PHOTOREDOX REACTIONS OF MIXED-VALENCE COMPOUNDS INDUCED BY INTER-VALENCE EXCITATION

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ABSTRACT

A variety of mixed-valence systems were shown to be photoactive in aqueous solution upon light absorption by the intervalence (IT) band. IT excitation leads to an electron transfer from a reducing to an oxidizing metal center. Co(III), Ru(III), Cr(III), and Os(III) complexes were used as electron acceptors while $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$, and $[Os(CN)_6]^{4-}$ served as electron donors. Inner- as well as outer-sphere systems were studied. The inner-sphere IT interaction was mediated by bridging cyanide ligands in binuclear complexes. Outer-sphere IT systems were formed by ion pairs of the oxidizing complexes as cations and the reducing hexacyanide anions. Light-induced metal to metal electron transfer was followed by secondary processes which yielded stable photoproducts.

INTRODUCTION

Photoredox reactions of transiton metal complexes play an important role in inorganic photochemistry. (ref. 1,2) Intra-molecular redox processes are usually initiated by light absorption into charge transfer (CT) bands. The classical reactive CT states are those of the metal to ligand and ligand to metal type. The light absorption itself is associated with the oxidation of the metal and reduction of the ligand and vice versa. Such a resonance mechanism does not apply to the majority of intermolecular photoredox reactions of metal complexes. In these cases an electron is transferred from an internally excited metal complex to a ground state molecule. Bimolecular excited state electron transfer reactions of this type have been investigated extensively during recent years.(ref. 3-5)

Light-induced electron transfer between two metal complexes may also occur by a resonance mechanism. In mixed-valence (MV) systems(ref. 4,6-10) the interaction of a reducing and oxidizing metal center leads to the appearance of a metal to metal CT or

intervalence transfer (IT) absorption band in the electronic spectrum. The electron transfer from the reducing to the oxidizing metal takes place directly by light absorption. In binuclear complexes the metal metal interaction can be mediated by a bridging ligand. The electron is then transfered by an intramolecular or inner-sphere process. The corresponding intermolecular or outer-sphere electron transfer may occur when both metal complexes exist separately but are in close contact.

Many MV systems have been studied during the last decade (ref. 6-10). The occurence of optical IT transitions and their relationship to thermal electron transfer processes found much attention (ref. 4,7,10,11). Although the analogy of thermal and light-induced redox reactions involving two metal centers is quite obvious, photoredox reactions induced by IT excitation were almost unknown. Of course, an IT excitation is a photoredox process by definition. However, it remains a photophysical phenomenon unless a permanent chemical change takes place by secondary processes following the light-induced charge separation.

In 1975 we started to explore photochemical reactions induced by IT transitions. At that time the discussion of MV systems was stimulated by the Creutz-Taube ion (ref. 12) and focussed on homo-binuclear, ligand-bridged, symmetric Ru^{II}, Ru^{III} complexes (ref. 4,10,13,14). Unfortunately, for a variety of reasons these com- . pounds are not well suited to observe a photochemical reaction leading to a permanent chemical change. First of all, in a symmetric MV complex an electron exchange does not cause a real chemical change, although the individual metal atoms have exchanged their oxidation state and hence their environment. But even in most homobinuclear complexes which are slightly asymmetric due to different ligands a rapid thermal electron exchange occurs. This situation interferes with the observation of light-induced electron transfer. Finally, the IT bands of the symmetric or nearly symmetric MV systems appear in the near IR which is not easily accessible by conventional irradiation sources and light detection devices. Consequently, photoactive MV systems should be designed according to these considerations.

Light-sensitivity will be most easily observed for strongly asymmetric MV systems. They may be stable towards thermal electron exchange and are expected to display their IT bands in the visible or UV region (see Fig. 1).
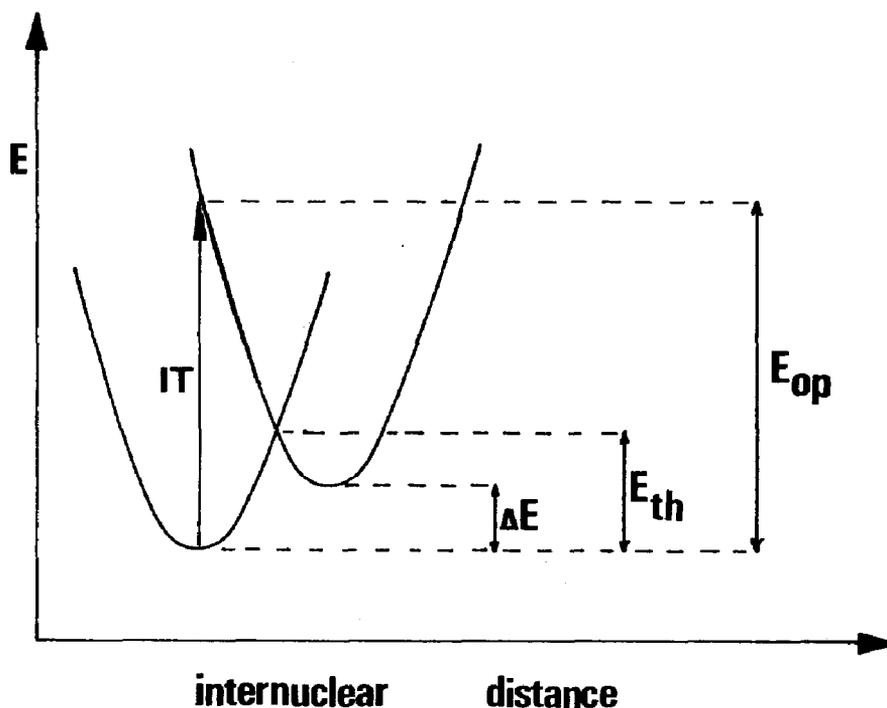
Fig.1. Potential energy versus internuclear distance for asymmetric mixed-valence systems.

ΔE is the energy difference between both redox isomers and a measure for the redox asymmetry. For thermal electron transfer the activation energy E_{th} is required.

According to this picture (Fig. 1) the relaxed IT state or redox isomer will not be stable but return rapidly to the starting point by back electron transfer. An irreversible formation of stable photoproducts can only be achieved if the redox isomer is able to undergo some further geometrical rearrangements. These secondary processes must be fast enough to compete with back electron transfer.

An asymmetric MV system may be constructed in two ways. In homo-binuclear complexes different ligands at both metals can be employed. For example, in a Ru^{II}, Ru^{III} complex a large redox asymmetry will be achieved if Ru^{II} is stabilized by π-acceptor ligands and Ru^{III} by π-donors. Much larger energy separations are possible in heteronuclear systems. The individual components of a MV system are selected according to their redox potentials. Another very important criterion for a proper choice is the antici-

pated reactivity of the redox isomer generated by IT excitation. For example, photoactivity is expected if $[Co(NH_3)_6]^{3+}$ is the oxidizing component of an IT system. Upon reduction $[Co(NH_3)_6]^{2+}$ is formed. It is kinetically very labile and undergoes a rapid decomposition in aqueous solution.

DISCUSSION

The spectroscopic properties of the light-sensitive MV systems are discussed on the basis of the Hush theory (ref. 7). For our purpose only the most simply approximations are used (ref. 7,14, 15,16). The application of some basic equations requires a weak coupling between the redox centers. This requirement seems to be fullfilled. The electronic spectra of our MV systems are composed of the spectra of the mononuclear components. In addition an IT band appears due to the interaction of the reducing and the oxidizing metals. According to Hush the energy of this band at the absorption maximum E_{op} depends on the energy difference ΔE between both redox isomers and the reorganizational energy χ:

$$E_{op} = \Delta E + \chi$$

In a first approximation ΔE can be expressed by the difference of the redox potentials of the reducing and oxidizing component of the MV system. The activation energy E_{th} for thermal electron transfer within the MV system and the halfwidth of the IT band are given by the following equations:

$$E_{th} = \frac{E_{op}^2}{4\chi} \quad \text{and} \quad \Delta\bar{v}_{1/2} = [2310(E_{op}-\Delta E)]^{1/2}$$
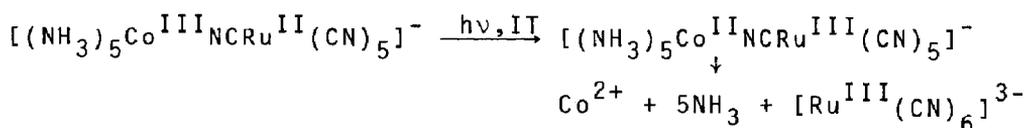
Inner-sphere intervalence excitation

As a first example we prepared a binuclear cyanide-bridged complex which contains Co(III) as oxidizing and Ru(II) as reducing metal center (ref. 17):

$$[Co(NH_3)_5H_2O]^{3+}+[Ru(CN)_6]^{4-} \rightarrow [(NH_3)_5Co^{III}NCRu^{II}(CN)_5]^-+H_2O$$
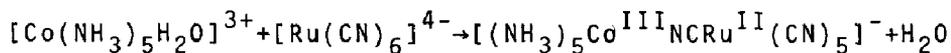
In aqueous solution this complex exhibits an IT ($Ru^{II} \rightarrow Co^{III}$) absorption band at λ_{max} = 375 nm or $\bar{v}_{max}$ = 26667 cm^{-1} (ε = 690). A bridging cyanide which coordinates via nitrogen can be considered to be similar to ammonia, at least with regard to its ligand field strength (ref. 17). The binuclear complex may then be viewed as

being composed of $[Co(NH_3)_6]^{3+}$ (E^0 = 0.11 V) (ref. 18) and $[Ru(CN)_6]^{4-}$ (E^0 = 0.86 V) (Ref. 18). This gives a reorganizational energy of χ = 59 kcal/mol provided these redox potentials apply also to the reduction of Co(III) and oxidation of Ru(II) in the binuclear complex. The experimental halfwidth of the IT band ($\Delta\bar{\nu}_{1/2}$ = 7280 cm^{-1}) differs from the calculated one (3740 cm^{-1}). The origin of this difference is not quite clear. Some possible explanations have been advanced by Meyer et al.(ref. 19,20). The activation barrier for thermal electron transfer is calculated to be E_{th} = 25 kcal/mol. Aqueous solutions of the binuclear complex are stable at room temperature but undergo a redox decomposition upon light absorption by the IT band with ϕ = 0.46 at λ_{irr} = 366 nm:

$$[(NH_3)_5Co^{III}NCRu^{II}(CN)_5]^- \xrightarrow{h\nu, IT} [(NH_3)_5Co^{II}NCRu^{III}(CN)_5]^-$$
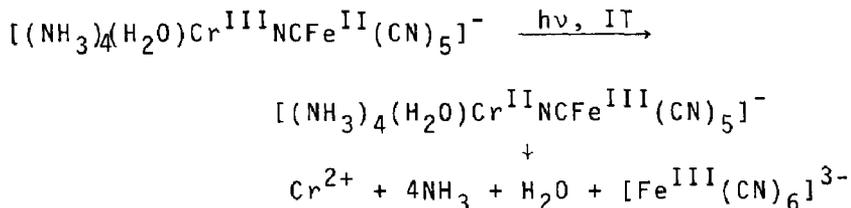$$\downarrow$$
$$Co^{2+} + 5NH_3 + [Ru^{III}(CN)_6]^{3-}$$

The redox isomer generated by IT excitation is not stable but decomposes due to the lability of Co(II).

An attempt to prepare the corresponding binuclear iron complex $[(NH_3)_5Co^{III}NCFe^{II}(CN)_6]^-$ failed. Upon mixing solutions of $[Co(NH_3)_5H_2O]^{3+}$ and $[Fe(CN)_6]^{4-}$ a rapid thermal outer-sphere electron transfer from Fe(II) to Co(III) takes place (ref.21) before the formation of the binuclear complex occurs. $[Fe(CN)_6]^{4-}$ is more reducing than $[Ru(CN)_6]^{4-}$ by 0.5 V.(ref. 19) Assuming the same reorganizational energy of χ = 58 kcal/mol for both binuclear complexes $[(NH_3)_5Co^{III}NCM^{II}(CN)_5]^-$ with M = Fe and Ru the activation barrier would be E_{th} = 17 kcal/mol for thermal electron transfer within the hypothetical complex $\{(NH_3)_5Co^{III}NCFe^{II}(CN)_5]^-$ in an aqueous solution.

In analogy to the binuclear Co^{III}, Ru^{II} complex the compound $Li[(NH_3)_4(H_2O)Cr^{III}NCFe^{II}(CN)_5]\cdot 3H_2O$ was synthesized(ref. 22). In the electronic absorption spectrum of an aqueous solution of this complex an IT ($Fe^{II} \rightarrow Cr^{III}$) band appears at λ_{max} = 376 nm or $\bar{\nu}_{max}$ = 26596 cm^{-1} (ϵ = 2500). From the redox potentials of both components $[Cr(NH_3)_5H_2O]^{3+}$ ($E_{1/2}$ = -0.9 V vs SCE) (ref. 23) and $[Fe(CN)_6]^{4-}$ ($E_{1/2}$ = +0.19 V) (ref. 19) which constitute the binuclear complex the reorganizational energy is calculated to be χ = 51 kcal. The measured halfwidth of the IT band (4000 cm^{-1}) is very close to the calculated halfwidth of 4500 cm^{-1}. The

thermal electron transfer would require E_{th} = 28 kcal. Upon light absorption by the IT band the aqueous complex decomposes yielding $[Fe(CN)_6]^{3-}$ and an unidentified chromium compound. It is suggested that the photoreaction proceeds according to:

$$[(NH_3)_4(H_2O)Cr^{III}NCFe^{II}(CN)_5]^- \xrightarrow{h\nu,\ IT}$$

$$[(NH_3)_4(H_2O)Cr^{II}NCFe^{III}(CN)_5]^-$$
$$\downarrow$$
$$Cr^{2+} + 4NH_3 + H_2O + [Fe^{III}(CN)_6]^{3-}$$

The redox isomer obtained by IT excitation is kinetically labile due to the Cr(II) center. It decays and releases Cr^{2+} which is re-oxidized by oxygen. In the presence of air $[Fe(CN)_6]^{3-}$ was produced with a quantum yield of $\sim 10^{-1}$ at λ_{irr} = 366 nm.

Binuclear complexes of the type $[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ with M = Fe, Ru, and Os constitute another series of light-sensitive heteronuclear MV compounds. The IT ($M^{II} \rightarrow Co^{III}$) band of the iron complex in aqueous solution appears at λ_{max} = 385 nm or $\bar{\nu}_{max}$ = 25974 cm^{-1} (ε = 630)(ref. 24). From the redox potentials of $[Co(CN)_6]^{3-}$ (-0.8 V)(ref. 25) and $[Fe(CN)_6]^{4-}$ (+0.36 V)(ref. 18) the reorganizational energy χ = 48 kcal and the barrier for thermal electron transfer E_{th} = 29 kcal can be calculated. The corresponding values of the binuclear complexes containing $[Ru(CN)_6]^{4-}$ (+0.86 V)(ref. 18,19) and $[Os(CN)_6]^{4-}$ (+0.56 V)(ref. 19) are: λ_{max} = 312 nm or $\bar{\nu}_{max}$ (IT) = 32051 cm^{-1} (ε = 460)(ref. 24), χ = 53 kcal, E_{th} = 39 kcal for M = Ru and λ_{max} = 360 nm or $\bar{\nu}_{max}$ (IT) = 27780 cm^{-1} (ε = 734)(ref. 26), χ = 48 kcal, E_{th} = 33 kcal for M = Os. The halfwidths of the IT bands were not determined due to the broad overlap with bands of other origin. In all cases the aqueous complexes undergo photoredox reactions upon IT excitation (ref. 24,26). The primary photochemical step is the dissociation of the dimer which follows the light-induced electron transfer:

$$[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-} \xrightarrow{h\nu,\ IT} [(NC)_5Co^{II}NCM^{III}(CN)_5]^{6-}$$
$$\downarrow$$
$$[Co^{II}(CN)_5]^{3-} + [M^{III}(CN)_6]^{3-}$$
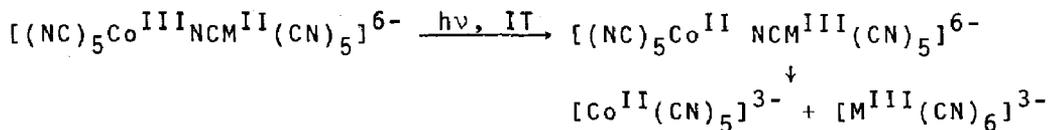
In the absence of air a complete regeneration of the binuclear complex occurs by a thermal inner-sphere electron transfer:

$$[Co^{II}(CN)_5]^{3-} + [M^{III}(CN)_6]^{3-} \rightarrow [(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$$
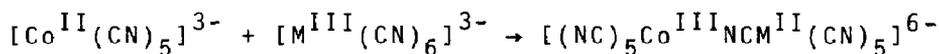
In distinction to ammine complexes of Co(II) which decay irreversibly the complex $[Co(CN)_5]^{3-}$ does not decompose in aqueous solution. The regeneration of the binuclear complexes by this thermal back electron transfer is not surprising at all since all three binuclear complexes are synthesized by this reaction. The iron complex was prepared by Haim and Wilmarth in 1961 according to this procedure. The photolysis of all three complexes induced by IT excitation leads to a permanent chemical change only in the presence of air. The complex $[Co(CN)_5]^{3-}$ can be intercepted by O_2:

$$2[Co(CN)_5]^{3-} + O_2 \rightarrow [(NC)_5Co^{III}(O_2^{2-})Co^{III}(CN)_5]^{6-}$$
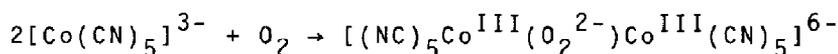
In acidic solution the peroxo complexes decomposes to yield H_2O_2 and $2[Co^{III}(CN)_5(H_2O)]^{2-}$ while in basic solution the peroxo complex is further oxidized to the superoxo complexes $[(NC)_5Co^{III}(O_2^-)Co^{III}(CN)_5]^{5-}$. The quantum yields for the formation of $[M^{III}(CN)_6]^{3-}$ are slightly wavelength-dependent due to the overlap of the IT bands with absorptions of other origin. The quantum yields may exceed unity because $[M(CN)_6]^{3-}$ is not only produced in the primary photochemical reaction but also by the oxidation of $[M(CN)_6]^{4-}$ by H_2O_2. The quantum yields are fairly large: $\phi = 1.6$ at $\lambda_{irr} = 405$ nm for M = Fe; $\phi = 0.39$ at $\lambda_{irr} = 313$ nm for M = Ru (ref. 24), and $\phi \sim 10^{-1}$ at $\lambda_{irr} = 366$ nm for M = Os (ref. 26).

It should be mentioned here that light-induced electron transfer between two metal centers was also observed for other ligand-bridged binuclear complexes. However, in all these cases the electron transfer was not achieved by direct IT excitation. The irradiation of heterobinuclear Co^{III}/Fe^{II} (ref. 28) and Co^{III}/Cu^{I} (ref. 29) complexes leads apparently to the generation of the redox isomers Co^{II}/Fe^{III} and Co^{II}/Cu^{II} which underwent an irreversible decomposition. In these compounds optical IT transitions were not observed. The redox isomers were populated by radiationless transitions from higher excited states of different origin. In a Ru^{II}/Cu^{II} dimer the redox isomer Ru^{III}/Cu^{I} was formed only as a short-lived transient which went back rapidly to the ground state (k = 7.8×10^3 s^{-1})(ref.30). In analogy to this observation the photochemical generation of an IT state was also observed for an asymmetric Ru^{II}/Ru^{III} dimer (ref. 31). Although this system dis-

plays an IT band, the redox isomer was only detected upon irradia-
tion of other absorption bands at shorter wavelength. The IT state
returned to the starting situation with k = 0.8×10^{10} s^{-1}. Again,
a permanent photochemical change did not take place. In a related
case an IT state was detected indirectly by emission spectroscopy
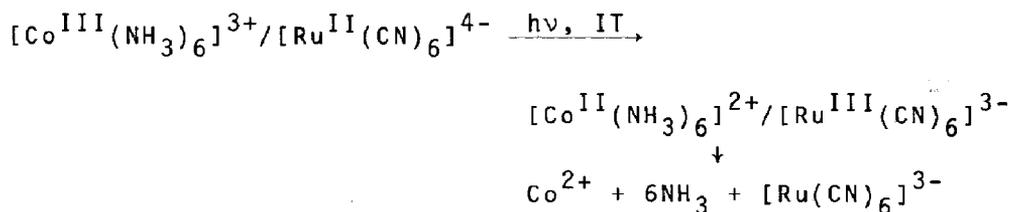(ref. 32). Similar processes seem to occur also in more complex
systems(ref. 33).

Outer-sphere intervalence excitation

The IT bands as they occur in the complexes
$[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ (ref. 24,26) will be hardly observed as
optical outer-sphere IT transitions. The mononuclear components
$Co^{III}(CN)_5(NC)^{3-}$ (or $Co^{III}(CN)_5(NH_3)^{2-}$ for comparison) and
$M^{II}(CN)_6^{4-}$ are both anionic. A considerable association of both
ions which is required to observe an outer-sphere MV interaction,
does certainly not occur. The situation is much more favorable if
the reducing and oxidizing complexes carry opposite charges. Ion
pair formation may take place by electrostatic attraction. Within
the ion pairs a MV interaction can occur giving rise to IT transi-
tions (ref. 19,34-36). Sometimes such ion pairs form precipitates
of low solubility. Unfortunately, an investigation in solution is
then excluded.

In contrast to the binuclear homoleptic cyanide complexes the
components of $[(NH_3)_5Co^{III}NCRu^{II}(CN)_6]^-$ (ref. 17) carry opposite
charges and should form ion pairs. In this case the comparison of
closely related inner- and outer-sphere MV systems would be pos-
sible. Indeed, $[Co(NH_3)_6]^{3+}$ and $[Ru(CN)_6]^{4-}$ form ion pairs which
show an IT (Ru^{II} → Co^{III}) band (ref. 37). In an aqueous solution
this band occurs at λ_{max} = 342 nm (ε = 243)(ref. 26), while in
DMSO it is shifted to λ_{max} = 360 nm (ε = 580)(ref. 37). Such a
red shift is expected since according to the Hush theory a decrease
of the solvent polarity decreases also the energy of the IT tran-
sition (ref. 38-40). A quantitative evaluation of this shift is
certainly not useful, because the degree of solvation and hence
the distance within the ion pair may be different in both solvents.
In addition, in aqueous solution hydrogen bonding could interfere
with simple solvation. On the other side, the comparison of the
IT bands of the ion pair and the binuclear counterpart
$[(NH_3)_5Co^{III}NCRu^{II}(CN)_6]^-$ (λ_{max} = 375 nm, ε = 690)(ref. 17), both
in aqueous solution, is certainly interesting. The red shift and

the increase in intensity of the IT band upon formation of the binuclear complex is in accordance with the expectation. The red shift is then caused by the decrease of the distance between both redox (ref. 40, 41) centers. Simultaneously, this facilitates also a stronger metal-metal interaction. Consequently, the IT band becomes more intense.

Upon IT excitation the ion pair $[Co(NH_3)_6]^{3+}/[Ru(CN)_6]^{4-}$ undergoes a photoredox decomposition quite analogous to that of the binuclear complex:

$$[Co^{III}(NH_3)_6]^{3+}/[Ru^{II}(CN)_6]^{4-} \xrightarrow{\ h\nu,\ IT\ }$$

$$[Co^{II}(NH_3)_6]^{2+}/[Ru^{III}(CN)_6]^{3-}$$
$$\downarrow$$
$$Co^{2+} + 6NH_3 + [Ru(CN)_6]^{3-}$$
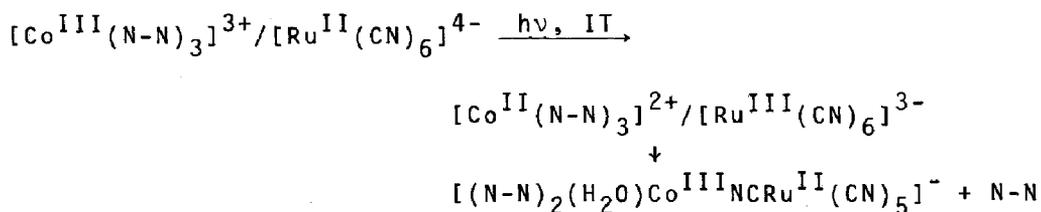
At λ_{irr} = 366 nm the quantum yield was ϕ = 0.034 in solutions of DMSO.(ref. 37) In aqueous solution the formation of a precipitate precluded the determination of reliable quantum yields.(ref. 26)

A variation of the distance between Co(III) and Ru(II) should not only effect the energy of the IT band, but also the quantum yield of the photoredox reaction. A larger quantum yield may be expected with increasing distance. The probability of back electron transfer which regenerates the starting ion pair should become smaller if the distance increases. We explored this possibility by changing the size of the cobalt complex, without changing the basic electronic structure. In addition to $[Co(NH_3)_6]^{3+}$ complexes of the type $[Co(N-N)_3]^{3+}$ were used. The ligand N-N represents a bidentate ligand derived from ethylendiamine (en). It is assumed that the complexes become larger upon substitution of the H atoms of en by groups of increasing size: ethylenediamine (en), 1,2-diaminopropane (pn), and trans-1,2-diaminocyclohexane (chn). This series is completed by $[Co(sep)]^{3+}$ (sep = sepulchrate).(ref. 42) Although the basic electronic structure is the same for all these $[Co(N-N)_3]^{3+}$ complexes the redox potentials are shifted to more negative values with increasing size of the complex (E^o vs. SCE) (ref. 43): $[Co(en)_3]^{3+}$ (-0.50 V), $[Co(pn)_3]^{3+}$ (-0.50 V), $[Co(chn)_3]^{3+}$ (-0.52 V), and $[Co(sep)]^{3+}$ ($E_{1/2}$ = -0.54 V vs. SCE) (ref. 42). It follows that the energy difference ΔE between $[Co^{III}(N-N)_3]^{3+}/[Ru^{II}(CN)_6]^{4-}$ and its redox isomer

$[Co^{II}(N-N)_3]^{2+}/[Ru^{III}(CN)_6]^{3-}$ increases along this series. In all cases the formation of the ion pairs in aqueous solution was accompanied by the appearance of an IT band. It was measured by differential spectroscopy yielding the "pure" IT bands: λ_{max} = 348 nm (Co en$_3{}^{3+}$); λ_{max} = 350 nm (Co pn$_3{}^{3+}$); λ_{max} = 355 nm (Co chn$_3{}^{3+}$); and λ_{max} = 372 nm (Co sep^{3+}).

These results are quite unexpected on the first view. With increasing size of the cobalt complex and increasing value of ΔE the IT band should move to higher energies. But the opposite behavior is observed. It seems likely that the increasing size of the cobalt complex leads actually to a decrease of the distance between the redox centers. This contradiction may find an explanation by the different degree of solvation of the complex cations. It is well known from the alkali cations that with increasing size the solvation of the cations becomes weaker and hence the diameter of the solvated ion smaller.
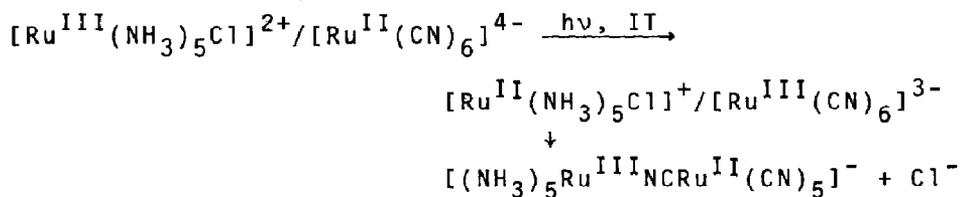
Upon IT excitation all of the ion pairs are photochemically active in aqueous solution with the exception of $[Co(sep)]^{3+}/[Ru(CN)_6]^{4-}$. Since $[Co(sep)]^{2+}$ is kinetically stable (ref. 42) the generation of the redox isomer $[Co(sep)]^{2+}/[Ru(CN)_6]^{3-}$ is simply followed by back electron transfer. In the case of the cobalt complexes containing the bidentate ligands another secondary reaction competes with back electron transfer:

$$[Co^{III}(N-N)_3]^{3+}/[Ru^{II}(CN)_6]^{4-} \xrightarrow{\ h\nu,\ IT\ }$$

$$[Co^{II}(N-N)_3]^{2+}/[Ru^{III}(CN)_6]^{3-}$$
$$\downarrow$$
$$[(N-N)_2(H_2O)Co^{III}NCRu^{II}(CN)_5]^- + N-N$$

The chelate ligands are apparently not released as rapidly as ammonia from Co(II). The formation of the binuclear complex may proceed by an inner-sphere electron transfer reaction in analogy to the formation of $[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ (see above). Although the photoproducts $[(N-N)_2(H_2O)Co^{III}NCRu^{II}(CN)_5]^-$ were not identified definitely, the spectral changes which accompany the photolysis support this assumption. The irradiation was followed by a red shift and intensification of the IT band of the ion pairs. These effects are also observed (see above), when the ion pair $[Co(NH_3)_6]^{3+}/[Ru^{II}(CN)_6]^{4-}$ is compared with the binuclear complex

$[(NH_3)_5Co^{III}NCRu^{II}(CN)_5]^-$. On the basis of these spectral changes estimates of quantum yields were made. For all three ion pairs the binuclear complexes $[(N-N)_2(H_2O)Co^{III}NCRu^{II}(CN)_5]^-$ were formed with efficiencies of approximately $\phi \sim 10^{-1}$ at λ_{irr} = 366 nm.

As outlined in the introduction MV compounds which are expected to undergo a permanent photochemical change upon IT excitation should not participate in thermal electron exchange between their metal centers. This can be avoided by the design of asymmetric MV systems which have large barriers for thermal electron transfer. The heterobinuclear MV compounds containing Co(III) and M(II) (M = Fe, Ru, Os) are good examples of this type of MV systems. In homonuclear complexes the redox asymmetry can be achieved by the coordination of different ligands at both metal centers. A large number of inner- (ref. 10-14) and outer-sphere (ref. 19,34) homonuclear MV systems containing Ru^{II} and Ru^{III} as asymmetric redox centers are known. Since the reorganizational energy of Ru^{II}, Ru^{III} systems is rather low it is difficult to design a MV system which does not undergo thermal electron exchange. The best candidates are those which contain π-accepting ligands for stabilization of Ru(II) and π-donors for Ru(III). One of the most favorable systems proved to be the combination $[Ru(NH_3)_5Cl]^{2+}/[Ru^{II}(CN)_6]^{4-}$. In aqueous solution this ion pair was formed with a stability constant of K = 216.(ref. 44) An IT ($Ru^{II} \rightarrow Ru^{III}$) band appeared at λ_{max} = 510 nm (ε = 20). This is the largest energy of an optical IT transition which has been observed for any Ru^{II}, Ru^{III} MV system. This observation is also consistent with the large difference of the redox potentials within the ion pair (ΔE = 0.9 V).(ref. 44) Accordingly the barrier for thermal electron transfer is calculated to be E_{th} = 22 kcal. Upon light absorption by the IT band (λ_{irr} = 546 nm) the aqueous ion pair is converted to a binuclear complex with a quantum yield of ϕ = 0.002. The reaction proceeds according to the following stochiometry

$$[Ru^{III}(NH_3)_5Cl]^{2+}/[Ru^{II}(CN)_6]^{4-} \xrightarrow{\ h\nu,\ IT\ }$$

$$[Ru^{II}(NH_3)_5Cl]^+/[Ru^{III}(CN)_6]^{3-}$$
$$\downarrow$$
$$[(NH_3)_5Ru^{III}NCRu^{II}(CN)_5]^- + Cl^-$$

The redox isomer generated by IT excitation may either return to

the starting situation by back electron transfer or diffuse apart. The complex $[Ru^{II}(NH_3)_5Cl]^+$ which has escaped to the bulk solution should undergo a rapid aquation to form $[Ru(NH_3)_5H_2O]^{2+}$. The substitutionally labile water ligand may be replaced by $[Ru(CN)_6]^{4-}$. This produces the binuclear complex $[(NH_3)_5Ru^{II}NCRu^{II}(CN)_5]^{2-}$. Finally, oxidation by $[Ru(CN)_6]^{3-}$ generates the binuclear MV complex as stable photoproduct.(ref. 44)

Quite recently we started to investigate a further series of photochemically active outer-sphere MV systems. Using again the reducing anions $[M(CN)_6]^{4-}$ with M = Fe, Ru, and Os we selected $[Os^{III}(NH_3)_5Cl]^{2+}$ as oxidizing counter ion. Since this Os(III) complex is rather stable towards reduction ($E_f = -0.56$ V), (ref. 45) the ion pairs are not susceptible to a rapid thermal electron transfer. All three ion pairs exhibit IT ($M^{II} \rightarrow Os^{III}$) bands in aqueous solutions. Some relevant data are collected in Table I.

TABLE 1

Spectroscopic and thermodynamic data of aqueous ion pairs $[Os(NH_3)_5Cl]^{2+}[M(CN)_6]^{4-}$

M	E_{op},[a] cm^{-1}	$\Delta\bar{v}_{1/2}$exp,[b] cm^{-1}	$\Delta\bar{v}_{1/2}$calc,[c] cm^{-1}	ΔE,[d] V	χ,[e] kcal/mol	E_{th},[f] kcal/mol
Fe	22831	5580	5494	1.21	37	25
Ru	26881	7200	5499	1.71	37	40
Os	25773	7520	5767	1.41	41	33

[a] Energy of the IT band at the maximum.
[b] Experimental halfwidth of the IT band.
[c] Calculated halfwidth.
[d] Difference of redox potentials of $[Os(NH_3)_5Cl]^{2+}$ and $[M(CN)_6]^{4-}$
[e] Calculated reorganizational energy.
[f] Calculated activation energy for thermal electron transfer.

The IT-bands were again measured by differential absorption spectroscopy. In all cases light absorption by the IT bands leads to the formation of the binuclear complexes $[(NH_3)_5Os^{III}NCM^{II}(CN)_5]^-$. It is assumed that the photoreactions proceed by the same or a similar mechanism which is suggested to apply to the ion pair $[Ru(NH_3)_5Cl]^{2+}/[Ru(CN)_6]^{4-}$. The binuclear Os^{III}, M^{II} complexes formed by the photolysis of the ion pairs were identified by their absorption spectra. They are characterized by IT ($M^{II} \rightarrow Os^{III}$)

bands: λ_{max} = 610 nm (M = Fe); λ_{max} = 485 nm (M = Ru); λ_{max} = 556 nm (M= Os). An independent preparation of these binuclear complexes was achieved by the thermal reaction of $[Os(NH_3)_5(O_2CCF_3)]^{2+}$ (ref. 45) with $[M(CN)_6]^{4-}$.

The aqueous ion pair $Cu^{2+}/[Mo^{IV}(CN)_8]^{4-}$ was recently shown by Hennig et al. to be photoactive upon IT ($Mo^{IV} \rightarrow Cu^{2+}$) excitation. (ref. 46-48) Light absorption by the IT band (λ_{max} = 495 nm) generates the redox isomer $Cu^+/[Mo^V(CN)_8]^{3-}$ which restores rapidly ($k = 1.3\times10^9$ s^{-1}) the starting ion pair by back electron transfer. (ref. 46) Interestingly, the intermediate $[Mo(CN)_8]^{3-}$ can be "scavenged" by photons. During the photolysis of $Cu^{2+}/[Mo(CN)_8]^{4-}$ the stationary state concentration of $Mo^V(CN)_8 3-$ is apparently large enough for a secondary photolysis by shorter wavelength irradiation (385 nm). Only bichromatic irradiation (λ_{irr} = 500 nm and 385 nm) is effective in this light-induced reaction. The secondary photolysis of $Mo(CN)_8^{3-}$ generates OH radicals which were intercepted by a spin trap.(ref. 47,48)

CONCLUSION

The photochemistry of MV systems is just beginning to emerge and is certainly a valuable addition to the field of inorganic photochemistry. It seems feasible to design a large variety of new photoactive heteronuclear MV compounds, particularly of the outer-sphere type. Under suitable conditions such systems might be useful for light energy conversion and storage. In contrast to the usual excited state electron transfer a long-lived internally excited state is not required, when the electron transfer is achieved directly by light absorption into IT bands.

More sophisticated applications can be anticipated for photochromic MV compounds. In systems with a small redox asymmetry ΔE but a large reorganizational energy χ a thermal electron transfer may not take place. But both redox isomers could then be reversibly interconverted by irradiation with light of slightly different wavelengths:

$$DA \underset{h\nu_2}{\overset{h\nu_1}{\rightleftarrows}} D^+A^-$$
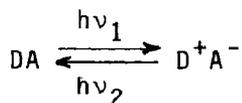
An optical information storage seems to be feasible on the basis of this mechanism. In inner-sphere complexes the light-induced electron transfer can be directed in space. (ref. 32) The direction of

electron flow would be reversed by changing the wavelength of light.

Finally, it should be emphasized that the concept of MV metal complexes can be extended to systems where the MV behavior is not based on reducing and oxidizing metals but rather on ligands. Accordingly, metal complexes of the type $L_{red}ML_{ox}$ represent a new class of MV compounds which are characterized by optical IT ($L_{red} \rightarrow L_{ox}$) transitions.(ref. 49) These complexes are largely unexplored. But a single observation on the photoactivity of a such ligand-based MV complex was recently reported.(ref. 50)

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