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Photochemistry of transition metal octacyanides and related compounds. Past, present and future*

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Abstract

The review is given on previous and recent developments in the solution photochemistry of $M(CN)_8^{4-}$, $M(CN)_8^{3-}$, ion pairs of $M(CN)_8^{4-}$ with counter cations and of mixed-ligand cyano-polypyridyl complexes of the type $W(CN)_6(NN)^{2-}$, (NN= 2,2'-bipyridyl and 1,10- phenanthroline). Unanswered questions that can serve as the basis for the future research are raised.

1. INTRODUCTION

Octacyanides of transition metals [M=Mo(IV,V), W(IV,V) and Nb(III,IV)] have been the subject of interest since many years (see papers [1]) from the point of view of their structure, reactivity and photochemistry, often with contradictory results. Their chemistry and photochemistry is similar, in many aspects to those of the much better known hexacyano complexes, but the higher coordination number of the central metal, possibility of changing the coordination polyhedra and coordination number during photochemical and thermal reactions make the study more difficult. Thus the number of papers published and the knowledge of problems including formation and behaviour of mixed-ligand compounds are much lower. In this paper we present a review on the structure, spectroscopy and photochemistry of octacyanides and related compounds, mainly that of molybdenum and tungsten. Niobium complexes discovered relatively lately [2] still wait for more detailed study.

2. STRUCTURE

The structures of $M(CN)_8^{n-}$ (n=2,3 or 4) ions are themselves of great interest and various investigations have been carried out to determine the geometries of these ions in the solid state and in solution. X-ray crystallographic studies have provided examples of square antiprismatic (D_{4d}), dodecahedral (D_{2d}) or bicapped trigonal prismatic (C_{2v}) configurations as well as

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*Dedicated to Professor Vittorio Carassiti on the occasion of his 70th birthday.

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those lying between the idealized polyhedrons (see Table 1).

Table 1.
The X-ray crystal structure of $[M(CN)_8]^{3-/4-}$ (M= Mo,W) anions with various cations.

Symmetry	**Complex formula**		**Ref.**
	Mo	**W**	
D_{4d}	$Cd_2[Mo(CN)_8]\cdot 2N_2H_4\cdot 4H_2O$	---	[3]
	a	$H_4[W(CN)_8]\cdot 6H_2O$	[4]
	---	$H_4[W(CN)_8]\cdot 4HCl\cdot$ $\cdot 12H_2O$	[5]
	$Ag_4(NH_3)_5[Mo(CN)_8]\cdot 1.5H_2O$	---	[6]
	a	$(4,4'bpyH_2)_2[W(CN)_8]\cdot$ $\cdot 4.5H_2O$	[7]
$D_{2d}{}^{b}$	$K_4[Mo(CN)_8]\cdot 2H_2O$	a	[8]
	$(n\text{-}Bu_4N)_3[Mo(CN)_8]$	---	[9]
	$(C_6H_6NO_2)_4[Mo(CN)_8]$	a	[10]
	$Rb_4[Mo(CN)_8]\cdot 3H_2O$	---	[11]
$D_{2d}+D_{4d}{}^{c}$	$(NH_4)_4[Mo(CN)_8]\cdot 0.5H_2O$	---	[11]
$D_{4d}-D_{2d}{}^{d}$	a	$Na_3[W(CN)_8]\cdot 4H_2O$	[12]
C_{2v}	$Cs_3[Mo(CN)_8]\cdot 2H_2O$	---	[13]
$D_{2d}-C_{2v}{}^{d}$	$(Et_3NH)_2(H_3O)_2[Mo(CN)_8]$	a	[14]

[a] Mo or W salts were found to be isomorphic; [b] this geometry was found also for $K_4[Nb(CN)_8]\cdot 2H_2O$ [2] and for $K_5[Nb(CN)_8]$ [15]; [c] two different environments of Mo atoms; [d] the coordination polyhedron can be described as about half-way between two idealized polyhedra.

The ESR and vibrational spectra indicate that in some cases in aqueous solution the structure of the anion changes from D_{2d} to D_{4d} [15,16] and from that between $D_{4d}-D_{2d}$ to D_{2d} [17]. In recent years we have found a new phenomenon of phase transitions observed for complexes with tetrabutylammonium cation [18]. The reorientation of different groups of the organic cation was found to be responsible for the phase transitions at the temperatures of 260K and 295K for Mo and 280K and 340K for W-complex.

3. THERMAL REACTIVITY

Thermodynamically stable and kinetically inert octacyanides [19,20] have been employed in the oxidation [M(V)] and in the reduction [M(IV)] of many classes of compounds in both basic and acidic media. Examples are the reduction of MnO_4^-,$S_2O_8^{2-}$,VO^{2+} $Ag(OH)_4^-$, IO_3^-, IO_4^- [21] and CrO_4^{2-} [22] as well as the oxidation of hydrazine and substituted hydrazines, hydroxylamine, formaldehyde, thiourea, thioacetamide and arsenite [21], iodide [23] manganate(VI) [24], iron (II) [25], benzoins [26] and ascorbic acid [27]. In most cases the simple experimental rate-law

$$\text{rate} = k_{obs}\,[Ox]\,[Red] \qquad (1)$$

and outer-sphere mechanism was proposed, but in some cases the influence of pH and ion-pair formation was also taken into consideration. Unfortunately, there is no detailed study on the reduction of $M(CN)_8^{3-}$ by the OH^- and CN^- ions and on the reactions of both octacyanides with hydrogen peroxide which, depending on pH, acts as a reducing or oxidizing agent [28]. All these reactions are important to understand the complicated photochemistry of M(V)-octacyanides especially that in alkaline medium. This prompted us to investigate recently the reduction of octacyanometallates(V) by OH^- ions in aqueous solution. A complicated experimental rate law was found [29]

$$\text{rate} = \frac{k'\,[M(CN)_8^{3-}]^2\,[OH^-]\,[K^+]}{k'' + k'''\,[M(CN)_8^{4-}]} \qquad (2)$$

The mechanism of the reaction involves the formation of OH radical as the intermediate and the final evolution of oxygen according to stoichiometric equation

$$4\,M(CN)_8^{3-} + 4OH^- = 4\,M(CN)_8^{4-} + O_2 + 2H_2O \qquad (3)$$

4. PROPERTIES OF THE GROUND STATE OF $M(CN)_8^{4-}$

Although the symmetry of $M(CN)_8^{4-}$ depends on the environmental effects it is common to discuss such complexes in terms of dodecahedral symmetry, where the ground electronic state is a singlet $^1A_1$. A typical absorption spectra [30,31] consists of metal-centered, MC, bands: two very weak singlet-triplet bands at 580 and 510 nm (Mo) and 625 and 600 nm (W) as well as three singlet-singlet bands at 427, 367 and 304 nm (Mo) and 433, 369 and 302 nm (W). In the ultraviolet part of the spectra there are two charge transfer bands: metal-to-solvent (MSCT) band at 267 nm (Mo) and 275 nm (W) [32] and metal-to-ligand (MLCT) charge- transfer band at 240 nm (Mo) and 249 nm (W) [31]. These transitions are illustrated in the energy level diagram in Figure 1.

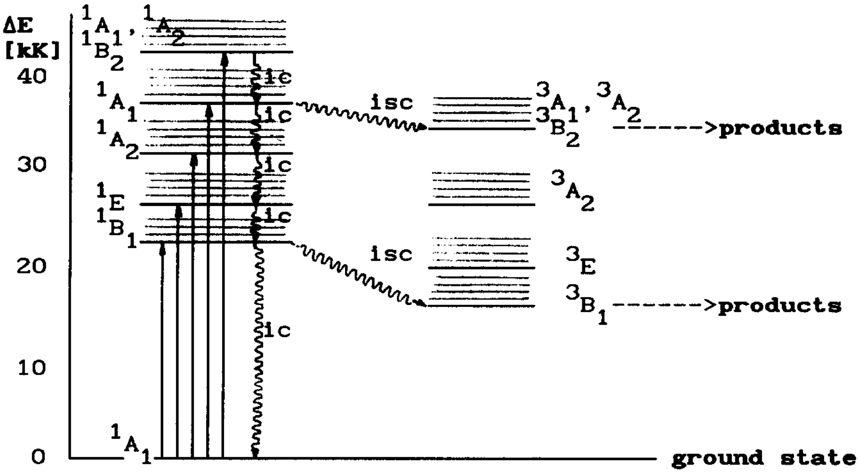


Figure 1. Simplified energy-level diagram of M(CN)$_8^{4-}$ complexes (based on calculation of A. Gołębiewski and R. Nalewajski [33]); ic denotes internal conversion, isc - intersystem crossing. Straight-line arrows refer to radiative transition, wavy-line arrows refer to nonradiative transitions.

5. PHOTOCHEMISTRY OF M(CN)$_8^{4-}$

The photochemistry of M(CN)$_8^{4-}$ has a long and noble history [34]. The general mechanism accepted for the photochemical reactions occurring under MSCT excitation can be described by the scheme [35]

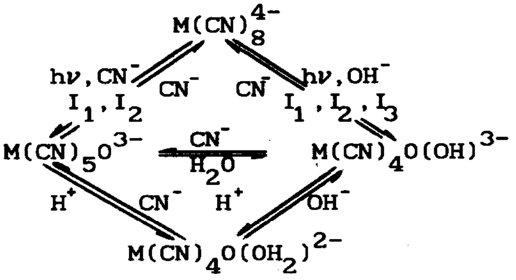
$$M(CN)_8^{4-} \xrightarrow{h\nu} [M(CN)_8]^{4-*} \longrightarrow M(CN)_8^{3-} + e^-_{aq} \quad (4)$$

The MSCT state can be reached either directly or by the internal conversion from MLCT transition (Figure 1). Upon continuous irradiation in aqueous solution at room temperature, this reaction becomes complicated by side reactions such as recombination and ligand substitution. However, when $CHCl_3$ is used as solvent, a clear, one-electron photo-oxidation without side reaction was observed [36].

The substitutional photochemistry of octacyanometallates described by the scheme

$$M(CN)_8^{4-} \xrightarrow{h\nu} [M(CN)_8^{4-}]^* \longrightarrow \text{photoaquation products} \quad (5)$$

was recognized early [1,37]. The systematic studies performed in the sixties by Carassiti et al [38], Adamson et al [37,39] and Jakób et al [40] were later continued by others [41-44]. These studies can be summarized in the Scheme 1



$I_1 = M(CN)_7(OH_2)^{3-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} M(CN)_7(OH)^{4-}$

$I_2 = M(CN)_6(OH_2)_2^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} M(CN)_6(OH)_2^{4-}$ or $M(CN)_6^{2-}$

$I_3 = M(CN)_5O^{3-}$

Scheme 1. Alkaline photolysis of octacyanometalate(IV) in the presence and absence of potassium cyanide.

valid for the natural pH (during photolysis the pH increases to *ca* 11) and for the alkaline aqueous solutions [43]. The spectral behaviour of irradiated $M(CN)_8^{4-}$ solution depends not only on the pH of solution but also on the concentration of the complex and the concentration of the added CN^-. In alkaline solution blue (Mo) and purple (W) $M(CN)_4O(OH)^{3-}$ is formed through hepta- (I_1), hexa- (I_2) and penta- (I_3) cyano-species as intermediates. Addition of CN^- stabilizes the green (Mo) and blue (W) oxopentacyanometallates(IV). $M(CN)_5O^{3-}$ easily hydrolyses, depending on pH, to $M(CN)_4O(OH)^{3-}$ or $M(CN)_4O(OH_2)^{2-}$. The initial quantum yields of heptacyanide formation is near to one whereas the final quantum yields of $M(CN)_4O(OH)^{3-}$ formation (at pH 13) is equal to 0.7 [43].

6. PHOTOCHEMISTRY OF ION PAIRS

The alkali metals octacyanides react with a number of bivalent and trivalent metal ions as well as with organic cations to give stable compounds [7]. Ion pairs which contain a reducing [M(IV)] and an oxidizing [Cu(II), Fe(III), Pt(IV), U(VI), Ph_2I^+ 2,2'-bpyH$^+$] cation show ion-pair charge-transfer (IPCT) bands in their absorption spectra [46-48]. Irradiation within IPCT bands followed by excitation within CT bands of $M(CN)_8^{3-}$ formed

$$\begin{tikzcd} Cu^{2+}, Mo(CN)_8^{4-} \arrow[r, "h\nu_1 (IPCT)"] & Cu^{+}, Mo(CN)_8^{3-} \arrow[d, shift left, "h\nu_2\ (CT)"] \\ & Cu^{+}, Mo(CN)_8^{4-} + \dot{O}H + H^{+} \arrow[u, shift left, "H_2O"] \end{tikzcd} \qquad (5)$$

results in the reduction of counter ion and formation of OH radical [46]. Similar reaction scheme we have found for the 2,2'-bpyH$^+$/$M(CN)_8^{4-}$ system. We are studying now the 4,4'-bpyH$_2^{2+}$ / $M(CN)_8^{4-}$ system for which IPCT band is observed at 480nm (Mo) and 550nm (W) (in solids at 590nm and 700nm respectively [7]).

7. PHOTOCHEMISTRY OF THE M(CN)$_8^{4-}$-POLYPYRIDYL SYSTEM

Photochemical substitution reactions of CN^- ligand in octacyanocomplexes by 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) have been reported [49]. We have found, however, that in fact, the photoaquation occurred, followed by thermal substitution of $M(CN)_5O^{3-}$ or $M(CN)_4O(OH)^{3-}$ (Scheme 1) by polypirydyls [50] leading to the $M(CN)_3(NN)O^-$ ions. The crystal structure of 1:2 phen adduct [51] and 1:0.5 bpy adduct [50] showed that the anions are distorted octahedrons. They exhibit low lying MLCT bands which are solvent dependent (Table 2) and can be correlated with acceptor number (AN) and Reichard's E_T parameter [50, 52].

Table 2.
λ_{max}[nm] (ε_{max} 10^{-3}) of MLCT bands for $M(CN)_3(NN)O^-$ and $M(CN)_6(NN)^{2-}$ ions in various solvents.

Solvent	$M(CN)_3(bpy)O^-$		$W(CN)_6(NN)^{2-}$	
	Mo	W	bpy	phen
H_2O	455(1.89)	385(a)	380(2.90)	340(a)
	645(0.17)	495(a)	565(4.90)	500(a)
		666(a)		552(a)
MeOH	367(1.89)	401(3.06)	409(3.20)	363(2.20)
	498(4.27)	432(3.53)	612(7.00)	606(11.2)
	642(0.78)	526(4.63)		
		684(3.23)		
EtOH	368(1.94)	402(3.08)	412(4.00)	365(a)
	506(4.43)	437(3.71)	615(8.30)	609(a)
	645(0.86)	531(4.56)		
		688(3.40)		
MeCN	379(2.20)	418(3.48)	440(3.90)	390(a)
	400(2.17)	455(4.92)	660(9.20)	656(a)
	525(5.14)	555(4.36)		
	655(1.22)	711(4.76)		
Me_2CO	393(2.53)	433(3.52)	--	--
	431(2.32)	477(6.28)		
	546(5.62)	562(3.27)		
	666(1.86)	737(5.68)		
DMSO	--	--	445(4.10)	397(a)
	--	--	670(9.90)	673(a)

^{a}not determined.

8. CHEMISTRY AND PHOTOCHEMISTRY OF CYANO-POLYPYRIDYL COMPLEXES

Although mixed-ligand cyano-polypyridyl complexes were not obtained on photochemical way, we obtained the complexes of the general type $W(CN)_6(NN)^{2-}$ thermally using appropriate ion pairs as substrates [52, 53]. They have, in many aspects, similar properties to that of the well known class of cyano-polypyridyls of transition metals [e.g. Fe(II), Ru(II) and Os(II)]. With their fairly high solvent sensitivity (Table 2) we expect these $W(CN)_6(NN)^{2-}$ anions to prove a useful indicator of solvation and local environment in water-rich media, including micellar systems and such "organized media". The redox potential of the reversible couples $W(CN)_6(NN)^{-}$ / $W(CN)_6(NN)^{2-}$ (cyclic voltammetry) is relatively high as compared with the $M(CN)_8^{3-}$/ $M(CN)_8^{4-}$ system (Table 3). For both bpy and phen complexes, electron withdrawing polypyridyls decrease the reducing ability of M(IV) complexes but some solvents increase it considerably.

Table 2.
Formal redox potentials [V] for $M(CN)_8^{3-/4-}$ and $W(CN)_6(NN)^{-/2-}$ complexes in different solvents (ionic strength 0.1).

Solvent	Formal redox potential			
	$Mo(CN)_8^{3-/4-}$	$W(CN)_8^{3-/4-}$	$W(CN)_6(bpy)^{-/2-}$	$W(CN)_6(phen)^{-/2-}$
H_2O	0.78	0.51	0.84	0.86
MeOH	0.58	0.32	0.75	0.78
Me_2CO	--	--	0.61	0.62
MeCN	0.51	0.26	--	--
DMSO	0.19	-0.06	0.60	--

Continuous photolysis of $M(CN)_6(NN)^{2-}$ ions in aqueous solution leads to substitution of polypyridyl ligand by two water (or hydroxy) molecules [53,54]. The wave-length independent quantum yields, Φ, increase from $\Phi= 3.1\times10^{-3}$ (at pH 1) to $\Phi= 7.2\times10^{-3}$ (at pH range 8.12-10.85) for NN=bpy and is equal to 8.5×10^{-3} (natural pH) for NN=phen. The photoreaction occurs from low- lying MC state [53,54]. The $W(CN)_6(NN)^{-}$ ions undergo photoreduction to W(IV) analogue with initial quantum yields $\Phi(365)= 0.17$ (bpy) in water and $\Phi(365)= 0.19$ (phen) in methanolic solution [53,54].

9. PHOTOCHEMISTRY OF $M(CN)_8^{3-}$

CT and MC photochemistry of $M(CN)_8^{3-}$ has been recently reviewed by Kemp [55] and Sieklucka [21]. The characteristic feature of CT photochemistry is that the mechanism of the primary act

$$M(CN)_8^{3-} + H_2O \xrightarrow{h\nu} M(CN)_8^{4-} + H^+ + \dot{O}H \qquad (6)$$

proposed for the first time by Carassiti and Balzani [55] and supported by us for W-compound [57] seems to be valid also for the Mo-analogue [58,59]. In the latter case intramolecular pathway

$$Mo(CN)_8^{3-} \xrightarrow{h\nu} Mo(CN)_8^{3-} + \dot{C}N \qquad (7)$$

has also been earlier proposed [60]. Initial quantum yields of $M(CN)_8^{4-}$ formation are lower than one [Φ=0.8 (W) and Φ *ca* 0.9 (Mo)] [57,58,60] and are independent on pH, whereas the final quantum yields are pH dependent and much higher than one in alkaline solution. The reduction by H_2O_2 formed by recombination of $\dot{O}H$ radicals and by OH^- ions seems to be responsible for high quantum yields.

A detailed study on W-complex revealed [61,62] that besides the photoredox process (equation 6), about 10% of reaction proceeds through the transient $W^{V}(CN)_7^{2-}$ which either becomes solvated or reacts with $W(CN)_8^{3-}$ giving several products characterized as $(CN)_6W^{VI}$-NC-$W^{VI}(CN)_6^-$, $(CN)_7W^{VI}$-NC-$W^{IV}(CN)_7^{5-}$ and $(CN)_7W^{VI}$-NC-$W^{IV}(CN)_6$-CN-$W^{VI}(CN)_7^-$. The photochemistry of $W(CN)_8^{3-}$ ion was found also to be intensity dependent. At high irradiation intensities a new absorption band appears (λ_{max} = 535 nm) assigned to $W^{IV}(CN)_7O_2^{3-}$ [63]. From irradiated water-methanolic solution two new complexes $W(CN)_6O^{2-}$ and $W(CN)_6OCH_3^-$ were isolated and characterized by crystal structure analysis [64].

10. FUTURE

As in all areas of research there are many unresolved problems and unanswered questions that will serve as the basis for future research.

1) What is the real composition and structure of several intermediates and final products in photochemistry of both $M(CN)_8^{3-}$ and $M(CN)_8^{4-}$? Photochemistry of niobium octacyanides is still unknown.
2) Acidic photolysis of $M(CN)_8^{4-}$ and alkaline photoreduction of $M(CN)_8^{3-}$ needs more details.
3) Details for nonaqueous solvents and mixed solvents are not available or only mentioned.
4) What is the energy of "thexi" states, their geometry and lifetimes. What is the formal redox potential for the excited states ?
5) Synthesis of new cyano-polypyridyl complexes (which can be finely "tuned" by alteration of type and number of ligands and by alteration of solvents) is necessary.
6) To what extent can $M(CN)_6(NN)^{2-}$ complexes be used in solar energy conversion and storage schemes ? Their photochemical and thermal stabilities, their spectroscopic and redox properties seem to be promising.

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