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Photocatalytic Systems. LXIII. Intervalence Transfer (IT) Behaviour and IT Photochemistry of Mixed-Valence Compounds with Cyanometallates

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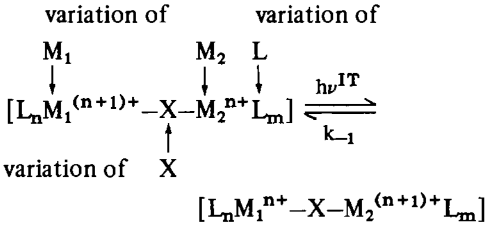
Cyanometallates such as octacyanomolybdate(IV), octacyanotungstate(IV), hexacyanoruthenate(II), and hexacyanoferrate(II) form mixed-valence compounds with appropriate copper(II), iron(III), uranium(VI) and vanadium(IV) compounds. Detailed spectroscopic investigations in solution show that the mixed-valence compounds under discussion are characterized by changes in the IT transitions. The IT behaviour is discussed within the framework of the conceptual approach of Hush. Photochemical investigations of the mixed-valence compounds described show low photoreactivity only, caused by fast back electron transfer processes. Both chemical and physical scavenging processes, the latter in the form of a new type of sequential two-photon processes, may be helpful in quenching the back electron transfer. The results obtained enable us to realize the concept of static spectral sensitization of photocatalytic systems based on light-sensitive coordination compounds.

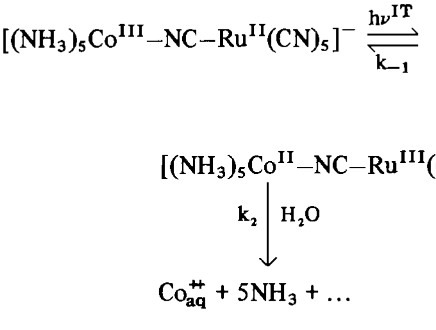
Introduction

Within the framework of our investigations of photocatalytic systems based on light-sensitive coordination compounds and their spectral sensitization [1], our interest has focused on the concept of static spectral sensitization [2]. The concept consists in the combination of the sensitizer S and the complex C to be spectrally sensitized in a closed unit. The aim is to avoid bimolecular reactions, which are the most decisive barrier in dynamic sensitization processes [3]. Among the experimental chances to realize the concept of static sensitization, mixed-valence compounds of the class II within the Robin-Day classification [4] are of considerable interest because they allow in principle the generation of 'optical windows' ranging from the ultraviolet up to the near infrared. Thus, depending on the redox asymmetry of both metal centers (M_1 and M_2), the kind of the bridging ligand X as well as the dielectric properties of the solvent systems used, it is possible to tune the spectral sensitivity of appropriate mixed-valence compounds primarily upon convenient synthetic conditions (1).



$$[L_nM_1^{(n+1)+}{-}X{-}M_2^{n+}L_m] \underset{k_{-1}}{\overset{h\nu^{IT}}{\rightleftharpoons}} [L_nM_1^{n+}{-}X{-}M_2^{(n+1)+}L_m] \qquad (1)$$

However, the well-known fast back electron transfer processes (k_{-1}) is a strong restricting factor concerning efficient electron transfer from the metal center M_2 to M_1 photochemically induced by IT excitation. Therefore in addition to the generation of optical windows it is our intention to search for very fast scavenging processes which are able to fix the valence isomeric mixed-valence species formed photochemically. There is a possibility to quench back electron transfer processes, as has been shown by Vogler [5, 6] by the first description of photochemical reactions of mixed-valence systems, which undoubtedly belong to the class II of the classification proposed by Robin and Day. Thus, the Vogler-Kunkely ion (2) is characterized by a very efficient formation of cobalt(II) induced upon irradiation into the IT region:



$$[(NH_3)_5Co^{III}{-}NC{-}Ru^{II}(CN)_5]^- \underset{k_{-1}}{\overset{h\nu^{IT}}{\rightleftharpoons}} [(NH_3)_5Co^{II}{-}NC{-}Ru^{III}(CN)_5]^- \xrightarrow[k_2]{H_2O} Co^{++}_{aq} + 5NH_3 + \ldots \qquad (2)$$

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This result is due to the well-known scavenging of the kinetically-labile cobalt(II) by fast aquation reactions. The aquation of cobalt(II) prevents the back electron transfer process with high efficiency and the cobalt(II) formed photochemically and spectrally sensitized can be used for catalytic purposes [1].

Further advantages of mixed-valence compounds belonging to class II in realizing the concept of static sensitization consist in predicting their spectral behaviour and the kinetics of light-induced electron transfer processes within the framework of the Hush theory [7, 8] and a general theory of electron transfer [23]. Here, we want to report our results concerning the IT behaviour and the photo redox reactions of mixed-valence compounds based on cyanometallates such as octacyanomolybdate(IV), octacyanotungstate(IV), hexacyanoferrate(II), and hexacyanoruthenate(II). Certain preliminary results have already been published [9–14]. The aim of these investigations is connected with the problem of spectrally sensitized photochemical generation of free cyanide which can be used within a photocatalytic cycle for the formation of heterocyclic 1.2-endioles [1, 15].

Experimental

$K_4[Mo(CN)_8]\cdot 2H_2O$ [44, 45], $K_4[Ru(CN)_6]\cdot 3H_2O$ [49], $K_4[W(CN)_8]\cdot 2H_2O$ [45, 50], $Na_3[Fe(CN)_5X]$ [46–48], and copper(II) diimine complexes [51] were prepared by standard techniques. Chemicals of analytical reagent grade and doubly distilled water and purified solvents were used in the preparation of solutions of the mixed-valence compounds. The solutions obtained were kept in the dark to avoid uncontrolled photoreactions.

The estimation of the dielectric properties of the solvent mixtures used was performed by refractometry (Abbé refractometer, VEB Carl Zeiss Jena) and by use of Looyenga's method [52].

Ultraviolet-visible spectra were obtained on a Cary Model 17 and on a Specord spectrometer (VEB Carl Zeiss Jena). ESR spectra were obtained on a Jeol JES-3BQ spectrometer.

Photochemical investigations were performed in the usual manner (high-pressure mercury lamp HBO 500, cut-off filters, interference-filters) and light-intensities were estimated according to Hatchard and Parker [53] and by reineckate actinometry [54], depending on the wavelength of irradiation. The quantitative analysis of cyanide was performed photometrically [56] using a modified König reaction.

Results and Discussion

Mixed-valence compounds of class II are generally characterized by the following properties, described at first by the Hush theory [8]: the electronic spectra of mixed-valence compounds do not exist merely as the sum of the spectra of their components. The position of IT band depends strongly on the dielectric properties of the solvents used. Furthermore, the position of the maxima of the IT bands is correlated with their band widths and depends strongly on the redox asymmetry of both metal centers. Finally, within the theoretical approach [8, 23] it is possible under certain circumstances to evaluate some of these dependencies and to compare them with the appropriate experimental results.

Aqueous solutions of the cyanometallates $[Mo(CN)_8]^{4-}$, $[W(CN)_8]^{4-}$, $[Fe(CN)_6]^{4-}$, and $Ru(CN)_6]^{4-}$ exhibit remarkable colour changes after addition of Fe(II), Cu(II), UO_2^{2+}, VO^{2+}, and Ce(IV) ions. This result can also be observed after the addition of special cobalt(III) ammine complexes [16]. The addition of Cr(III), Co(II), Ni(II), Zn(II), Hg(II), and Tl(I) leads to electronic spectra characterized as the sum of the components without any further additional bands.

Typical electronic spectra of mixed-valence compounds characterized by IT behaviour and consisting of octacyanomolybdate(IV) and appropriate other metal centers are shown in Fig. 1 (see also Table I).

TABLE I. Experimental Data of the Ion Pair Associates $M^{n+}/[Mo(CN)_8]^{4-}$.[a]

M^{n+}	ΔE^{o} [b]	$\bar{\nu}_{IT}$ [c]	$\Delta\bar{\nu}_{1/2}$ [c]	ϵ^{max}	K [d]	C_{IP}/C_{Mo} [e]	$C_{Mo(V)}/C_{Mo}$ [f]
Fe^{3+}	–0.07	12.5	7.4	1300 ± 50	750 ± 50	0.33	0.28 ± 0.07
Cu^{2+}	0.67	20.2	6.4	750 ± 50	2250 ± 250	0.52	0.04 ± 0.02
UO_2^{2+}	0.79	24.65 [g]	10.9	385 ± 20	2100 ± 400	0.51	0.03
VO^{2+}	0.87	29.0	9.6	860 ± 40	∞	1.0	0.01

[a] Aqueous solutions, $10^{-3}M$. [b] E^{o} $(Mo(CN)_8^{3-}/Mo(CN)_8^{4-})$ = 0.84 V [18]. [c] Data in 10^3 cm^{-1}. [d] Association constants of the reaction: $M^{n+} + [Mo(CN)_8]^{4-} \rightleftharpoons M^{n+}[Mo(CN)_8]^{4-}$. [e] Ratio of the amount of ion pairs to the whole amount of $[Mo(CN)_8]^{4-/3-}$. [f] Ratio of Mo(V) (estimated by ESR-spectroscopic measurements) related to the whole amount of Mo. [g] A second band was found near $19.4\cdot 10^3$ cm^{-1}.

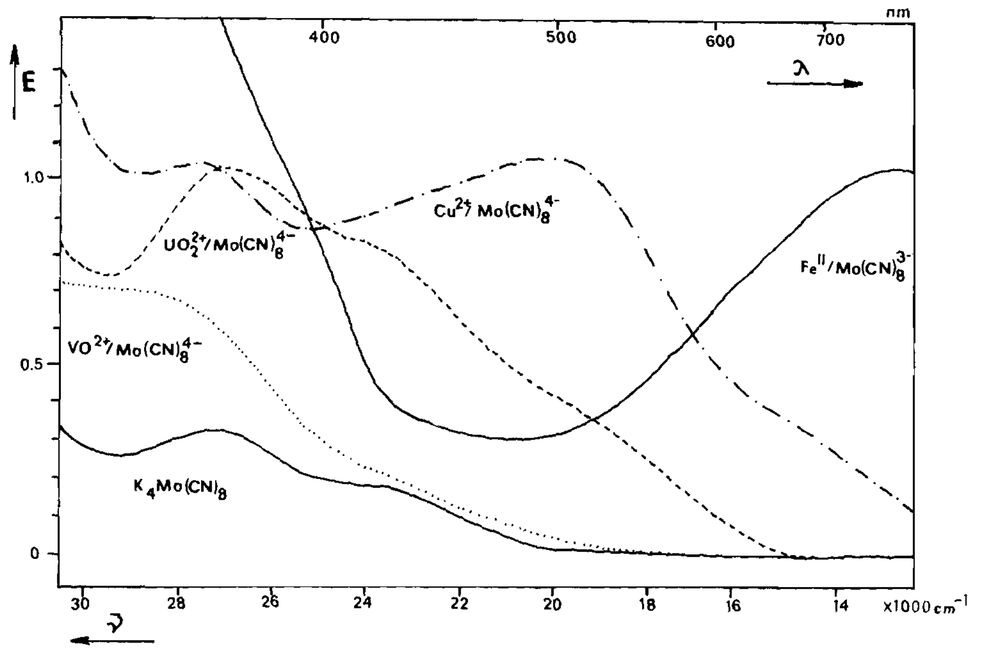

Fig. 1. Ultraviolet-visible spectra of mixed-valence compounds of octacyanomolybdate(IV) in aqueous solution compared with the spectrum of $K_4[Mo(CN)_8]$.

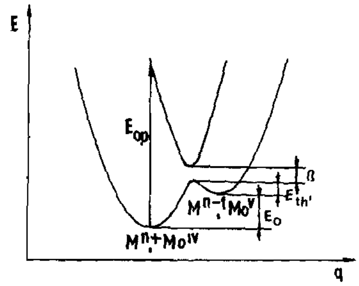

Fig. 2. Potential energy diagram (energy E *vs.* nuclear coordinate q) of mixed-valence compounds with extremely weak coupled metal centers (M^{n+}, Mo^{IV}: precursor complex; M^{n+1}, Mo^V: successor complex; E_{op}: optical IT transition; E_o: enthalpy difference between precursor and successor compound; E_{th}': enthalpy of thermal back electron transfer; β: resonance energy).

Here, IT bands are very broad compared with the usual CT bands. Furthermore, optical transitions can be achieved throughout the complete visible spectral region, depending however on the second metal center occupying the other position within the mixed-valence system. The low-energy limit of the IT transitions is given by the thermal electron transfer reactions between both metal centers. This can be explained on the basis of simple potential curve description of both valence isomeric forms of mixed-valence compounds (see Fig. 2) [8, 23]. Thus, by adding Ce(IV) ions to aqueous solutions of $[Mo(CN)_8]^{4-}$, thermal formation of Ce(III) and $[Mo(CN)_8]^{3-}$ can be observed. This result agrees with the redox potentials of both metal centers ($E^o_{Ce(III)/(IV)} = 1.71$ V [17], $E^o_{[Mo(CN)_8]^{4-/3-}} = 0.84$ V [18]).

Generally, under the condition of other combinations of metal centers to mixed-valence compounds, thermally-induced electron transfer processes have to be considered depending on the appropriate redox potentials. Thus, when combining iron(III) with $[Mo(CN)_8]^{4-}$ the thermal formation of the valence isomeric form $Fe(II)/[Mo(CN)_8]^{3-}$ has been observed by ESR-spectroscopic investigations [10] (see Table I).

By using Job's method [19] in combination with the method of Rose and Drago [20] it has been estimated in agreement with earlier results [21, 22] that in a concentration interval of $c > 5 \cdot 10^{-2}$ *M* the mixed-valence systems under discussion consist of 1:1 associates. By increasing the concentration of UO_2^{2+}, associates of 1:2 are formed. This result could explain the appearance of a second IT transition at lower energies such as of $UO_2^{2+}/[Mo(CN)_8]^{4-}$ mixed-valence compounds (see Fig. 1).

According to the theoretical approach [7, 8, 23], the position of the IT bands correlates to both the optical and dielectric properties of the solvent used, as well as to the redox potentials of the donor and acceptor site of the appropriate mixed-valence system.

Because the energy of the optical IT transition (E_{op}) is correlated to the energy contributions coming from both the inner-sphere ($E_{r,i}$) and outer-sphere reorganization ($E_{r,o}$), from enthalpy differences (ΔE) between both valence isomeric forms of mixed-valence compounds, and from the change of electrostatic interactions (ΔE_{el}) after the optical IT transition (3)

$$E_{op} = E_{r,i} + E_{r,o} + \Delta E + \Delta E_{el} \qquad (3)$$

the position of λ_{max}^{IT} depends linearly on the solvent term $(1/D_{op} - 1/D_s)$, as derived from the continuum theory ($E_{r,o} = f(1/D_{op} - 1/D_s)$). The concurrence of our experimental data with calculated values is represented in Fig. 3.

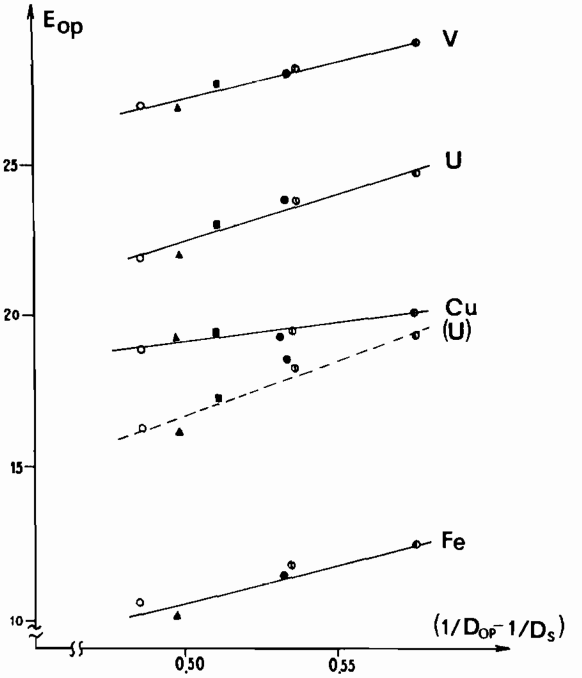

Fig. 3. Dependence of the maximum of the optical IT transition (E_{op}) in $10^3 \cdot cm^{-1}$ of the mixed-valence compounds M^{n+}, $[Mo(CN)_8]$ ($M^{n+} = VO^{++}$, UO_2^{++}, Fe^{3+}, Cu^{2+}) on the solvent term $(1/D_{op} - 1/D_s)$ of solvent/water mixtures (○: DMSO, ▲: DMFA, ■: acetone, ●: MeCN, ⦶: MeOH, ◐: H_2O).

When considering the influence of the dielectric properties of solvents and the redox potential of the metal centers combined with cyanometallates, the position of λ_{max}^{IT} can be influenced also by changing the coordination sphere of the metal centers from water to other ligands. Thus, as seen with copper(II), *i.e.*, it is easily possible to change the redox potential of the acceptor site by going from copper(II) aquo species to complexes with σ-donor and π-acceptor ligands. Therefore it is possible to shift the maximum of the IT transition from about 360 nm ($[Cu(en)_2]^{++}/[Mo(CN)_8]^{4-}$) up to about 660 nm ($[Cu(dmp)_2]^{++}/[Mo(CN)_8]^{4-}$) (see Table II). Interestingly enough, in the case of the mixed-valence system $[Cu(dmch)_2]^{++}/[Mo(CN)_8]^{4-}$ thermal electron transfer processes have been observed due to inadequate redox potentials of the copper(II) complex site. Furthermore, hexa-coordinated and penta-coordinated copper(II) complex units like $[Cu(en)_3]^{++}$, $[Cu(phen)_3]^{++}$ and $[Cu(NH_3)_5]^{++}$ do not show any IT transitions in aqueous solutions. This result can be explained by the formation of cyano-bridged mixed-valence compounds as a condition of the appearance of IT bands, whereas outer-sphere mixed-valence compounds with IT behaviour are not formed in this case. We have been able to prove the formation of cyano-bridged dimers [10] by evaluations according to the models of Marcus [24], Levich [25], Doganadze [26], and Cannon [23, 27], respectively.

TABLE II. Position of the IT-bands of the System $[CuL_n]^{2+}/[Mo(CN)_8]^{4-}$.

CuL_n^{2+}	$\tilde{\nu}_{IT}$ (in 10^3 cm^{-1})^a	E_{Red} (in V)^b
$Cu(phen)Br_2$	17.8	
$Cu(phen)Cl_2$	17.0	
$Cu(phen)(NO_3)_2$	17.0	
$Cu(phen)_2Br_2$	18.0	
$Cu(phen)_2Cl_2$	18.0	
$Cu(phen)_2(NO_3)_2$	17.5	+0.174
$Cu(ach)_2(NO_3)_2$	18.5	
$Cu(bpy)_2(NO_3)_2$	18.0	
$Cu(5\text{-mp.})_2(NO_3)_2$	16.9	+0.337
$Cu(dmp)_2(NO_3)_2$	15.2^c	+0.594
$Cu(dmch)_2(NO_3)_2$	–^{d}	+0.675
$Cu(en)_2(NO_3)_2$	27.8	–0.38

(phen = 1,10-phenanthroline; ach = 8-aminoquinoline; bpy = 2,2′-bipyridine; 5-mp = 5methyl-1,10-phenanthroline; dmp = 2,9-dimethyl-1,10-phenanthroline; dmch = 4,4′-dimethyl-3,3′-dimethylene-2,2′-diquinoline (cuprotest); en = ethylendiamine; PPN = triphenyl-phosphine-iminium). ^{a}Spectra in methanol, concentrations: $5 \cdot 10^{-4}$ *M* $[CuL_n]^{2+}$, $5 \cdot 10^{-4}$ *M* $[CuL_n]^{2+}$, $5 \cdot 10^{-4}$ *M* $(PPN)_4[Mo(CN)_8]$, error of estimation: $\pm 0.1 \cdot 10^{-3}$ cm^{-1}. ^{b}Redox potentials at 298 K. ^{c}Error: $\pm 0.5 \cdot 10^3$ cm^{-1}; 33% formation of $Cu^+/[Mo(CN)_8]^{3-}$. ^{d}Complete thermal reaction is to be observed.

Another possibility of shifting the position of the λ_{max}^{IT}-value consists in varying the 1st coordination sphere of the donor site of the mixed-valence systems under investigation. Thus, with $[Fe(CN)_5X]^{3-}$ in the donor site we have been able to show a strong influence of the λ_{max}^{IT}-value depending on X, as summarized in Table III. As already mentioned, the variation of X within a row of mixed-valence compounds may influence the energy of optical IT transitions considerably. The combination of both variation of the metal centers of the acceptor site and of X within the donor site leads to transitions from about 350 nm up to 800 nm (see Table III).

Furthermore, varying both metal centers of the mixed-valence system offers another possibility of shifting the λ_{max}^{IT}-values. Thus, optical IT transitions

TABLE III. Energy of the IT Transitions in Dependence on the Variation of the First Coordination Sphere of the Donor Site within the System $M^{n+}/[Fe(CN)_5X]^{3-}$.

M^{n+}	$\bar{\nu}_{IT}\,[10^3\ cm^{-1}]$ [a]		
	$[Fe(CN)_5H_2O]^{3-}$	$[Fe(CN)_5NH_3]^{3-}$	$[Fe(CN)_5DMSO]^{3-}$ [b]
Fe^{3+}	13.1	12.7	16.0
Cu^{2+}	21.8	20.1	23.9
UO_2^{2+}	24.0	23.6	25.9
VO^{2+}	27.5	27.5	29.4

[a] The estimation of the absorption maxima was performed with freshly prepared solutions ($c = 10^{-3}\ M$; error $\pm 0.1 \cdot 10^3\ cm^{-1}$).
[b] $E^o = 0.89$ V.

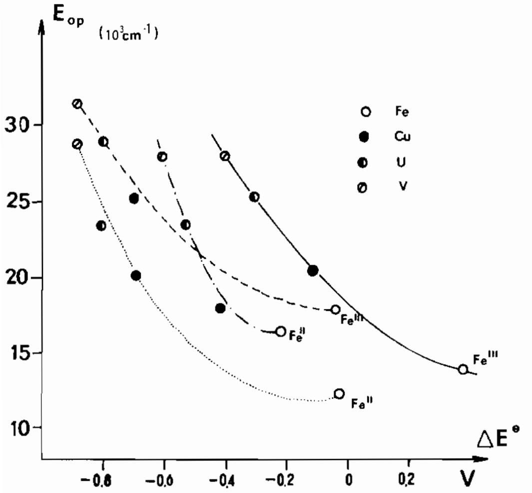

Fig. 4. Optical IT transition (E_{op} in $10^3 \cdot cm^{-1}$) of different mixed-valence compounds M_1^{n+}, $[Me_2(CN)_m]$ (——: $[Fe(CN)_6]^{4-}$; —·—: $[W(CN)_8]^{4-}$; – – –: $[Ru(CN)_6]^{4-}$; ....: $[Mo(CN)_8]^{4-}$) in dependence on their redox potentials (ΔE^o in V).

shown in Fig. 4 can be achieved in aqueous solution between about 330 and 830 nm (see also Table I) depending on the redox asymmetry of both metal centers.

Because of certain experimental difficulties in estimating the thermal redox behaviour of these particular mixed-valence systems by different electrochemical methods, the redox potentials of separated redox couples could not be taken fully into consideration. However, despite inaccuracy concerning the values of redox potentials of the mixed-valence compounds, the potentials of the separated complexes seem to be a very valuable measure for predicting the position of the IT bands in their dependence on various metal centers. According to these considerations we draw the conclusion that the shift of the IT bands into the low-energy region is limited because of the occurence of thermal electron transfer processes. However, it is generally possible to generate optical IT transitions along the complete visible spectral region up to the near infrared by constructing of appropriate mixed-valence systems.

Furthermore, all our experimental results support the suggestion that the mixed-valence systems described belong to class II, according to the Robin-Day classification [4]: the delocalization parameter α^2 provides a good measure for distinguishing between mixed-valence compounds of the classes I, II, and III, respectively. The value of α^2 has been calculated by the following eqn. (4) [28]

$$\alpha^2 = (4.24 \cdot 10^{-4} \cdot \epsilon_{max} \cdot \Delta\bar{\nu}_{1/2})/(\bar{\nu}_{IT} \cdot d^2) \qquad (4)$$

based on appropriate experimental data (ϵ_{max}, $\Delta\bar{\nu}_{1/2}$, $\bar{\nu}_{IT}$) and with values of the distance d between both metal centers as calculated either by the method of Cannon [23, 27] or by that proposed by Marcus [24], Levis [25], and Doganadze [26]. The α^2-values obtained are within a range of 0.0005 (UO_2^{++}, $[Mo(CN)_8]^{4-}$) and 0.0121 (Fe(III), $[Mo(CN)_8]^{4-}$) [10]. These values point out unambiguously the extremely weak coupling between both metal centers as required in mixed-valence compounds belonging to class II.

Finally, in addition to their behaviour discussed before, the IT bands exhibit a very broad band width. As far as the band width of heteronuclear mixed-valence compounds ($E \neq 0$) and at higher temperatures ($kT > h\nu_{IT}$) is concerned the following relation is proven to be valid (5) [7].

$$\bar{\nu}_{IT} = \Delta E + (16kT \cdot \ln 2)^{-1}(\Delta\bar{\nu}_{1/2})^2 \qquad (5)$$

The calculated values for $\Delta\bar{\nu}_{1/2}$ are in good agreement with the experimental results [10], which provides an additional argument of these mixed-valence compounds belonging to class II.

Up to now few results are known concerning photo redox reactions of class II mixed-valence compounds initiated by IT excitation only. Thus, in addition to the Vogler-Kunkely ion [5, 6] further examples can be classified within the weakly coupled mixed-valence systems of class II and characterized by photo redox reactivity [29, 30]. Compared to these results other light-induced redox reactions of mixed-valence compounds with heterocyclic bridging ligands like pyrazine and its derivatives [31, 8] as well as unsaturated carbonic acid derivatives [32, 33], seem to be induced by MLCT excitation. The appearance of MLCT bands instead of IT bands is due to the higher electron delocalization between both metal centers through the bridging ligands (class III compounds). The same must be assumed in the case of the Creutz-Taube ion [8, 34].

In the case of heteronuclear mixed-valence compounds consisting of octacyanomolybdate(IV) and the appropriate counter ion a light-induced electron transfer caused by IT excitation is to be expected. The light-induced electron transfer leads to the formation of the vibrationally-excited valence isomeric species (see Fig. 2) consisting of octacyanomolybdate(V) and the appropriate other reduced metal center. Because of the well known kinetic lability of $[Mo(CN)_8]^{3-}$ [35–38] fast cyanide splitting can be expected, which could compete successfully with the back electron transfer.

Unfortunately the other cyanometallates under investigation do not show comparable changes of their kinetic behaviour caused by the changing of their formal oxidation number. Therefore they have not been investigated photochemically. However, in mixed-valence compounds based on $[Mo(CN)_8]^{4-}$ it should be possible generally to achieve the generation of free cyanide spectrally sensitized to accomplish the photocatalytic cycle described elsewhere [15] as light-sensitive over the whole visible spectral region. We have checked our assumptions concerning the photoreactivity of mixed-valence systems based on $[Mo(CN)_8]^{4-}$ by photochemical investigations of the $Cu(II)/[Mo(CN)_8]^{4-}$ system.

The primary step following from the irradiation is achieved by IT excitation of $Cu(II)/[Mo(CN)_8]^{4-}$ associates. This step can be accompanied by consecutive thermal reactions leading to free cyanide (6).

$$\begin{tikzcd} Cu(II)/[Mo(CN)_8]^{4-} \arrow[r, shift left, "h\nu"] & Cu(I)/[Mo(CN)_8]^{3-} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_S\ {[S]}"'] \arrow[dr, "k_2"] & \\ & Cu^+{-}S & CN^- + \dots \end{tikzcd}$$

$k_2, k_S > k_{-1}$ (S = scavenger) (6)

The problem is the competition of the values of k_2 and k_S, respectively, compared with k_{-1}.

The photochemical investigations have been performed by both monochromatic and polychromatic irradiations at appropriate wave-lengths. Low concentrations of copper(II) and octacyanomolybdate(IV) have been used for their low solubility of the polymeric structures from prussian blue type [56] as formed at higher concentrations. Therefore the analytical estimation of free cyanide seems to be the best indicator concerning photochemical reactions according to eqn. (6). The following results were obtained. No significant photochemical reactions of the mixed-valence compound have been observed compared with $K_4[Mo(CN)_8]$ up to wave-length of irradiation from about 500 nm. However, irradiation above 500 nm leads to increasing formation of free cyanide in the case of mixed-valence compounds. In order to investigate the efficiency of the spectrally-sensitized formation of free cyanide we estimated the photochemical turnover U instead of the quantum yield value (7).

$$U = n_{CN^-}/(I_o \cdot t) \qquad (7)$$

(n_{CN^-} = number of cyanide formed in mol; I_o = intensity of the incident light; t = time of irradiation)

The advantage of estimating U instead of the usual quantum yield values follows from practical aims, because the concentration of free cyanide formed photochemically in relation to the number of incident photons (U) as compared to absorbed photons (ϕ) is of greater interest as far as the question of its practical efficiency of spectral sensitization is concerned. Table IV points out the increase of the photochemical formation of cyanide mediated by IT excitation (above 500 nm) of $Cu(II)/[Mo(CN)_8]^{4-}$ compared with $K_4[Mo(CN)_8]$.

However, despite this increase of the spectrally sensitized formation of cyanide by a factor of approximately 5 (see Table IV) the real concentration is low. The reason for this low efficiency is due to the fact that the rate (k_1) of cyanide substitution of $Cu(I)/[Mo(CN)_8]^{3-}$ can not compete sufficiently enough with the back electron transfer (k_{-1}).

The evaluation of k_{-1} from results derived from the spectroscopic investigation of the IT behaviour of mixed-valence compounds of class II may be achieved according to the conceptual approach of the Hush theory.

Hence, k_{-1} can be obtained from experimental results by the following eqn. (8) or in a modified version according to Grätzel [40].

$$k_{-1} = \nu_{et} \cdot \exp[-E_{th}'/kt] \qquad (8)$$

The value of E_{th}' is easily obtainable from experimental data (E_{op}, E_o and α), whereas the factor ν_{et} can be evaluated according to eqn. (9) [39].

$$\nu_{et} = 4\beta/h \qquad (9)$$

(β follows from spectroscopic data)

The calculated values of k_{-1} as well as the lifetime τ of mixed-valence compounds based on octacyanomolybdate(IV) are summarized in Table V. Table V represents that we have to consider the very short lifetime of the valence isomeric $Cu(I)/[Mo(CN)_8]^{3-}$

TABLE IV. Results of the Photochemical Investigation of the system $Cu^{2+}/[Mo(CN)_8]^{4-}$.[a]

Wave-length of irradiation (nm)	Quantum yield[b]		Turnover U[c]		$U_{IT}/U_{K_4}[Mo(CN)_8]$[f]
	IT-system	$K_4[Mo(CN)_8]$	IT-system	$K_4[Mo(CN)_8]$	
313	1.38	2.61	1.30	1.95	0.67
436	0.27	0.42	0.19	0.12	1.58
495	0.062	0.60	0.048	0.018	2.67
509	0.058	0.95	0.044	0.009	4.89
546	0.025	0[e]	0.017[d]	0[e]	

[a] Aqueous solutions (10^{-3} *M*, 30 ml, d = 2cm, t^{irr} = 0–5h). [b] Quantum yield concerning the formation of CN^- (error ± 15%). [c] Turnover: CN^- formed photochemically in relation to incident light (error ±15%). [d] Error > 15%. [e] Very small concentration of CN^- which was not estimated quantitatively. [f] Ratio of the turnover U of the IT-system compared to that in pure $K_4[Mo(CN)_8]$ solutions.

TABLE V. Calculated Parameters (β, E_{th}', ν_{et}) for Estimating of the Rate Constant k_{-1} and τ of the Mixed-Valence Systems $M^{n+}/[Mo(CN)_8]^{4-}$.

ion pair	β (kJ·mol^{-1})	E_{th}'·(kJ·mol^{-1})	ν_{et}[a]	k_{-1}[b]	τ(s)
$Fe^{2+}/[Mo(CN)_8]^{3-}$	16.44	22.7	1.65	$1.57\cdot10^{10}$	$6.37\cdot10^{-11}$
$Cu^{2+}/[Mo(CN)_8]^{4-}$	15.26	32.4	1.53	$2.78\cdot10^{8}$	$3.60\cdot10^{-9}$
$UO_2^{VI}/[Mo(CN)_8]^{4-}$	6.59	52.0	0.66	$4.09\cdot10^{4}$	$2.45\cdot10^{-5}$
$VO^{IV}/[Mo(CN)_8]^{4-}$	21.10	48.7	2.12	$4.95\cdot10^{5}$	$2.02\cdot10^{-6}$

[a] (10^{14}·s^{-1}), T = 295 K. [b] (s^{-1}), T = 295 K.

mixed-valence system generated by IT excitation (τ = $3.6\cdot10^{-9}$ s). Compared to this the higher lifetime of the appropriate $UO_2^+/[Mo(CN)_8]^{3-}$ species (τ = $2.45\cdot10^{-5}$ s) is due to the formation of outer-sphere mixed-valence systems [10], which lead to an increasing thermal barrier E_{th}'.

In order to check the values of k_{-1} and τ calculated according to Hush's theoretical approach we tried their experimental estimation. We have been able to estimate k_{-1} by low-temperature ESR investigations, as published very recently [14]. The results of these investigations are in surprisingly good agreement with the values calculated theoretically (k_{-1}^{exp} = $(2.74 \pm 1.2)\cdot10^{-4}$ s^{-1}; k_{-1}^{theor} = $8.2\cdot10^{-4}$ s^{-1}; T = 93 K). The lifetime of the $Cu(I)/[Mo(CN)_8]^{3-}$ valence isomeric species is obviously too short compared with the rate of the thermal substitution of kinetically labile octacyanomolybdate(V).

Furthermore, as illustrated in Table V, the lower the energy of E_{op} the lower the lifetime of the vibrationally excited valence isomeric species generated by IT excitation. Because of the short lifetime of $Cu(I)/[Mo(CN)_8]^{3-}$ relative to the rate of the thermal substitution of octacyanomolybdate(V), we have tried to use fast scavenging reactions selective for copper(I). However, simple kinetic considerations have shown (10) that high concentrations of scavengers are required when the back electron transfer is almost totally quenched.

$$k_S\cdot[S] = 100\cdot k_{-1} \qquad (10)$$

([S] = concentration of scavenger)

Thus, in the case of $Cu(I)/[Mo(CN)_8]^{3-}$ (k_{-1} = 10^8 s^{-1}) a concentration of about 1 M of scavenger is required even if the scavenging process is diffusion controlled (k_S = 10^{10} M^{-1} s^{-1}). However, it is unfortunately impossible to achieve in aqueous solutions appropriately high concentrations of neutral scavengers such as benzonitrile, triphenylphosphine, various phenol derivatives, $[Co(NH_3)_3(N_3)_3]$ and others. Whereas acetonitrile already undergoes thermal redox reactions with the mixed-valence compound $Cu(II)/[Mo(CN)_8]^{4-}$ itself, ionic scavengers such as oxalatoferrate(III), $[Co(NH_3)_5N_3]^{++}$, and appropriate diazonium compounds, *e.g.* lead to uncontrolled influences on the association equilibria of the mixed-valence system. For that reason we were unable to overcome the barrier of fast back electron transfer by chemical scavenging processes. Therefore one should consider that chemical quenching of back electron transfer processes can be achieved preferably by extremely fast scavenging reactions occurring within the excited valence isomeric species itself. Such extremely fast scavenging reactions may be obtained especially by the substitution of the reduced or oxidized site of the valence isomer by the solvent as described for the Vogler-Kunkely ion [5, 6]. As far as we know only one example of chemical scavenging with an additional scavenger has been described [6]: the scavenging reaction of $[Co(CN)_5]^{3-}$ by oxygen (11).

$$[(CN)_5Co^{III}\text{–}NC\text{–}Fe^{II}(CN)_5]^{6-} \xrightarrow{h\nu^{IT}}$$

$$\begin{array}{c} [(CN)_5Co^{II}\text{–}NC\text{–}Fe^{III}(CN)_5]^{6-} \\ \downarrow \\ \vdots\ {+O_2} \\ \downarrow \\ [(CN)_5Co\text{–}O_2\text{–}Co(CN)_5]^{6-} + \ldots \end{array} \qquad (11)$$

However, in addition to chemical scavengers we have used the physical scavenger light to quench back-electron transfer in the mixed-valence isomers consisting of $M^{n+}/[Mo(CN)_8]^{3-}$ [9, 13]. Because of the well-known photo reactivity of octacyanomolybdate(V) itself there is reason to believe in inducing an unusual type of sequential two-photon processes initiated by irradiation with light of energy sufficient enough to generate primarily the valence isomeric species $Cu(I)/[Mo(CN)_8]^{3-}$ from the appropriate precursor compound, and secondarily to initiate the photooxidation of water by the $[Mo(CN)_8]^{3-}$-site according to eqn. (12).

$$Cu(II)/[Mo(CN)_8]^{4-} \underset{k_{-1}}{\overset{h\nu_1^{IT}}{\rightleftharpoons}}$$

$$\begin{array}{l} Cu(I)/[Mo(CN)_8]^{3-} \\ \quad H_2O \Big\downarrow h\nu_2 \\ Cu(I)/[Mo(CN)_8]^{4-} + OH^{\bullet} + H^{+} \\ \qquad\qquad\qquad\quad k_S \Big\downarrow S \\ \qquad\qquad\qquad\quad S\text{–}OH \end{array} \qquad (12)$$

The most interesting fact here is the formation of hydroxide radicals characterized by a prolonged lifetime ($\tau = 3.65 \cdot 10^{-5}$ s) as compared with $Cu(I)/[Mo(CN)_8]^{3-}$. Therefore $OH^{\bullet}$ radicals can be scavenged very easily by 4-nitroso-dimethylaniline (4-NDMA) [41].

Scavenging experiments with 4-NDMA and appropriate kinetic investigations show unambiguously the formation of $OH^{\bullet}$ radicals according to eqn. (12) initiated by secondary photolysis of $Cu(I)/[Mo(CN)_8]^{3-}$ [13]. This result indicates that the reaction pathway (12) may be interpreted as a sequential two-photon process [9, 13, 14].

Various experiments suggest the appearance of a sequential two-photon process to be responsible for the formation of $OH^{\bullet}$ radicals which have also been detected by spin-trapping [9]. Thus, $OH^{\bullet}$ radicals have been observed only under conditions of IT excitation, whereas irradiation at wavelengths of 365 nm and 492 nm did not yield any comparable result. Furthermore, octacyanomolybdate(V) synthesized by oxidation of $[Mo(CN)_8]^{4-}$ with Ce(IV) does not show any thermal formation of $OH^{\bullet}$ radicals. The $OH^{\bullet}$-scavenger 4-NDMA itself is light-insensitive under our experimental conditions, and does not react with copper(II), octacyanomolybdate(IV), and the mixed-valence compound $Cu(II)/[Mo(CN)_8]^{4-}$ either under thermal or photochemical conditions. Furthermore, the direct photochemical generation of octacyanomolybdate(V) has been avoided by cutting-off light of higher wavelength than $27 \cdot 10^3$ cm^{-1}. Moreover, the estimation of the stationary concentration of $Cu(I)/[Mo(CN)_8]^{3-}$ in relation to both the extinction of $[Mo(CN)_8]^{3-}$ is to be expected and the number of photons absorbed at appropriate wavelength confirms unambiguously the appearance of a two-photon process. Final experiments of simultaneous irradiation with two laser-beams of distinct wavelength ($\lambda_1 = 520$ nm; $\lambda_2 = 365$ nm) and of tuned intensity are in preparation to exclude any further light-sensitive intermediates.

As far as we know in the case of coordination compounds sequential two-photon processes have only been described when occurring in secondary excitation of higher electronically excited states (see *e.g.* [42, 43]). But sequential two-photon processes as described in eqn. (12) distinguish themselves from others by the following factors: the first (13) as well

$$Cu(II)/[Mo(CN)_8]^{4-} \xrightarrow{h\nu_1} Cu(I)/[Mo(CN)_8]^{3-} \qquad (13)$$

as the second excitation (14) lead to vibrationally excited ground states.

$$Cu(I)/[Mo(CN)_8]^{3-} \xrightarrow[H_2O]{h\nu_2} Cu(I)/[Mo(CN)_8]^{4-} + + OH^{\bullet} + H^{+} \qquad (14)$$

Therefore it would also be possible to discuss that reaction as secondary photolysis. Furthermore, in contrast to usual two-photon processes, photons of distinct energy are required to initiate the sequential two-photon process according to eqns. (13) and (14). Finally, instead of laser irradiation required in case of electronically excited state sequential two-photon processes usual light sources can be used.

In summary one can say that mixed-valence compounds belonging to class II are of considerable interest regarding the possibility to generate optical windows from the ultraviolet up to the near infrared. These optical transitions can be shifted systematically by varying the metal centers, and their coordination spheres, as well as by changing the bridging ligand in case of inner-sphere mixed-valence compounds. Furthermore, the dielectric properties of various solvents can be used to shift the position of the $\lambda_{max}{}^{IT}$–values. The position of the maximum of IT bands can be predicted approximately by applying the theoretical approach of Hush.

However, as far as the advantages of mixed-valence compounds with respect to static spectral sensitization of photocatalytic systems [1] is concerned fast back electron transfer processes are to be considered. However, the back electron transfer can be quenched by either fast chemical scavenging processes, preferably within the valence isomeric species of the appropriate precursor mixed-valence compounds or by physical scavengers such as light. Thus we were able to demonstrate that a new type of sequential two-photon processes might be helpful in overcoming the restrictions of fast back electron transfer processes.

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