Coordination Chemistry Reviews, *125* (1993) 1–12

Inorganic Photochemistry – – Then and Now

Arthur W. Adamson

Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0744

Abstract

Some of the early quantitative history of inorganic photochemistry is recalled and some of the early experiences of the writer. Conceptual landmarks in the progress to the present are outlined. The role of the Italian school of photochemistry in this development is noted. The current state of the field is discussed briefly along with some predictions.

1. INTRODUCTION

It was a pleasure to have been part of the symposium honoring Vittorio Carassiti and his career. This introductory paper is written with the intent of conveying some of the history of the development of modern inorganic photochemistry and to do so from a personal, retrospective point of view. Attention will be paid to how my own laboratory developed and how it related to the major school of inorganic photochemistry than began and grew under Carassiti's leadership.

2. EARLY TIMES

Numerous early mentions of color changes of coordination compounds on exposure to sunlight can be found – – after all, the color fastness of dyes and pigments was a matter of some importance. I will mention a few quantitative early studies, most of them with oxalato complexes. An 1880 example is that of Eder's reaction, the photo-reduction of $HgCl_2$ to Hg(I) in the presence of oxalate, with the formation of CO_2 [1]. An excellent 1917 paper by Vranek [2] gives the ratio, R of the rate of photo-decomposition of $Co(C_2O_4)_3^{3-}$ to the absorbed light *energy* per second. It provides an interesting perspective to note that Einstein's law of photochemical equivalence was not yet taken for granted. Thus Vranek cites literature proposing variously that R should

0010-8545/93/$24.00

generally be independent of wavelength, λ, that it should be proportional to λ, or that log (Rε) should be inversely proportional to λ, ε being the frequency of the light. His actual finding was that R decreased linearly with increasing λ. He calculates as an afterthought a few quantum yields as we would define them today. The flavor became distinctly more modern in a 1930 paper introducing the uranyl oxalate actinometer [3]. There were early studies of Cr(III) and Co(III) complexes by Schwarz and co-workers in the 1920's [4] and by Linhard and Weigel in the early 1950's [5]. These last authors showed laboriously produced absorption spectra and to some extent related spectral features with the type of photochemistry.

Our own first experience with photochemistry fell within this period. In a study of the thermal exchange of $^{14}CN^-$ with various cyano complexes we found the rate of exchange with $Mo(CN)_8^{4-}$ to be independent both of CN^- and of complex concentration! We then realized that the exchange was induced by the newly installed fluorescent lights, and so reported it in 1950 [6]. That's the way it was forty years ago.

3. THE BEGINNINGS OF CONTEMPORARY INORGANIC PHOTOCHEMISTRY--THE WAY IT WAS FOR US

Our own interest really began with a sabbatical visit in 1954 to the laboratory of J. Bjerrum in Copenhagen. I was impressed by the collection of Cr(III) and Co (III) complexes dating from the days of S.M. Jørgensen and by anecdotal mentions of their sensitivity to sunlight, reinforcing our earlier experience with $Mo(CN)_8^{4-}$. It was after this visit that we started a serious study of the photochemistry of Werner-type complexes, using a bolometer made in our departmental shops. The first results were reported at the 1957 International Conference on Coordination Chemistry (ICCC) in Rome. It was the only photochemical paper; the emphasized topics were spectroscopy, especially infrared (IR), stability constants, structure, and magnetic properties. It was at this meeting that I met and became acquainted with Vittorio Carassiti and his work on optical activity. Our photochemical paper was published the following year [7]. The Italian school of photochemistry started about then and developed rapidly--the first of an eventual flood of papers from Carassiti and his group appeared in 1959 [8], followed by one with Vincenzo Balzani [9], both greatly clarifying the photochemistry of octacyano complexes. Other important contemporary papers were those by Plane and Hunt [10] on the photo-exchange of $H_2{}^{18}O$ with $Cr(H_2O)_6^{3+}$and by Parker and Hatchard on ferrioxalate actinometry [11] (oxalates again!). We later added an actinometry system involving Reinecke's salt, $KCr(NH_3)_2(NCS)_4$, which functioned at longer wavelengths [12].

Other schools of photochemistry developed during the 1960's, such as that of H.L. Schläfer in Frankfurt. There were, in addition, groups whose primary interest was in synthetic chemistry or in the kinetics or the spectroscopy of coordination compounds and who also published important photochemical papers. Examples include those by W. Strohmeier and co-workers in Germany [13], on carbonyl complexes, G. Emschwiller in France, on cyano complexes, and A. A. Grinberg in Russia on platinum ones. The Italian group began expanding--L. Moggi joined Balzani and Carassiti in 1964 with a paper on the photochemistry of some Fe(II) cyano complexes [14]. By the late 1960's and early 1970's laboratories such as those of H.F. Wasgestian in Germany, G.B. Porter and A.D. Kirk in Canada, J.F. Endicott and M.Z. Hoffman, P. Ford, H.B. Gray, and M. Wrighton in the U.S. became known. Some of this development is cited in our 1968 review paper [15]. As a typical first, the Carassiti group provided in 1970 a now classic monograph [16]. Other books followed [17-19] but the most current reference, published in 1991, is again from the Italian school [20].

Inorganic photochemists at first presented their work at meetings and symposia as lonely and scattered contributions within some larger topic. We appeared, for example, at ICCC meetings, at other symposia on coordination chemistry such as Gordon Conferences and the 1974 Bressanone meeting, at national chemical society meetings, at spectroscopic society meetings, and at organic photochemical symposia. We would collect on such occasions as a small fraternity (we even composed our own "photosongs"). As the field grew, our papers became grouped in their own sessions. We developed our own satellite conference preceding some more general event, and then our own symposium, the International Symposium on the Photophysics and Photochemistry of Coordination Compounds, or ISP^{2}C^2. Locally, we initiated an annual student symposium which rotated among five Southern California universities, the first being held in 1975 at my university's marine research station on Catalina Island. This early brotherhood has weakened as the field has matured and developed its own sub-specialities such as laser photophysics, organometallic and bio-inorganic photochemistry, solar energy conversion, thin film systems, modified electrodes, etc.. These sub-areas again have started as components of larger meetings, and have now begun anew the process of developing their own, separate symposia. It has been quite an evolutionary process.

In what follows, I outline my experiences with the developmental history of inorganic photochemistry and then describe a major development, that of sensitization and other bimolecular excited state processes.

4. JOURNEYS OF DISCOVERY--EXCITED STATE CHEMISTRY

Theoretically minded chemists began evolving the crystal field theory of physicists into ligand field theory and in a form usable by coordination chemists, and this process was well developed by the early 1960's [21-24]. This, and the advent of the recording uv-visible spectrophotometer which made it easy to obtain accurate and detailed absorption spectra, permitted coordination photochemists to make probably correct or at least informative excited state assignments. This aspect showed up in our 1968 review paper [15] and more so in the book by Balzani and Carassiti [16].

Qualitative generalizations could be made. Irradiation of a charge-transfer-to-metal, CTTM, band of a Co(III) complex led to redox decomposition, while the ligand field bands were photo-inert (later, we showed this last to be a matter of degree [25]). Spin-allowed ligand field bands of Cr(III) complexes were active toward ligand substitution. Discussion began to focus on the specific chemical reactivity of various excited states. Of help was the obtaining of partial quantum yields, that is, separate yields for two or more reaction modes, as in the wavelength dependence of the ratio $\phi_{redox}/\phi_{aquation}$ for $Co(NH_3)_5Br^{2+}$ [26]. We proposed a cage mechanism [7], an enduring although sometimes disputed model [27]; a version of it was used by the Italian group in explaining the photo-linkage isomerization of $Co(NH_3)_5(NO_2)^{2+}$ [28] (correcting our mistaken report of photoaquation). With the help of an Italian collaborator, Edoardo Zinato, we similarly determined the variation with wavelength of ϕ_{NH_3} and ϕ_{NCS^-}, the two photoaquation products of $Cr(NH_3)_5(NCS)^{2+}$ [29], as shown in Fig. 1. Note that not only were the yields different but their *ratio* was different on irradiation of the quartet bands vs. the doublet band. The results suggested different chemistries for different excited states and reinforced an earlier set of generalizations on Cr(III) photochemistry that came to be known as "Adamson's Rules" [30]. These rules recognized that with Cr(III) ammines the photoproduct was not neccessarily the same as that for the thermal aquation reaction, that is, the photochemistry could be *antithermal*. The stereochemistry also could be different from that expected from thermal

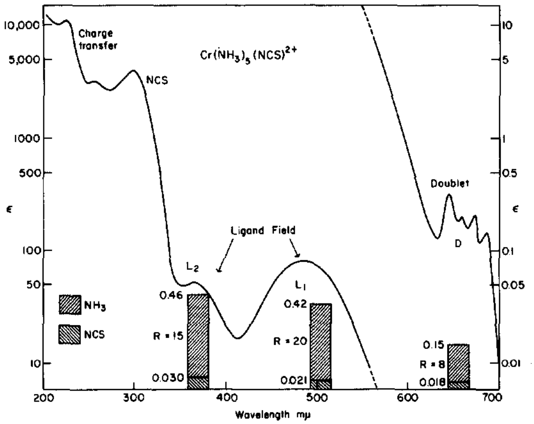

Figure 1. Absorption sperctrum for $Cr(NH_3)_5(NCS)^{2+}$ in aqueous solution. Bars show quantum yields for ammonia and for thiocyanate aquation at the indicated wavelengths and R is their ration. From Ref. 29.

substitutional chemistry. Thus *trans*-$Cr(en)_2Cl_2^+$(endenoting ethylenediamine) photoaquates Cl^-, as predicted by the rules, but gives predominantly *cis*-$Cr(en)_2(H_2O)Cl^{2+}$ [31]. In a further Italian collaboration, we established by isotopic labelling that the rules did predict which actual ligand would be photo-labilized in a Cr(III) ammine complex, but also concluded that the reactive excited state was probably not octahedral in geometry, but was significantly distorted [32]. Where such distortion was prevented by the ligand framework, as in *trans*-$Cr(cyclam)Cl_2^+$ (cyclam is a ring ligand having four coordinating amine functions) which is incapable of giving a *cis*-aquo product, the complex was photo-inert [33]. Various laboratories have pursued this matter of Cr(III) photophysics and excited state stereochemistry, in Italy most notably that of Zinato.

A great advance in sophistication came when chemists learned from spectroscopists that many coordination compounds show photo-excited emission, usually first reported for low temperature crystals or glasses, and carried such studies to room temperature aqueous solution. Thus while low temperature emisson spectra and lifetimes for the doublet excited state of Cr(III) complexes had been reported fairly early [34], it was rather later that the positions of emission maxima (but no lifetimes) were reported under aqueous conditions [35]. The Italian group also made use of emission intensities [36]. It was exciting to us, however, to make our first emission *lifetime* measurements under photochemical conditions (with the use of a pulsed laser at the University of Utah) [37]. We then acquired a powerful Nd glass laser of our own, and in due course made a number of lifetime measurements in room temperature solutions; some additional "rules" were generated for Cr(III) emissions [38].

The question of what excited state is the chemically active one was, of course, of great interest. H.L. Schläfer had proposed as early as 1957 that Cr(III) photochemistry was due to the doublet excited state [39], and this mechanism became popular. Adamson's rules, however, strongly indicated that the first excited quartet state was the reactive one; there ensued a period of lively experimentation and discussion. A type of excited state diagram that we favored is shown in Fig. 2. It now appears that, depending on the particular Cr(III) complex, one or the other excited state may be the principal one leading to chemical reaction; the important point, however, is that each excited state can have different, distinctive substitutional chemistry and stereochemistry.

I can use Fig. 2 to illustrate an additional matter. There is a considerable Stokes' shift between the absorption band maximum and that of the emission in the case of the spin-allowed transitions of octahedral complexes, and of Cr(III) ones in particular. Optical transitions are expected by the Franck-Condon principle to be "vertical" and the presence of the Stokes' shift implies that absorption of a light quantum produces an excited state with a degree of vibrational excitation, a *Franck-Condon* state. This state then thermally equilibrates before undergoing emission; the process is indicated by the slanted vibrational ladder in the figure. We called such thermally equilibrated states *thexi* states in a collaborative review with G. Sartori and concluded that it is from thexi states that photochemical reactions generally occur [40].

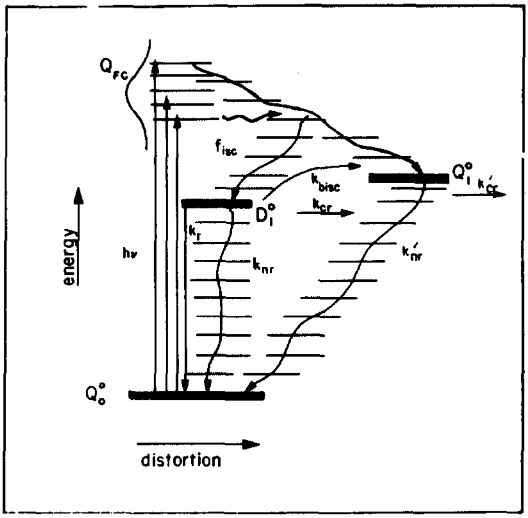

Figure 2. Schematic excited state scheme for a Cr(III) complex. Q and D denote quartet and doublet state, respectively; light horizontal lines indicate vibrational levels. Superscripts zero denote thermally equilibrated states; subscripts zero and one denote ground state and excited state, and PC denotes a Franck-Condon state. Optical transitions are shown as vertical arrows, and radiationless processes, as wavy arrows.

As I have indicated, a major mechanistic concern among inorganic photochemists was with the question of which is the reactive excited state for octahedral complexes. The detailed mechanism by which that state reacted could only be approached indirectly, as through the stereo-chemical behavior. The situation was thus somewhat in contrast with a major preoccupation of coordination chemists during the 1950's and 1960's, namely the detailed *mechanism* of thermal substitution reactions of transition metal complexes. There was exciting controversy in this area [41]; the terms S_N1, S_N2, S_N1CB had passionate advocates. We tended to assume tacitly that whatever mechanism applied to ground state ligand substitution was likely to hold for the excited state process. Only occasionally was some thought given to the fact that excited state distortion constituted a serious complication. In brief, we tended to be more concerned with the nature of the excited state than with that of the transition state.

The photochemistry of many other classes of coordination compounds was studied during the 1960's and 1970's, as is evident from Refs. 15-19. F. Basolo and co-workers, for example, had an early publication on some Rh(III) and Ir(III) complexes [42]. For a period the Carassiti group was very interested in cyano complexes (e.g. Refs. 8, 9, 14) but the attention of the Italian group quickly expanded to include Co(III) and Pt(II) complexes (e.g. Refs. 27, 28), those of Cr(III) (e. g. Ref. 36) and other families. In due course, we looked at Rh(III) ammines [43] and Pt(II) complexes such as Zeise's salt, $Pt(C_2H_2)Cl_2$ [44]. The range of ligands used expanded, as with the use of the cyclam ligand mentioned above, and the equatorial ligand PnAO, here again with Italian collaboration [45], and the use of sepulchrates [46] and cryptates [47] by the Italian school.

New kinds of photoreactions were investigated, an interesting one being that of photo-electron production. This was reported for $Fe(CN)_6^{4-}$ in 1963 [48] and we later found the same process for $Mo(CN)_8^{4-}$ and other cyano complexes, as well as for $IrCl_6^{3-}$ [49]. It was our first experience with flash photolysis--the equipment was of the old high voltage flash tube kind, using an adapted x-ray transformer as the voltage source.

4. JOURNEYS OF DISCOVERY—BIMOLECULAR EXCITED STATE PROCESSES

Excitation energy transfer between coordination compounds in the solid state was reported in the 1960's by H.L. Schläfer's group [50], along with similar observations from those of L.S. Forster [51] and G.A. Crosby [52]. The related process of sensitization, that is, chemical reaction induced by excitation energy transfer, had been studied in the early 1960's by organic photochemists [53, 54]. It was not until 1968, however, that A. Vogler in my laboratory found that common organic sensitizers such as benzophenone could sensitize coordination compounds, in this case various Co(III) ammines [55]. We extended the phenomenon to Cr(III) ammines, again with an Italian collaborator [56]. Carassiti's group followed closely in showing in 1969 that one could avoid potential mechanistic questions by using a sensitizer that did not have hydrogen abstraction ability [57]. I remember the animated discussion on sensitization during a visit to Bologna that year. Other examples of excitation energy transfer followed quickly. An important feature at this stage of development was that kinetic, that is, Stern-Volmer plots now allowed a relation between the donor excited state lifetime and the bimolecular rate constant for the donor-acceptor energy transfer. One of our more elegant little papers, with Kane-Maguire and co-workers, demonstrated reversible excitation energy transfer between $Cr(NH_3)_5(NCS)^{2+}$ and $Cr(CN)_6^{3-}$ and showed what complexity could be studied with the use of a pulsed laser [58].

The next voyage of discovery began for us with the arrival of J. Demas, bringing interesting experiences with the unusually strong emission from $Ru(2,2'\text{-bipyridine})_3^{2+}$, which we came to call *rubipy*. He found in rubipy a new sensitizer and probably the first case of excitation energy transfer between two transition metal complexes in room temperature fluid solution. [59]. Rubipy proved to be a widely used sensitizer; the Italian group, for example, tested the quenching of its emission by Co(III) and Ni(II) complexes of various charges [60]. A whole new adventure began with the finding by H. Gafney, another arrival to our group, that rubipy not only sensitized the redox decomposition of $Co(NH_3)_5Br^{2+}$ but in so doing gave $Ru(2,2'\text{-bipyridine})_3^{3+}$ as a product. We proposed the then controversial idea of excited state electron transfer [61]. Additional work confirmed the mechanism as did work in other laboratories such as that of N. Sutin [62]. Actually, the idea of excited state electron transfer came naturally to us because of our experience with photo-electron production--after all, transfering an electron to a reducible complex is less drastic than forcing one into solvent water. The finding was exciting to us as a new phenomenon in inorganic photochemistry; it also allowed us to write redox cycles leading to the photo-induced decomposition of water, that is, to solar energy conversion. A by-product of our discovery was the boost it gave to electron transfer kineticists looking for high-energy redox reactions in their testing of Marcus theory. These various aspects of rubipy photochemistry have stimulated probably thousands of papers. We restricted our own pursuits in this area--my philosophy in such matters is described informally in this journal in a 1991 interview by R. Bau [63].

Another type of bimolecular excited state reaction involves the use of a quencher to inhibit emission and photochemistry. Examples now abound in the literature; a pleasing one for us was in the study of $W(CO)_5L$ complexes. We were able to place the energy of the reactive excited state through the use of a series of acceptor species [64]. The Italian group has, in particular, pursued the challenge of estimating all of the various rate contstants in an excited state scheme such as that of Fig. 2, through the use of a spectrum of photochemical and photophysical techniques [65].

Some less widely studied types of inorganic photochemical behavior are the following, the references being mostly to our work but which will in turn cite that of other laboratories. The phenomena are: photochromism [66], photocalorimetry [67] and the photoacoustic effect [68], chemiluminescence [69], and pulsed laser triboluminescence [70].

This outline of our work and that of the Italians brings us to the mid 1980's. Most of the basic types of phenomena have been mentioned and much of contemporary research builds on this background. The current state of affairs and possible new directions are noted in the concluding section.

5. JOURNEYS IN PROGRESS

One of the important contemporary explorations is instrumental. Laser equipment which, for us allowed exploration down to short nanoseconds, has been extended in capability to the picosecond and long femtosecond time scale [71]. It is possible to observe state-to-state processes, that is, to determine particular vibronic initial and final states. My own feeling, however, is that it is more important to the coordination photochemist to characterize reactive thexi states. Note that "state" in this connotation refers to a thermodynamic ensemble, not a spectroscopic state; thexi states have energy, entropy, standard redox potentials, and their rate processes can be treated by conventional chemical kinetics. They also have structure, and an important achievement has been the use of excited state Raman spectroscopy, as in the case of rubipy [72]. ESIR or excited state IR spectroscopy, an important structure determing tool, has come more slowly. We investigated the use of the plasma formed by an intense laser pulse as a source of white IR radiation, but did not complete the project [73]. Recently, Woodruff and co-workers have made successful use of IR pulses from the beat frequency of two laser sources to obtain actual ESIR spectra [71]. This is an important matter. We should know much more than we do now about the electronic and geometric structures of thexi states; such states are, after all, the "reagents" of photochemistry. The equipment involved in ESIR spectroscopy is specialized and expensive and for this reason there will likely be increasing cooperation between photochemical and molecular spectroscopy laboratories in joint ventures. Such information is bound to come; much successful use has already been made of IR spectra of reactive intermediates such as $M(CO)_5$ species produced photochemically in low temperature matrices [74].

There is much contemporary activity in the matter of solar energy conversion; a major laboratory is that of M. Grätzel [75]. An important, continuing activity is that of the surface modification of electrodes by attaching coordination compounds of the rubipy type [76]. This brings us to what Balzani has called "supramolecular" photochemistry, or the devising and study of multicentered photochemical systems. The field has been well described by the Italian group [20] and is a growing one. We can expect in due course the development of practical solar electrochemical cells using coordination compounds.

Finally, the area of inorganic, organo-metallic, and bio-organic photochemistry in solution remains a vast one. Research now and to come will be increasingly physical chemical in using all the techniques described earlier to obtain detailed excited state schemes and rate constants. Detailed mechanisms of thexi state reactions will be pursued. There will be increasing numbers of studies of photochemistry and photophysics at interfaces and within porous solids [77] and gels [78].

For us and for the Italians, inorganic photochemistry has come a long ways from the 1950's. To adopt a famous phrase, our field indeed has an endless frontier !

6. REFERENCES

1 J. Eder, Chem. Ber., 13 (1880) 166.
2 J. Vranek, Z. Electrochem., 23 (1917) 336.
3 W. G. Leighton and G. S. Forbes, J. Amer. Chem Soc., 52 (1930) 3139.
4 For example: R. Schwarz and K. Tede, Ber., 60B (1927) 69.
5 For example: A. Linhard and M. Weigel, Z. anorg. allgem. Chem., 266 (1951) 49.
6 A. W. Adamson, J. P. Welker, and M. Volpe, J. Amer. Chem. Soc., 72 (1950) 4030. Note: Welker's thesis gives a quantum yield of 7.5 for the exchange, based on uranyl oxalate actinometry, and notes an interesting sequence of color changes.
7 A. W. Adamson and A. H. Sporer, J. Amer. Chem. Soc., 80 (1958) 3865. The same paper appears in a Supplement to La Ricerca Scientifica (1958) 1.
8 V. Carassiti and M. Claude, Ann. di Chimica, 49 (1959) 1697.

9 V. Carassiti and V. Balzani, Ann. di Chimica, 50 (1960) 630.
10 R. A. Plane and J. P. Hunt, J. Amer. Chem. Soc., 79 (1957) 3343.
11 C. A. Parker and C. C. Hatchard, J. Phys. Chem., 63 (1959) 22.
12 E. E. Wegner and A. W. Adamson, J. Amer. Chem. Soc., 88 (1966) 394.
13 For example: W. Strohmeier and D. von Hobe, Chem. Ber., 94 (1966) 761.
14 V. Balzani, V. Carassiti, and L. Moggi, Ann. di Chimica, 54 (1964) 251.
15 A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P.D. Fleischauer, and R. D. Lindholm, Chem. Rev., 68 (1968) 54.
16 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, New York, 1970.
17 A. W. Adamson and P. D. Fleischauer (eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975.
18 G. L. Geoffroy and M. S. Wrighton, Organometallic Photochemistry, Wiley, New York, 1979.
19 G. J. Ferraudi, Elements of Inorganic Photochemistry, Wiley, New York, 1988.
20 V. Balzani and F. Scandola, Supramolecular Photochemistry, Ellis Horwood, New York, 1991.
21 C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962.
22 C. K. Jørgensen, Absorption Spectra and Bonding in Complexes, Pergamon, New York, 1962.
23 T. M. Dunn, D. D. McClure, and R. G. Pearson, Crystal Field Theory, Harper & Row, New York, 1965.
24 B. N. Figgis, Introduction to Ligand Fields, Interscience, New York, 1966.
25 R. A. Pribush, C. K. Poon, C. M. Bruce, and A. W. Adamson, J. Amer. Chem. Soc., 96 (1974) 3027. Note: this was our first use of a continuous laser, with which we could use a long path-length, small diameter photolysis cell in the study of very low quantum yield systems.
26 A. W. Adamson, Disc. Far. Soc., No. 29 (1960) 163.

27 V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, Inorg. Chim. Acta Rev., 1 (1967) 7.
28 V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, Inorg. Chem., 7 (1968) 1398.
29 E. Zinato, R. D. Lindholm, and A. W. Adamson, J. Amer. Chem Soc., 91 (1969) 1076.
30 A. W. Adamson, J. Phys. Chem., 71 (1967) 798.
31 A. D. Kirk, K. C. Moss, and J. G. Valentin, Can. J. Chem., 48 (1971) 1524.
32 E. Zinato, P. Riccieri, and A. W. Adamson, J. Amer. Chem. Soc., 96 (1974) 375.
33 C. Kutal and A. W. Adamson, J. Amer. Chem. Soc., 93 (1971) 5581.
34 For example: K. DeArmond and L. S. Forster, Spectrochim. Acta, 19 (1963) 1687.
35 N. A. P. Kane-Maguire and C. H. Langford, Chem. Comm., (1971) 895.
36 R. Ballardini, G. Varoni, H. F. Wasgestian, L. Moggi, and V. Balzani, J. Phys. Chem., 77 (1973) 2947.

37 A. W. Adamson, C. Geosling, R. Pribush, and R. Wright, Inorg. Chim. Acta, 16 (1976) L5.
38 R.T. Walters and A.W. Adamson, Acta Chim. Scand., A33 (1979) 53.
39 H.L. Schläfer, Z. physik. Chem., 11 (1975) 65: J. Phys. Chem., 69 (1965) 2201.
40 P.D. Fleischauer, A.W. Adamson, and G. Sartori, Inorganic Reaction Mechanisms, Part II, J.O. Edwards (ed)., Wiley, New York, 1972. See also A.W. Adamson, Advances in Chemistry Series, No. 150, R.B. King (ed.), American Chemical Society, Washington, D.C., 1976, p. 128.
41 For example: F. Basolo and R.G. Pearson. Mechanisms of Inorganic Reactions, Wiley, New York, 1958; J. Lewis and R.G. Wilkins. Modern Coordination Chemistry, Intersciuence, New York, 1960. The flavor of the times is well captured in the monograph: R.K. Murmann, R.T.M. Fraser, and J. Bauman, Mechanisms of Inorganic Reactions, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D.C., 1965.
42 R.A. Bauer and F. Basolo,. J. Amer. Chem. Soc., 90 (1968) 2437.
43 C. Kutal and A.W. Adamson, Inorg. Chem., 12 (1973) 1454.
44 P. Natarajan and A.W. Adamson, J. Amer. Chem. Soc., 93 (1971) 5599
45 F. Diomedi-Camassei, E. Nocchi, G. Sartori and A.W. Adamson, Inorg. Chem., 14 (1975) 25.
46 For example: F. Pina, M. Ciano, Q.G. Mulazzani, M. Venturi, V. Balzani, and L. Moggi, Scientific Papers of the Institute of Physical and Chemical Research, 78 (1984) 166.
47 N. Sabbatini, M. Ciano, S. Dellonte, A. Bonazzi and V. Balzani, Chem. Phys. Lett., 90 (1982) 265.
48 M.S. Matheson, W.A. Mulac, and J. Rabini, J. Phys. Chem., 67 (1963) 2613.
49 W.L. Waltz, A.W. Adamson and P.D. Fleischauer, J. Amer. Chem. Soc., 89 (1967) 3923; W.L. Waltz and A.W. Adamson, J. Phys. Chem., 73 (1969) 4250.
50. H. Gausmann and H.L. Schläfer, J. Chem. Phys., 48 (1968) 4056.

51. D.J. Binet, E.L. Goldberg, and L.S. Forster, J. Phys Chem., 72 (1968) 3017.
52. G.A. Crosby, R.E. Whan, and R.M. Alire, J. Chem Phys., 34 (1961) 743.
53. J.G. Calvert and J.N. Pitts, Jr., Photochemistry, Wiley, New York, 1966.
54. For example: G.S. Hammond and J. Saltiel, J. Amer. Chem. Soc., 84 (1962) 4983.
55. A. Vogler amd A.W. Adamson, J. Amer. Chem. Soc., 90 (1968) 5943.
56. A.W. Adamson, J.E. Martin, and F. Diomedi-Camassei, J. Amer. Chem. Soc., 91 (1969) 7530.
57. M.A. Scandola, F. Scandola, and V. Carassiti, Mol . Photochem., 1 (1969) 403.
58. N.A.P. Kane-Maguire, C.G. Toney, B. Swiger, A.W. Adamson, and R. E Wright, Inorg. Chim. Acta, 22 (1977) L11.
59. J.N. Demas and A.W. Adamson, J. American Chem Soc., 93 (1971) 1800.
60. F. Bolleta, N, Maestri, L. Moggi, and V. Balzani, J. Amer. Chem. Soc., 95 (1973) 7864.
61. H.D. Gafney and A.W. Adamson, J. Amer. Chem. Soc., 94 (1972) 8238.

62. G. Navon and N. Sutin, Inorg. Chem. , 13 (1974) 2159.
63. R. Bau, Coor. Chem Rev., 110 (1991) 1.
64. A.J. Lees and A.W. Adamson. J. Amer. Chem Soc., 104 (1982) 3804.
65. For example: V. Balzani, F. Bolletta, and F. Scandola, J. Amer. Chem. Soc., 102 (1980) 2152.
66. C. Geosling, A.W. Adamson, and A.R. Gutierrez, Inorg, Chim Acta, 29 (1978) 279.
67. A.W. Adamson, A. Vogler, H. Kunkeley, and R. Wachter, J. Amer. Chem. Soc., 100 (1978) 1298.
68. K. Peters, Science, 241 (1988) 1053.
69. L. El-Sayed and A.W. Adamson, Inorg. Chim. Acta, 132 (1987) 105.
70. G.E. Hardy, B. P. Chandra, J.F. Zink, A.W. Adamson, R.C. Fukuda, and R.T. Walters, J. Amer. Chem. Soc., 101 (1979) 2787.
71. See for example: S.K. Doorn, P.O. Stoutland, R.B. Dyer, and W.H. Woodruff, J. Amer. Chem. Soc., 114 (1992) 3133.
72. R.F. Dallinger and W.H. Woodruff, J. Amer. Chem. Soc., 101 (1979) 4391.
73. A.W. Adamson and M. Cimolina, J. Phys. Chem., 88 (1984) 488.
74. See for example: R.N Perutz and J, Turner, Inorg. Chem., 14 (1975) 262; M.A. Graham, A.J. Rest, an J.J. Turner, J. Organomet. Chem., 24 (1970) C54.
75. For example: P. Liska, N. Vlachopoulus, M.K. Nazeerruddin, P. Comte, and M. Grätzel, J. Amer. Chem. Soc., 100 (1988) 3686.
76. C.A. Bignozzi and F. Scandola, J. Amer. Chem. Soc., 112 (1990) 7099.
77. T. Kennelly, H.D. Gafney, and M. Braun, J. Amer. Chem. Soc., 107 (1985) 4431.
78. A. Alama-Schwok, M. Ottoleeghi, and D. Avnir, Nature, 365 (1992), Jan. 16 issue.