Coordination Chemistry Reviews
159 (1997) 271–294

Photosubstitution and photoredox behaviour of cyanometallates: reaction models

Zofia Stasicka *, Ewa Wasielewska

Department of Inorganic Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland

Contents

Abstract

This paper surveys thermal and photochemical reactivities of the cyanometallates. The thermal reactivity is described in connection with the unique properties of the cyanide ligand, whereas photochemical behaviour is discussed with reference to characteristics of the relevant excited states. For some hexacyano and pentacyanonitrosyl complexes the reactivity is interpreted using a simple INDO-type method. The modelling procedure for the thermal reactivity consists in interpreting the characteristics of the frontier orbitals, bond orders and charge distributions in the ground state, whereas photochemical reactivity is modelled by calculating the electronic structure of the selected excited states and analyzing the differences between the features of the ground and excited states. © 1997 Elsevier Science S.A.

Keywords: Photosubstitution; Photoredox behaviour; Cyanometallates

1. Introduction

One of the most important recent applications of transition metal complexes is to build them into supramolecular species in which chromophoric and reactive or

---

* Corresponding author.

PII S0010-8545(96)01310-0

luminophoric components are covalently linked together. An inexhaustible source of such systems involves the chemistry of ligands efficiently bridging metal ion centres. One of the most intriguing members of this group is the cyanide ligand. The uniqueness of its behaviour is revealed by a versatility in bonding, variety of complex structures and diversity of photochemical modes. The variety of complex structures includes such rare geometries as columnar compounds, cyanoclathrates, clusters, cyanospinels and compounds with different CN bridges. The photochemical modes lead to generation of various species of potential importance in catalysis such as CN^- ions, cyano or solvent radicals, solvated electrons, and complexes unsaturated coordinatively or in a reactive oxidation state.

The aim of this article is to survey the photochemical reactivity of cyano complexes and the trends in its theoretical interpretation in order to elucidate the correlation between reactivity patterns and electronic structures.

The survey is limited to the mononuclear complexes and mainly presents the material which has not been covered in previous review articles and books [1–11].

2. General characteristics of cyanide as a ligand and thermal reactivity of cyano complexes

The unique properties of the CN^- ligand make the photochemistry of its complexes unconventional and diverse. For a mechanistic study one can have at one's disposal an exceptionally wide variety of systems, e.g., complexes in low and high oxidation numbers or/and with low or high coordination numbers differing remarkably in lability, in redox reactivity, etc. Moreover, a sophisticated play of weakening and strengthening of both σ- and π-bonding is often involved in activation or photoactivation processes. This is of special significance in the case of mixed-ligand complexes.

(i) One of the most important features of the ligand consists in its ambidentate but strongly asymmetric behaviour: both carbon and nitrogen can act as donor atoms, but there is a significant difference in their bonding ability [12]. Although R–CN and R–NC isomers are quite common in organic chemistry, virtually all the cyano complexes of transition metals, wherein CN^- is coordinated as a monodentate ligand, have been recognized as C-bonded. In a few cases the formation of an N-bonded species was claimed [3] but only for the $[Co(CN)(H_2O)(dmgH)_2]$ complex (where $dmgH_2$ = dimethyl-glioxime) has the existence of the cyano and the less stable isocyano isomer been verified crystallographically [13].

The strong C-atom basicity originates from the HOMO σ-orbital mostly localized on the carbon atom. The nitrogen end is appreciably less basic due to lower energy of the σ_s^* orbital localized mainly on the N-atom [14]. This is manifested by a considerable difference in hardness of the two donor atoms: when bonding through the C-atom, cyanide is one of the softest ligands (Δ = 2 kcal) due to a narrow HOMO-LUMO gap, whereas for N-bonded isomers Δ is much higher (12 kcal) [15].

(ii) C-bonded CN^- is a strong field ligand belonging (together with CO, NO^+, C_2H_4, C_2H_2) to a group of strong σ-donors and good π-acceptors [16]. The π-acceptor ability of CN^- is the lowest within the isoelectronic CN^-, CO, NO^+ series, mainly due to its negative charge. In spite of this, the consequences of π-bonding are of key importance. The back-donation prevents accumulation of a large negative charge on the metal atom, and contributes substantially to the M–C bond strength, thus enhancing d-orbital splitting energy. This is why cyanides are counted among the low spin complexes with all the consequences for structure and properties. The predominance of σ- over π-bond reinforces the C–N bond upon coordination to a metal. Thus, the stretching frequencies, ν(CN), are generally higher for cyano complexes than for free CN^-, whereas the opposite prevails in the case of the CO ligand [1,3,17].

It is generally assumed that the contribution of π-acceptance to the total energy is responsible for stabilization of central metal ions with a large number of electrons, as a consequence of which there exists a broad variety of cyano complexes of late transition elements in a low oxidation state. The importance of the contribution increases when the energy difference between the filled metal d-orbitals and the empty π*-orbitals of the ligand decreases, and therefore the sensitivity to the nature of co-ligands bound to the metal ion is observed. Consequently, mixed-ligand cyano complexes at low oxidation numbers usually contain other π-acceptors, like CO, NO^+. Examples of such complexes are: a large family of the $[M(CN)_5NO]^{n-}$ complexes, $[Fe(CN)_5CO]^{3-,2-}$ ions [1–5,18–27], $Re_3(CN)_3(CO)_{12}$ and $[Os_3H_2(CN)(CO)_{10}]^-$ clusters [28,29] or mixed valence Mo(0) or W(0) complexes [30].

The contribution of π-back donation also depends on the nature of the central metal atom, which can be illustrated by its decrease in the series $[Fe(CN)_6]^{4-} > [Co(CN)_6]^{3-} > [Cr(CN)_6]^{3-}$ [31].

The π-acid properties together with the nonbulky shape of the CN ligand assist the d_{z^2} and p_z orbitals of the adjacent metal atoms to overlap effectively. Consequently, the M–M bonds are formed leading to one-dimensional stacks of the square-planar $[M(CN)_4]$ units. Such structures are typical of d^8 complexes of Ni(II), Pd(II) and Pt(II) [32–37].

The π-acid properties are also responsible for stability of d^{10} cyano complexes. These were reported to exist in the form of cubic cyanospinels of the formula $M_2[M'(CN)_4]$ (where $M = K^+$ or Rb^+ and $M' = Zn(II)$, Cd(II) or Hg(II)) [38].

(iii) The overlap of the filled cyanide π-orbitals with the relevant metal empty d_π-orbitals can also stabilize the central metal ion with a low number of electrons. In such a case cyanide resembles other π-basic ligands like those with F- or O-donor atoms, which stabilize the early transition elements in a high oxidation state [1,2,39]. This is mostly accomplished with coordination numbers higher than 6, especially with larger central atoms from the second and third transition series. The d^4 and d^3 systems can be stabilized by seven CN^- ligands, whereas d^2 and d^1 configurations are known to be stable in the $[M(CN)_8]^{n-}$ complexes [39].

The importance of the π-donor contribution increases when the energy difference between the orbitals decreases being sensitive to the nature of the co-ligands bound to the metal ion. This is why there exists a large number of oxocyano complexes at high oxidation numbers. The mixed oxocyano ligands were recently reported to stabilize even the d^0 configuration in W(VI) complexes [40,41]. The oxoligands are also known to act as bridges in oxocyanocomplexes, which can be exemplified by μ-oxo-bis[oxotetracyanorhenium(V)] [42]. Also fluoro or nitrido co-ligands are effective in stabilization of the low number of electrons, e.g., the d^2 configuration of osmium(VI) in $[Os(CN)_5N]^{2-}$, or rhenium(V) in $[ReN(L)(CN)_4]^{2-}$ complexes (where $L = H_2O$ or N_3^-) [43,44].

The amphoteric nature of π-bonding of the CN^- ligand is, however, strongly asymmetric: the π-acceptor capability dominates, whereas the π-donor ability is appreciable only in systems with a low number of electrons.

(iv) The versatility in π-bonding of the CN^- ligand is manifested in the formation of stable cyano complexes both by early and late transition elements, by hard and soft acids and by metal ions with low and high oxidation numbers.

It is not uncommon for the CN^- ligand to form stable complexes in two or even three successive oxidation states (e.g., for Cr, Mn and Fe [45]), and in this respect CN^- resembles ligands such as 2,2′-dipyridine and 1,2-dithiolenes.

Moreover, the cyano ligand is known to form stable complexes with two or even three successive coordination numbers at the same centre (e.g., Ni(II), Cu(I), Ag(I), Hg(II)). This phenomenon is accompanied by an unusually wide range of stereochemical configurations among which are also unconventional ones: linear (e.g., in $[Ag(CN)_2]^-$), triangular (e.g., in $[Cu(CN)_2]_n^{n-}$), square planar (e.g., in $[Pt(CN)_4]^{2-}$), square pyramidal (e.g., in $[Ni(CN)_5]^{3-}$), pentagonal bipyramidal (in heptacyanides of V(III), Mo(II), and Re(III)), square antiprismatic (e.g., in $H_4[M(CN)_8]$, where M = Mo(IV), or W(IV)), and dodecahedral (examples may be $[Nb(CN)_8]^{4,5-}$, or $K_4[Mo(CN)_8]\cdot 2H_2O$) [1–3,39].

(v) Although the basicity of the nitrogen end is appreciably lower than that of the C-atom, it appears to be enhanced upon formation of the M–CN bonding. Coordination by both C- and N-atoms lead to a decrease in charge on the ligand and consequently to an increase in contribution from the π-acceptance with a simultaneous reduction in the σ-component of the M–C bond. This results in weakening of the M–C bond and reinforcement of the M–N bond, so that their strengths become comparable within the bridge. Consequently, bridging is accompanied by an increase in the C–N bond order, which is responsible for shifting the CN stretching band to a higher and ν(MC) to a lower frequency [1,3,17,46].

This effect induces mononuclear cyano complexes to behave as nucleophiles which is demonstrated in their interaction with electrophilic solvents, in protonation, in methylation and in bridging to other metal or non-metal atoms with formation of di- or poly-nuclear compounds. Usually cyanide ligands form the end-on type strong bridges between two metal atoms, M–CN–M′, between a metal and another electrophile, M–CN–R, or between two non-metal atoms [1–3,14].

Due to different donor atoms in bridges, substances which seem to be simple cyanides can contain nonequivalent metal atoms, like $Co(CN)_2$ or $Ni(CN)_2$.aq [1]. The structures may involve transition metals in carbon and nitrogen polyhedra, although sometimes the CN bridges appear to be totally end-for-end disordered [47]. In the case of homoleptic octahedra, the difference in splitting energy results in low-spin MC_6, whereas MN_6 centres are high-spin as it was shown for the Prussian blue, $Fe_4[Fe(CN)_6]_3$ and its analogues [1,48,49].

For mixed-metal complexes, the problem of preferential sites and bridged linkage isomerism (L_mM-μ-CN-$M'L'_n$ and L_mM-μ-NC-$M'L'_n$) should be taken into account. The linkage isomerism was found, however, only in few cases, examples being $[(CN)_5Co(CN)Co(NH_3)_5]$ [50,51], $[NiCoCl(CN)_2(dmgH)_2(dpe)]$ (dmgH = dimethylglyoximato ligand, dpe = bis(diphenyl-phosphino)ethene) [52], $[(H_2O)_5Cr(CN)Co(CN)_5]$ [53] and $(C_6F_5)_2Pd[(CN)Pd(C_6F_5)(PPh_3)_2]$ or similar Pd(II) and Pt(II) complexes [54].

The bridges determine the specific properties of the compounds. Most of their interesting functions are related to the occurrence of intramolecular electron and energy transfer processes mediated by the CN bridges [14,55–60]. As relatively simple units, the dimers and polymers can serve as models and starting points for understanding electron transmission phenomena through more complex chemical and biological systems. Some of the polymers were also used as model substances for the investigation of spin interaction via cyanide groups [49,61–63].

Interaction between the metal centres through the cyano bridge often lead to a change in spectral properties of the polymers as compared to the mononuclear species. Although the CN^- ligand is not chromophoric, new bands at relatively low energy are observed, especially in mixed-valence systems containing one metal centre of oxidizing and another one of reducing character. These bands arise mainly from an optically induced charge transfer between the metal centres through the bridging group. The intervalence transitions often cause the polymers to be intensely coloured, the best example being Prussian blue, $Fe_4[Fe(CN)_6]_3$ or $M^IFe[Fe(CN)_6]$, and its analogues [1–3,64–75].

(vi) The CN bridges may be found in many crystalline cyano complexes and involve chains, sheets, or three-dimensional structures. The bridges are mostly linear as singly bonded M–CN groups, less common are structures with bridges somewhat deviating from linearity at N- or at both the atoms, whereas structures entirely different from linearity are rare.

Some of the CN-bridged polymers occur in columnar forms which enable a long-range transfer. Such unique symmetry was found in stacked cyano-bridged porphyrinato complexes of Co(III), Rh(III), Fe(III), Cr(III) and Mn(III) which show good semiconducting properties [60].

Cadmium cyanide, $Cd(CN)_2$, and other polymeric cyanocadmates were reported to build mineralomimetic multi-dimensional structures consisting of tetrahedral and octahedral units [76–78]. A number of clay-like 2D layered, cristobalite-like or zeolite-like 3D framework host structures with cavities of molecular scale accommodate a variety of organic guest molecules and onium cations of different geometry.

Other inclusion compounds of multi-dimensional cyanometal complex hosts are those derived from the Hoffmann clathrate of general formula $ML_2Ni(CN)_4 \cdot xG$, where M = Ni(II), Cd(II), Mn(II), Cu(II) or other metal, L = neutral ligand such as amine, diamine, phosphine or arsine [76,79]. The compounds consist of square planar $[Ni(CN)_4]$ and octahedral $[ML_2(NC)_4]$ units linked by the CN bridges nonlinear at the N end (angle at the N-atom within 150–170°). As several kinds of guest aromatic molecules (G) can be included into the intercalation compounds, their application is important especially for development of novel separation technologies [80,81]. Similar nonlinear bridges were found recently in other polymeric cyanides generated by hexacyanide of Fe(II) [82–88].

CN-bridged complexes are of special interest in organometallic chemistry owing to the ability of the CN bridge to act as a charge transfer mediator. One of the most intriguing compounds from this series is organotin(IV) coordination polymer, $[(Me_3Sn)_4Fe(CN)_6 \cdot 2H_2O \cdot C_4H_8O_2]_\infty$ that was reported to form a three-dimensional host-guest network involving "cascade-type" guests [88]. Other examples from this new class consisted of anionic di- and tri-nuclear organotin adducts for which an X-ray analysis showed a Sn–CN–Ag bridging interaction non-linear at the N-atom (167.7°) [89].

Among numerous polymeric cyano complexes the compounds with CN bridges deviating from linearity at both ends are extremely rare [51,90]. A few examples of CN bridges, more typical of CO than of CN^- ligand, were also reported [2,91,92]. The cyanide ion was shown to bridge the Mo–Mo bond in the η^2 fashion wherein two electrons are donated to one Mo from the CN σ-pair and two are donated to the other Mo from the CN π-bond. The (σ + π) bonding, which is common in μ-CO complexes, was found in the $Et_4N[Cp_2Mo_2(CO)_4(CN)]$ dimer [92].

The $CuCN \cdot NH_3$ complex was for a long time considered to be unique in featuring a tridentate CN bridge which links the metal atoms into plane nets via the grouping $(Cu)_2C$–N–Cu [93]. It was recently shown, however, that the tridentate CN bridge is bound to three diverse metallic atoms (2Ru and 1Mn) in Ru_3-cluster derivatives [94]. The structure demonstrated the ability of the CN ligand to link different organometallic units and to stabilize unusual electron counts in organometallic complexes.

(vii) Many of inert mononuclear cyano complexes may be protonated generating reasonably stable acids containing M–CN–H groupings. The protonation causes a shift of the reduction potential to more positive values [64]. The cyano ligands may be also alkylated to produce isonitrile complexes, M–CN–R, that are the subject of continued interest [14,95]. Many other electrophiles react with terminal cyanide ligands to form compounds with the CN bridges between metal and non-metal atoms. The basicity of the nitrogen end was also demonstrated by adduct formation with BX_3 to give materials such as $K_2[Ni(CN \cdot BF_3)_4]$ and $K_4[Fe(CN \cdot BF_3)_6]$ [14]. The addition of a proton or another electrophile to the nitrogen end of cyanide results in a decrease in σ-bonding and increase in π-bonding to a metal [1–3,14]. The basicity of the CN ligand coordinated to one centre results also in interaction between cyano complexes and solvent molecules, depending strongly on the nature of solvent, especially on its acceptor number and hydrogen bonding formation [96–104]. The second-sphere interactions bring about environment-sensitivity of the spectroscopic, photophysical and redox properties of cyanides.

The nitrogen atoms involvement in hydrogen bonds, $MCN \cdots H \cdots NCM$ leads to different structures of acids, hydrated salts and mixed-ligand cyano complexes [99,105,106].

The basicity of the N-end is also demonstrated by metal complexes with a

CN-substituted organic ligand L–CN, and therefore compounds with M–NC–L–M′ groupings are produced that may be treated as having (NC–L) bridges [105,107].

3. Excited states and photophysical deactivation

(i) Large splitting energy and large extent of delocalization both in the ground and in excited states constitute special features of the cyano complexes. This is illustrated by characteristics of the HOMO in mixed-ligand pentacyanonitrosyl complexes of the first transition metal series (Table 1) as calculated using the SINDO method [108,109].

Despite the significant delocalization, it is still of practical use in discussing the spectroscopy, photophysics and photochemistry of cyano complexes to classify their excited states similarly to other complexes. The usual criterion of such a classification is the predominant electron density transfer due to the relevant excitation (Table 2). In many cyanide systems, however, an unequivocal classification of the transitions is not feasible. This question, less important for homoleptic complexes, is of great significance for mixed-ligand cyanides, especially those with other π-acceptors [108–115] (Table 3).

(ii) An additional complexity in interpreting the electronic spectra results from interactions between cyano complexes and solvent molecules. The interactions are

Table 1
Characteristics of the highest occupied orbitals in the $[M(CN)_5NO]^{n-}$ complexes of the first transition metal series (adapted from Refs. [108,109])

M^a HOMO	Cr(II) 8e	Cr(I) 8e	Mn(II) 8e	Fe(III) $2b_2$	Cr(0) $2b_2$	Mn(I) $2b_2$	Fe(II) 8e	Fe(I) 9e
% d	24	22	22	54	57	57	24	21
% NO	50	55	46				39	48
% CN_{eq}	20	18	26	46	43	43	29	17
% CN_{ax}	6	5	6				8	14

[a] The NO ligand is assumed as being formally NO^+.

Table 2
Charge changes accompanying transitions in homoleptic $[M(CN)_6]^{n-}$ complexes of Cr(III) and Fe(II) (adapted from Refs. [110,111])

Complex	$[Cr(CN)_6]^{3-}$			$[Fe(CN)_6]^{4-}$		
Transition:	$2t_{2g}\rightarrow 4e_g$	$4t_{1u}\rightarrow 2t_{2g}$	$1t_{1g}\rightarrow 2t_{2g}$	$2t_{2g}\rightarrow 4e_g$	$2t_{2g}\rightarrow 2t_{2u}$	$2t_{2g}\rightarrow 5t_{1u}$
Δq_M	+0.04	−0.31	−0.29	+0.25	+0.46	+0.46
Δq_{CN}	−0.01	+0.05	+0.05	−0.04	−0.08	−0.08
Δq_N	+0.05	−0.01	0.00	+0.05	+0.08	+0.08
q_{CN}	−0.51	−0.46	−0.46	−0.60	−0.64	−0.64
Main character	MC	LMCT	LMCT	MC + MLCT	MLCT	MLCT

Table 3
Charge changes accompanying transitions in mixed-ligand $[Fe(CN)_5L]^{n-}$ complexes ($L = CO$ and NO^+; adapted from Refs. [109,111,114])

Complex	$[Fe(CN)_5CO]^{3-}$			$[Fe(CN)_5NO]^{2-}$		
Transition:	$2b_2 \to 9e$	$8e \to 9e$	$1a_2 \to 9e$	$2b_2 \to 9e$	$8e \to 9e$	$1a_2 \to 9e$
Δq_M	+0.36	+0.37	+0.06	+0.06	+0.05	−0.14
Δq_{CNeq}	+0.02	+0.03	+0.13	0.00	+0.01	+0.12
Δ_{Neq}	+0.09	+0.08	+0.11	+0.04	+0.02	+0.06
Δq_{CNax}	−0.04	−0.08	−0.14	−0.07	−0.05	−0.14
Δq_{Nax}	+0.04	+0.08	−0.05	−0.05	+0.00	−0.10
Δq_L	−0.39	−0.40	−0.44	−0.0[illegible]	−0.04[a]	−0.20[b]
Main character	MLCT + MC	MLCT	LLCT	MC	MC + LC	LMCT + LLCT

[a] In this case an appreciable charge transfer within the NO ligand is observed ($\Delta q_N = -0.15$ and $\Delta q_0 = +0.11$).

[b] The charge transfer is localized mostly on the N-atom resulting in its charge decrease (from +0.50 to +0.31).

sensitive to the nature of solvent, and have their influence not only on the CTTS transitions but also on other bands of CT character [96–104,116–118]. These features render the excited states difficult to unequivocal labelling and lead to variety in the photochemistry of cyanometallates.

(iii) As in other systems, the vibrational relaxation of the excited states can be accompanied by radial and/or angular distortions. This leads to a change in bond lengths and/or in symmetry in the excited state as compared to the ground state. Emission and resonance Raman spectra were the basis for estimation of the excited state distortions in some complexes, among others in $[Cr(CN)_5NO]^{3-}$, $[Fe(CN)_5NO]^{2-}$ [119,120] and $[Ru(bipy)_2(CN)_2]^{n-}$ (bipy = 2,2′-bipyridine and $n = 0$–2) [121].

The distortions can be evaluated by changes in bond orders and/or in the diatomic contributions to the total energy accompanying excitation calculated by the SINDO method [108–111,114,122]. For hexacyanides of Cr(III) and Fe(II) (Table 4) an elongation of the M–CN bonds can only be expected in consequence of the

Table 4
Changes in: σ- and π-bond orders (p^{σ}_{Fe-CN} and Δp^{π}_{Fe-CN}), two-centre contributions to the total energy (ΔE_{M-CN}) and charges (Δq_N) accompanying transitions in hexacyanides of Cr(III) and Fe(II) (adapted from Refs. [110,111])

Complex	$[Cr(CN)_6]^{3-}$			$[Fe(CN)_6]^{4-}$		
Transition:	$2t_{2g} \to 4e_g$	$4t_{1u} \to 2t_{2g}$	$1t_{1g} \to 2t_{2g}$	$2t_{2g} \to 4e_g$	$2t_{2g} \to 2t_{2u}$	$2t_{2g} \to 5t_{1u}$
Δp^{σ}_{M-CN}	−0.186	−0.025	−0.021	−0.146	+0.030	+0.023
Δp^{π}_{M-CN}	−0.109	+0.110	+0.100	+0.012	−0.049	−0.031
ΔE_{M-CN}	+3.16	+0.12	+0.09	+2.13	−0.10	+0.28
Δq_N	+0.05	−0.01	0.00	+0.05	+0.08	+0.08

$2t_{2g} \rightarrow 2e_g$ excitation, whereas for pentacyanoferrates (Table 5) all excitations result in a significant weakening of the π-bonding between Fe and CO or NO–ligand, leaving the Fe–CN bond orders practically unchanged or even slightly increased. Consequently, an elongation of the Fe–L, and constancy or even slight shortening of the Fe–CN bonds, can be anticipated here. For higher energy states also a difference between axial and equatorial CN–ligand cannot be excluded.

(iv) The fate of an excited-state species and its lifetime depend not only on its character but also on other intrinsic factors such as the nature of the central metal ion, stereochemistry of the complex and the nature of CN^- and of other ligands. The CN^- ligand is classified as a poor quencher due to its large ligand field splitting, thermal inertness of cyano complexes and lack of a high-frequency intraligand mode (like ν(OH) or ν(NH)) that can be effective in quenching excited states [123–125]. It was suggested that these features are responsible for relatively long excited-state lifetimes of cyano complexes (see, e.g., Refs. [6,123–129]). A spectacular illustration of this phenomenon is provided by the $[Cr(CN)_{6-n}(H_2O)_n]^{n-3}$ series for which the lifetime of the ^2E excited state decreases by a factor of 250 and radiationless decay rate k_{nr} increases from 0 to $>6\times10^4$ when n varies from 0 to 6 [124].

Among other structural factors influencing the excited-state lifetime, the spin-orbit coupling should be mentioned. The lifetime of the $^3T_1$ triplet was found to decrease in the order

$$[Co(CN)_6]^{3-} \gg [Rh(CN)_6]^{3-} > [Ir(CN)_6]^{3-},$$

which is consistent with increasing values of the spin-orbit coupling constants of the central metal atom [126]. Spin-orbit coupling was assumed to be responsible for a variation in the radiative rate constants of mixed-ligand chromium(III) complexes [125].

(v) Thanks to the relatively long lifetimes of the excited states, their absorption spectra could be measured in some cases [130–134]. Considerable attention was

Table 5

Changes in: bond orders ($\Delta p^{\sigma}_{Fe\text{-}L}$ and $\Delta p^{\pi}_{Fe\text{-}L}$) and two centre contributions to the total energy ($\Delta E_{Fe\text{-}CN}$) accompanying transitions in mixed-ligand $[M(CN)_5L]^{n-}$ complexes (L=CO and NO^+) (adapted from Refs. [109,111,114])

Complex	$[Fe(CN)_5CO]^{3-}$			$[Fe(CN)_5NO]^{2-}$		
Transition:	$2b_2\rightarrow9e$	$8e\rightarrow9e$	$1a_2\rightarrow9e$	$2b_2\rightarrow9e$	$8e\rightarrow9e$	$1a_2\rightarrow9e$
$\Delta p^{\sigma}_{Fe\text{-}L}$	+0.038	+0.054	+0.030	−0.011	−0.003	+0.004
$\Delta p^{\pi}_{Fe\text{-}L}$	−0.590	−0.522	−0.355	−0.469	−0.619	−0.364
$\Delta p^{\sigma}_{Fe\text{-}CNeq}$	+0.019	+0.010	−0.034	−0.005	−0.014	−0.037
$\Delta p^{\pi}_{Fe\text{-}CNeq}$	−0.028	+0.050	+0.103	+0.105	+0.072	+0.122
$\Delta p^{\sigma}_{Fe\text{-}CNax}$	−0.005	+0.013	−0.008	−0.010	−0.007	−0.014
$\Delta p^{\pi}_{Fe\text{-}CNax}$	+0.002	+0.130	+0.110	+0.100	+0.204	+0.156
$\Delta E_{Fe\text{-}L}$	+4.94	+4.18	+3.87	+5.01	+6.62	+4.15
$\Delta E_{Fe\text{-}CNeq}$	−0.08	−0.18	−0.66	−0.69	−0.05	−0.23
$\Delta E_{Fe\text{-}CNax}$	+0.04	−1.12	−1.82	−0.65	−1.50	−0.80

attracted especially to the light-induced metastable states (MSI and MSII) of the $[Fe(CN)_5NO]^{2-}$ complex which are remarkable for their extremely long lifetime ($\tau > 10^7$ s at $T \cong 0$ K) [135–139]. The NO ligand seems to be a prerequisite for the existence of such metastable states. Besides nitrosylpentacyanoferrate(II), also in $[Ru(CN)_5NO]^{2-}$ and $[Os(CN)_5NO]^{2-}$, photochromic effects have been detected [136, 140]. The photochromic materials draw some interest for their potential application in construction of fast and efficient optical switches and as possible optical memory devices with a high storage capacity.

(vi) Beside the intrinsic there are also environmental factors such as temperature and pressure and as well as matrix factors, that contribute to the excited-state relaxation behaviour. Due to the tendency of the cyanide ligand to give second-sphere donor–acceptor interactions, the cyano complexes are exceptionally sensitive to the environment: their absorption spectra, emission spectra, luminescence quantum yields, luminescence lifetimes and electrochemical properties are affected by the nature of solvent, nature and concentration of counter-ions as well as by acidity [97–104, 141–143]. The solvent effects are of special meaning. In this case, with the growing acceptor number of the solvent and/or with the growing tendency to form hydrogen bonds, the stronger become the interactions. Consequently, different behaviour was observed in hydroxylic and nonhydroxylic solvents [117, 118]. The detailed study performed for mixed-ligand cyano-polypyridine Ru(II) complexes has shown good linear correlations between the spectroscopic energies and solvent acceptor numbers [116, 117, 141–144].

In the case of quasi one- and two-dimensional interactions within $M_2[Pt(CN)_4]$ and $Cs[Au(CN)_2]$, respectively, pressure was reported to have a significant effect on the excited state energy due to a decrease in the band gap energy [145–147]. In the solid phase, the magnetic effect or M–M interactions may also contribute to the excited-state energy [148–150].

All these factors contribute to typical kinetic competitiveness of various deactivation modes, such as radiative and non-radiative transitions, bimolecular quenching and photochemical reactivity. More details on the kinetic aspects of the exited-state decay may be found elsewhere [6, 7, 10, 11, 58].

(vii) Considering the properties of cyano complexes in excited states, their acid-base and redox behaviour must be taken into account. The effect of protonation on photophysics of mixed-ligand Ru(II) cyano complexes with a-diimines, $[RuL(CN)]$ (L = 2,2′-bipyridine, 1,10-phenantroline, 2,2′-biquinoline or their derivatives) and $[Ru(bipy)(CN)_4]^{2-}$ has been thoroughly investigated [141, 150–154]. The complexes with protonated CN^- ligands appeared to be such strong acids on excitation and they deprotonated so rapidly that only emission from the unprotonated form was observed. The proton-transfer excited-state equilibrium thus proved to be fast with respect to excited-state deactivation [150]. At lower temperature (77 K) emission from the protonated forms occurred but the protonation of the –CN to $-CNH^+$ resulted in decreased electron density at the Ru centre thus shifting the Ru–L MLCT excited state to higher energy while leaving levels of π–π* ligand-centred orbital origin practically unaffected. The energy spacing of the d–π* and π–π* levels is so strongly affected that in concentrated acids the energy ordering of the MC, LC and MLCT is reversed [150,151]. Similar behaviour was reported for (α-diimine)-cyanotricarbonyl-rhenium(I) for which the emitting state could be changed from the MLCT to π→π* type by varying acidity, ligand L and temperature [155]. The alteration resulted in large changes in emission spectra and lifetimes, which suggested application as environmental probes [155,156]. Similarly to the -CNH ligand, isonitriles, -CNR, stabilize the t_2 level as was reported for $[RuL_2(CNR)_2]$ and $RuL(CNR)_4]^{2-}$ [156]. The effect can invert the order of the lowest MLCT and π→π* excited states with radical changes in luminescence properties.

The origin of the changes in the CN ligand basicity can be understood considering the electron density redistribution at the N-end [108,110–112,157]. The survey of the Δq_N values calculated for some hexa- and pentacyanometallates (Tables 2 and 3) shows that the acid-basic properties at the terminal N-atom depend not only on the type of transition but also on the CN ligand position in relation to the co-ligand. The most spectacular example of the behaviour is provided by the difference between the charge of axial and equatorial N-atoms produced by the $1a_2 \rightarrow 9e$ excitation in the $[Fe(CN)_5L]^{n-}$ complexes (cf. Table 3).

Although more general conclusions on the CN ligand basicity in excited state could be drawn only on the basis of much larger accumulation of experimental and theoretical data, the following factors should be considered as influential: type of excitation, nature of the central atom, nature and position of co-ligand. In the case of mixed-ligand cyanides, a similar procedure could be used to predict changes in basicity of the L ligand.

(viii) As other complexes, cyanides in excited states are more powerful oxidants and reductants than in the ground state. The origin of the enhanced redox behaviour has been elucidated basing on the generalised Förster cycle [157] or on changes in ionization potential and electron affinity due to changes in occupation number of the HOMO and LUMO orbitals [6,10,11,158–161]. The nearly linear correlation between HOMO energy and oxidation potential reported for binuclear cyano-bridged manganese complexes demonstrates usefulness of the approach [162].

(ix) Population of excited states in quenching processes is a common procedure. Cyano complexes are widely used to quench excited states of other species, mostly polypyridyl $^*[M(NN)_3]^{2+}$ complexes (where M = Ru(II) or Os(II), and ammine Cr(III) complexes [163,164]). The cyanides are unique quenchers in that they span a wide range of excited-state energies and redox potentials making a delineation between the various quenching pathways possible. The predominant mechanism found was the reductive electron transfer from a quencher to $^*[Ru(NN)_3]^{2+}$ which is rather rare with inorganic quenchers [163]. This was accomplished with the cyano quenchers with low oxidation numbers, Mo(IV), Fe(II), Ru(II) and Os(II), whereas the cyanometallates of Co(III) and Fe(III) displayed oxidative electron transfer. The quenching rate constants for a series of the $[Fe^{II}(CN)_5L]^{n-}$ complexes paralleled the increasing reductive power of these complexes. It was suggested that energy transfer accompanies electron transfer in the case of the $[Fe(CN)_6]^{4-,3-}$ and $[Ni(CN)_4]^{2-}$ quenchers [163]. The reversible energy transfer was reported to be of the quenching mechanism displayed by the doublet excited state of $[Cr(tacn)(NCS)_3]$ (primary donor, tacn = 1,4,7-triazacyclononane), and $[Cr(CN)_6]^{3-}$ (primary acceptor) [165].

(x) Cyanometallates play an important role as photosensitizers due to extreme sensitivity of their spectroscopic and photophysical properties to the environment: absorption and emission spectra as well as excited-state lifetimes depend strongly on the solvent, nature and concentration of counter-ions and acidity. Quenching of electronically excited states of cyanometallates has been a subject of many investigations [163–168]. One of the systems studied consisted of $^*[Ru(bipy)_2(CN)_2]$ and $[Fe(CN)_6]^{4-,3-}$: both energy and electron transfer were reported, the latter being of reductive and oxidative character for the Fe(II) and Fe(III) complexes, respectively [163].

(xi) A growing interest in the energy or electron transfer processes displayed by polynuclear systems focused attention on the cyano-bridged complexes. The cyano bridge not only covalently links together chromophoric and luminophoric molecular components, but also enables fast and efficient energy transfer to produce luminophore emission following chromophore absorption. The complexes behave in many respects as supramolecular antenna systems [133,163–174]. The CN-bridged polymers display also electron transfer processes; the key problem, however, is fast back electron transfer which prevents using the systems for light-promoted charge separation. [55,58,175,176].

4. Photochemical reactivity

Homoleptic cyanide complexes are known to undergo photosubstitution (photosolvation) of a cyanide ligand

$$[M(CN)_n]^{m-} + L \xrightarrow{h\nu} [M(CN)_{n-1}L]^{1-m} + CN^- \qquad (1)$$

It was found in several hitherto studied systems, such as $[Cr(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$ and $[W(CN)_8]^{4-}$ complexes, that the reaction has a dissociative or dissociative interchange mechanism [6,177,178]. The experimental data are, however, not ample to draw general mechanistic conclusions.

Mixed-ligand cyanide complexes, being mostly of the $[M(CN)_5L]^{m-}$ type, can undergo not only cyanide [179–183] but also ligand L photosubstitution (photosolvation) [1,3,6,7,23,184]

$$[M(CN)_5L]^{m-} + L' \xrightarrow{h\nu} [M(CN)_5L']^{m-} + L \qquad (2)$$

The choice of substituted ligand, mechanism and quantum yield were found to depend on the parameters of the co-ligand, on the nature of the donor atom in particular. The photosubstitution pathways have been analyzed in terms of the Adamson's semi-empirical rules and of the Vanquickenborne-Ceulemans model [185] as well as basing on the SINDO approach [109–111,114].

Photoredox behaviour is usually demonstrated by homoleptic cyanide complexes as a result of reactive decay of an excited state being of the charge-transfer character [6,8]. Photoreduction proceeds by either inter- or intra-molecular pathway [186,187]

$$[M(CN)_n]^{m-} + D \xrightarrow{h\nu} [M(CN)_n]^{(m+1)-} + {}^{\bullet}D^{+} \tag{3}$$

$$[M(CN)_n]^{m-} + \text{solv} \xrightarrow{h\nu} [M(CN)_{n-1}(\text{solv})]^{m-} + {}^{\bullet}CN \tag{4}$$

In the case of mixed-ligand cyanides intramolecular photoreduction may also include the L ligand [188–192]

$$[M(CN)_5L]^{m-} + \text{solv} \xrightarrow{h\nu} [M(CN)_5(\text{solv})]^{(m+1)-} + {}^{\bullet}L^{+} \tag{5}$$

Intermolecular photooxidation leading to solvated electron production, is the only photooxidation pattern demonstrated by the homoleptic cyano complexes [1,6,8–11],

$$[M(CN)_n]^{m-} + \text{solv} \xrightarrow{h\nu} [M(CN)_n]^{1-m} + e^{-}_{\text{solv}} \tag{6}$$

whereas intramolecular photooxidation accompanied by solvation

$$[M(CN)_5L]^{m-} + \text{solv} \xrightarrow{h\nu} [M(CN)_5(\text{solv})]^{1-m} + L^{-} \tag{7}$$

was observed in some mixed-ligand cyanides, above all in $[Fe(CN)_5NO]^{2-}$ [6,8,188–191,193,194].

Systems composed of a cyano complex linked in some way to one or more units have recently generated great interest due to their uncommon properties and prospects for use in molecular engineering. The goal may be achieved not only by formation of CN bridges but also by formation of other covalent bonds or even by electrostatic interactions between the partners. In the latter case a number of ion-pairs were reported where the main cyano partners (and reducing species) were $[Fe(CN)_6]^{4-}$, $[Ru(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$, whereas the cation usually belonged the amino-complexes of Co(III), Ru(III), Os(III) [45,51,176,195–199].

The photochemistry and photophysics of the covalently linked systems also depend on the interaction strength between the units. Because of the asymmetry of the CN bridge, not only energy but also symmetry of the relevant states must be taken into account [175,199–208].

5. Modelling of the photochemical reactivity

The first insight into the problem was calculation of the electronic spectra, which was done with use of the SCCC MO method involving only the ground state [209]. Next, separate calculations of the ground and excited states were developed based on INDO-type [108–111,114,122], DFT-type [210,211] or ab initio SCF methods

[112,113,212–214]. The ab initio SCF CI calculations carried out for the series of hexacyanometallates of V, Cr, Mn and Fe, resulted in excellent agreement between the calculated and experimentally measured electronic spectra within LF transitions [214]. The scaled INDO method leads to much less precise results but instead it provides a possibility of modelling both thermal and photochemical reactivities.

Modelling of thermal reactivity of cyanometallates consisted in interpreting the characteristics of the frontier orbitals, bond orders and charge distributions in the ground state [109]. To find the most important factors which make the photochemical decay of excited states proceed along a specified photochemical mode, the reactivity was analyzed in relation to excitation-induced changes in charge distribution, bond orders and two-centre contributions to the total energy.

5.1. *Effect of the central atom*

To have an insight into the way in which the photochemical reactivity of cyano complexes depends upon the metal atom parameters, the photochemistry of hexacyanochromate(III) and hexacyanoferrate(II) were analyzed using the SINDO method [110,111].

Both the above hexacyanides undergo photosubstitution of the CN^- ligand upon the LF excitation (Eq. (1)) [8,130]. This is consistent with an appreciable decrease in the M–CN bond order and increase in the E_{M-CN} two-centre contribution to the total energy accompanying the LF transition ($2t_{2g} \rightarrow 4e_g$) (Table 4). The result is unique for the LF transition, and the changes in E_{M-CN} for other transitions may be treated as negligible. The latter suggests that neither photosubstitution (Eq. (1)) nor intramolecular photoreduction (Eq. (4)) can be expected as a result of the excitations.

Indeed, the modes were not found experimentally, although the CT excitation in the both cases leads to a photochemical reaction. A divergent photoredox behaviour has been observed here, i.e., photooxidation of $[Fe(CN)_6]^{4-}$ (Eq. (6)) and photoreduction of $[Cr(CN)_6]^{3-}$ (Eq. (3)) [8,9,179,186]. To interpret the behaviour, changes in charges accompanying transitions had to be considered (Table 2). These are negligible for the LF transition at $[Cr(CN)_6]^{3-}$, but are significant in other cases. The result is consistent with the interpretation of the charge transfer excitations of $[Cr(CN)_6]^{3-}$ made using the ab initio SCF method [113]. A considerable shift of the negative charge towards the Cr-atom due to the CT excitation together with lack of M–CN bond weakening are prerequisites for the intermolecular photoreduction (Eq. (3)) [179,186].

The reverse electron shift is observed for the $[Fe(CN)_6]^{4-}$ complex: the first three excitations lead to charge transfer from the metal to ligand, being more significant for the $2t_{2g} \rightarrow 2t_{2u}$ and $2t_{2g} \rightarrow 2t_{1u}$ transitions. The increase in the Fe-charge, lack of the weakening of the Fe–CN bond and substantial accumulation of negative charge at the CN ligand are assumed to be responsible for the transfer of an electron to the solvent and the outer sphere photooxidation mode (Eq. (6)) [111].

Comparing the results for both the hexacyanometallates (Tables 2 and 3, see also Ref. [6]) it can be seen that their first excited states should be similar in reactivity and their decay should lead to the photosubstitution mode (Eq. (1)). However, the different nature of the central atoms is decisive for the characteristics of the next excited states. For the chromium complex they are LMCT, not MLCT in character. The charge transfers and lack of the Cr–CN bond weakening indicate that photoreduction and photooxidation are the only possible modes following reactive decay of the excited states of chromium(III) and iron(II) complexes, respectively.

To model the reactivity of mixed-ligand cyanometallates, the $[M(CN)_5NO]^{x-}$ family was chosen which is known for diverse reactivity despite similarity in geometry and bonding [1,20,21]. Their thermal reactivity can be conveniently illustrated by a fragment of the periodic table (Fig. 1), which demonstrates a diagonal relationship of the reactivity: the complexes at the top-right side are stable in acids, whereas in alkaline media they undergo a nucleophilic attack followed by a substitution of the NO^+ ligand. The pentacyanonitrosylmetallates from the lower-left side are resistant towards bases, whereas in acidic media a substitution of the CN^- ligand takes place as a consequence of an electrophilic attack [20,24,108,109]. They are stronger reducing agents than the former group; some of them ($[Cr(CN)_5NO]^{4-}$, $[Fe(CN)_5NO]^{3-}$) are even unstable towards molecular oxygen.

The analysis made with the use of the SINDO method showed that their thermal behaviour is consistent with characteristics of the frontier orbital, i.e., LUMO or HOMO energy and charge on the nitrogen atoms of both the NO ligand (qN(NO)) and equatorial CN ligand (qN(CNeq). The results (Fig. 1) show that the predisposition of the $[M(CN)_5NO]^{x-}$ complexes to undergo a nucleophilic attack depends on oxidation number of the central metal ion and its nature. For the same central atom the predisposition increases with its oxidation number

$$M(0) < M(I) < M(II) < M(III)$$

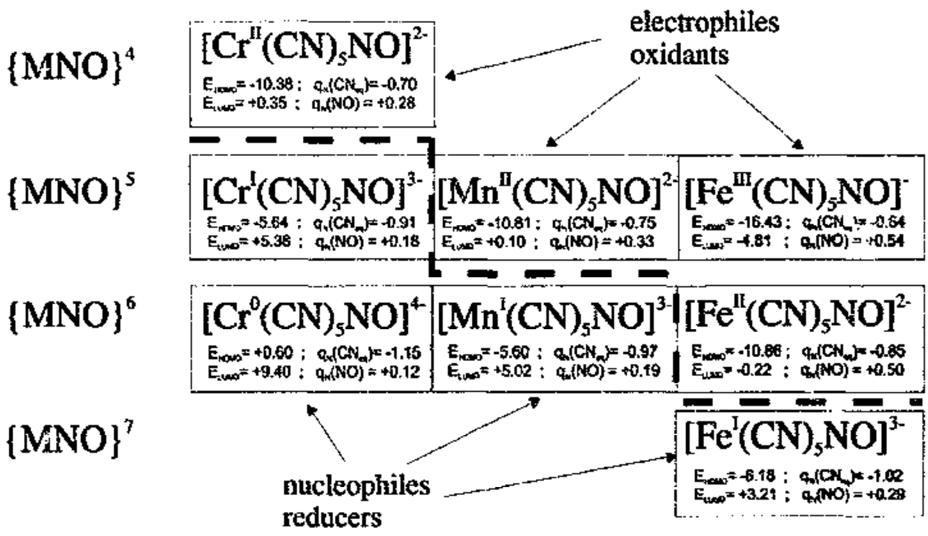

Fig. 1. Graph of correlations between reactivity and electronic structure of $[M(CN)_5NO]^{x-}$ complexes.

whereas for different centres it grows in the order

$$\mathrm{Cr} < \mathrm{Mn} < \mathrm{Fe}$$

both in the isoelectronic series (d^5 or d^6) and in the series at the same formal oxidation number (I or II).

Electrophilic properties of the whole $[\mathrm{M(CN)_5NO}]^{n-}$ family were ordered as follows:

$$\mathrm{Cr(0)} < \mathrm{Cr(I)} < \mathrm{Mn(I)} < \mathrm{Fe(I)} \leq \mathrm{Cr(II)} < \mathrm{Mn(II)} < \mathrm{Fe(II)} < \mathrm{Fe(III)}$$

which is consistent with experimental oxidation and reduction sequences [24,109].

The SINDO calculations have shown that the redox and electrophilic behaviour of the $[\mathrm{M(CN)_5NO}]^{n-}$ complexes for the first transition-metal series are strongly dependent on the number of electrons and nature of the metal atom. When the complexes are tabulated according to these features, the diagonal relationship of their reactivity becomes evident (Fig. 1). The results may be useful for assessing unknown redox potentials or electrophilic reactivity of the complexes as well as to create a point of departure for predicting their photochemical reactivity [24,108,109,122].

5.2. *Effect of co-ligand*

The effect of co-ligand has been studied by interpreting thermal and photochemical reactivity of the isoelectronic $[\mathrm{Fe^{II}(CN)_5L}]^{m-}$ complexes ($\mathrm{L}=\mathrm{CN^-}$, CO, $\mathrm{NO^+}$) by the SINDO type calculations carried out for the ground and selected excited states. The results reflect the differences in photoredox behaviour of the complexes and for the L, not $\mathrm{CN^-}$, photosubstitution mode in the carbonyl and nitrosyl complexes [111].

The complexes are known to undergo photoaquation of the L ligand (Eq. (2), Fig. 2), yielding aquopentacyanoferrate(II), $[\mathrm{Fe^{II}(CN)_5H_2O}]^{3-}$, and the ligand L ($\mathrm{CN^-}$, CO or $\mathrm{NO^+}$) [1,8,25,191,215,216]. Furthermore, hexacyanoferrate(II) undergoes intermolecular photooxidation (Eq. (6)) generating solvated electrons with a relatively high quantum yield [1,8,130]. The intermolecular photooxidation

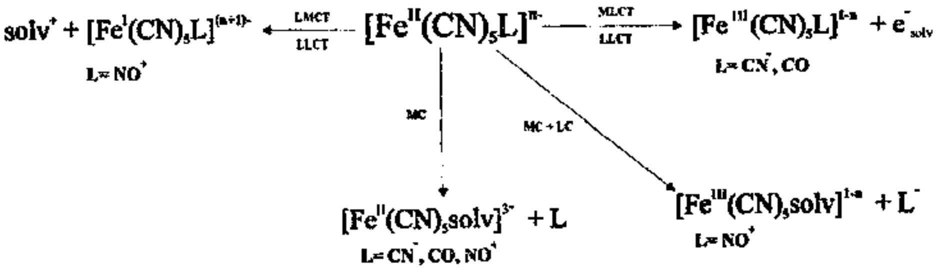

Fig. 2. Main photochemical pathways of $[\mathrm{Fe(CN)_5L}]^{n-}$ complexes ($\mathrm{L}=\mathrm{CN^-}$, CO, $\mathrm{NO^+}$) and characters of the relevant excited states.

mode was detected recently to proceed also in solutions of $[Fe(CN)_5CO]^{3-}$ [27]. It was postulated that in the case of $[Fe(CN)_5NO]^{2-}$ the mode proceeds in a glassy state [217], but it was never observed in solution. On the contrary, the intramolecular photooxidation and solvation of the NO ligand (Eq. (7)) was found to be the major photochemical mode detected in aqueous and non-aqueous media [8,130,190,191,193,216]. Moreover, the intermolecular photoreduction (Eq. (3)) was found to proceed in non-aqueous solutions. The latter process results in generation of $[Fe^{I}(CN)_5NO]^{3-}$, which undergoes a fast first-order decay with loss of cyanide to give $[Fe(CN)_4NO]^{2-}$ [190,218]. Neither intramolecular photooxidation nor photoreduction were detected for the $[Fe(CN)_5L]^{n-}$ complexes with L=CO, CN^- (Fig. 2).

Thus, within the isoelectronic $[Fe(CN)_5L]^{m-}$ series, a tendency to undergo intermolecular photooxidation decreases within the series

$$[Fe(CN)_6]^{4-} > [Fe(CN)_5CO]^{3-} \gg [Fe(CN)_5NO]^{2-}$$

whereas susceptibility to undergo intramolecular photooxidation or photoreduction increases along the series.

The behaviour was interpreted in terms of the bond order characteristics and appeared to be consistent with the expectation that the π-acceptor ability of the ligand L, increasing in the series $CN^- < NO^+$, plays the crucial role. This was recognized by the increase in the π-bond contribution to the Fe–L bond along the series, accompanied by simultaneous reduction in the π contribution to the Fe–CN bond and practically unchanged σ-bond orders of Fe–CN and Fe–L [111].

In the case of the $[Fe(CN)_5CO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ of complexes the $2b_2 \rightarrow 9e < 8e \rightarrow 9e < 1a_2 \rightarrow 9e$ excitations are accompanied by a considerable weakening of the Fe–L bonding and increase in the $E_{Fe\text{-}L}$ energy, whereas the Fe–CN bonds, both in *cis* and *trans* positions, are either unchanged or even strengthened (Table 5). The weakening of the Fe–L bonding results primarily from the decrease in the π-bond order, whereas the σ-bond order remains nearly unchanged. The changes in bond-order substantiate photosubstitution of the L ligand and point at photosubstitution of the CN^- ligand as less probable mode.

The decrease in the Fe–L bond order provides evidence that the ^1E ($2b_2 \rightarrow 9e$) and $^1A_2$, $^1B_1$, $^1B_2$ ($8e \rightarrow 9e$) states should be those mainly responsible for the photosubstitution. This conclusion is consistent with the experimental data except the ^1E excited state ($2b_2 \rightarrow 9e$) in $[Fe(CN)_5NO]^{2-}$ that was reported to be unreactive [8,114,130,191,193,216].

In other cases the changes in charges are larger and somewhat similar both for $[Fe(CN)_5CO]^{3-}$ and $[Fe(CN)_5NO]^{2-}$. All the transitions result in an electron transfer from the equatorial CN^- to axial ligands (both CN^- and L) which is indicative of larger or smaller contribution of the ligand to ligand charge transfer $L_{eq}L_{ax}CT$).

On the other hand, the charge changes on the iron atom in both complexes (Table 3) are opposite to each other. In the case of $[Fe(CN)_5CO]^{3-}$, all the studied transitions lead to an increase in charge, whereas for $[Fe(CN)_5NO]^{2-}$ the changes are either negligible ($2b_2 \rightarrow 9e$ and $8e \rightarrow 9e$) or q_{Fe} is decreased ($1a_2 \rightarrow 9e$). These findings prove the opposite CT character of the excited states of the carbonyl and nitrosyl complexes: there is a considerable Fe→CO MLCT contribution to all transitions in $[Fe(CN)_5CO]^{3-}$, whereas in the nitrosyl complex the first two transitions are partly d–d and partly within the NO ligand, and only the third transition ($1a_1 \rightarrow 9e$) is similar for both the complexes. The third transition leads to the charge transfer from the equatorial CN^- ligands to all other parts of the complex. It involves only ligands (L=CO) or is also partly $CN_{eq} \rightarrow Fe$ LMCT in character ($L=NO^+$).

The results substantiate the reported photoredox behaviour of the complexes (Fig. 2), i.e., susceptibility of $[Fe(CN)_5CO]^{3-}$ to intermolecular photooxidation and predisposition of $[Fe(CN)_5NO]^{2-}$ to photoreduction induced by reactive decay of the ^1E ($1a_1 \rightarrow 9e$) state. It can also be concluded, that the nitrosyl is the only ligand that has the π-acceptor character strong enough to facilitate photoreduction of the iron atom in the $[Fe^{II}(CN)_5L]^{m-}$ complex.

It was suggested that intramolecular photooxidation and solvation of the NO ligand (Eq. (5)), that follows the $8e \rightarrow 9e$ excitation in $[Fe(CN)_5NO]^{2-}$, results both from weakening of the Fe–NO bond and from a considerable charge shift within the NO ligand (Table 3) [114,191]. The intramolecular photooxidation cannot be excluded also in the case of $[Fe(CN)_5CO]^{3-}$, for which susceptibility to reduction of the CO ligand was found to be enhanced by exposure [27].

Owing to the weakest π-acceptor character of CN^- among the ligands discussed, excitation-induced charge changes in $[Fe(CN)_6]^{4-}$ are closer to those in the carbonyl than the nitrosyl complex. In particular, all transitions in $[Fe(CN)_6]^{4-}$ (Tables 2 and 3) lead to an increase in the net charge on the Fe atom showing that the transitions are of MLCT character, mainly ($2t_{2g} \rightarrow 2t_{2u}$ and $2t_{2g} \rightarrow 5t_{1u}$) or partly ($2t_{2g} \rightarrow 4e_g$). The same direction of charge transfer is also observed in several successive more energetic transitions. It can be concluded from this finding that photooxidation is the only possible photoredox mode in $[Fe(CN)_6]^{4-}$. The highest HOMO energy amongst the $[Fe(CN)_5L]^{m-}$ complexes explains the observed intermolecular photooxidation and solvated electron production of the $[Fe(CN)_6]^{4-}$ complex. Comparing the values of charge changes, the $2t_{2g} \rightarrow 2t_{2u}$ and $2t_{2g} \rightarrow 5t_{1u}$ transitions seem to be those leading to photooxidation. Additionally, the both transitions are accompanied by insignificant changes in the Fe–CN bond order (Table 4) and in the two centre Fe–CN contribution to the total energy.

On the other hand, the first transition, $2t_{2g} \rightarrow 4e_g$, although leading to the smallest charge transfer, results both in an appreciable decrease in the Fe–CN σ-bond order and in an increase in E_{Fe-CN}. These changes are consistent with the excitation-induced photosubstitution of the CN^- ligand.

6. Conclusions

The review shows a variety of thermal and photochemical behaviours of cyano complexes, mixed-ligand cyanometallates in particular. Their interpretation becomes easier when the flexibility of the CN^- ligand and specific character of the excited states are considered.

The scaled INDO method was thus recognized as a useful tool for predicting both thermal reactivity and tendency of reactive decay of an excited state of cyanometallates; the procedure, however, should be acknowledged as a model, that is a point of departure for further refinement.

Nevertheless, the approach enables to predict the properties of the excited states under consideration and to interpret photochemical modes, their mechanisms and even their efficiencies.

Acknowledgements

The authors gratefully acknowledge financial support from KBN, grant No 0976/83/93/04; COST/PECO, grant No D3/0005/93.

References

[1] A.G. Sharpe, The Chemistry of Cyano Complexes of the Transition Metals, Academic Press, London, 1976.

[2] A.G. Sharpe in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987, Vol. 2, pp. 7–11.

[3] A.M. Goluo, H. Köhler and V.V. Skopenko (Eds.), Chemistry of Pseudohalides, Elsevier, Amsterdam, 1986, pp. 77–185.

[4] W.P. Griffith, Coord. Chem. Rev., 17 (1975) 177.

[5] D.H. Macartney, Rev. Inorg. Chem., 9 (1988) 101.

[6] B. Sieklucka, Prog. Reaction Kinetics, 15 (1989) 175.

[7] G. Stochel, Coord. Chem. Rev., 114 (1992) 269–295.

[8] V. Balzani and V. Carassiti Photochemistry of Coordination Compounds, Academic Press, London, 1970.

[9] A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley Interscience Publ., New York, 1975.

[10] G.J. Ferraudi, Elements of Inorganic Photochemistry, Wiley Interscience Publ., New York, 1988.

[11] J. Sykora and J. Sima, Photochemistry of Coordination Compounds, Elsevier, Amsterdam, 1990.

[12] J. Burmeister, Coord. Chem. Rev., 105 (1990) 77.

[13] S. Alwarez and C. Lopez, Inorg. Chim. Acta, 64 (1982) L99.

[14] D.F. Shriver, Struct. Bond., 1 (1967) 32.

[15] R.G. Pearson, Coord. Chem. Rev., 100 (1990) 430.

[16] C.A. Tsipis, Coord. Chem. Rev., 108 (1991) 163.

[17] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd edn., Wiley and Sons, New York, 1978, pp. 259–267.

[18] R.C. Maurya, D.D. Mishra, S.K. Jaiswal and I. Dubey, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 25 (1995) 521.

[19] R.C. Maurya, D.D. Mishra, S. Mukherjee and J. Dubey, Polyhedron, 14 (1995) 1351.

[20] A. McCleverty, Chem. Rev., 79 (1979) 53.

[21] H. Swinehart, Coord. Chem. Rev., 2 (1967) 385.

[22] J.H. Enemark and R.D. Feltham, Coord. Chem. Rev., 13 (1974) 339.

[23] A.R. Butler and D.L.H. Wiliams, Chem. Soc. Rev., 16 (1987) 361.

[24] Z. Stasicka, G. Stochel and E. Wasielewska, in F. Pruchnik (Ed.), Progress in Inorganic and Organometallic Chemistry, Wrocław, 1995, in press.

[25] A. Vogler and H. Kunkely, Z. Naturforsch. Teil B, 30 (1975) 335.

[26] E. Toma and F.T.P. Lellis, An. Acad. Bras. Cienc. 59 (1987) 165.

[27] T. Jarzynowski and E. Wasielewska, Proc. 6th SOPTROCC, Smolenice-Bratyslava, Czechoslovakia, 1988, p. 61.

[28] F. Calderazzo, U. Mazzi, G. Pampaloni, R. Poli, F. Tisato and P.F. Zanazzi, Gazz. Chim. Ital., 119 (1989) 241.

[29] A.J. Deeming, S. Donovan-Mtunzi, S.E. Kabir, A.J. Arce and Y. De Sanctis, J. Chem. Soc., Dalton Trans., (1987) 1457.

[30] W.M. Laidlaw and R.G. Denning, Polyhedron, 13 (1994) 1875.

[31] M. Sano, H. Kashiwagi and H. Yamatera, Inorg. Chem., 21 (1982) 3837.

[32] W. Holzapfel, H. Yersin and G. Gliemann, Z. Kristallogr., 157 (1981) 47.

[33] T. Ziegler, J.K. Nagle, J.G. Snijders and E.J. Baerends, J. Am. Chem. Soc., 111 (1989) 5635.

[34] Ch.M. Che, L.Y. He, Ch.K. Poon and Th.C.W. Mak, Inorg. Chem., 28 (1989) 3081.

[35] V.H. Houlding and A.J. Frank, NATO ASI Ser., Ser. C 174 (1986) 199.

[36] A.E. Underhill in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987, Vol. 6, pp. 133–154.

[37] H.K. Yip, T.F. Lai amd Ch.M. Che, J. Chem. Soc., Dalton Trans., 1991, 1639.

[38] L. Wiehl and S. Haussühl, Z. Kristall., 156 (1981) 117.

[39] D.L. Kepert in G. Wilkinson (Ed.), Comprehensive Coordination Chemistry, Pergamon Press, Oxford, 1987, Vol. 1, pp. 31–107.

[40] B. Sieklucka, N.W. Alcock, T.J. Kemp and D.J. Stufkens, J. Chem. Soc., Dalton Trans., 1990, 2331.

[41] B. Sieklucka, R. Dziembaj and S. Witkowski, Inorg. Chim. Acta, 187 (1991) 5.

[42] P.O. Lumme, U. Turpeinen and Z. Stasicka, Acta Crystallogr., C47 (1991) 501.

[43] Ch.M. Che, M.H.W. Lam, Th.C.W. Mak, J. Chem. Soc., Chem. Commun., (1989) 1529.

[44] W. Purcell, L.J. Damoense and J.G. Leipold, Inorg. Chim. Acta, 195 (1992) 217.

[45] Z. Stasicka, Proc. 12th Conf. Coord. Chem., Smolenice-Bratislava, Czechoslovakia, 1989, p. 359.

[46] B.J. Coe, T.I. Meyer and P.S. White, Inorg. Chem., 34 (1995) 3600.

[47] F.B. Stocker, Inorg. Chem.. 30 (1991) 1472.

[48] V.B. Nechitayilo, V.I. Styopkin, Z.A. Tkachenko, Y.G. Goltsov, V.P. Sherstyuk and V.V. Zhilinskaya, Electrochim. Acta, 40 (1995) 2501.

[49] W.R. Entley and G.S. Girolami, Inorg. Chem., 33 (1994) 5165.

[50] R.A. de Castello, C.P. MacColl and A. Haim, Inorg. Chem., 10 (1971) 203.

[51] F.R. Fronczek and W.P. Schaefer, Inorg. Chem., 13 (1974) 727.

[52] M.J. Bermejo and S. Alvarez, Inorg. Chim. Acta, 82 (1984) L23.

[53] D. Gaswick and A. Haim, J. Inorg. Nucl. Chem., 40 (1978) 437.

[54] R. Uson, J. Fornies, M.A. Uson and M.L. Mas, Inorg. Chim. Acta, 168 (1990) 59.

[55] A. Vogler in M.A. Fox and M. Chanon (Eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988, part D, Ch. 5.5, p. 179.

[56] V. Balzani, L. Moggi and F. Scandola, NATO ASI Ser., Ser. C 14 (1987) 1.

[57] F. Scandola and C.A. Bignozzi, NATO ASI Ser., Ser. C 214 (1987) 121.

[58] V. Balzani and F. Scandola, Supramolecular Photochemistry, Ellis Horwood, New York, 1991.

[59] F. Scandola, M.T. Indelli, C. Chiorboli and C.A. Bignozzi, Top. Curr. Chem., 158 (1990) 73.

[60] N. Fahmy and M. Hanack, Recl. Trav. Chim. Pays-Bas, 109 (1990) 235 and Refs. therein.

[61] R. Klenze, B. Kanellakopulos, G. Trageser and H.H. Eysel, J. Chem. Phys., 72 (1980) 5819.

[62] H. Miyasaka, N. Matsumoto, H.O. Kawa, N. Re, E. Gallo and C. Floriani, Angew. Chem. Int. Edn. Engl., 34 (1995) 1446.

[63] M. Orendac, A. Orendacova, B. Borzenets, I. Cernak and A. Feher, IEEE Trans. Magnetics, 30 (1994) 1109.

[64] S. Siddiqui, W.W. Henderson and R.E. Shepherd, Inorg. Chem., 26 (1987) 3101.

[65] P. Forlano, L.M. Baraldo, J.A. Olabe and C.D. Dellavedova, Inorg. Chim. Acta, 223 (1994) 37.

[66] G. Tsaur, M.C. Wu and A. Yeh, J. Chinese Chem. Soc., 41 (1994) 431.

[67] V.G. Poulopoulou, Z.W. Li and H. Taube, Inorg. Chim. Acta, 225 (1994) 173.

[68] L.A.A. Deoliveira, L. Dellaciana and A. Haim, Inorg. Chim. Acta, 225 (1994) 29.

[69] D.M. Duggan and D.N. Hendrickson, Inorg. Chem., 13 (1974) 1911.

[70] W.M. Laidlaw and R.G. Denning, Polyhedron, 13 (1994) 2337.

[71] W.B. Yan, Z.H. Zhou, H. Zhang, X.Y. Tang and Z.G. Xu, Chem. J. Chines Jniv.-Chinese, 16 (1995) 133.

[72] K. Winkler, J. Electroanal. Chem., 388 (1995) 151.

[73] Z.W. Li, A. Yeh and H. Taube, Inorg. Chem., 33 (1994) 2874.

[74] M. Martinez, M.A. Pitarque and R. van Eldik, J. Chem. Soc., Dalton Trans., (1994) 3159.

[75] D.E. Khosthariya, R. Billing, M. Ackermann and R. van Eldik, J. Chem. Soc. araday Trans., 91 (1995) 1625.

[76] T. Iwamoto in J.L. Atwood, J.E.D. Davies and D.D. MacNicol (Eds.), Incl sion Compounds, Oxford Univ. Press, Oxford, 1991, Vol. 5.

[77] T. Kitazawa, S. Nishikiori and T. Iwamoto, Mater. Sci. Forum, 91–93 (1992) 7.

[78] T. Kitazawa, S. Nishikiori, A. Yamagishi, R. Kuroda and T. Iwamoto, J. C em. Soc., Chem. Commun., 413 (1992) and Refs. therein.

[79] S. Nishikiori, T. Hasegawa and T. Iwamoto, J. Inclusion Phen., 11 (1991) 137 nd Refs. therein.

[80] S. Nishikiori and T. Iwamoto, Anal. Sci., 4 (1988) 25.

[81] K. Park and T. Iwamoto, J. Chem. Soc., Chem. Commun., 72 (1992).

[82] N. Karacan and Y. Tufan, Spectrosc. Lett., 28 (1995) 773.

[83] E. Ruiz and S. Alvaraz, Inorg. Chem., 34 (1995) 3260.

[84] T. Soma and T. Iwamoto, Chem. Lett., 4 (1994) 821.

[85] Z. Kantarci, N. Karacan and B. Davarcioglu, J. Mol. Struct., 323 (1994) 53.

[86] D.F. Mullica, E.L. Sappenfield and H.O. Perkins, J. Solid. State Chem., 78 (1 9) 301.

[87] C.R. Johnson, C.M. Jones, S.A. Asher and J.E. Abola, Inorg. Chem., 30 (1991 2120.

[88] M. Adam, A.K. Brimah, R.D. Fischer and L. Xing-Fu, Inorg. Chem., 29 (199 1595.

[89] M. Carcelli, C. Ferrari, C. Pelizzi, G. Pelizzi, G. Predieri and C. Solinas, J. C em. Soc., Dalton Trans., 1992, 2127.

[90] J.A. Davies, F.R. Hartley, S.G. Murray and M.A. Pierce-Butler, J. Chem. S ., Dalton Trans., 1983, 1305.

[91] M.A. Pavlosky and J.A. Larrabee, J. Am. Chem. Soc., 110 (1988) 5349.

[92] M.D. Curtis, K.R. Han and W.M. Butler, Inorg. Chem., 19 (1980) 2096.

[93] D.T. Cromer, A.C. Larson and R.B. Roof Jr., Acta Crystallogr., 15 (1962) 39

[94] B. Oswald, A.K. Powell, F. Rashwan, J. Heinze and H. Vahrenkamp, Chem. B , 123 (1990) 243.

[95] B.N. Storhoff and H.C. Lewis Jr., Coord. Chem. Rev., 23 (1977) 1.

[96] P. Riccieri and E. Zinato, Polyhedron, 11 (1992) 71.

[97] I. Tejera, R. Jimenez, A. Rodriguez, F. Sanchez and M.L. Moya, React. Kin . Catal. Lett., 46 (1992) 427.

[98] N.A. Lewis, R.R. Mcneer and D.V. Taveras, Inorg. Chim. Acta, 225 (1994) 89

[99] J. Szklarzewicz, A. Samotus, J. Burgess, I. Fawcett and D.R. Russell, J. Chem. S ., Dalton Trans., 18 (1995) 3057.

[100] W.M. Laidlaw and R.G. Denning, J. Chem. Soc., Dalton Trans., 13 (1994) 19 .

[101] M. Podsiadla, J. Rzeszotarska and M.K. Kalinowski, Monatsh. Chem., 125 (1 4) 827.

[102] A. Rodriguez, P. Pereztejeda, R. Imenez, F. Sauchez, P. Lopez, I.I. Calvente an M.L. Moya, Int. J. Chem. Kinetics, 27 (1995) 807.

[103] V. Holba and M. Hankova, Collect. Czech. Chem. Commun., 60 (1995) 537.

[104] V. Holba and M. Hankova, Chem. Zvesti, 48 (1994) 310.

[105] H.Y. Huang, W.J. Chen, Ch.Ch. Yang and A. Yeh, Inorg. Chem., 30 (1991) 18 2.

[106] I. Cernak, M. Kanuchova, I. Chomic, I. Potocnak, I. Kamenicek and Z. Zak, cta Crystallogr. Sect. C, 50 (1994) 1563.

[107] O. Angelova, J. Macicek, M. Atanasov and G. Petrov, Inorg. Chem., 30 (1991) 943.

[108] E. Wasielewska, Inorg. Chim. Acta, 113 (1986) 115.

[109] E. Wasielewska and Z. Stasicka in J.J. Ziółkowski (Ed.) Coordination Chemis y and Catalysis, World Scientific, Singapore, 1987, pp. 440–457.

[110] E. Wasielewska, Inorg. Chim. Acta, 122 (1986) L1.

[111] E. Wasielewska and Z. Stasicka, J. Inf. Rec. Mater., 17 (1989) 441.
[112] L.G. Vanquickenborne, L. Haspeslagh, M. Hendrickx and J. Verhulst, Inorg. Chem., 23 (1984) 1677.
[113] L.G. Vanquickenborne, L. Haspeslagh and M. Hendrickx in A.B.P. Lever (Ed.), Excited States and Reactive Intermediates, ACS Symposium Series 307, Washington, DC, 1986, p. 12.
[114] A. Gołębiewski and E. Wasielewska, J. Mol. Struct., 67 (1980) 183.
[115] E. Waldhor, J. Poppe, W. Kaim, E.H. Cutin, M.E.G. Posse and N.E. Katz, Inorg. Chem., 34 (1995) 3093.
[116] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd edn., Elsevier, Amsterdam, 1984, Chapter 5.
[117] V. Gutmann and G. Resch, Monatsh. Chem., 119 (1988) 1251.
[118] N. Kitamura, M. Sato, H.B. Kim, R. Obata and S. Tazuke, Inorg. Chem., 27 (1988) 651.
[119] J.I. Zink, Coord. Chem. Rev., 64 (1985) 93.
[120] J.I. Zink, L. Tutt and Y.Y. Yang, in A.B.P. Lever (Ed.), Excited States Reaction Intermediates, ACS Symp. Ser., 307 (1986) 39.
[121] J.B. Cooper and D.W. Wertz, Inorg. Chem., 28 (1989) 3108.
[122] E. Wasielewska and A. Gołębiewski, Polish J. Chem., 55 (1980) 1099.
[123] E. Zinato, A.W. Adamson, J.L. Reed, J.P. Puaux and P. Riccieri, Inorg. Chem., 23 (1984) 1138.
[124] A. Ghaith, L.S. Forster and J.V. Rund, Inorg. Chim. Acta, 116 (1986) 11.
[125] J.F. Endicott, R.B. Lessard, D. Lynch, M.W. Perkovic and Ch.K. Ryu, Coord. Chem. Rev., 97 (1990) 65.
[126] M.E. Frink and P.C. Ford, Inorg. Chem., 24 (1985) 3494.
[127] J.R. Winkler and H.B. Gray, Inorg. Chem., 24 (1985) 346.
[128] X. Song and J.F. Endicott, Inorg. Chem., 30 (1991) 2214.
[129] N.A.P. Kane-Maguire, W.S. Crippen and P.K. Miller, Inorg. Chem., 22 (1983) 696.
[130] Z. Stasicka and A. Marchaj, Coord. Chem. Rev., 23 (1977) 131.
[131] L. Viaene, J. D'Olieslager, A. Ceulemans and L.G. Vanquickenborne, J. Am. Chem. Soc., 101 (1979) 1405.
[132] J.W. Schindler, R.C. Fukuda and A.W. Adamson, J. Am. Chem. Soc., 104 (1982) 3596.
[133] C.A. Bignozzi, M.T. Indelli and F. Scandola, J. Am. Chem. Soc., 111 (1989) 5192.
[134] K. Matsui, Md.K. Nazeeruddin, R. Humphry-Baker, M. Grätzel and K. Kalyanasundaram, J. Phys. Chem., 96 (1992) 10587.
[135] U. Hauser, W. Klimm, L. Reder, T. Schmitz, M. Wessel and H. Zellmer, Phys. Lett. A, 144 (1990) 39.
[136] Th. Woike, W. Krasser, H. Zöllner, W. Kirchner and S. Haussühl, Z. Phys. D, 25 (1993) 351 and Refs. therein.
[137] H.U. Güdel, Chem. Phys. Lett., 175 (1990) 262.
[138] Y. Morioka, Spectrochim. Acta, Part A, 50 (1994) 1499.
[139] K. Lughausen, H. Siegert, T.H. Woike and S. Haussuhl, J. Phys. Chem. Solids, 56 (1995) 1291.
[140] J.A. Guida, O.E. Piro and P.J. Aymonino, Inorg. Chem., 34 (1995) 4113.
[141] P. Belser, A. von Zelewsky, A. Juris, F. Barigelletti and V. Balzani, Gazz. Chim. Ital., 115 (1985) 723.
[142] C. Conti and L.S. Forster, J. Chem. Soc., 99 (1977) 613.
[143] P.E. Hoggard and K.W. Lee, Inorg. Chem., 27 (1988) 2335.
[144] M. Kozik, N. Sutin and J.R. Winkler, Coord. Chem. Rev., 97 (1990) 23.
[145] M. Stock and H. Yersin, Solid State Commun., 27 (1978) 1305.
[146] U. Riedl, G. Gliemann, H. Yersin and K.J. Range, Abstracts of the ISPPCC, Fribourg, 1991, p. 57.
[147] U. Rössler and H. Yersin, Phys. Rev. B, 26 (1982) 3187.
[148] J.H. Lacasce Jr., W.A. Turner, M.R. Corson, P.J. Dolan Jr. and J.K. Nagle, Chem. Phys., 118 (1987) 289.
[149] Z. Assefa, F. DeStefano, M.A. Garepapaghi, J.H. LaCasce Jr., S. Ouellete, M.R. Corson, J.R. Nagle and H.H. Patterson, Inorg. Chem., 30 (1991) 2868.
[150] S.H. Peterson and J.N. Demas, J. Am. Chem. Soc., 101 (1979) 6571.
[151] A. Juris, F. Barigelletti, V. Balzani, P. Belser and A. von Zelewsky, J. Chem. Soc., Faraday Trans., 83 (1987) 2295.
[152] M.T. Indelli, C.A. Bignozzi, A. Marconi and F. Scandola, in H. Yersin and A. Vogler (Eds.),

Photochemistry and Photophysics of Coordination Compounds, Springer-Verlag Berlin, 1987, p. 159.
[153] J. Davila, M.T. Indelli, A. Marconi, C.A. Bignozzi and F. Scandola, XII IUPAC Symp. Photochem., Bologna, 1988, p. 271.
[154] M.T. Indelli, A. Marconi and F. Scandola, XII IUPAC Symp. Photochem., Bologna, 1988, p. 393.
[155] R.M. Leasure, L.A. Sacksteder, D. Nesselrodt, G.A. Reitz, J.N. Demas and B.A. DeGraff, Inorg. Chem., 30 (1991) 3722.
[156] M.T. Indelli, C.A. Bignozzi, A. Marconi and F. Scandola, J. Am. Chem. Soc., 110 (1988) 7381.
[157] Z.R. Grabowski and W. Rubaszewska, J. Chem. Soc., Faraday Trans., I (1977) 1.
[158] V. Balzani, F. Bolletta, M.T. Gandolfi and M. Maestri, Top. Curr. Chem., 75 (1978) 1.
[159] V. Balzani, F. Bolletta, M. Ciano and M. Maestri, J. Chem. Educ., 60 (1983) 447.
[160] Z. Stasicka, Wiad. Chem., 39 (1985) 571.
[161] K. Kalyanasundaram, M. Grätzel and Md.K. Nazeeruddin, Inorg. Chem., 31 (1992) 5243.
[162] G.A. Carriedo, N.G. Connelly, S. Alvarez, E. Perez-Carreno and S. Garcia-Granda, Inorg. Chem., 32 (1993) 272.
[163] N. Serpone in M.A. Fox and M. Chanon (Eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988, part D, Ch. 5.3, p. 47.
[164] A.D. Kirk and S.R.L. Fernando, Inorg. Chem., 33 (1994) 4435.
[165] A.D. Kirk and C. Namasivayam, J. Phys. Chem., 93 (1989) 5488.
[166] C.A. Bignozzi, M.T. Indelli and F. Scandola, XII IUPAC Symp. Photochem., Bologna, 1988, p. 395.
[167] C. Chiorboli, C.A. Bignozzi, M.T. Indelli, M.A. Rampi and F. Scandola, Coord. Chem. Rev., 11 (1991) 267.
[168] M. Nishizawa and P.C. Ford, Inorg. Chem., 20 (1981) 2016.
[169] C.A. Bignozzi, S. Roffia, C. Chiorboli, J. Davila, M.T. Indelli and F. Scandola, Inorg. Chem. 28 (1989) 4350.
[170] Y. Lei, T. Buranda and J.F. Endicott, J. Am. Chem. Soc., 112 (1990) 8820.
[171] F. Scandola, C.A. Bignozzi, C. Chiorboli, M.T. Indelli and M.A. Rampi, Coord. Chem. Rev., 97 (1990) 299.
[172] C.A. Bignozzi, M.T. Indelli and F. Scandola, 10 ISPPCC, Sendai, 1993, p. 7.
[173] R. Amadelli, R. Argazzi, C.A. Bignozzi and F. Scandola, J. Am. Chem. Soc., 112 (1990) 7099.
[174] C.A. Bignozzi, R. Argazzi, C. Chiorboli, S. Roffia and F. Scandola, Coord. Chem. Rev., 111 (1991) 261.
[175] V. Balzani and F. Scandola in M.A. Fox and M. Chanon (Eds.), Photoinduced Electron Transfer, Elsevier, Amsterdam, 1988, part D, Ch. 5.4, p. 148.
[176] A. Vogler, A.H. Osman and H. Kunkely, Coord. Chem. Rev., 64 (1985) 159.
[177] J. Szklarzewicz and A. Samotus, Trans. Met. Chem., 20 (1995) 174.
[178] S.I. Ali, A.M.A. Ansari and N.K.S. Pundhir, Indian J. Chem. Sect. A, 34 (1995) 423.
[179] H.B. Quang, Z. Stasicka, B. Mainusch and F. Wasgestian, J. Photochem. Photobiol., A. Chem., 99 (1996) 149.
[180] G. Stopa and Z. Stasicka, Polyhedron, 3 (1984) 247.
[181] J. Oszajca, G. Stopa and Z. Stasicka, Proc. 11th Conf. Coord. Chem., Smolenice-Bratislava, Czechoslovakia, 1987, p. 293.
[182] G. Stopa, Z. Stasicka and D. Rehorek, Polish J. Chem., 65 (1991) 649.
[183] A. Marchaj and F. Wasgestian, Inorg. Chim. Acta, 102 (1985) L13.
[184] J. Szklarzewicz, A. Samotus, O. Traverso and S. Sostero, Polyhedron, 13 (1994) 1755.
[185] L.G. Vanquickenborne and A. Ceulemans, Coord. Chem. Rev., 48 (1983) 157.
[186] A. Marchaj, Z. Stasicka and D. Rehorek, Polyhedron, 2 (1983) 1281 and Refs. therein.
[187] E. Joselevich and I. Willner, J. Phys. Chem., 99 (1995) 6903.
[188] Z. Stasicka, A. Marchaj and G. Stochel, Proc. 8th Conf. Coord. Chem. Smolenice-Bratislava, Czechoslovakia, 1980, p. 373.
[189] G. Stochel and Z. Stasicka, Proc. 10th Conf. Coord. Chem. Smolenice-Bratislava, Czechoslovakia,
[190] G. Stochel and Z. Stasicka, Polyhedron, 4 (1985) 1887.
[191] G. Stochel, R. van Eldik and Z. Stasicka, Inorg. Chem., 25 (1986) 3663.

[192] E. Hejmo, E. Porcel-Ortega, T. Senkowski and Z. Stasicka, Bull. Pol. Acad. Sci., Ser. Chem., 36 (1988) 351.

[193] M.G. Deoliveira, G.J. Langley and A.J. Rest, J. Chem. Soc., Dalton Trans., 12 (1995) 2013.

[194] A. Ulveczky and A. Horvath, Inorg. Chim. Acta, 236 (1995) 173.

[195] J.C. Curtis and T.J. Meyer, Inorg. Chem., 21 (1982) 1562.

[196] A. Vogler and J. Kisslinger, J. Am. Chem. Soc., 104 (1982) 2311.

[197] G. Stochel, J. Achrem-Achremowicz, A. Karocki, B. Osman, D. Rybniewska and Z. Stasicka, J. Pol. Chem., in press.

[198] H. Kunkely, G. Stochel and A. Vogler, Z. Naturforsch., 44b (1989) 145.

[199] G. Stochel, Polyhedron, 13 (1994) 155.

[200] M. Nishizawa and P.C. Ford, Inorg. Chem., 20 (1981) 2016.

[201] M. Zhou, B.W. Pfennig, J. Steiger, D. van Engen, and A.B. Bocarsly, Inorg. Chem., 29 (1990) 2456.

[202] A.C. Dash and G.C. Pradhan, Indian J. Chem. Sect. A, 33 (1994) 661.

[203] D.E. Khoshtariya, R. Billing, M. Ackermann and R. van Eldik, J. Chem. Soc., Faraday Trans., 91 (1995) 1625.

[204] C.A. Bignozzi, S. Roffia and F. Scandola, J. Am. Chem. Soc., 107 (1985) 1644.

[205] C.A. Bignozzi, C. Paradisi, S. Roffia and F. Scandola, Inorg. Chem., 27 (1988) 408.

[206] B.W. Pfennig and A.B. Bocarsly, Abstracts of the ISPPCC, Fribourg, 1991, p. 79.

[207] J.B. Cooper, T.M. Vess, W.A. Kalsbeck and D.W. Wertz, Inorg. Chem., 30 (1991).

[208] W.W. Henderson and R.E. Shepherd, Inorg. Chem., 24 (1985) 2398.

[209] J.J. Alexander and H.B. Gray, J. Am. Chem. Soc., 90 (168) 4260.

[210] A. Aizman and D. Case, Inorg. Chem., 20 (1981) 528.

[211] M. Sano, H. Adachi and H. Yamatera, Bull. Chem. Soc. Jpn., 54 (1981) 2898.

[212] M. Sano, H. Yamatera and Y. Hatano, Chem. Phys. Lett. 60 (1979) 257.

[213] L.G. Vanquickenborne, M. Hendrickx, I. Hyla-Kryspin and L. Haspeslagh, Inorg. Chem., 25 (1986) 885.

[214] K. Pierloot, E. Van Praet and L.G. Vanquickenborne, J. Phys. Chem., 97 (1993) 12220.

[215] H.E. Toma, N.M. Moroi and N.Y.M. Iha, A. Acad. Brasil. Ci., 54 (1980) 585.

[216] T. Jarzynowski, T. Senkowski and Z. Stasicka, Polish J. Chem., 10 (1980) 902.

[217] M.C.R. Symons, J.G. Wilkinson and D.X. West, J. Chem. Soc., Dalton Trans., (1982) 2001.

[218] E.F. Hockings and I. Bernal, J. Chem. Soc., 1964, 5029.