

PHOTOCHEMISTRY OF COORDINATION COMPOUNDS OF THE MAIN GROUP METALS

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SUMMARY

A general concept is developed which relates characteristic excited states of main group metal complexes to typical photoreactions. With regard to their electronic spectra and photochemistry the main group metals are classified according to their ground state electron configuration ns^2np^2 . The photochemistry is generally dominated by the reactivity of metal-centered sp and ligand to metal charge transfer excited states which in most cases initiate inter- and intramolecular photoredox processes.

INTRODUCTION

The discussion of the photochemistry of coordination compounds is almost exclusively restricted to complexes of transition metals (refs. 1-4). Although some scattered observations on the light sensitivity of coordination compounds of main group metals have been reported, this important aspect of inorganic photochemistry has been largely ignored. To some degree this lack of knowledge seems to be related to the kinetic lability of complexes of main group metals. In many cases well-defined compounds do not exist in solution, particularly in water. However, in organic solvents which are weakly coordinating many main group metal complexes dissolve without decomposition and are thus susceptible to detailed photochemical studies. In many cases the investigation of the photochemistry of transition metal complexes was stimulated by the accidental observation of their light sensitivity. This is especially true for colored compounds which are photolyzed by visible irradiation. On the contrary, most main group metal compounds are colorless and may be sensitive only to UV light.

During recent years we have tried to develop a general concept which relates characteristic excited states to typical reactions of main group metal complexes. This review is the first attempt to summarize these observations and ideas. It is not intended to present a comprehensive survey but rather selected examples of the nature and reactivity of excited states of main group metal compounds. Organometallics are omitted here. Although many of these compounds are known to be photosensitive the nature of their excited states is less clear due to the extensive electron delocalization and covalent bonding in these molecules.

ELECTRON CONFIGURATIONS OF THE MAIN GROUP METALS

In analogy to the transition metals the main group metals can be classified according to the electron configuration in their ground states. The valence orbitals of the main group elements are ns and np orbitals. Starting with an empty valence shell stable complexes are formed with the electron configurations s^0 , s^1 , s^2 , s^2p^2 , and s^2s^4 . In contrast to the transition metals the main group metals form generally diamagnetic complexes with an even number of valence electrons. In the case of the s^1 configuration stable complexes contain two metals which are linked by a metal-metal bond.

 s^0

When all valence electrons are removed the highest oxidation state with the s^0 configuration is obtained. Typical metal ions are those of the third to fifth main group: Ga^{III} , In^{III} , Tl^{III} , Ge^{IV} , Sn^{IV} , Pb^{IV} , and Sb^V . These metal ions form a large number of coordination compounds particularly those with an octahedral structure. The metals of the first two groups (alkali and earth alkali) are not included in our discussion since the valence orbitals of the M^+ and M^{2+} ions are very unstable. Low-energy electronic transitions involving the metal ions do then not occur. Consequently, there is no photochemistry initiated by irradiation with conventional light sources. On the other side, Hg^{II} is discussed here although it is not considered to be a main group metal. However, with regard to its spectroscopic and photochemical properties Hg^{II} is not different from other s^0 metals.

 s^1

The s^1 configuration is rather exceptional and forms stable compounds only as diamagnetic dimeric complexes which contain a metal-metal bond. In addition to Ga^{II} and In^{II} mercury(I) is a typical example of a s^1 metal.

 s^2

Next to s^0 the s^2 configuration is most important for main group metals. Typical ions include Ga^I , In^I , Tl^I , Ge^{II} , Sn^{II} , Pb^{II} , Sb^{III} , Bi^{III} , and Te^{IV} . The coordination numbers and structures are variable. The lone s^2 electron pair exerts a strong influence on the molecular structure by s-p orbital mixing. A rather exotic but interesting example of a s^2 metal is the mercury atom which can be studied in solution under ambient conditions.

 p^2

Ions with a partially filled p subshell can be found only on the right side of the periodic table. Te^{II} and I^{III} are typical examples of p^2 metals.

Although these elements may not be considered to be metals, their coordination compounds are not different from those of any other main group metal. Square planar structures are characteristic for p^2 ions.

p^4

There are only a few cases of coordination compounds with a p^4 configuration. Iodine(I) may be taken as an example. Such complexes have a linear structure.

ELECTRONIC TRANSITIONS AND ABSORPTION SPECTRA

Much information on the electronic structures and electronic transitions of main group metal complexes can be found in various chapters of Jørgensen's books (refs. 5-7). We classify the absorption spectra according to the electron configuration as outlined above.

s^0 complexes

In analogy to the d^0 configuration of transition metals (e.g. CrO_4^{2-} , MnO_4^-) the only electronic transition which can occur for s^0 complexes is of the ligand to metal charge transfer (LMCT) type. However, in contrast to the d^0 complexes the oxidation strength of a s^0 metal increases from the top to the bottom of the main groups. The energy of the LMCT transitions decrease then in the same direction. This fact is also reflected by the colors of the compounds. While the LMCT band of $[PbCl_6]^{2-}$ extends to the visible and causes the yellow color of the complex the corresponding tin complex $[SnCl_6]^{2-}$ is colorless since the LMCT absorption is shifted to the UV (refs. 8,9). LMCT bands of the same type were also detected in the absorption spectra of Hg^{II} complexes (refs. 8,10,11) such as $[Hg(N_3)_3]^-$ (ref. 12).

Detailed assignments were made for several octahedral s^0 complexes (refs. 8,9,13). The acceptor orbitals for LMCT transitions are the σ -antibonding a_{1g} (s) and t_{1u} (p) MOs. LMCT absorptions were generally assigned to the transition of a ligand π or σ electron to the antibonding s orbital (a_{1g}). Transitions terminating in the p-orbitals (t_{1u}) occur at much higher energies. The corresponding LMCT bands may thus not appear in the accessible wavelength region. The absorption spectra of some tin(IV) and lead(IV) complexes may serve as suitable examples. The allowed low-energy LMCT transitions $t_{1u}(\pi^b) \rightarrow a_{1g}$ and $t_{1u}(\sigma^b) \rightarrow a_{1g}$ cause intense long-wavelength absorptions of $[SnCl_6]^{2-}$ (278 and 222 nm) (refs. 8,9,13,14), $[PbCl_6]^{2-}$ (307 and 208 nm) (refs. 8,9,14), $[Sn(N_3)_6]^{2-}$ (264 and 236) (ref. 15), and $[Pb(N_3)_6]^{2-}$ (390 and 318 nm) (refs. 15,16).

Besides LMCT absorptions bands of a different origin may be observed in special cases. Porphyrin complexes of s^0 metals are characterized by low-energy intraligand (IL) porphyrin absorptions (ref. 17). Ligand to ligand charge transfer (LLCT) transitions were assigned to absorption bands of the s^0 complexes $[\text{Be}(\text{bipy})\text{X}_2]$ (ref. 18) ($\text{bipy} = 2,2'$ -bipyridyl and $\text{X}^- = \text{halide}$) and $[\text{Tl}(\text{bipy})_2\text{I}_2]^+$ (ref. 19).

s^1 complexes

Absorption spectra of the s^1 complexes $[\text{Cl}_3\text{M}^{\text{II}}\text{M}^{\text{II}}\text{Cl}_3]^{2-}$ with $\text{M} = \text{Ga}$ and In were not reported. But there is little doubt that these spectra are rather similar to that of the isoelectronic Hg_2^{2+} ion. The metal-metal bond of this dimeric ion is essentially based on the interaction of the mercury 6s orbitals. This generates a bonding and an antibonding σ MO. The intense long-wavelength absorption of $[\text{H}_2\text{O}-\text{Hg}^{\text{I}}-\text{Hg}^{\text{I}}-\text{H}_2\text{O}]^{2+}$ at $\lambda_{\text{max}} = 237 \text{ nm}$ is then assigned to the allowed $\sigma^b \rightarrow \sigma^*$ transition (ref. 20).

s^2 complexes

For s^2 complexes there exists a larger variety of electronic transitions. Most important are the metal-centered $s \rightarrow p$ transitions. Detailed assignments are frequently complicated by a rather low symmetry of the s^2 complexes. Generally, this is due to the presence of a stereochemically active lone pair which is not any more a pure s electron pair but gains some p character by sp orbital mixing. In addition, the solution structure of s^2 complexes is often unknown since they can undergo excessive ligand dissociation due to their kinetic lability. Therefore the assignments of sp bands are frequently given as those of the free s^2 ions (refs. 5-7). All sp absorption bands occur in the UV spectral region. The two lowest-energy transitions are spin-forbidden ($^1S_0 \rightarrow ^3P_1$ and $^1S_0 \rightarrow ^3P_2$). The corresponding absorption bands can be of considerable intensity ($\epsilon \sim 10^3$) since spin-orbit coupling is very strong for the heavy metals such as Tl^{I} , Sb^{III} , Bi^{III} , and Te^{IV} . The first spin-allowed sp transition ($^1S_0 \rightarrow ^1P_1$) appears at higher energies. The spin-forbidden $^1S_0 \rightarrow ^3P_1$ transition appears as a narrow intense band at $\lambda_{\text{max}} = 255 \text{ nm}$ also for atomic mercury in solutions of a variety of solvents (ref. 21). While in the gas phase of mercury this transition appears as an absorption line it is broadened in solution due to the perturbation of the mercury atoms by the solvent.

In some cases such as $[\text{SbCl}_6]^{3-}$ or $[\text{TeBr}_6]^{2-}$ regular octahedral complexes are formed. The lone pair preserves its s-character since sp mixing does not take place. Classical ligand field theory leads then to a detailed assignment of the sp absorption bands in the octahedral ligand field (refs.

22,23,24,25). Their energy increases in the following order:

$$^1A_{1g} \rightarrow ^3T_{1u} (^1S_0 \rightarrow ^3P_1) < ^1A_{1g} \rightarrow ^3T_{1u} (^1S_0 \rightarrow ^3P_2) < ^1A_{1g} \rightarrow ^1T_{1u} (^1S_0 \rightarrow ^1P_1).$$

In addition to sp, LMCT transitions of s^2 complexes are possible since the p-orbitals are empty. These transitions occur generally at much higher energies than the LMCT transitions of s^0 complexes which have also empty s orbitals. However, LMCT bands appear only in the accessible wavelength region if the s^2 metal is fairly oxidizing. While a LMCT band was not detected in the spectrum of $[SbCl_5]^{3-}$ (refs. 24,25) it appears at $\lambda_{max} = 270$ nm for $[TeBr_6]^{2-}$ (ref. 22) which contains the much more oxidizing Te^{IV} .

Generally, s^2 metals are not oxidizing but reducing due to the presence of the lone pair. Accordingly, low-energy metal to ligand charge transfer (MLCT) transitions should occur for s^2 complexes with suitable ligands such as 2,2'-bipyridyl (bipy) or 1,10-phenanthroline (o-phen). Such MLCT bands were indeed identified in the spectra of $M^{III}(bipy)_3$ with $M = Sb$ and Bi and $X^- = Cl^-, Br^-$ and I^- (ref. 26). The energy of the bands increases from Sb^{III} to Bi^{III} in agreement with the change of the reducing strength of these metals. There is also a dependence of the energy of the MLCT bands on the ligand X^- . It has been suggested that this effect is caused by the extent of sp mixing at the metal. MLCT assignments were also made for absorption bands of the complex $[Sn^{II}(C_5Me_5)bipy]^+$ (ref. 27) and metalloporphyrins of Sn^{II} , Sb^{III} , and Bi^{III} (ref. 17).

s^0/s^2 mixed-valence complexes

Mixtures of s^0 and s^2 complexes of the same metal such as $Sn^{II/IV}$ or $Sb^{III/V}$ show low-energy $s^2 \rightarrow s^0$ metal to metal charge transfer (MMCT) bands (ref. 28). Bridging halide ligands facilitate the mixed-valence interaction. MMCT transitions were assigned to long-wavelength absorption bands of $[M_2Cl_{10}]^{2-}$ with $M = Sn$ (ref. 29) and Sb (ref. 30).

p^2 complexes

Simple p^2 complexes are expected to possess metal-centered $p \rightarrow p$ and LM(p)CT transitions at low energies. This assumption was confirmed for the square-planar complex $[ICl_4]^-$. The longest wavelength band at $\lambda_{max} = 335$ nm is assigned to the Laporte forbidden pp transition $2a_{2u} (p_z) \rightarrow 3e_u (p_{x,y})$ (refs. 31,32). The more intense band of $[ICl_4]^-$ at shorter wavelength belongs certainly to a LMCT transition from the chloride ligands to the empty $3e_u$ orbitals of the oxidizing I^{III} ion (ref. 32).

p^4 complexes

The linear p^4 complexes $[I^I Cl_2]^-$, $[I(pyridine)_2]^+$ and $[I^I(CN)_2]^-$

(ref. 33) should certainly show low-energy pp transitions from the non-bonding HOMO $2a_u$ ($p_{x,y}$) to the antibonding LUMO $3\sigma_u$ (p_z) (ref. 31). In the spectrum of $[\text{ICl}_2]^-$ this pp band appears at 335 nm (refs. 31,32). In addition to pp absorptions LMCT bands and in the case of $[\text{I}(\text{pyridine})_2]^+$ and $[\text{I}(\text{CN})_2]^-$ MLCT bands are expected to occur. The spectra of these two complexes have not yet been recorded.

EMISSION SPECTRA

While s^0 complexes with a LMCT state as lowest excited state are generally not luminescent many s^2 complexes are emissive. The emission originates from the lowest-energy sp excited triplet. Frequently the luminescence can be observed even at room temperature and in solution. The aquo or halide complexes of Tl^{I} (refs. 34-39), Sn^{II} (refs. 39,40), Pb^{II} (refs. 37,39,40), and Sb^{III} (refs. 25,40) are typical examples of s^2 metals which luminescence under ambient conditions. For instance, the aquo complex of Tl^+ emits with a quantum yield of $\phi = 0.17$ and a lifetime of $\tau \sim 10^{-6}$ s at $\lambda_{\text{max}} = 368$ nm ($\lambda_{\text{exc}} = 238$ nm) in water (ref. 38). The sp triplet $^3T_{1u}$ of $[\text{SbCl}_6]^{3-}$ undergoes a luminescence with $\phi \approx 2.5 \times 10^{-3}$ and $\tau \leq 5 \times 10^{-9}$ s at $\lambda_{\text{max}} = 520$ nm in CHCl_3 (ref. 25). The rate constants for the phosphorescence and radiationless deactivation are $k = 4.8 \times 10^4 \text{ s}^{-1}$ and $k = 2.0 \times 10^7 \text{ s}^{-1}$. The emission is quenched by oxygen with a second order rate constant $k = 2.7 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$.

If the lowest excited state is of the IL type it may undergo an emission regardless of the electron configuration at the metal. Porphyrin complexes of s^0 and s^2 metals are well known to luminesce from the lowest $\pi\pi^*$ states of the porphyrin ligand (ref. 17).

Luminescence of s^1 , p^2 , and p^4 complexes has not yet been observed.

PHOTOCHEMISTRY

In analogy to transition metal complexes coordination compounds of the main group metals might be expected to undergo essentially two types of photochemical reactions: ligand substitutions and photoredox reactions. Photosubstitutions should originate from the metal-centered sp and po excited states which undergo certainly large distortions (ref. 41). Such substitutions may indeed occur but do not yield stable products. Due to the kinetic lability of many main group metal complexes a regeneration of the starting compounds would prevent the observation of photoactivity. Of course, time resolved spectroscopy may show the existence of short-lived intermediates.

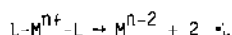
The photochemistry of main group metal complexes is thus dominated if not restricted to photoredox reactions. They take place as intra- and inter-

molecular processes which are initiated by metal-centered and CT excited states.

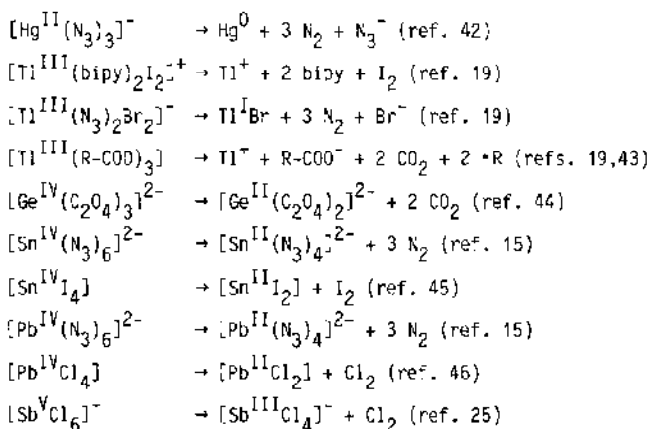
There is not yet much information available on mechanistic details of these reactions. However, in many cases a clear relationship between the nature of the excited state and the type of photoreaction has been established. Most photolyses were carried out in organic solvents of low coordinating ability to exclude extensive dissociation of ligands.

s^0 complexes

The majority of main group metal complexes which have been studied photochemically consists of compounds with a s^0 electron configuration. Since the electronic transitions of these complexes are exclusively of the LMCT type it is not surprising that electronic excitation is followed by the reduction of the metal and oxidation of the ligands. Stable products are obtained by a two-electron reduction of the metal and one-electron oxidation of two ligands. LMCT states undergo thus a reductive elimination:

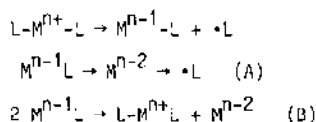


According to our experience almost any s^0 complex will undergo such a photochemical reductive elimination upon LMCT excitation. This behavior is illustrated by the following examples:

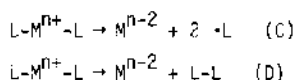


The overall stoichiometric equations of these photoreactions are certainly correct although the molecular identity of the products is not known in some cases.

The optical LMCT excitation is a one-electron transfer whereas stable products are formed by a two-electron process. For the molecular mechanism several possibilities must be considered. An intermediate formation of an unstable s^1 radical may be followed by the reduction of this radical (A) or its disproportionation (B) in a secondary thermal process:



As an alternative the LMCT state could undergo the reductive elimination in a concerted fashion. The metal is then reduced by a simultaneous $2e^-$ -transfer from two ligands, which may be split off as radicals $\cdot L$ (C) or released as a new molecule $L-L$ (D):



Low-temperature experiments led to the conclusion that the photolysis of $[M(N_3)_6]^{2-}$ with $M = Sn$ and Pb proceeds according to equation (C) (ref. 45). This reaction has its counterpart in the photochemistry of certain transition metal complexes. The reductive photoelimination of $[Pt(CN)_4(N_3)_2]^{2-}$ takes place by the same mechanism (ref. 47). Flash photolysis studies of $[PbCl_4]$ have shown that in this case $PbCl_3$ and Cl atoms are probably primary photoproducts (ref. 46). For the other photochemical reductive eliminations which are described above mechanistic studies were not yet carried out. The photolysis of $[Hg(N_3)_3]^-$ in ethanol is of special interest since the formation of mercury atoms can be observed under ambient conditions (ref. 42).

s^1 complexes

Irradiation of the $\sigma^b(M-M) \rightarrow \sigma^*(M-M)$ absorption of $[Hg_2(H_2O)_2]^{2+}$ in an air-saturated aqueous solution leads to the photooxidation of $Hg(I)$ according to the equation (ref. 48):

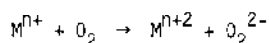


In the absence of O_2 the complex does not appear to be light-sensitive. It is suggested that the $\sigma\sigma^*$ excitation is associated with a homolytic splitting of

the Hg-Hg bond. The Hg^{I} radicals undergo an efficient regeneration of Hg_2^{2+} if they are not intercepted by oxygen which oxidizes these radicals to Hg^{II} . However, it cannot be excluded presently that another photochemical mechanism is in operation. As an alternative the $[\text{Hg}_2(\text{H}_2\text{O})_2]^{2+}$ ion could undergo a direct excited state electron transfer to O_2 . But the photohomolysis of the metal-metal bond is a very general process for binuclear transition metal complexes (refs. 3,49) and does thus probably apply also to $[\text{Hg}_2(\text{H}_2\text{O})_2]^{2+}$.

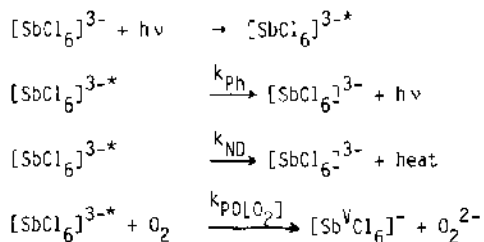
s² complexes

Complexes of reducing s² metals such as Tl^{I} (refs. 34,35), Sn^{II} (refs. 39,50,51), and Sb^{III} (ref. 52) are well known to undergo a photooxidation in the presence of O_2 . This reaction proceeds according to the equation:



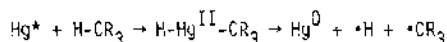
The photooxidation of Sn^{II} is used for electroless metal deposition (refs. 50,51). Nevertheless, the nature of the reactive excited state and the mechanism of photooxidation has not been studied until recently. Previous observations were made mainly in aqueous hydrochloric acid. Under these conditions an equilibrium of several chloro complexes seems to exist. In order to work with a well-defined complex we investigated the photochemistry of Sb^{III} in CHCl_3 (ref. 25). In the presence of an excess of chloride $[\text{SbCl}_6]^{3-}$ is formed.

Irradiation of $[\text{SbCl}_6]^{3-}$ ($\lambda_{\text{irr}} < 350 \text{ nm}$) leads to the population of the lowest so triplet ($^3\text{T}_{1\text{u}}$) which phosphoresces at room temperature and in solution. In the presence of oxygen this luminescence is partially quenched. Simultaneously, the complex is photooxidized to $[\text{SbCl}_6]^-$ with the concomitant formation of O_2^{2-} . In an air-saturated solution the photooxidation occurs with $\phi = 0.08$. These results can be explained by the following reaction scheme (ref. 25):

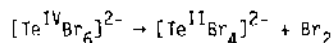


From the experimental data individual rate constants were calculated. The phosphorescence and the nonradiative deactivation take place with $k_{ph} = 4.8 \times 10^4 \text{ s}^{-1}$ and $k_{ND} = 2.0 \times 10^7 \text{ s}^{-1}$. The photooxidation is an excited state electron transfer which proceeds with the second order rate constant $k_{PO} = 2.7 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$. The calculated quantum yield of photooxidation ($\phi = 0.37$) is much larger than the experimental value. It is assumed that the photooxidation is partially reversed by back electron transfer. It is not yet known whether the photooxidation occurs by two subsequent one-electron transfer processes or by a two-electron transfer in a concerted fashion.

Another interesting s^2 metal is mercury in its atomic state. In solution (refs. 53,54) as well as in the gas phase (ref. 55) mercury atoms photosensitize the dehydrodimerization of organic compounds. It has been suggested that this very efficient CH bond activation takes place via the formation of some kind of exciplex (ref. 55). In view of the electron transfer ability of other excited s^2 metals (see above) it seems feasible that this dehydrodimerization could also proceed as a photochemical oxidative addition to excited mercury atoms and a subsequent reductive elimination:



If the s^2 metal is fairly oxidizing LMCT transitions occur at relatively low energies. For example, the complex $[\text{TeBr}_6]^{2-}$ shows a LMCT band in addition to longer-wavelength sp absorptions (ref. 22). LMCT excitation leads to an efficient reductive elimination (ref. 56):



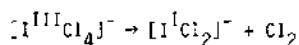
This photoredox behavior extends also to the sp region at low energies although with lower quantum yields. It has been suggested that the sp excited state has a certain probability to cross over to the reactive LMCT state.

s^0/s^2 mixed valence complexes

As shown by radioactive labeling the mixed-valence system $[\text{Sn}^{\text{II}}\text{Cl}_4]^{2-}/[\text{Sn}^{\text{IV}}\text{Cl}_6]^{2-}$ does not undergo a rapid thermal ligand exchange between both complexes. However, upon irradiation of the $\text{Sn}^{\text{II}} \rightarrow \text{Sn}^{\text{IV}}$ MMCT band a facile ligand exchange was indeed observed (ref. 57). It is remarkable that this reaction was already studied in 1951 long before transition metal complexes were shown to have reactive MMCT states (ref. 58).

p² complexes

Upon LMCT excitation the p² complex [ICl₄]⁻ undergoes a reductive elimination (ref. 32):



Light absorption by the pp-band at longer wavelength leads to the same reaction but with a lower quantum yield. This reduced efficiency may be explained by a mechanism which accounts also for the wavelength-dependent quantum yield of the photochemical reductive elimination of [TeBr₆]²⁻ (ref. 56).

OUTLOOK AND CONCLUSION

At this point it is certainly of interest to compare the photochemistry of coordination compounds of the main group metals with that of transition metal complexes. Our discussion has shown that there are many similarities but also some pronounced differences. Due to the kinetic lability of simple main group metal complexes photosubstitutions of ligands cannot be observed while this type of photoreaction is important for transition metal complexes (refs. 1-4). Photoredox reactions are common for both metal groups. However, transition metal complexes undergo frequently one-electron photoredox processes while the main group metals change their oxidation states almost always by two units.

With regard to potential applications the main group metals offer certain advantages over the transition metals. As photocatalysts the main group metals may have a better capability for reactions which require multi-electron transfer processes such as water splitting or transformations of organic compounds. For excited state electron transfer the kinetic lability of main group metal complexes is not necessarily a disadvantage. This kinetic lability may even prevent a gradual decomposition of the photocatalyst in an undesirable side reaction. On the other side, applications may be presently hampered by the fact that most main group metal compounds are colorless and require irradiation in the UV region. However, a photolysis with visible light is certainly feasible by using appropriate sensitizers. Applications of the photochemistry of main group metal complexes are yet rare (refs. 50,51). Nevertheless, we anticipate that this short review will stimulate further research of this interesting branch of inorganic photochemistry. Important applications may be developed on the basis of a better knowledge of the photochemistry of main group metal complexes.

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