studied by Brown *et al.* (15), enable a two-electron reduction to take place:



Although Rh_2b_4^+ , produced in aqueous solutions by reductive quenching, does not appear to reduce water to H_2 quickly enough to compete with back electron transfer, the possibility remains that hydride formation and hydrogen production by such species could be encouraged in strongly acidic solution for complexes of other bridging isocyanides.

Recently, we have been studying another class of polynuclear complexes, the cubic molybdenum and tungsten cluster halide ions, $\text{M}_6\text{X}_{14}^{2-}$. These are luminescent in aqueous and nonaqueous solutions at room temperature (Fig. 4), and the ion $\text{Mo}_6\text{Cl}_{14}^{2-}$ in particular shows an unusually long lifetime for any kind of transition metal complex (180 μsec in acetonitrile) (34). The absorption and emission bands do not display fine structure, making a detailed description of electronic structure difficult. Still, the emissive excited states do appear to be associated with transitions centered on the hexanuclear (M_6) core structure. These cluster halides, therefore, contain

a metal atom core which is bound strongly enough to resist degradation in its lowest excited states.

The $\text{Mo}_6\text{Cl}_{14}^{2-}$ ion can be oxidized in a simple one-electron step; the oxidation has been achieved both electrochemically and photochemically, in the latter case by reaction of the ion's phosphorescent excited state with various electron acceptors. A modified Latimer diagram for $\text{Mo}_6\text{Cl}_{14}^{2-}$, derived from emission spectra and quenching reactions, appears in Fig. 5. Examination of the photoredox reactions of these cluster ions in aqueous solution may indicate a basis for solar energy storage reactions of the type discussed above.

In two classes of polynuclear metal complexes, then, we have been able to associate photoredox activity with strong metal-metal bonding in the excited state. Photophysical studies with $\text{Re}_2\text{Cl}_8^{2-}$ (35) and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ (36) are also of interest: they suggest that, in addition to the high-energy photoionization processes described above (Table 3) for quadruply bonded species, lower energy excited states are available with long lifetimes. The luminescent excited state of $\text{Re}_2\text{Cl}_8^{2-}$, indeed, undergoes both oxidative and reductive quenching (37).

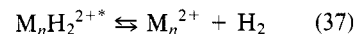
We hope to make use of these photochemically attractive properties in a scheme based on two photochemical studies described earlier in this article. In the hexachloroiridate system, the dramatic increase in photooxidation quantum yield with acidity suggests the consumption of a protonated or hydridic species in the rate-determining step. In the case of $\text{Mo}_2\text{Cl}_8^{4-}$, such an intermediate, $\text{Mo}_2\text{Cl}_8\text{H}^{3-}$, was actually observed. Cluster species offer an advantage over these mono- and binuclear complexes in planning systems for photoredox reactions: in ions such as $[\text{Nb}_6\text{Cl}_{12}]^z$ ($z = 2+, 3+, 4+$) (38) and $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_4]^z$

($z = -, 0, +, 2+$) (39), facile multielectron redox processes occur without major structural change.

In the next phase of photochemical experiments with metal clusters, then, these features should be combined: the possibility of protonation in strongly acidic solutions, and the chance for efficient photoredox reactions without degradation of the clusters. We propose that a metal cluster (M_n) can exist in acidic aqueous solution as an equilibrium mixture of protonated species:



Protonation should be particularly favorable for anionic clusters such as $\text{M}_6\text{X}_{14}^{2-}$. The cluster excited state formed on visible irradiation might then react with a proton in solution to make hydrogen (compare reaction 26), or it might eliminate H_2 directly in its doubly protonated form:



Both processes would lead to the formation of M_n^{2+} , which would (at least in the $\text{Mo}_6\text{Cl}_{14}^{2-}$ system) be an extremely powerful oxidant. In hydrohalic acid solution M_n^{2+} might easily oxidize the solvent, forming oxygen or a halogen while regenerating M_n .

Concluding Remarks

The eventual role of the solar chemistry of metal complexes in fuel production is uncertain. Although there are now several systems that meet many of the criteria demanded for practical solar chemical conversion (40), the cost and especially the lack of durability of the sensitizers and cocatalysts are two critical factors that stand in the way of large-scale applications. It was partly the need for more durable systems that stimulated our research on all-inorganic clusters such as $\text{Mo}_6\text{Cl}_{14}^{2-}$, which could prove to be sturdier in solar chemical cycles than complexes containing organic ligands. It is likely that more clusters will be found whose electronic excited states can undergo oxidation-reduction reactions that store chemical energy.

References and Notes

- See, for example, A. W. Maverick and H. B. Gray, *Pure Appl. Chem.* **52**, 2339 (1980); V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, M. Gleria, *Science* **189**, 852 (1975).
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Determination of Nucleotide Sequences in DNA

Frederick Sanger

In spite of the important role played by DNA sequences in living matter, it is only relatively recently that general methods for their determination have been developed. This is mainly because of the very large size of DNA molecules, the smallest being those of the simple bacteriophages such as ϕ X174 (which contains about 5000 base pairs). It was therefore difficult to develop methods with such complicated systems. There are, however, some relatively small RNA molecules—notably the transfer RNA's of about 75 nucleotides, and these were used for the early studies on nucleic acid sequences (1).

Following my work on amino acid sequences in proteins (2) I turned my attention to RNA and, with G. G. Brownlee and B. G. Barrell, developed a relatively rapid small-scale method for the fractionation of 32 P-labeled oligonucleotides (3). This became the basis for most subsequent studies of RNA se-

quences. The general approach used in these studies, and in those on proteins, depended on the principle of partial degradation. The large molecules were broken down, usually by suitable enzymes, to give smaller products which were then separated from each other, and their sequence was determined. When sufficient results had been obtained they were fitted together by a process of deduction to give the complete sequence. This approach was necessarily rather slow and tedious, often involving successive digestions and fractionations, and it was not easy to apply it to the larger DNA molecules. When we first studied DNA some significant sequences

of about 50 nucleotides in length were obtained with this method (4, 5), but it seemed that to be able to sequence genetic material a new approach was desirable and we turned our attention to the use of copying procedures.

Copying Procedures

In the RNA field these procedures had been pioneered by C. Weissmann and his colleagues (6) in their studies on the RNA sequence of the bacteriophage Q β . Phage Q β contains a replicase that will synthesize a complementary copy of the single-stranded RNA chain, starting from its 3' end. These workers devised elegant procedures involving pulse-labeling with radioactively labeled nucleotides, from which sequences could be deduced.

For DNA sequences we have used the enzyme DNA polymerase, which copies single-stranded DNA as shown in Fig. 1. The enzyme requires a primer, which is a single-stranded oligonucleotide having a sequence that is complementary to, and therefore able to hybridize with, a region on the DNA being sequenced (the template). Mononucleotide residues are add-

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