Coordination Chemistry Reviews
219–221 (2001) 881–921

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Advances in the coordination chemistry of $[M(CN)_5L]^{n-}$ ions (M = Fe, Ru, Os)

Luis M. Baraldo, Paula Forlano, Alejandro R. Parise,
Leonardo D. Slep, José A. Olabe *

Departamento de Química Inorgánica, Analítica y Química Física, Inquimae,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón 2,
Ciudad Universitaria, C1428EHA Buenos Aires, Argentina

Received 16 November 2000; received in revised form 13 March 2001; accepted 26 March 2001

Contents

---

* Corresponding author. Tel.: +54-11-4576-3358; fax: +54-11-4576-3341.
E-mail address: olabe@q1.fcen.uba.ar (J.A. Olabe).

PII: S0010-8545(01)00383-6

Abstract

New developments in the synthesis, crystal and molecular structure, spectroscopy and kinetic properties of the $[M(CN)_5L]^{n-}$ ions ($M^{II,III}$ = Fe, Ru, Os; L = H_2O, NH_3, amines, CN^-, *N*-heterocyclic ligands, etc.), performed over the last decade, are reviewed. The properties of dinuclear complexes containing pentacyano-fragments bridged by pyrazine, cyanide or other bridging ligands, are also considered, with emphasis on mixed-valent systems. The influence of the solvent and other medium effects on the electronic structure, as well as on the modification of the reactivity of L upon coordination is addressed particularly. Some catalytic processes relevant to bioinorganic chemistry are discussed, involving either ligand oxidation (hydrazine, thiolates) or reduction (nitrosyl).

Keywords: Pentacyano-L-metalates; Mixed-valent complexes; Cyanide-bridged systems; Reactions of coordinated ligands

---

1. Introduction

The chemistry of the $[M(CN)_5L]^{n-}$ complexes, with M = Fe, Ru, Os and L a variable ligand (H_2O, CN^-, NH_3, amines, NO, NO_2^-, *N*-heterocyclic molecules, CO, etc.) has received much attention, and systematic investigation of their electronic structure and reactivity are currently pursued [1]. The study of the iron- and ruthenium series was developed mainly in 1970s and 1980s, respectively. Work on iron complexes was reviewed in 1988 [2], but since then important developments have been achieved, particularly for the ruthenium and osmium series chemistry.

In the present review we address significant new results regarding crystallography, electronic structure, spectroscopy, electrochemistry and reactivity of these compounds and considering also the influence that the medium exerts on the above mentioned properties. The complexes with *N*-heterocyclic ligands, namely pyrazine (pz), pyridine (py) and their derivatives, deserve special attention, as they allow fruitful comparisons between the three metal series. We also consider the use of pentacyano-fragments for synthesizing dinuclear and oligonuclear entities, with either *N*-heterocyclic molecules [3] or cyanide groups [4] as bridging ligands.

We focus specially on the reactivity of Fe, Ru and Os pentacyanonitrosyl complexes. Some modern aspects of NO chemistry have been highlighted recently [5], including the photoinduced reversible linkage-isomerization of –NO to –ON in $[Fe(CN)_5NO]^{2-}$ ion and related complexes, and therefore these are not discussed in this review. Also, recently reviewed issues like the photosubstitution and photoredox studies on cyanometalates [6] and the solid state chemistry of Prussian blue-type compounds [7] are not included, with the exception of photoreactivity in the mixed-valence complexes.

2. The coordination of L ligands. Structure, ligand interchange and redox reactivity

2.1. Crystallography

Through the mid-1980s, structural data for salts of the $[M(CN)_5L]^{n-}$ anions were lacking, with some exceptions like $Na_4[Fe(CN)_6]\cdot 10H_2O$, $K_4[Fe(CN)_6]\cdot 3H_2O$, $K_3[Fe(CN)_6]$, $Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$ and $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ [1,2]. The crystal structures of $Na_4[M(CN)_6]\cdot 10H_2O$ [8] and of $Na_2[M(CN)_5NO]\cdot 2H_2O$ [9] (M = Ru, Os) were obtained subsequently, and found to be isostructural with the iron analogs. Recently, the molecular structure of $Na_3[Fe^{II}(CN)_5NH_3]\cdot 7H_2O$ has been solved [10]. The Fe^{II}–N distance is 0.06 Å longer than in the Fe(III) analog [11], and the *trans*-Fe^{II}–C bond is 0.05 Å shorter than the *cis*-Fe^{II}–C bonds. This could be ascribed to the *trans*-CN ligand receiving a greater electron density, given that NH_3 is not a competing π-acceptor. This behavior is at variance with the one previously found for $[Fe(CN)_5NO]^{2-}$ [12]; here, the electron-withdrawing ability of NO^+ makes the *trans*-CN ligand less basic than the *cis*-ones. These facts are a manifestation of the different structural *trans*-effects of NO^+ versus NH_3 [13].

A sodium salt containing the $[Fe^{II}(CN)_5CO]^{3-}$ anion was studied [14]. No differences exist in the *cis*- and *trans*-Fe–C bond lengths corresponding to the cyanide ligands (1.91 Å, av.) but the Fe–C bond is remarkably short for the carbonyl ligand (1.79 Å). This can be associated with the strength of the metal π-interaction with carbonyl, which is larger than that with cyanide, even though the σ-binding capability of the CO ligand is the weakest [15].

Aymonino, Varetti and coworkers carried out comprehensive work on the differently hydrated salts of the nitroprusside ion containing Groups 1 and 2 cations [16]. The crystal and molecular structures and the vibrational spectra reflect the interactions of the anion with the different types of waters and cations, but no systematic variations show up in the internal relevant parameters of the anion, with the exception of a decrease of the NO stretching-wavenumber upon dehydration (ca. 20–40 cm^{-1}). The latter shift reflects the loss of the specific donor interactions of cyanides with water in the solid phase. The interactions also show up in the solution chemistry of cyanide-complexes (see Section 5).

2.2. Synthesis and general properties

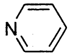
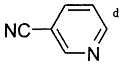
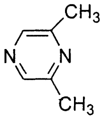
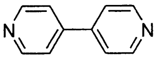
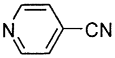
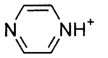
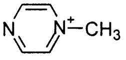
2.2.1. Iron

New complexes of pentacyanoferrate with different L ligands have been prepared and characterized spectroscopically. With purine and pyrimidine nucleic bases, nucleosides and 5′-mononucleotides, stable complexes were obtained by direct coordination to the $[Fe^{II}(CN)_5H_2O]^{3-}$ ion, or, alternatively, by adding the ligands to solutions of the nitroprusside ion subjected to irradiation or base addition. Intense metal-to-ligand charge transfer (MLCT) transitions are typical of coordination to the $Fe^{II}(CN)_5^{3-}$ fragment (as for L = adenine, $\lambda_{max} = 330$ nm); on the other hand, ligand-to-metal charge transfer (LMCT) transitions around 500–600 nm appear for Fe(III) complexes with hypoxanthine, cytosine, cytosine monophosphate, adenine and adenosine [17a]. A similar spectroscopic and kinetic characterization in aqueous solution was made with complexes of Fe(II) and Fe(III) with adenosine, 1-methyladenosine, tubercidin and 2- and 3-aminopyridines. The first three Fe(II)-complexes bind through the N-1 of the nucleic acid and are labile toward dissociation, k_{-L} ca. 0.1–0.6 s^{-1}. The amino-pyridine complexes behave as expected for other py-derivatives, showing an enhancement of the dissociation rate for the 2-aminopyridine ligand compared to the 3-isomer due to steric effects [17b]. Yeh also performed spectroscopic and kinetic characterization of some new complexes of Fe(II) and Fe(III) with pyridine derivatives, namely 4- and 3-hydroxypyridine, as well as 4- and 3-methoxypyridine. The results are in agreement with those reported for related complexes; interestingly, however, the rate of formation of the 4-hydroxypyridine complex is three orders of magnitude smaller than the others, probably because of the favorable tautomeric equilibrium of the 4-hydroxypyridine ligand to its keto-form, the latter being unable to bind to pentacyanoferrate(II) [17c]. As to the 3-(3′-pyridyl)sydnone complex, this is shown to be very stable compared to other 3-substituted py-derivatives; the electronic spectrum and the high redox potential (0.54 V vs. NHE) reveal that the sydnone substituent is a strong electron withdrawing agent [17d]. The characterization of the Fe(II) and Fe(III) pentacyano-complexes of aniline has been studied, and the spectral and kinetic data are consistent with those of other ammines. The Fe(II)-complex is less stable, however ($K = 319$ M^{-1}), in line with the high dissociation rate of aniline, ca. 1 s^{-1}. The latter value can be explained by the weak basicity of aniline, compared with those of ammonia and other amines, which form more stable complexes (K around 10^4–10^5 M^{-1}). The electrochemical results show two reversible waves, although only one should be expected for a mononuclear $[Fe^{III,II}(CN)_5aniline]^{2,3-}$ redox couple. The additional wave was attributed to unreacted aquapentacyanoferrate(II); the reported cyclic voltammogram (CV) pattern suggests, however, that a cyanide-bridged mixed-valent complex can be present at the concentration level employed, 10^{-3} M [17e]. Other fairly unstable complexes (K generally lower than 10^3 M^{-1}) were formed by acetonitrile and related ligands [17f]. Shepherd et al. report a comprehensive study of the coordination of 2-substituted imidazoles and imidazolates, using different spectroscopic, electrochemical and kinetic techniques, revealing the influence of the substituents on the binding properties, as well as on the rate- and stability constants [17g]. Toma studied the reaction of aquapentacyanoferrate(II) with the 2-amino pyrazine ligand, which yields a mixture of isomers coordinated at the amino and aromatic N-groups. The amino-coordinated isomer converts to the N-aromatic isomer, with $k = 0.57$ s^{-1} (25 °C). The latter, more stable isomer, was characterized electrochemically and spectrophotometrically in aqueous solution [17h]. Pentacyanide-complexes of Fe(II) and Fe(III) with triethylphosphite were prepared. The ligand behaves as a very strong π-acid, similar to cyanide; the bond with Fe(II) is very inert toward dissociation, and no cyanide-*trans* effect was found, in contrast with the behavior of the ruthenium pentaammines. Aquation of $P(OCH_2CH_3)_3$ as well as of cyanide is observed upon irradiation, in contrast with the general behavior during the photolysis of pentacyano-L-ferrates(II), where no cyanide is released [6]. However, the *cis*- or *trans*-nature of labilized cyanide was not determined [17i]. Stable Fe(II)-complexes were also obtained with triphenyl-substituted phosphines, P(Ph–*p*-X)$_3$ (X = H, F, Cl, OCH_3, CH_3, CF_3). The redox potentials of the $Fe^{III,II}$ couples shift positively for X becoming more electron-acceptor. It was concluded that the triphenylphosphines are stronger π-acceptors than the trialkyl-derivatives [17j]. However, the σ-donor ability of the ligands also changes, influencing the values of the redox potentials. Borges et al. prepared some complexes with sulfur-binding heterocyclic ligands (1,4-thioxane, 1,4- and 1,3-dithiane), which were characterized by electronic, IR and Mössbauer spectroscopies. Rate saturation behavior for the dissociation processes suggests a D mechanism. The rate constants are around $3–6 \times 10^{-4}\ s^{-1}$, at 25 °C, similar as for *N*-binding ligands [17k]. The basicities of bound pyrazine were studied with the three pentacyanometalate-fragments; the pK_a values for the $[M(CN)_5pzH]^{2-}$ ions are: Fe (1.24) > Os (0.53) > Ru (0.41) [17i]. Although it was stressed that none of the pK_a, NMR or electronic spectral results provide a quantitative approach to individual σ–π contributions, nevertheless the order of the pK_as could be determined mainly by the π-interactions [17l]. This had been previously proposed by Toma and Stadler [17m], by studying the coordination of 2,6-dimethylpyrazine (dmpz) with pentacyanoferrate(II) and pentacyanoruthenate(II). They also suggested that Fe was a stronger π-donor than ruthenium, in agreement with previous NMR results [18].

2.2.2. Ruthenium

An extensive series of $[Ru(CN)_5L]^{n-}$ complexes with pz- and py-derivatives has been prepared [18]. Advantage was taken of direct substitution of L into the $[Ru(CN)_5H_2O]^{3-}$ ion, which had been previously characterized ($\lambda_{max} = 310$ nm) after the reaction of $[Ru(CN)_6]^{4-}$ with bromine. For $[Ru(CN)_5H_2O]^{3-}$, λ_{max} was later reported to be 308 nm, with $\varepsilon = 1640\ M^{-1}\,cm^{-1}$ [19a]. Table 1 shows the wavelength maxima and the molar absorptivities for the MLCT transitions of a selected group of *N*-heterocyclic ligands for which comparable data also exist for the iron and osmium analogs [17l,17m,19a,20,21,22a,23]. For the three metal series, it can be seen that the energies decrease and the intensities increase with the acceptor abilities of L. While the first is expected behavior for weakly coupled systems, the latter might be a sign of increasing M–L coupling. Comparison of the UV–vis spectra of the $[Ru(CN)_5L]^{n-}$ and $[Ru(NH_3)_5L]^{n+}$ ions shows that the MLCT transitions are shifted to higher energies for the cyano-complexes, reflecting the stabilization of the metal orbitals by the strong-field cyano-ligands. Consistently, the degree of back-donation from the pentacyanoruthenate fragment to the L ligand is smaller than that for the pentaammines, and was estimated to be lower than 10% [18]. Other solids in addition to L = pz were prepared, with L = cyanopyridines (4- and 3-CNpy) [22], hydrazine, ethylenediamine and dimethylsulfoxide (dmso) compounds [24]. For the ruthenium complexes with L = CN^-, dmso, pz, NH_3 and H_2O, spin-allowed d–d bands appear in the range 250–310 nm. The energies vary in agreement with the spectrochemical series, and a correlation exists with the dissociation-rate constants for L release, which increases in the above order. A new value of 10Dq = 42 000 cm^{-1} was proposed for the $[Ru(CN)_6]^{4-}$ ion,

Table 1
Wavelength maxima (λ, nm) and molar absorptivities (ε, M^{-1} cm^{-1}) for selected $[M^{II}(CN)_5L]^{n-}$ complexes (M = Os, Ru, Fe)

L	Os[a]	Ru	Fe
	318 (5460)	317 (5020)[b]	362 (3715)[c]
 [d]	354 (5560)	342 (5500)[e]	414 (3200)[f]
	372 (6590)	364 (7700)[g]	440 (5500)[g]
	374 (7770)	368 (8800)[b]	432 (5623)[c]
	386 (6435)	370 (5040)[b]	452 (5012)[c]
 [h]	398 (6320)	388 (5900)[e]	477 (5700)[f]
	514 (12700)[i]	504 (6540)[i]	636 (6900)[i]
	532 (14970)	522 (6840)[b]	655 (12022)[c]

[a] Data of the asymmetric band. See Ref. [20] for the two disclosed absorptions, obtained by Gaussian deconvolution.
[b] Ref. [19a].
[c] Ref. [21].
[d] N-nitrile binding.
[e] Ref. [22a].
[f] Ref. [23].
[g] Ref. [17m].
[h] N-heterocycle binding.
[i] Ref. [17l].
[h] N-heterocycle binding.
[i] Ref. [17l].

based on a modified assignment of the d–d bands [25]. Thus, 10Dq for $[Ru(CN)_6]^{4-}$ is now greater than that for $[Fe(CN)_6]^{4-}$ (32 800 cm^{-1}), consistent with ligand field model predictions [26].

2.2.3. Osmium

Only electronic (MLCT but not d–d) and vibrational spectroscopic properties of the $[Os(CN)_6]^{4-}$ ion have been reported [1,2,26]. Salts with substituted pentacyano-derivatives have been obtained recently, $K_2[Os(CN)_5N_2H_5]\cdot 2H_2O$ [20] and $K_3[Os(CN)_5NH_3]\cdot 2H_2O$ [27]. They were prepared from the nitrosyl compound [9b], and can be used for preparing other L derivatives by direct substitution of the ammine ligands.

A comprehensive study on the synthesis and properties of the $[Os(CN)_5L]^{n-}$ compounds with *N*-heterocyclic ligands has been published [20]. Table 1 shows the MLCT absorption data for selected ligands. Fig. 1 shows the splitting of the $Os^{II} \rightarrow \pi^*(L)$ MLCT band into two components, a distinctive spectroscopic feature with respect to iron- and ruthenium complexes. Fig. 2 shows an excellent correla-

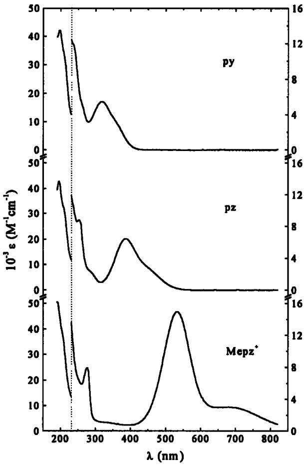


Fig. 1. Electronic spectra of $[Os^{II}(CN)_5L]^{n-}$ complexes with L = py, pz, mepz$^+$, in aqueous solution.

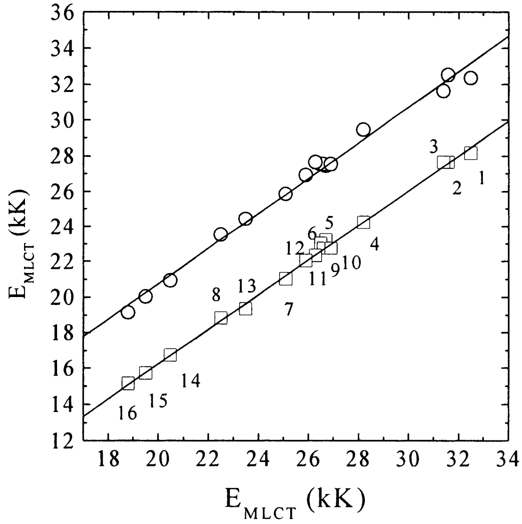


Fig. 2. Correlation between the MLCT band energies in $[M^{II}(CN)_5L]^{n-}$ complexes, M = Fe (squares), Ru (circles) and the MLCT band of higher energy for the osmium analogs.

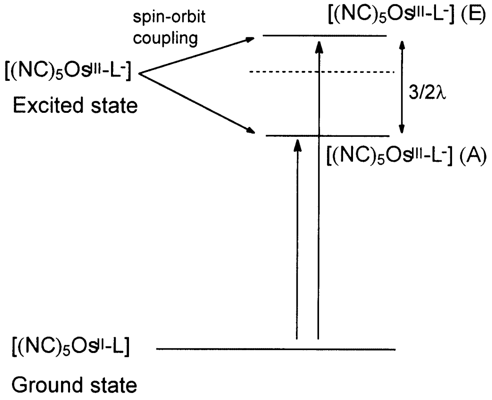
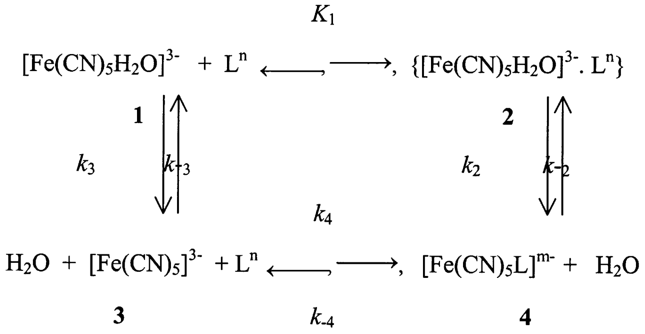


Fig. 3. Splitting of the MLCT excited state in $[Os^{II}(CN)_5L]^{n-}$ under spin–orbit coupling.

tion (nearly unit slope) between the absorption energies, E_{MLCT}, in water, for the three metal series, suggesting that even for L ligands with very different π-acceptor abilities, the metal–cyanide interactions are dominant in the bonding scheme. It also suggests that the degree of M–L back bonding is low for the three metal fragments. It was shown that the slopes of the E_{MLCT} plots deviate considerably from unity when one of the $[MX_5]$ fragments is a much stronger π-donor; this can be seen in the plots of the E_{MLCT} energies of the Ru- or the Os-pentaammines against E_{MLCT} for the pentacyanide complexes [18]. The difference in energy between the split MLCT transitions is independent of L; this fact was assigned to a spin–orbit coupling effect. Fig. 3 shows a simplified model for the two transitions, which yields a value of $\lambda_{Os} = 2900 \pm 200$ cm^{-1} for the spin–orbit coupling constant, as reported in the literature [28]. Strikingly enough, the splitting pattern does not agree with the previous observations on the $[Os^{II}(NH_3)_5L]^{n+}$ series [29], in which the energy differences for the two bands were found to be strongly dependent on L. A comprehensive theoretical description of electronic transitions in these $\{MX_5L\}$ systems ($M = Fe$, Ru, Os; $X = CN^-$, NH_3; $L = N$-heterocyclic ligands) has been recently published [20b].

2.3. Ligand substitution (dissociation and formation reactions)

Kinetic rate constants for ligand interchange have been obtained for Fe(II) [17c,e,f,30,31] and Fe(III) [32] pentacyano-L-complexes. The new results for the dissociation reactions of Fe(II) species are in agreement with the mechanism previously proposed for the reactions with other L ligands [2]. Evidence for the proposed D mechanism (cf. Scheme 1, route 4–3–1) includes saturation kinetics with respect to the concentration of the entering ligand, the dependence of rate dissociation constants on the binding ability of L, and the significantly positive values of $\Delta S^{\#}$ and $\Delta V^{\#}$ [31].



Scheme 1.

In contrast, the mechanism of the dissociation reactions of Fe(III) complexes has not been established so firmly; the aquation of $[Fe^{III}(CN)_5NO_2]^{3-}$ was shown to be acid-catalyzed, following protonation of the nitro ligand. Activation volumes are slightly positive, but the interpretation is not conclusive since $\Delta V^{\#}$ is a composite function, and it is therefore difficult to predict the magnitude of $\Delta V^{\#}(k)$, associated with the rate-determining step [32a].

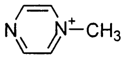
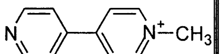
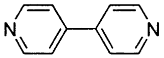
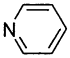
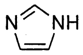
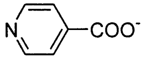
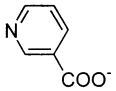
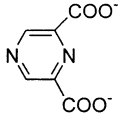
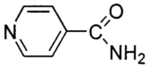
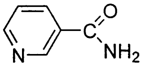
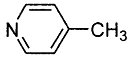
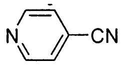
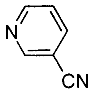
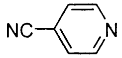
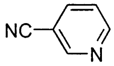
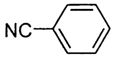
In the case of the formation reactions, the new results for the Fe(II) complexes confirm the marked dependence of the rate constants on the charge of the entering ligand L, and the lack of variation of $\Delta H^{\#}$ with L [2]. For a series of dicationic ligands of the type $[R(CH_2)_nR]^{2+}$, the rate constants for the formation reactions depend on the polymethylene chain length n, decreasing in the order R = pz > 4,4′-bipyridine (bpy) > *trans*-1,2-bis(4-pyridyl)ethylene (bpe), as the donor nitrogen atom is further removed from the site of the positive charges [30]. Saturation kinetics were observed, consistent with an ion-pair dissociative mechanism, I_d (cf. Scheme 1, route 1–2–4), with $[Fe(CN)_5H_2O/L]^-$ ion-pair constants in the range 40–100 M^{-1}. From these, the rate-determining loss of the coordinated aqua-ligand was calculated, decreasing to ca. 100 s^{-1}, compared with the value estimated for neutral ligands, ca. 300 s^{-1} [2]. This was traced down to the interaction of cyanides with the positive charges, thus making the dissociation of water slower. Van Eldik et al. reported that the above results, together with all the previous ones on the formation reactions [2], can be explained alternatively by a limiting D mechanism [31a]. The proposal is based on a previously measured $\Delta V^{\#}$ value, 13.5 $cm^3\ mol^{-1}$, obtained for the coordination of cyanide into $[Fe^{II}(CN)_5H_2O]^{3-}$ [31b], as well as on a series of experiments with neutral and negative ligands (imidazole, histidine, methionine, glutathione, glycine, β-alanine), for which ion-pairing was minimized. Although the meaningful $\Delta V^{\#}(k_3)$ must be disclosed from the experimental value (which is a composite one), a careful analysis seems to validate route 1–3–4 (D) against route 1–2–4 (I_d). In fact, the nearly constant values of $\Delta V^{\#}$ estimated for step k_3 for the different ligands are similar to the one found for cyanide coordination, and correspond to the theoretical value, $+13\ cm^3\ mol^{-1}$, expected for the dissociation of a water molecule from the octahedral complex. The choice of a D against I_d mechanism is also supported by consideration of microscopic reversibility, given that forward and reverse reaction steps cannot proceed according to different mechanisms involving different transition states. Analogous arguments are used for validating the D mechanism in a study of the aquation and formation reactions of the amminepentacyanoferrate(II) ion [31c]. A volume profile analysis was undertaken for both types of processes, and the activation entropies and activation volumes were found to be around 13–14 $cm^3 mol^{-1}$, in agreement with the results previously commented.

In the reactions of $[Fe^{III}(CN)_5H_2O]^{2-}$ with L = cytosine, cytidine and cytidine-5-monophosphate, the pseudo-first-order rate constants exhibit the behavior $k_{obs} = k_f[L] + k_d$ for the overall reaction leading to $[Fe^{III}(CN)_5L]^{n-}$. The temperature and pressure dependences of k_f and k_d, as well as of the equilibrium constant K $(= k_f/k_d)$ were studied. By looking at the positive values for $\Delta S^{\#}$ and $\Delta V^{\#}$, an I_d mechanism is proposed reasonably for both the formation and dissociation reactions, mainly because $\Delta V^{\#}$ values are found to be significantly smaller than those reported for the substitution reactions of Fe(II) complexes [32b].

Kinetic and mechanistic studies for ruthenium pentacyano-complexes have been also published [19,22,24,25]. The picture resembles the behavior of pentacyanoferrates. Table 2 shows the specific rate constants for the formation and dissociation reactions of the $[Ru^{II}(CN)_5L]^{n-}$ ions, at 25 °C. The dissociation rate constants are one to two orders of magnitude lower than that for the iron analogs [19,22,24,25]. Activation parameters cover the range: $\Delta H^{\#} = 22–30$ kcal mol^{-1} and $\Delta S^{\#} = 0–15$ cal $K^{-1} mol^{-1}$, in agreement with a dissociative mechanism. It has been suggested that a shift from D to I_d could be operative, based on the low activation entropies with respect to the iron-derivatives; this is not yet conclusive, given the absence of activation volume data. For the formation processes, the rates are also lower than the values for iron, and depend on the charge of the entering ligand L [19,22,24]. As with the iron complexes, the $\Delta H^{\#}$ values are around 13–20 kcal mol^{-1}; these values are significantly smaller than those for dissociation. This is due to the fact that these rates are controlled by the release of water, which is much faster than that for other L ligands. Some contrasting results appear for the activation entropies because either positive values (in the range 0–7 cal $K^{-1} mol^{-1}$) [19a], or negative values (in the range -12 to -26 cal $K^{-1} mol^{-1}$) [19b,22a] were found for several *N*-heterocyclic ligands, as well as for other ligands. The positive values are more compatible with the dissociative mechanism generally accepted for these compounds. A value of ca. 10 s^{-1} was estimated for the water exchange rate on $[Ru^{II}(CN)_5H_2O]^{3-}$ [19a], based on the acceptance of an I_d mechanism. Taking into account the previous discussion for the pentacyanoferrates, a distinction between D and I_d cannot be established before a more comprehensive set of measurements, including activation volumes, is performed.

Kinetic measurements with Os(II) complexes are still emerging. The $[Os^{II}(CN)_5pz]^{3-}$ ion is remarkably inert toward the dissociation of pyrazine. The rate dissociation constant is around 10^{-8} s^{-1} (25 °C), four orders of magnitude lower than in the ruthenium analog, due to the stronger Os–N bond [20]. The limiting saturation behavior and activation parameter data also suggest a dissociative mechanism; a detailed kinetic study is underway for several L ligands [27].

Table 2
Rate constants for the formation (k_f) and dissociation (k_d) reactions in $[Ru^{II}(CN)_5L]^{n-}$ complexes at 25 °C

L	k_f, M^{-1}, s^{-1} [a]	$10^5 \times k_d$, s^{-1}
	47.0[b] 8.6[d]	6.31[c] 7.3[d,e]
	44.4[b]	4.17[c]
	14.4[b]	6.79[c]
	10.9[b] 0.96[d]	1.77[c] 2.4[d,e]
	5.4[b] 0.95[d]	3.34[c] 3.4[d,e]
	5.1[b]	10.7[c]
	3.5[b]	1.67[c]
	0.28[d]	-
	1.8[b]	-
	1.3[d]	2.8[d,e]
	1.2[d]	5.0[d,e]
	1.2[d]	3.8[d,e]
	0.76[f]	2.5[d,f]
	0.35[f]	6.0[f]
	0.44[f]	130[f]
	0.45[f]	240[f]
	0.49[f]	180[f]
NH_3	-	37[g]
$[N_2H_5]^+$	0.33[h]	280[h]
N_2H_4	0.40[h]	15[h]
$[enH]^+$	0.83[i]	11.4[i]
en	0.89[i]	6.3[i]
$[NO_2]^-$	0.15[e,j]	20[j]
$[ONO]^-$	0.23[j]	100[j]
dmso	13.1[c] 1.6[k]	0.85[c] 1.6[k]

[a] I = 0.1 M, unless otherwise indicated.
[b] Ref. [19a].
[c] Ref. [22b].
[d] Ref. [19b].
[e] I = 1.0 M.
[f] Ref. [22a].
[g] Ref. [25].
[h] Ref. [24a].
[i] Ref. [24b].
[j] Ref. [19c].
[k] Ref. [24c].

2.4. Redox chemistry

The Os(II) pentacyano-complexes can be oxidized reversibly to the Os(III) states in water, and a range of E_{ox} values (V vs. NHE) is obtained by changing the L ligands, from py (0.63 V) to *N*-methylpyrazinium (mepz$^+$, 0.96 V) [20]. The E_{ox} values are intermediate between those for the iron and ruthenium analogs, as was also found for the hexacyanometalates [33]. Fig. 4 shows that E_{ox} for the osmium compounds correlate with the pK_as of the L ligands, as well as with the E_{ox} values for the iron analogs. This suggests that a significant, dominant σ-bonding contribution is present, which determines the energy of the HOMO, in addition to the low π-interaction. The oxidized compounds show a set of bands in the visible–near UV region, as found with $[Os^{III}(CN)_6]^{3-}$ [26], whose energies are almost independent of L (LMCT, $CN^- \rightarrow \pi$ (Os)). The Os(III) complexes are stable for hours, with the exception of $[Os^{III}(CN)_5mepz]^-$, which decomposes in a few minutes. New UV–vis and magnetic circular dichroism (MCD) spectroscopic measurements at 4.2 K confirmed the assignments for the LMCT transitions in the $[M(CN)_6]^{3-}$ anions (M = Ru, Os). Earlier d–d assignments on Os(III) and Fe(III) hexacyano-complexes have been questioned. Near IR MCD allowed a preliminary observation of intraconfigurational d–d transitions in the osmium complex [34].

The coordinated mepz$^+$ ligand was reduced reversibly in the three metal complexes, with surprisingly similar values of $E_{red} = -0.53 \pm 0.01$ V (water), also coincident with the value for the reduction of free mepz$^+$. This was traced down to compensating contributions of σ- and π-interactions, which should increase and decrease the E_{red} values upon complexation, respectively. The quantitative relation: $E_{MLCT} = (E_{ox} - E_{red}) + \chi$, shows values of ca. 0.6 eV for χ, which includes contribu-

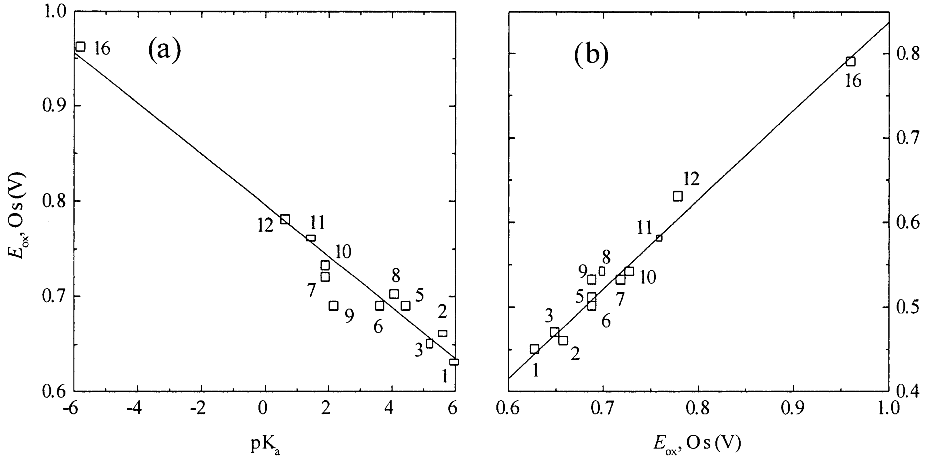


Fig. 4. (a) Correlation between the potentials of the $Os^{III,II}$ redox couple in $[Os^{II}(CN)_5L]^{n-}$ complexes, E_{ox}, and the pK_a of the free ligands. (b) Correlation between E_{ox} (Fe) and E_{ox} (Os) for several L ligands. Ligand numbers correspond to: 1, 4-mepy; 2, 3-mepy; 3, py; 4, 3-CNpy; 5, 4,4′-bpy; 6, isn; 7, 4-CNpy; 8, mebpy$^+$; 9, pdz; 10, dmpz; 11, 2-mepz; 12, pz; 13, pzO; 14, dmpzH$^+$; 15, pzH$^+$; 16, mepz$^+$.

tions from intramolecular relaxation and solvent reorganization after MLCT excitation [35]. The bound mepz radical was characterized by spectroelectrochemical techniques and by EPR in the $[\mathrm{Os^{II}(CN)_5mepz}]^{3-}$ ion; the ruthenium and iron analogs, however, are unstable toward the release of a cyanide ligand, a situation resembling the behavior of the nitrosyl complexes upon reduction (see Section 6). The EPR spectra of the $[\mathrm{M^{II}(CN)_4mepz}]^{2-}$ (M = Fe, Ru) resulting species were assigned [36]. The *p*-aminophenoxyl radical was also stabilized by coordination to $[\mathrm{Fe^{II}(CN)_5}]^{3-}$, as a result of the reaction of the $[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-}$ ion with *p*-aminophenol [37].

2.5. Electron transfer

The kinetics of the electron self-exchange reactions of the $[\mathrm{M^{II,III}(CN)_6}]^{4-/3-}$ couples (M = Ru, Os) were investigated in different media, by using ^{13}C-NMR line-broadening techniques [38]. Through measurements at different pHs, at $I = 1$ M ($\mathrm{Na^+}$), k_{ex} decrease from 8.9×10^4 $\mathrm{M^{-1}\,s^{-1}}$ to 2.8×10^4 $\mathrm{M^{-1}\,s^{-1}}$ and 1.8×10^3 $\mathrm{M^{-1}\,s^{-1}}$ for the non-protonated, mono- and di-protonated Os(II) species, respectively. The pK_{a} values for the $[\mathrm{Os^{II}(HNC)(CN)_5}]^{3-}$ and $[\mathrm{Os^{II}(HNC)_2(CN)_4}]^{2-}$ ions were calculated as 1.9 ± 0.1 and 0.6 ± 0.2, respectively. k_{ex} also depends on the type of electrolyte countercation, increasing in the sense $\mathrm{H^+} < \mathrm{Li^+} < \mathrm{Na^+} < \mathrm{NH_4^+} < \mathrm{K^+}$ (about a five-fold increase from $\mathrm{H^+}$ to $\mathrm{K^+}$). A first-order behavior was observed for k_{ex} against the concentration of sodium ion, increasing from ca. 4×10^3 (0.04 M) to 9×10^4 $\mathrm{M^{-1}\,s^{-1}}$ (1 M), indicating that the cation catalyzes the electron-exchange reaction. When the effects of the concentration and the nature of the cation in the electrolyte are taken into consideration, the k_{ex} values for the Os couple are very similar to the ones for Fe and Ru complexes (25 °C) [38]. The cations are presumed to reduce the electrostatic repulsion between the reactants, based on the correlations of electron-transfer rate constants with crystal radii and the polarizability of the cations. As for other complexes, the Ru- and Os-hexacyanide self-exchange rate constants can be predicted with reasonable success by using the semi-classical model for outer-sphere bimolecular electron-exchange reactions [39].

$$k_{\mathrm{ex}} = K_{\mathrm{A}} \nu_{\mathrm{n}} \kappa_{\mathrm{el}} \Gamma'_{\mathrm{n}} \exp\{-(\Delta G^*_{\mathrm{in}} + \Delta G^*_{\mathrm{out}})/RT\} \tag{1}$$

Thus, the exchange rate constant, k_{ex}, may be expressed (Eq. (1)) as the product of a pre-equilibrium constant K_{A}, an effective nuclear frequency ν_{n}, an electronic factor κ_{el}, an inner-sphere nuclear tunneling factor, Γ_{n}, and a nuclear factor that contains terms for both inner-sphere (ΔG^*_{in}) and solvent ($\Delta G^*_{\mathrm{out}}$) reorganization energies. Values of about 3 and 28 kJ mol^{-1} were estimated for ΔG^*_{in} and $\Delta G^*_{\mathrm{out}}$, respectively, for $[\mathrm{Os(CN)_6}]^{4-/3-}$. The first one is consistent with the transfer of an electron occupying a non-bonding orbital. Thus, the calculated value for k_{ex} was $2 \pm 1 \times 10^5$ $\mathrm{M^{-1}\,s^{-1}}$, in acceptable agreement with the experimental value at $I = 1.0$ M. Studies on several cross-reactions with different reactants have been performed, using the Marcus relationship [40]. For ascorbic acid and substituted dihydroxybenzenes, consistent k_{ex} values for the cyanometalate couples were obtained and found to be in agreement with those predicted by the semi-classical model [41a]. Similarly, the outer-sphere reduction of the biologically relevant $[Fe^{III}(CN)_5NO_2]^{3-}$ ion by the ascorbate anion, HA^-, led to $k_{ex} = 4.5 \times 10^4$ $M^{-1}\,cm^{-1}$ (25 °C, $I = 0.3$ M) [41b], a value that is expectedly close to that found for the hexacyanoferrate(III/II) couple. In the latter work, negative activation volumes ($\Delta V^{\#}_{12(exp)} = -10.0$ $cm^3\,mol^{-1}$) were also obtained for the cross-reaction, and these were found to be in agreement with the value predicted by the Marcus–Hush–Stranks model [42], taking into account the contributions from the volume changes arising on coulombic work, the solvent rearrangements and the electrolyte effects. Similar results for the reduction of the three $[M^{III}(CN)_6]^{3-}$ ions with ascorbic acid [41c] were obtained at different pHs, accounting for the reactivity of ascorbic acid, H_2A, and the ascorbate anion, HA^-. In the latter case, the activation parameters are consistent with the previously described work. However, a volume profile analyses led the authors to consider that the oxidation of ascorbic acid may not proceed through a simple adiabatic process. It could imply the formation of a bicyclic intermediate after the primary one-electron, outer-sphere oxidation of ascorbic acid, in which the open-chain ascorbate radical is supposed to be formed. A consequence of neglecting the cyclization step implies that the k_{ex} values for the $H_2A^{\bullet +}/H_2A$ and $HA^{\bullet}/HA^-$ couples so far estimated from the Marcus cross-relation may not be valid.

Metelski and Swaddle studied the self-exchange processes for the hexacyanometalate anions as a function of pressure, temperature and added-electrolyte concentrations. A catalytic effect of the alkali metal ions was also found. The positive activation volumes for self-exchange, $\Delta V^{\#}_{ex}$, suggest that cation desolvation occurs prior to bridging to the anions [43]. It was also demonstrated that the cyanometalates agree with the 'fifty-percent rule', $\Delta V^{\#}_{el} = 1/2\Delta V^{\#}_{ex}$, where $\Delta V^{\#}_{el}$ is the volume of activation measured electrochemically [44]. This is an extension of Marcus' prediction that the free energies of activation, $\Delta G^{\#}$, for homogeneous (bimolecular) electron transfer and for electrode reactions should be related similarly [40]. The relation also holds for a great number of redox couples that react through an outer-sphere mechanism [45].

A high pressure study suggests an outer-sphere mechanism for the reduction of several $[Fe^{III}(CN)_5L]^{n-}$ complexes ($L = CN^-$, NO_2^-, H_2O) with oxymyoglobin [46]. The precursor complex formation and the observed rate constants were found to be smaller for the aqua-complex in comparison with the other two complexes. This was explained by the smaller negative charge on the aqua-complex, assuming that electrostatic interaction between the redox partners plays an important role in the overall electron transfer process. A modeling of the specific site on the protein surface supports the above proposal.

Studies on the cross reactions between $[Fe^{II}(CN)_6]^{4-}$ and several $[Co^{III}(NH_3)_5X]^{3+}$ complexes ($X = H_2O$, py, dmso) show that outer-sphere mechanisms are operative. Activation parameters, including volumes of activation, were interpreted on the basis of solvational changes on the individual ions within the ion-pair precursor, of which the largest effect originates from the iron center [47a]. This is in contrast with previous interpretations of Saito and coworkers [47b] on the predominance of intrinsic volume changes during the outer-sphere and intra-molecular electron-transfer processes. The oxidation of $[Fe^{II}(CN)_6]^{4-}$ with $[Co^{III}(RNH_2)_5(H_2O)]^{3+}$ (R = H, Me, Et) reveals correlations between size and ion-pair formation constants, electron-transfer rate constants and thermal and pressure activation parameters. The volumes of activation show again that solvational changes during electron transfer are mainly responsible for the values obtained [47c]. Outer-sphere mechanisms were also proposed for the oxidation of $[Fe^{II}(CN)_5L]^{n-}$ ions with $Fe^{VI}O_4^{2-}$ [48].

The reductive quenching of differently charged ruthenium polypyridyl sensitizers by cyanometalate complexes (Mo and W octacyano- and Fe, Os-hexacyanometalates) was studied by laser flash photolysis/transient absorbance and emission spectroscopies [49]. The hexacyanometalates exhibit much lower cage escape efficiencies than the octacyanomolybdates, and this was assigned to the different rates of geminate ion pair electron transfer in the two cases (the reverse-electron-transfer rate is expected to be slower in the case of the larger octacyanometalate ions).

The reactions of $[Fe^{II}(CN)_6]^{4-}$ with several oxidants relevant to oscillatory systems were investigated [50]. A study with bromate as oxidant was done in the pH range 3.6–5.8 [50a]. A complex mechanism was proposed on the basis of numerical simulations, based on the $[Fe^{II}(CN)_5H_2O]^{3-}$ ion as the active species (the aquation is facilitated by light and/or protonation of cyanides). A fast, reversible substitution of bound water by bromate is proposed to occur by rapid oxygen exchange between the coordinated water molecule and the bromate ion, without breaking the Fe–OH_2 bond. Then, a comparatively slow electron-transfer step would lead to the oxidized aqua-ion and the $BrO_2^{\bullet}$ radical. Subsequent rapid reactions were proposed to explain the formation of bromide and $[Fe^{III}(CN)_6]^{3-}$ as final products. In fact, inspection of the value for the independently measured rate constant for reaction of $[Fe^{II}(CN)_5H_2O]^{3-}$ with bromate, 6.8 $M^{-1} s^{-1}$, suggests that, alternatively, a substitution-controlled loss of water from $[Fe^{II}(CN)_5H_2O]^{3-}$ could be followed by coordination of bromate and electron-transfer. A final step involving the formation of a cyanide-bridged mixed-valent dimer, $[Fe_2(CN)_{11}]^{6-}$ cannot be accepted in terms of such a high rate constant value, 10^4 $M^{-1} s^{-1}$. Other mechanisms for the loss of $[Fe^{II}(CN)_5H_2O]^{3-}$ could be proposed instead. In a related study, the oxidation of $[Fe^{II}(CN)_6]^{4-}$ by H_2O_2 was shown to be catalyzed by trace quantities of aqueous Fe(III) or Fe(II), under conditions where the concentration of the aquapentacyanoferrate(II) ion (which is known to be an active catalyst) was made negligible [50b]. The catalysis would be promoted by facile oxidation of the aqueous iron species by H_2O_2, as supported by the rate decrease upon addition of chelating agents. The autoxidation of $[Fe^{II}(CN)_5H_2O]^{3-}$ was proposed to occur in a similar way [51]. Finally, studies with the known H_2O_2–SO_3^{2-}–$[Fe^{II}(CN)_6]^{4-}$ pH oscillator were performed by adding bromocresol purple; through the modification of the sensitivity of the system to light, new non-linear interactions are observed [50c]. Modifications on the same pH oscillator by adding horseradish peroxidase were also performed [50d].

As for H_2O_2, the outer-sphere oxidation reactions of $[Fe^{II}(CN)_5L]^{n-}$ with peroxydisulfate are also slow but measurable processes, and can be described by a Marcus-type linear free-energy relationship [52,53]. They can be catalyzed by traces of $[Ru^{II}(NH_3)_5L]^{n+}$ ions [54]. The catalysis is apparently favored by ion association, due to the opposite charge of the Ru(II) species, and could be also aided by the specific interactions between peroxydisulfate and the bound ammines [55]. In a systematic, comprehensive study, it has been shown that assisted rapid oxidation of pentacyanoferrates(II) can be obtained in dinuclear species such as $[(NC)_5Fe^{II}LRu^{II}(NH_3)_5]^n$ (L = 1,2-bis(4-pyridyl)ethane, imidazolate, 4- and 3-CNpy, and cyanide). The assistance is promoted by the pentaammine-fragments, which react much faster than pentacyanoferrates(II) with peroxydisulfate. The rate of these stoichiometric (not catalytic) reactions depends mainly on the redox potential at the $Ru^{II,III}$ couple, and the crucial role of electronic isomerization processes in the dinuclear mixed-valence systems has been understood [53,55–57].

3. Solvent influence on the electronic structure and on the reactivity of L

A general review on the medium effects on charge transfer in metal complexes is available [58] Strong solvatochromism has been reported early for compounds of the type $[Fe^{II}(LL)_2(CN)_2]$, where LL = 2,2′-bipyridine and related ligands [59]. A systematic study was performed with a large number of mixed-ligand iron and ruthenium complexes containing different amounts of cyanide and of *N*-heterocyclic L ligands [60]. Both the redox potential, $E_{0,}$ and the MLCT energies, E_{MLCT} ($Fe^{II} \rightarrow \pi^*$ (L)) shift to greater values when going from weak to strong acceptor solvents, in the Gutmann scale [61]. This was traced down to donor–acceptor interactions between cyanides (donor) and solvent molecules (acceptor), leading to the stabilization of the metallic HOMO. The magnitude of the shifts depends additively on the number of bound cyanides for a given metal, as found for a series of Fe(II) [60a,b] and Ru(II) complexes [60c]. The π-electron withdrawing and σ-electron donation influence of the sixth ligand L also affect the donor ability of cyanides, as shown by the slopes of the plots of E_{MLCT} against the acceptor number, AN, which decrease in the order: py > pz > $mepz^+$ > NO^+ [62–64]. Fig. 5 shows the dependence of E_{MLCT} on AN for both components of the MLCT band in the $[Os(CN)_5pz]^{3-}$ ion. Other complexes with different ligands, L, behave similarly, but remarkably in the $[Os(CN)_5mepz]_2$-ion, the two MLCT present very different sensitivity to the solvent, along with a deviation from the linear behavior for small AN values [20b]. The reactivity of L can be influenced significantly by cyanide–solvent interactions, and several examples follow. The dissociation rate of 2,6-dimethylpyrazine (dmpz) from $[Fe(CN)_5dmpz]^{3-}$ ion increases slightly in methanol compared to water, but it increases about 100-times when going from aqueous to pure acetone or acetonitrile solutions, an effect that was described as due to the solvent assisted transfer of the leaving ligand to the solvation shell [65]. Electronic effects could also be important, as the energy of the HOMO is greater in acetonitrile as compared with water; this was shown to correlate with the dissociation rates of L [25]. We conclude that the relative importance of electronic and medium effects is not easy to disclose in these systems. The stretching wavenumber, ν_{NO}, for the $[Fe(CN)_5NO]^{2-}$ ion in water, 1937 cm^{-1}, decreases to 1892 cm^{-1} in

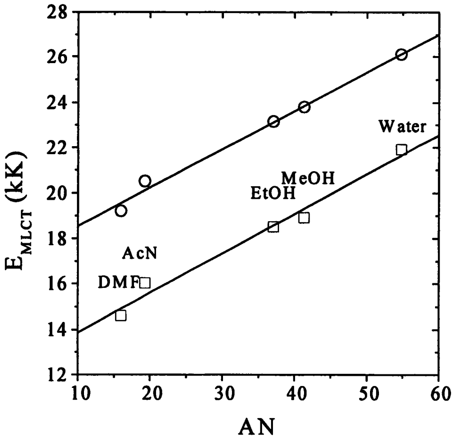


Fig. 5. Plot of E_{MLCT} for both transitions in $[\mathrm{Os^{II}(CN)_5L}]^{n-}$, against solvent acceptor number, AN (Gutmann's scale).

acetonitrile [66]. A similar shift is observed when measuring the solid state spectra and replacing sodium with tetrabutylammonium ions as the countercations. The same behavior occurs with the ruthenium- and osmium–nitrosyl compounds [67,68]. An increase in the back-bonding ability of the $[\mathrm{M(CN)_5}]$ fragment in weak acceptor solvents (or in the presence of weakly interacting cations) has been invoked to explain the weakening of the NO bond.

For the amphiphilic pentacyano(4-octadecylaminopyridine)ferrate(III) complex [69], the energy of the LMCT band ($\pi\ (\mathrm{L}) \rightarrow \mathrm{Fe^{III}}$) increases when going from water to weak-acceptor solvents, in an expected reverse way [70] as compared with the changes in the MLCT bands for Fe(II) complexes. Similarly, the energy of the LMCT transitions in some $[\mathrm{Fe^{III}(CN)_5L}]^{2-}$ complexes depends on the type of closed-shell countercations, shifting to lower energies when the cation charge is increased [71]. Solutions of $\{\mathrm{Et_4N}\}_3[\mathrm{Fe^{III}(CN)_6}]$ in mixed-solvents display tunable potentials of the $\mathrm{Fe^{III,II}}$ redox couple, potentially useful for reactions in organic media [72]; this is indeed also the general case for the members of the $[\mathrm{M^{III}(CN)_5L}]^{2-}$ series [20,62,63].

The basicity of pyrazine toward protonation is significantly greater in $[\mathrm{Ru(NH_3)_5pz}]^{2+}$ than in the $[\mathrm{Ru(CN)_5pz}]^{3-}$ ion, as measured by the pK_as, 2.5 versus 0.6, respectively [17i]. The difference reflects the contrasting behavior of ammine and cyanide as auxiliary ligands; ammines are charge donors, promoting the back bonding from an electron-rich metal to pyrazine; cyanides are strong π-acceptors and withdraw charge from the metal, weakening its back-bonding ability. DFT calculations in vacuum, however, showed that pz was *more* basic in the cyanide-complex, but an appropriate modeling of the cyanide environment introducing discrete water molecules led to an agreement with the experimental results [73].

The sensitivity of cyanides toward changes in the medium also manifests itself through the influence of the addition of either electrolytes or micelles on the rates of different reactions [74]. Salt effects can be explained by the binding of cations to donor cyanides, in a similar way as with solvents and H-acceptor interactions. Thus, the dissociation rates of L ligands from pentacyano-L-ferrates(II) decrease with increasing concentration of salts [75], and the same occurs for the formation reactions, which are controlled by the loss of water [76]. The oxidation of the $[Fe(CN)_6]^{4-}$ ion by peroxydisulfate in AOT–oil–water microemulsions was studied (AOT = sodium bis(2-etylhexyl) sulfosuccinate), showing a rate enhancement compared to aqueous solutions, which was assigned to different factors [77]. The intramolecular electron-transfer within the dinuclear complex formed by $[Fe^{II}(CN)_5H_2O]^{3-}$ and tetraamminepyrazinecarboxylatocobalt(III) was studied in binary aqueous media, showing the role of specific interactions on reactivity [78]. Micellar effects on the electron-transfer reaction within the ion pairs formed by some $[Co^{III}(NH_3)_5L]^{3+}$ complexes and $[Fe^{II}(CN)_6]^{4-}$ were interpreted within Marcus' theory, after separating the ion-pair formation equilibria from the true electron transfer rate constants [79]. Finally, the supercomplexation of $[Fe^{III}(CN)_6]^{3-}$ by a polyammonium macrocycle was shown to influence significantly the thermal and photoinduced reactions with iodide [80].

4. The 'Creutz–Taube' analogs and other related complexes

The specific cyanide–solvent interactions show up in the stabilities and metal–metal coupling in the $[(NC)_5M\text{–pz–}M(CN)_5]^{5-}$ mixed-valent ions (M = Fe, Ru, Os) [3a], which are related closely to the Creutz–Taube (CT) ion, $[(NH_3)_5\text{-}Ru\text{–pz–}Ru(NH_3)_5]^{5+}$ [3b]. In aqueous solution, the $[(NC)_5Fe\text{–pz–}Fe(CN)_5]^{5-}$ ion behaves as a weakly coupled, localized class II compound in terms of the Hush model [81], with a small comproportionation constant ($K_c = 50$), and a broad intervalence charge transfer (IVCT) band at 1300 nm ($\varepsilon = 3180\ M^{-1}\ cm^{-1}$) [82]. This is apparently consistent with the competing π-acceptor ability of the cyanides toward pyrazine in aqueous solutions, in contrast with the donor ammines favoring a stronger interaction between the ruthenium metal centers ($K_c = 10^{6.8}$) through the pyrazine bridge [29a]. In aprotic solvents such as acetonitrile, the three pentacyanide dinuclear complexes are much more stable toward disproportionation into the isovalent states than in protic solvents (Table 3), and can be characterized in the fully reduced (II, II), fully oxidized (III, III) (except the Ru member) and mixed-valent (II, III) states. Table 3 also shows that the IVCT bands in the iron- and osmium complexes [83,84] are more intense and show significantly smaller bandwidths than in the ruthenium analog [85]; the bandwidths are close to the value found for the CT ion [3b]. For $[(NC)_5Ru\text{–pz–}Ru(CN)_5]^{5-}$, it was slightly greater than that calculated according to the Hush model predictions, $\Delta\nu_{1/2} = (2310\ \nu_{max})^{1/2} = 3623\ cm^{-1}$ suggesting a localized, Class II behavior [81]. Infrared spectroscopy is a useful tool for revealing the electronic delocalization in the three compounds. For the iron mixed-valent complex (Fig. 6), a broad, asymmetric band

Table 3
Electrochemical and spectroscopic data for the $[(NC)_5M–pz–M(CN)_5]^{5-}$ mixed-valent ions

M [a]	Fe	Ru	Os
ΔE (mV) [b]	0.32	0.28	0.34
K_c [c]	$10^{6.5}$	$10^{4.7}$	$10^{5.8}$
λ_{max} (nm) (ε, M^{-1} cm^{-1})	745 (8000) MLCT	530 (8000) MLCT	574 (29 000) MLCT
	599 (7300) MLCT	620 sh	840 (7900) MLCT
	2475 (3900) IVCT	1760 (2600) IVCT	1395 (6600) IVCT
$\Delta\nu_{1/2}$ (cm^{-1})	1500	4200	1450
IR ν_{CN} (cm^{-1}) [d,e]	2044 sh	2057 s	2054 s
	2070 s, br	2091 w	2080 sh
	2112 w	2111 w	2108 m

[a] Ref. [83], Fe; Ref. [84], Os; Ref. [85], Ru.

[b] Difference in half-wave potentials for the two reversible one-electron processes.

[c] $K_c = e^{nF\Delta E/RT} = ([M–pz–M]^{5-})^2/([M–pz–M]^{4-})([M–pz–M]^{6-})$; measured in CH_3CN, 248 K (Fe); CH_2Cl_2, 298 K (Ru); CH_3CN, 298 K(Os).

[d] Other bands, including triplet absorptions: 2016 (950); 2530 (–); 4032 (960); 5071 (220).

[e] Pyrazine-ring stretching at 1583 (Fe), 1585 (Ru), 1582 (Os) cm^{-1}.

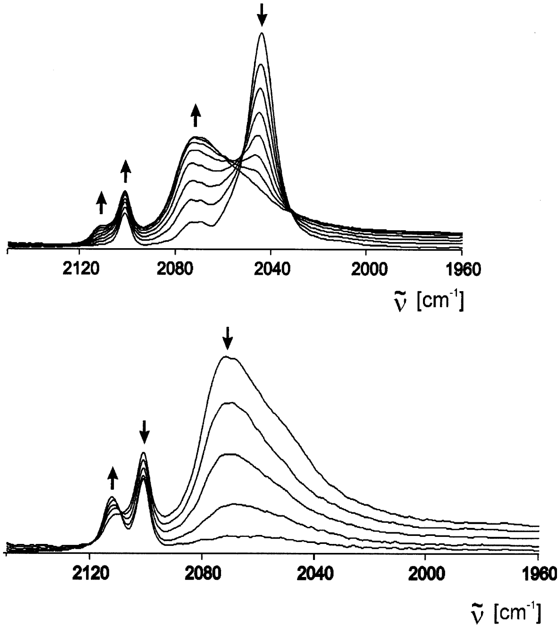


Fig. 6. Successive IR spectra in the cyanide stretching region of the $[(NC)_5Fe–pz–Fe(CN)_5]^{n-}$ complexes from OTTLE spectroelectrochemistry (in acetonitrile/0.1 M Bu_4NPF_6). Upper: fully reduced ($n = 6$) to mixed-valent ($n = 5$). Lower: mixed-valent ($n = 5$) to fully oxidized ($n = 4$). The band at 2100 cm^{-1} is attributed to hexacyanoferrate(III), based on comparison with an authentic sample.

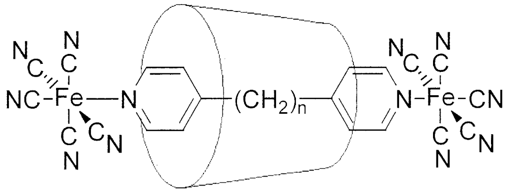
emerges at 2070 cm^{-1}; weak absorptions are still present at 2045 and 2110 cm^{-1}, which are values characteristic of cyanide stretching when bound to Fe(II) and Fe(III), respectively. This suggests an incomplete averaging of valencies, also supported by the emergence of a very weak band at 1583 cm^{-1} (symmetric pyrazine ring stretching) upon oxidation of the II, II ion to the II, III one, and its disappearance upon further oxidation to the symmetric III, III complex. The observed ν_{CN} pattern, however, indicates fast metal–metal electron transfer compatible with the vibrational timescale [86]. The values of K_c and $\Delta\nu_{1/2}$ are similar to the values for the CT complex. This was described as a Class III delocalized compound [3b,87], and thus we conclude that the iron mixed-valent complex in acetonitrile is a true borderline case, with features of both a localized and delocalized situation on the vibrational time scale [88]. The picture is similar for the osmium compound, although the band pattern shows additional transitions associated to spin–orbit coupling, as previously described in the ammine-analog [29]. The iron system exhibits the strongest $d\pi-\pi^*$ (pz) interaction, probably because of a better energy match as compared with the osmium analog, also suggested by the basicity trends of pyrazine in the $[M(CN)_5pz]^{3-}$ complexes (Fe > Os > Ru) [17i]. The EPR measurements for the iron- and osmium-dinuclear mixed-valent pz-complexes display a similar pattern of g components as the CT ion, suggesting a similar electronic structure. In the same line of reasoning, the complex $[(NC)_5$-Fe–L–$Fe(CN)_5]^{5-}$, with L = s-tetrazine, shows a shift in K_c from 10^8 to 10^{19} when going from aqueous to acetonitrile solutions. All the spectroscopic evidence, including Mössbauer studies, suggests that it is a fully delocalized species [89].

In summary, weak acceptor solvents favor the coupling between the two metal centers. The borderline situation can be detected for an efficient coupling bridge such as pyrazine, but not for some larger ligands, which induce a typical Class II behavior independent of the solvent, namely the pentacyanoferrate dimers bridged by 4,4′-bpy [83,90] and bpe [83]. The 4,4′-bpy-complex showed significant shifts of the IVCT band upon stepwise ionic association [91]. SERS and FT-SERS investigations of the fully reduced pz- and 4,4′-bpy dimers were performed upon adsorption on silver and gold electrodes [92a]. Similar dimers bridged by 4-picolylamine [92b], *p*-benzoquinonediimine [92c] and thiocyanato [92d] ligands have also been characterized.

Complexes of the bridging ligand 4,4′-dithiodipyridine (DTDP) were prepared with the pentacyanometalate (M = Fe, Ru) as pendant fragments [93]. For M = Fe, H_{ab} and K_c values were calculated from the near-IR absorption spectrum of the mixed-valent species, in aqueous solution, and a Class II behavior was proposed. The data for the [py–S–S–py] bridged compound suggest a stronger electronic coupling than that for [py–CH=CH–py] (bpe), a related bridge of a similar size. Unsymmetrical dinuclear complexes bridged by pz and pz-derivatives have been prepared with pentacyanoferrate(II) [56,93,94], and pentacyanoruthenate(II) [57,93,95] fragments at one end and pentaammineruthenium fragments at the other end. The complexes have been characterized spectroscopically as mixed-valent species and sometimes as the fully reduced and fully oxidized species as well; the kinetics of the formation and dissociation reactions were determined in most cases, together with the rates of the redox reactions, predominantly with peroxydisulfate. Intramolecular electron transfer from pentacyanoferrate(II) to pentaammine-cobalt(III) mediated by several bridging ligands was studied in order to assess the adiabaticity and the role of distance between metal centers [96].

Spectroscopic and kinetic formation studies were performed with the linear trinuclear complex $[(NC)_5Fe^{II}–pz–Ru^{II}(NH_3)_4–pz–Fe^{II}(CN)_5]^{4-}$, including mixed-valent chemistry [97a]. A series of di- to heptanuclear pz-bridged complexes was prepared by reaction of the tris(bipyrazine)ruthenium(II) ion with several aquapentacyanoferrate(II) ions; these were characterized spectroscopically and kinetically [97b].

An interesting application of the properties of pentacyanoferrates(II) with *N*-heterocyclic ligands was provided by the synthesis of dimeric, bridged species, from which some specific supramolecular aggregates can be obtained, called *rotaxanes* [98a,b]. The rotaxanes are complexes in which a cyclic molecular bead is threaded by a linear chain bearing bulky end units, which prevent the complex from dissociating into its cyclic and linear molecular components. By using cyclodextrins (CD) as cyclic components, stable self-assembling rotaxanes have been reported of the type $[(NC)_5Fe\{R(CH_2)_nR\cdot\alpha\text{-CD}\}Fe(CN)_5]^{4-}$, where the linear thread is a dicationic bridging ligand of the type $[R(CH_2)_nR]^{2+}$ ($n = 8–12$) and R is 4,4′-bipyridinium, pyrazinium or 3- and 4-cyanopyridinium entities [98c–e]. Other bridging ligands were of the [pyRpy] type, i.e. neutral 4,4′-bis-(pyridine) ligands with a variety of R functional groups connecting the 4 and 4′ pyridine carbons [98f]. These bridging ligands form stable inclusion complexes with CD by threading the 4,4′-bipyridinium groups through the CD cavity such that the hydrophobic alkyl chain resides within the cavity and the cationic bipyridinium end groups extend from either end. The pentacyanoferrate(II) groups can bind to the exposed N-atoms of the heterocyclic ligands, thus behaving as bulky end units (stoppers). The ligand substitution properties of the pentacyanoferrates are suitable for the self-assembly of the rotaxane complexes, which can be achieved in several ways, independently of the order of addition of the metal precursor ($[Fe^{II}(CN)_5H_2O]^{3-}$), the CD or the bridging ligand.



Rate and activation parameters and CD inclusion stability constants have been determined by studying the formation and dissociation reactions of the semirotaxanes, $[(NC)_5Fe\{pyRpy\cdot CD\}]^{3-}$, and the rotaxanes. The mechanistic features have been investigated by using visible and NMR spectroscopies, thus tracing the changes in the rate constants and in the MLCT transitions to the nature of the CD hosts and the R linkage on the [pyRpy] guests. All these studies have been performed with Fe(II) complexes, several bridging ligands and α- and β-CDs, and a broad picture of different molecular and intermolecular interactions develops upon the systematic variations. An interesting derivation could probably be attained by the preparation of mixed-valent rotaxane species where the intermetallic coupling could be controlled by the degree of intermolecular interactions of the bridging ligand with the host cyclic component.

5. Use of $[M(CN)_5L]^{n-}$ complexes in the synthesis of cyanide-bridged complexes

Cyanide-bridged oligonuclear complexes have been investigated intensively in the last 15 years. This work has been reviewed [4], and we only highlight here the progress in the preparation, spectroscopic and kinetic characterization of new complexes with mixed-valence (including photoreactivity) properties, containing pentacyanometalate(II) moieties and several $[M^{III}X_5]$ acceptors: $[M^{III}(CN)_5]$ (M = Fe, Ru) [99,100], $[Os^{III}(NH_3)_5]$, $[Os^{III}(CN)_5]$, $[Cr^{III}(NH_3)_5]$ [101], $[Ru^{III}(NH_3)_5]$ [53,102–104], $[Ru^{III}(edta)]$ [105], $[Co^{III}azamacrocycle]$ [106], $[Pt^{IV}(NH_3)_5]$ [107], aquacobalamin [108].

Table 4 displays a list of complexes with the electronic spectral properties (wavelength maxima, molar absorptivities and bandwidths) associated with the measured IVCT absorptions occurring in a region comprised by the near-UV up to the near-IR. In most cases, the dinuclear complexes can be obtained by substitution of the $[M^{III,II}(CN)_6]^{n-}$ anion into the corresponding aqua-complex, $[M^{II,III}X_5H_2O]^n$. This reaction may involve an electron transfer reaction prior to the proper

Table 4
Intervalence charge-transfer parameters in cyanide-bridged complexes of formula $[X_5M^{III}–NC–M^{II}(CN)_5]^{n-}$ (M = Fe, Ru, Os)

Complex	λ_{max} (nm)	ε (M^{-1} cm^{-1})	$\Delta\nu_{1/2}$ (cm^{-1})	Reference
$[(NC)_5Fe^{III}–NC–Fe^{II}(CN)_5]^{6-}$	1300	3180	5100	[99a]
$[(NC)_5Ru^{III}–NC–Ru^{II}(CN)_5]^{6-}$	1094	7140	4500	[99b]
$[(NH_3)_5Os^{III}–NC–Fe^{II}(CN)_5]^{-}$	628	1640	4320	[101a]
$[(NH_3)_5Os^{III}–NC–Ru^{II}(CN)_5]^{-}$	490	1840	4520	[101a]
$[(NH_3)_5Os^{III}–NC–Os^{II}(CN)_5]^{-}$	559	2090	6130	[101a]
$[(NH_3)_5Cr^{III}–NC–Fe^{II}(CN)_5]^{-}$	376	2400	6310	[101a]
$[(NC)_5Co^{III}–NC–Fe^{II}(CN)_5]^{6-}$	385	630	–	[101a]
$[(NC)_5Os^{III}–NC–Ru^{II}(CN)_5]^{6-}$	312	460	–	[101b]
$[(NC)_5Os^{III}–NC–Os^{II}(CN)_5]^{6-}$	360	730	–	[101b]
$[(NH_3)_5Ru^{III}–NC–Fe^{II}(CN)_5]^{-}$	980	3000	4100	[102a]
$[(NH_3)_5Ru^{III}–NC–Ru^{II}(CN)_5]^{-}$	680	2800	–	[95a]
$[(NH_3)_5Ru^{III}–NC–Os^{II}(CN)_5]^{-}$	825	3450	6700	[102b]
$[(edta)Ru^{III}–NC–Fe^{II}(CN)_5]^{5-}$	969	3200	4434	[105b]
$[(edta)Ru^{III}–NC–Ru^{II}(CN)_5]^{5-}$	678	2700	5172	[105b]
$[(edta)Ru^{III}–NC–Os^{II}(CN)_5]^{5-}$	792	3400	6892	[105b]
$[aza^{15}Co^{III}–NC–Fe^{II}(CN)_5]^{6-}$	528	420	4550	[106a]
$[(NH_3)_5Pt^{IV}–NC–Fe^{II}(CN)_5]^{0}$	421	540	7820	[107]

substitution. In addition to the appearance of the IVCT band, evidence of bridge-formation was obtained sometimes through electrochemical techniques: the redox potential of the hexacyanide couple shifts positively upon complex formation by ca. 0.2–0.3 V, whilst the one of the $[M^{III,II}X_5NC]$ couple decreases by ca. 0.1 V (compared to the $M^{III,II}X_5H_2O$ redox couple). An upward shift of $\nu_{CN_{br}}$, the stretching of the bridging cyanide, to ca. 2100 cm^{-1} is also observed, compared to the equatorial and axial modes, which appear at lower values.

Table 4 shows that, in general, for a given donor, lower wavelengths and lower molar absorptivities are obtained as the acceptor $M^{III}X_5$ fragments become less oxidizing. The bandwidths are broad (more evidently for the Os^{II} donors, with seemingly composite bands associated to spin–orbit coupling), and have been interpreted in terms of the Hush model for weakly coupled, Class II compounds [81]. The experimental values are usually in agreement or greater than the theoretical values. The electronic coupling elements, H_{ab}, calculated on the basis of the above model, lead to values in the range 1500–2000 cm^{-1}, which are certainly higher than expected for systems which are weakly coupled (ca. 500 cm^{-1}) [3b]. A caveat can be raised on the applicability of the Hush model for this type of cyanide-bridged system.

For a given $[M^{III}X_5]$ acceptor, the IVCT band energies change with M in the order: Ru > Os > Fe, as observed for the MLCT transitions in $[M^{II}(CN)_5L]^{n-}$ systems. This is in agreement with the trends in the redox potentials of the hexacyanide-couples.

The results for the mixed-valent complexes containing symmetric pentacyanide-fragments on both sides are particularly interesting. The $[(NC)_5Fe^{III}NCFe^{II}(CN)_5]^{6-}$ ion was earlier prepared as a sodium salt by mixing $[Fe^{III}(CN)_5NH_3]^{2-}$ with hexacyanoferrate(II), and was characterized properly spectroelectrochemically [99a]. The ruthenium analog was obtained upon irradiation of mixed solutions of $Co(gly)_3$ (gly = glycinato) and $[Ru^{II}(CN)_6]^{4-}$. The same product resulted by electron transfer from hexacyanoruthenate(II) to the luminescent state of $[Ru(bpy)_3]^{2+}$, as well as by electrolysis of a solution of hexacyanoruthenate(II) at a platinum electrode [99b]. All the spectral parameters point to the absorption of the product being an IVCT transition in the $[(NC)_5Ru^{III}NCRu^{II}(CN)_5]^{6-}$ ion. The mechanism of the photoinduced process has been discussed, but the proposed final step leading to the mixed-valent complex involves a diffusion-controlled reaction between $[Ru^{II}(CN)_6]^{4-}$ and $[Ru^{III}(CN)_6]^{3-}$. This is unlikely, as an aquated pentacyanide reactant should be seemingly present. Irrespective of the actual mechanism, the identity of the mixed-valent ruthenium dimer seems reasonably well established in aqueous solution, even though the preparation of pure solid salts, as well as complementary spectral and electrochemical measurements is desirable. It would be also interesting to prepare the missing osmium-dinuclear complex, in order to make complete assignments. On the basis of the above discussion on the C-T analogs, it is tempting to explore the transition from a class II localized system to a class III delocalized one, by tuning the solvent properties in order to assess the coupling ability of the cyanide bridge.

Photoinduced intermolecular electron transfer has been observed with concentrated solutions of $[Fe^{II}(CN)_6]^{4-}$ and $[Fe^{III}(CN)_6]^{3-}$ ions, by irradiating the weak ($\varepsilon = 20–50\ M^{-1}\,cm^{-1}$) IVCT bands appearing in the NIR region [100a–d]. The alkali metal ions play a key role in the ion-pair electron transfer dynamics, as well as in the solvent reorganization changes on the reactants, which have been studied by changing the temperature and pressure and by using solvent isotope effects [100e].

The behavior upon IVCT irradiation of the mixed-valent complexes $[(NH_3)_5Os^{III}NCM^{II}(CN)_5]^-$ (M = Fe, Ru, Os), $[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]^-$ and $[(NC)_5Co^{III}NCOs^{II}(CN)_5]^{6-}$ was explored by Vogler et al. [101a]. The latter complex could be photolyzed upon IVCT excitation, as previously observed with the iron(II) and ruthenium(II) pentacyano-derivatives [101b]: the transiently formed redox isomer, $[(NC)_5Co^{II}NCOs^{III}(CN)_5]^{6-}$ dissociates into $[Os^{III}(CN)_6]^{3-}$ and $[Co^{II}(CN)_5]^{3-}$. The latter ion can be trapped by dioxygen giving a peroxo-complex, $[Co_2(CN)_{10}O_2]^{6-}$. The $[(NH_3)_5Cr^{III}NCFe^{II}(CN)_5]^-$ ion also underwent photolysis; the spectral changes are consistent with the formation of $[Fe^{III}(CN)_6]^{3-}$, along with Cr^{2+} and $5NH_3$, as a result of a fast decomposition of the initially produced [Cr^{II}, Fe^{III}] redox isomer. In contrast with this behavior, the three $[(NH_3)_5Os^{III}$-$NCM^{II}(CN)_5]^-$ ions were not light-sensitive upon IVCT excitation. As the redox isomers initially formed are expected not to be labile toward substitution, a rapid back electron transfer apparently regenerates the original Os^{III}/M^{II} complexes.

Comprehensive studies on the preparation, spectroscopy, electrochemistry, and the kinetics of substitution reactions were performed on the cyanide-bridged complexes containing $[M^{II}(CN)_5]^{3-}$ as donor fragments, and $[Ru^{III}(NH_3)_5]^{3+}$ [102–104] or $[Ru^{III}(edta)]^-$ [105] as acceptor fragments Studies of temperature and pressure effects on the IVCT bands and on the formal redox potentials of the component metal centers were carried out with $[(edta)Ru^{III}–CN–M(CN)_x]^{5-}$ (M = Fe^{II}, $x = 5$; M = Mo^{IV}, $x = 7$) [105c]. By also performing IR and NMR spectroscopic measurements, the role of hydrogen-bonded interactions with the different fragments was investigated, suggesting the participation of different edta-conformers in both dinuclear complex formation and optical electron-transfer absorption.

The complex $[(NC)_5Ru^{II}–CN–Ru^{III}(NH_3)_5]^-$ has also been characterized by anchoring on films of TiO_2 dispersed on silica-gel surfaces [103]; the spectroscopic and electrochemical properties are similar to those in solution phase, without significant matrix effects. Studies were also performed in aqueous–alcohol salt solution mixtures [104].

Two cyanide-bridged compounds of the series presently discussed were first characterized structurally in 1999 by single-crystal X-ray diffractometry, as well as by electronic and IR spectroscopies and cyclic voltammetry. The first one was Na{*trans*-$[L^{15}Co^{III}NCFe^{II}(CN)_5]$} · $4H_2O$, with L^{15} = 10-methyl-1,4,8,12-tetraazacyclopentadecan-10-amine [106a] and the second one, $[(NH_3)_5Pt^{IV}NCFe^{II}$-$(CN)_5] \cdot 6H_2O$ [107]. The study on the first complex was followed by a related report on similar complexes with other macrocyclic ligands [106b]. The studies on the Pt(IV) complex were performed in an effort to develop a full understanding of the photophysics of a related trinuclear complex containing the $Fe^{II}–Pt^{IV}–Fe^{II}$ chain (discussed later). The photochemistry of the dinuclear complex leads to irreversible charge transfer with formation of hexacyanoferrate(III) and some unidentified Pt(II) species.

Aquacobalamin and $[Fe^{II}(CN)_6]^{4-}$ react to produce the dinuclear anion [cobalamin-μ-NC–$Fe(CN)_5]^{3-}$, which was isolated as a zinc salt [108a]. The anation reaction was studied, together with similar reactions with other entering anions (N_3^-, $[Fe^{II}(CN)_5NO]^{2-}$ $[Fe^{III}(CN)_5H_2O]^{2-}$). From the variation of the rate constants observed and the positive entropies and activation volumes, a dissociative mechanism was proposed [108a]. No definite IVCT absorption could be detected for the dinuclear product, as the band is probably hidden by the intense corrin intraligand absorption (at ca. 400 nm). The occurrence of photolysis was interpreted as arising in IVCT excitation from Fe(II) to Co(III), as with the above discussed $[(NC)_5Co^{III}NCM^{II}(CN)_5]^{6-}$ complexes. On the other hand, the ruthenium analog, [cobalamin-μ-NC–$Ru(CN)_5]^{3-}$ did not show photolytic behavior, probably because the fraction of light absorbed by the IVCT band is negligible [108b].

Complexes with $[Ru^{II}(bpy)_2py]^{2+}$ [109] and $[Pt^{II}(py)_2Cl]^+$ [110] as donors, and $[Fe^{III}(CN)_5]$ as acceptor have also been reported. In the first one, the IVCT band shows up at 700 nm ($\varepsilon = 2000$ M^{-1} cm^{-1}). On the other hand, no IVCT absorptions were detected with the platinum complexes.

A series of mixed-valent compounds was prepared and characterized through the coordination of one to three $[Fe^{III}(CN)_6]^{3-}$ moieties to the $[Re^I(dmb)(CO)_3]^+$ ion (dmb = 4,4′-dimethyl-2,2′-bipyridine) [111]. The different complexes were characterized by IR, UV–vis and electrochemistry. The dinuclear complex shows an IVCT band ($Re^I \rightarrow Fe^{III}$) at 497 nm ($\varepsilon = 165$ M^{-1} cm^{-1}); by coordinating more Re^I units to the cyanide ligands, the IVCT band energies shift toward lower energies, with an increase in molar absorptivity. The application of the Hush model reveals a Class II behavior, with $H_{ab} = 670$ cm^{-1} for the dinuclear complex, which decreases upon the binding of more Re^I units. The small coupling between the metal centers is associated with the large difference in redox potentials, which decreases from 1.32 to 1.05 and 0.76 V by coordination of one to three Re^I units.

Cyanide-bridged trinuclear complexes have been prepared by using pentacyanometalate(II) fragments. The $[(NC)_5Ru^{II}NCCo^{III}(CN)_4CNCo^{III}(NH_3)_5]^{3-}$ ion shows an IVCT absorption at 370 nm, associated with electron transfer from $[Ru^{II}(CN)_5]^{3-}$ to the central Co^{III} center. By irradiating the IVCT band, a photoredox process leads to $[Ru^{III}(CN)_5H_2O]^{2-}$, $[Co^{III}(CN)_6]^{3-}$, aqueous Co(II) and $5NH_3$. It was proposed that the initial absorption step is followed by a charge shift from the central Co(II) to the Co(III) ammine moiety, with a subsequent rapid irreversible decay [112a]. The $[NH_3)_5Ru^{III}NCRu^{II}(CN)_4CNCo^{III}(NH_3)_5]^{2+}$ ion shows two IVCT bands at 647 and 372 nm, associated with charge transfer from the central Ru(II) to the Ru^{III} and Co^{III} metal centers, respectively. A photoredox process leads to Co(II) and some Ru(III) amine-complex, with a much larger quantum yield when irradiation occurs at 366 nm than at 577 nm. The spectrum as well as the photoreactivity scheme were discussed on the basis of a Hush diagram comprising three redox-active metal centers [112b]. With the $(NMe_3Cet)_6[(NC)_5Ru^{II}CNTi^{IV}(C_5H_5)_2NCRu^{II}(CN)_5]$ compound (Cet = cetyl), an intense IVCT band was observed at 630 nm, assigned as a $Ru^{II} \rightarrow Ti^{IV}$ transition. The complex also showed photoreactivity by irradiation at 577 nm, leading to $[Ru^{III}(CN)_6]^{3-}$ and Ti^{III}, which further reduced the solvent ($CHCl_3$). Analogous trinuclear complexes with Zr and Hf were prepared in solution, with IVCT bands at 420 and 365 nm, respectively [113].

Pfennig and Bocarsly prepared two series of trinuclear compounds and studied the relevant optical and thermal charge-transfer processes [114a]. The first group has the general formula $Na_2[L(NC)_4Fe^{II}CNPt^{IV}(NH_3)_4NCFe^{II}(CN)_4L]$, with L = py, pz and derivatives), and the second one: $\{Pt(NH_3)_4\}_2[(NC)_5M^{II}CNPt^{IV}(NH_3)_4NCM^{II}(CN)_5]$ (M = Fe, Ru, Os). All the compounds show IVCT bands in the visible region, whose parameters were interpreted in terms of the Marcus–Hush theory [81] in order to estimate the reorganization energies for the IV process, electron-transfer rate constants, thermal activation barriers, and the degree of delocalization. Also, the kinetics of formation, photochemical decomposition and the influence of the solvent on the charge-transfer processes were discussed. Complementary results were obtained by using ethylenediamine in place of NH_3, bound to the central Pt^{IV} metal [114b].

Recently, Pfennig et al. prepared several cyano-bridged trinuclear compounds of the form $[(NH_3)_5M\text{–}NC\text{–}Fe^{II}(CN)_4\text{–}M'(NH_3)_5]^{n+}$ ($M = Ru^{III}$, Os^{III}, Cr^{III}, Pt^{IV}; n = 2–4). IVCT absorption spectral and electrochemical results were used with the aim of estimation of the degree of electronic coupling between the metal centers, including the remote ones [115].

By oxidative polymerization of the above mentioned monomer, $\{Pt(NH_3)_4\}_2[(NC)_5Fe^{II}CNPt^{IV}(NH_3)_4NCFe^{II}(CN)_5]$, polymeric films of $[Fe^{II}(CN)_6\text{–}Pt^{IV}(NH_3)_4]_n$ were prepared on optically transparent indium–tin oxide (ITO) electrode surfaces [116]. By irradiation at 457 nm into the IVCT band of the polymer, the cleavage of bridging –CN– to Pt bonds leads to the dissociation of the film into shorter-chain $[Fe\text{–}Pt]_n$ oligomers, $[Pt(NH_3)_4]^{2+}$ and $[Fe^{III}(CN)_6]^{3-}$. When photolysis is carried out with the modified surface immersed in an aqueous solution containing transition metal cations, M^{n+} ($M = Ni^{+2}$, Fe^{+2}, Mn^{+2}, Cr^{+3}) the latter react with photogenerated $[Fe^{III}(CN)_6]^{3-}$ to form mixed metal cyanometalates on the electrode surface, thus incorporating M^{n+} into the interfacial lattice only at the irradiated regions. This leads to a film of a color different from to the original $[Fe\text{–}Pt]_n$ polymer. These multicomponent modified surfaces may be used as image-developing systems. The multicomponent electrodes could also find applicability as molecular electronic devices.

A trinuclear complex was prepared, $[(dmb)(CO)_3Re^I\text{-}\mu\text{-bpy–}Ru^{III}(en)_2\text{-}\mu\text{-NC–}Fe^{III}(CN)_5]Br$, with the purpose of studying charge separation processes following photoexcitation. Irradiation of the Re(I) → bpy MLCT band in the presence of phenothiazine (PTZ) leads, via a series of electron transfer reactions, to $[(dmb)(CO)_3Re^I\text{-}\mu\text{-bpy–}Ru^{III}(en)_2\text{-}\mu\text{-NC–}Fe^{II}(CN)_5]$ and PTZ^+. Thus, the pentacyanoferrate(III) behaves as a quencher of the back-reaction following irradiation at the Re^I center, and phenothiazine is used as a sacrificial donor [117].

The problem of intermetallic coupling mediated by a cyanide bridge is an open, hot subject, and has been addressed by using different modern experimental techniques. Time-dependent resonance-enhanced Raman scattering has been used to assess dynamic structural parameters (force constants, bond-length displacements and energy components of the vibrational activation barrier) involving MM′CT reactions in homogeneous media in $[(NC)_5M\text{–}CN\text{–}M'(NH_3)_5]^-$ ($M = Ru^{II}$, Fe^{II}; $M' = Ru^{III}$, Os^{III}) [118]. The same methodology has been used for an interfacial intervalence charge transfer process occurring with $[Fe^{II}(CN)_6]^{4-}$ adsorbed on colloidal TiO_2 [119]. In both homogeneous and heterogeneous reactions, the vibrational activation shows the participation of around ten modes, with the cyanide-bridging mode providing the largest contribution to the vibrational barrier. Even some surface modes (Ti–O and Ti–N stretchings) are enhanced during optical electron transfer. With adsorbed $[Fe^{II}(CN)_5L]^{n-}$ complexes (L = cyanide, py and py- or pz-derivatives), first evidence for fast, inverted, interfacial rate behavior was found in the thermal recovery reaction of Fe(II) species after photoexcitation of the Fe(II)–TiO_2 surface charge-transfer transition [120]; a good linear behavior (negative slope) was observed between $\log k_{ET}$ (the back reaction between excited TiO_2 and $[Fe^{III}(CN)_5L]^{(n-1)-}$) and the redox potential of the $Fe^{III,II}$ couple. The coupling between the metal centers has been studied by electrochemical [121], resonance Raman and NIR spectroscopies [122], and electroabsorption (Stark) techniques [123]. The latter method allows an estimation of charge transfer distances through the measurement of changes in dipole moment and polarizabilities due to the electronic transitions. Red-shifted infrared cyanide stretching frequencies have been used to estimate the vibronic coupling in related dinuclear complexes [124].

6. The reactivity of nitrosyl

The reactivity of nitrosyl, either free or bound to transition metal centers, has a great significance in chemistry [125], and particularly in modern biochemical studies [126]. The $[Fe(CN)_5NO]^{2-}$ ion has been studied extensively and is used as an hypotensive agent. Several reviews on its chemistry [127] and biochemistry [128] are available. The ion is very unreactive toward the dissociation of nitrosyl, because of multiple Fe–N bonding. In $[Fe(CN)_5NO]^{2-}$, NO may be considered a three electron donor (i.e. formally NO^+), with strong back-donation from the low-spin d^6 Fe(II) center, which populates the π^* (NO) orbital [125]. This is an arbitrary formalism, because the [Fe–N–O] moiety is in fact highly delocalized [129]; however, some conclusions can be obtained for the redox interconversions of bound nitrosyl, $NO^+ \leftrightarrow NO \leftrightarrow NO^-$, still considering the one-electron processes as predominantly centered at the NO ligand.

As mentioned above, the ruthenium- and osmium nitrosyl derivatives have been prepared [9]. Table 5 shows the electronic and IR spectral data, together with those for the iron analog. It can be seen that the energies of the electronic absorptions, assigned either to MLCT ($M \rightarrow \pi^*$ (NO)) or d–d transitions, increase in the order: Fe < Ru < Os. This seems to reflect the dominance of the $M\text{–}\pi^*$ (NO) interaction in controlling the energy of the relevant ground- and excited states; thus, the order can be explained by the stronger overlap of the d orbitals when going from Fe to

Table 5
Electronic and IR spectral data, equilibrium and nucleophilic rate constants for the $[M(CN)_5NO]^{2-}$ ions (M = Fe, Ru, Os)

	$[Fe(CN)_5NO]^{2-}$	$[Ru(CN)_5NO]^{2-}$	$[Os(CN)_5NO]^{2-}$
Electronic spectra [a] ν (cm^{-1}) (ε_{max}, $M^{-1}\,cm^{-1}$)			
$M \rightarrow \pi^*$ (NO)	20 080 (8) 25 380 (25)	22 988 (26) 28 985 (39)	23 420 (89) 31 850 (97)
d–d	30 300 (40) 37 800 (900) 42 000 (700)	39 215 (1550)	45 450 (6500)
$M \rightarrow \pi^*$ (CN)	50 000 (24 000)	50 000 (9400)	52 080 (15 600)
IR [a]			
ν_{NO} (cm^{-1})	1945	1926	1897
K_{eq} [a,b] (M^{-2})	1.5×10^5	4.4×10^6	4.2×10^1
k_{OH^-} [a,c] ($M^{-1}\,s^{-1}$)	0.55	0.95	1.37×10^{-4}
k_{SH^-} [a,c] ($M^{-1}\,s^{-1}$)	170	ca. 160	ca. 0.13

[a] Ref. [9b] and references therein.

[b] Correspond to $[M(CN)_5NO]^{2-} + 2OH^- \rightleftarrows [M(CN)_5NO_2]^{4-} + H_2O$.

[c] Specific second-order rate constants for the addition of OH^-, SH^-.

Ru and Os. The decrease of the NO stretching wavenumber in the same sense is also consistent with the increase in back-bonding to NO. Note, however, that this is in contrast to the order found for the three metals with the MLCT transitions to the pyrazine ligand. In that case, dominance of cyanides in the bonding scheme translated into a different order of the MLCT energies, as well as of other properties; also, it was shown that the π-contribution in the M–pz interaction might be very low.

The one-electron reduction of $[Fe(CN)_5NO]^{2-}$ is electrochemically reversible ($E = -0.37$ V vs. SCE) and leads to $[Fe^{II}(CN)_5NO]^{3-}$, a species that is in equilibrium with respect to the release of cyanides [130,131] (Eq. (2))

$$[Fe(CN)_5NO]^{3-} \rightleftarrows [Fe(CN)_4NO]^{2-} + CN^- \qquad (2)$$

The equilibrium (2) shifts with pH, and it is supposed that $[Fe(CN)_5NO]^{3-}$ predominates at pH values > 8. At pH values < 7 another cyanide ligand may be lost from the product in reaction 2.

The $[Fe(CN)_5NO]^{3-}$ ion has been also generated by pulse radiolysis [131] or by chemical reduction, either with sodium in liquid ammonia, dithionite, ascorbic acid or borohydride [132]. It has been characterized by EPR [132a] and IR ($\nu_{NO} = 1568$ cm^{-1} [132b]). The electronic spectrum shows two bands at 345 nm ($\varepsilon = 3500$ $M^{-1}\,cm^{-1}$) and 440 nm ($\varepsilon = 550$ $M^{-1}\,cm^{-1}$) [131], although combined bulk-electrolysis and absorption spectral measurements suggest that only the first one is characteristic of the one-electron reduction product, while the second band would be associated to two-electron reduction processes [130]. The latter could be the $[Fe^{II}(CN)_5NO]^{4-}$ species or, more probably, the protonated one,

$[Fe^{II}(CN)_5HNO]^{3-}$. Thus, probably one-electron and two-electron reduction products are obtained by pulse-radiolysis, as well as with the above mentioned chemical reductants. In the addition reaction of glutathione to $[Fe(CN)_5NO]^{2-}$, IR measurements detected the presence of N_2O [133], suggesting that two-electron processses must be also considered when using thiolates as reductants. A crystal structure is available for the tetraethylammonium salt of the square-pyramidal $[Fe(CN)_4NO]^{2-}$ ion, for which a Fe^I–NO^+ distribution has been proposed [134]. However, no crystal structure is available of any salt containing the $[Fe(CN)_5NO]^{3-}$ anion, and insufficient experimental evidence exists on the important but elusive species with bound NO^- (or any related form with N(I)). The two-electron electrochemical- and further processes are complex; the $[Fe(CN)_4NO]^{2-}$ species (Eq. (1)) can be reduced in a pH-dependent way ($E = -0.6$ vs. SCE, pH > 9); on the other hand, the $[Fe(CN)_5NO]^{3-}$ ion is reduced irreversibly at −1.32 V versus SCE, at pH 9, leading to bound hydroxylamine [130].

The $[Ru(CN)_5NO]^{2-}$ ion has been reduced electrochemically in a similar way as the iron analog [135]. The one-electron reversible reduction occurs at −0.39 V, and the second one, irreversible and multielectronic, at −1.60 V, in aqueous solution. In acetonitrile, the potentials shift toward more negative values, because of the increased electron density at the nitrosyl group when going from water to the organic solvent (see Section 3). Spectroelectrochemical experiments in acetonitrile show that the cyanide and nitrosyl stretching frequencies shift from 2136 to 2084 cm^{-1} and from 1884 to 1600 cm^{-1}, respectively, upon reduction at a controlled potential. The ν_{NO} stretching value agrees with the reported one for the iron–NO reduced complex (discussed earlier), and supports that the added electron is localized at the NO ligand. The latter fact is also consistent with epr measurements and DFT calculations [67]. Similar results were obtained for the reduction of $[Os(CN)_5NO]^{2-}$ [68]. In the latter work, NO was apparently labile toward dissociation on the minute time scale, leading to the $[Os(CN)_5pz]^{3-}$ ion when the reduction was done under excess of pyrazine. No kinetic rate constants have been published, however. It would be important to know about the dissociation ability of NO from the $[Fe(CN)_5NO]^{3-}$ ion, a process that probably could be present at high pHs when cyanide is not released. It must be stressed that a general lack of information exists on the rate of NO interchange in transition metal complexes, with the exception of emerging work with metal porphyrins [136].

The photoreduction of NO^+ in $[Fe(CN)_5NO]^{2-}$ could be achieved by irradiating in the visible region. A charge transfer process happened, leading to $[Fe^{III}(CN)_5H_2O]^{2-}$ and free NO as main photochemical products. These studies have been reviewed [6], but have not been extended to the ruthenium and osmium analogs.

In the above context of the reduction reactions of the NO^+ ligand, we come back to the results of Aymonino et al. with the different cationic salts of the nitroprusside anion [16]. By performing thermal analysis (DTA, TGA) of the solids in anaerobic media, the loss of hydration water was observed around 100 °C, followed by redox decomposition at greater temperatures. Eq. (3) shows the stoichiometry for the sodium complex, which has also been reported to be essentially valid for the other cationic salts:

$$4Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_6] + 4NO + 2C_2N_2 + Fe_2[Fe(CN)_6] + 4NaCN \qquad (3)$$

Inspection of the data indicates that the endothermic decomposition peak temperatures in DTA runs increase with the charge of the cation (around 260–300 °C for Group 1 and 330–370 °C for Group 2), as well as with the decrease in the radii for either Group 1 or 2 elements. As the net process involves an intramolecular charge transfer from cyanide to the NO^+ ligand, it appears that the cyanides become weaker reductants when the polarizing power of the cation is increased, thus increasing the decomposition temperature. The results reflect the specific interactions of the cyanides with the second-sphere cations, favoring the irreversible redox conversion upon thermal activation. It also represents an interesting type of solid state reaction, which probably could deserve a more detailed mechanistic analysis, as far as the apparently rate-determining step associated to the redox intramolecular electron transfer appears to be followed by an exothermic process leading to reorganized products.

For the pentacyanonitrosyl complexes, experimental and theoretical studies show that the N-atom of nitrosyl can be the site of electrophilic reactivity [137]. This is also a general case for other $[X_5M–NO]$ complexes, for which the electron density at NO can be controlled by selecting M or X. Table 5 shows the values of the rate constants for the nucleophilic addition reactions on the pentacyanonitrosylmetalates. The simplest reactions are those with OH^- (Eq. (4)), because no redox-chemistry appears. The accepted mechanism involves a rate-determining step for the addition of OH^-, with a further fast deprotonation of the adduct $[Fe(CN)_5NO_2H]^{3-}$ by the second OH^-, and formation of the *N*-nitrito-complex [9b,19c,138].

$$[M(CN)_5NO]^{2-} + 2OH^- \rightleftarrows [M(CN)_5NO_2]^{4-} + H_2O \qquad (4)$$

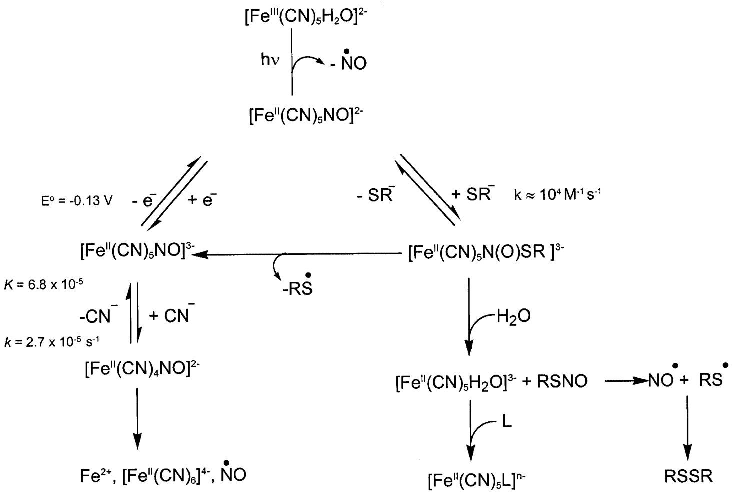
A rough correlation exists between the equilibrium constants for the nucleophilic additions (Eq. (4)) and the ν_{NO} frequencies; values in the range 1860–2000 cm^{-1} suggest that the complexes might be reactive [139]. Care must be taken when comparing rate-constant values (which are generally scarce in the literature) for different complexes, since the metal, the co-ligands and the overall charge influence the nucleophilic reactivity. For the three pentacyanonitrosylmetalates, the rates of OH^- addition agree with the trends in the IR stretching frequencies. The low value for the osmium complex is another example of the remarkable strong π-donor ability of Os(II) [9b]. The similar values for the iron and ruthenium complexes were ascribed to the likely greater polarizability of the ruthenium species favoring a faster process, thus compensating for the higher electron density on bound NO, as measured by the lower IR wavenumber [19c].

Recently, the pentacyanonitrosyl fragments have been used as building blocks for cyanide-bridged species such as:

$$[(NH_3)_5Ru^{II,III} - NC - M(CN)_4NO]^n \quad (M = Fe,\ Ru,\ Os)$$

The compounds display intense charge transfer bands between the distant Ru(II) and the acceptor moiety comprising the $[M^{II}(CN)_4(NO)]$ fragment, probably associated with the good electronic coupling mediated by the bridging cyanide. Even more impressively, the reactivity of the bound nitrosyl toward OH^- is increased by five orders of magnitude when switching the oxidation state at the distant cyanide-bridged ruthenium from II to III [140], evidence of charge withdrawal upon oxidation.

The reactions of SH^- and thiolates, SR^-, with $[Fe(CN)_5NO]^{2-}$ are much faster ($k = 10^2$–10^4 M^{-1} s^{-1}) than with OH^- [141,142], given the greater polarizability of the sulfur species. These nucleophiles, as other *N*-binding species such as ammonia, amines, hydroxylamine, etc., undergo irreversible redox reactions following the initial adduct formation [137]. The mechanism of the reactions of $[Fe(CN)_5NO]^{2-}$ with thiolates has been considered [142] (Scheme 2).



Scheme 2.

Some uncertainties still remain, such as the timing of NO release to the medium, as well as the competition between nitrosothiolate dissociation, redox conversion leading to NO and oxidized thiolate, and the role of pH in the overall process. The relative stability of the adducts formed by different thiolates with $[Fe(CN)_5NO]^{2-}$ has been reported [143], but the detailed mechanism comprising the complex pattern of successive and competitive reactions arising after the first equilibrium adduct formation appears as an open subject. A recent study of the photochemistry of $[Fe(CN)_5NO]^{2-}$ in the presence of thiolates shows that the nitrosothiol can be delivered in situ after visible light irradiation [144].

The addition reactions of ammonia and amines were studied in the 1970s and have been reviewed [137]. The reaction of trioxodinitrate $[ON{=}NO_2]^{2-}$ with $[Fe(CN)_5NO]^{2-}$ follows a complex mechanism, showing nitrosative cleavage of the N=N bond in trioxodinitrate upon adduct formation, leading to NO_2^-, NO and

N_2O in different stages of the reaction [145]. Recently, it has been shown that hydrazine acts a nucleophile toward $[Fe(CN)_5NO]^{2-}$, leading to N_2O and NH_3 as products [146] (Eq. (5))

$$[Fe(CN)_5NO]^{2-} + N_2H_4 + H_2O \rightleftarrows [Fe(CN)_5H_2O]^{3-} + N_2O + NH_3 + H^+ \quad (5)$$

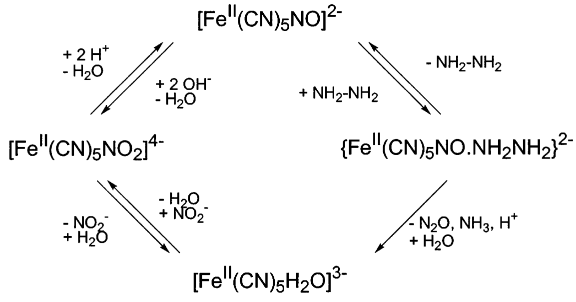
This is a remarkable fact, given the alternative formation and stabilization of bound azide for other nitrosyl complexes of ruthenium and osmium [137]. This shows that the mode of adduct decomposition can be dependent on the properties of the electrophilic metal fragment (such as the overall charge) for a given reaction type. The products of Eq. (5) are also indicative of a mechanistic pathway leading to a unusual product of hydrazine oxidation, N_2O; also, a novel path is shown, by which ammonia is generated by a two-electron oxidant, a mechanistic feature not previously found for hydrazine oxidation reactions [147].

The addition reactions to $[Fe(CN)_5NO]^{2-}$ should be sensitive to the solvent; in weak acceptor solvents, the electronic density at the nitrosyl group is enhanced, and we expect a decrease in the nucleophilic reactivity compared to aqueous solutions. This was found to be the case for the addition of *n*-butylamine in acetonitrile; the latter was also found to be a plausible route for obtaining aliphatic diazonium ions, stabilized by coordination to the iron center, whose π-donor ability must be also comparatively enhanced in acetonitrile [148].

7. Catalytic processes. The $[Fe^{II}(CN)L]^{n-}$ ions as labile metal centers

It is known that transition metal ions behave as catalysts in the reactions of many inorganic and organic substrates, particularly in redox processes. Coordination of the substrates to the metal is generally assumed as a key condition for activation, but the labile nature of most aqua-ions makes it difficult to disclose mechanistic pathways. For the pentacyanoferrate systems, sometimes the otherwise reactive intermediates can be spectroscopically characterized on the minute-time scale, because the back-bonding interactions with the Fe(II) center keeps the intermediate kinetically stabilized. This is the case for the autoxidation of hydrazine, evolving to coordinated diazene and to the labile dinitrogen molecule. Eventually, the $[Fe^{II}(CN)_5H_2O]^{3-}$ ion is able to bind the excess hydrazine, forming the $[Fe^{II}(CN)_5N_2H_4]^{3-}$ ion (a well-characterized species), which can be further oxidized when enough oxygen is present [149]. A similar mechanism probably occurs in the catalyzed autoxidation of thiolates by the same pentacyano-fragment, as suggested by the blue $[Fe^{III}(CN)_5SR]^{3-}$ intermediates which form and decay rapidly when the aquapentacyanoferrate(II) ion is put in contact with cysteine (or related thiolates) in the presence of excess oxygen [150]. The problems for disclosing the mechanistic details in the catalytic processes mediated by the $[Fe^{II}(CN)_5H_2O]^{3-}$ ion arise with the identification of possible Fe(III) intermediates and the formation of dimeric species, as for the hydrazine oxidation reaction [149]. In fact, it was previously shown that Fe(II) ions catalyzed the autoxidation of $[Fe^{II}(CN)H_2O]^{3-}$, and this is probably related to the demands of two-electron oxygen reduction met by some type of inner-sphere association between the reactants [51].

Recently, a catalytic process has been proposed in evidence for the reduction of nitrite by hydrazine [146] (Scheme 3).



Scheme 3.

The moderately fast nucleophilic attack of hydrazine on the $[Fe^{II}(CN)_5NO]^{2-}$ ion (Eq. (5), $k = 0.4\ M^{-1}\ s^{-1}$), leads to N_2O, NH_3 and the $[Fe^{II}(CN)H_2O]^{3-}$ ion. The latter may bind more nitrite (which converts to NO^+ upon coordination) and enter a new process, as long as hydrazine is available. Similar catalytic reactions (leading to N_2) have been published in the literature with ammonia and amines as nucleophilic reagents, but the reactions are much slower [151]. For the nucleophilic attack of hydroxylamine on $[Fe^{II}(CN)_5NO]^{2-}$, N_2O is formed and the aqua-ion could enter into a similar catalytic cycle for nitrite reduction. This is complicated, however, by another parallel process: the disproportionation of hydroxylamine, leading to mixtures of N_2, N_2O and NH_3 [152].

An interesting cycle was shown for the autooxidation of cysteine to cystine catalyzed by the $[Fe^{II}(CN)_5NO]^{2-}$ ion [142a]. In contrast to the reactions described above involving $[Fe^{II}(CN)H_2O]^{3-}$, cysteine forms a red adduct with the nitrosyl complex, followed by a redox reaction leading to bound NO and cystine. The NO complex can be oxidized again by dioxygen to the NO^+ form, and up to 10 moles of cysteine can be processed, with catalysis associated with the to NO^+/NO redox cycling. The reaction is complicated by the cyanide release occurring upon reduction of NO^+ and, probably, by two-electron reduction of NO^+ leading to N_2O.

8. Concluding remarks

Despite the significant advances obtained with the compounds of the three metal-series, this broad field seems ready for new developments. Valuable information was obtained on the solid state molecular structures for Os(II) and Ru(II) complexes, and those of the substituted pentacyanide-L complexes with Fe(II) are emerging. An expansion of crystallographic data is still needed, particularly searching for the *trans*-influences of the L ligands. The absence of data is more evident with the M(III) species (no crystal structures for the Ru(III) and Os(III) hexacyanides are available yet).

Although the main spectroscopic (IR, electronic) features of Fe(II) and Ru(II) complexes have been assigned, this is not the case with Os(II), particularly for the electronic d–d transitions. The $[Os(CN)_5H_2O]^{3-}$ ion has not been properly characterized, although its presence can be inferred as an intermediate during the synthesis of the $[Os(CN)_5L]^{n-}$ compounds. With the available new techniques, complexes with other L ligands for the latter series can be prepared at will.

The splitting of the MLCT transitions for the $[Os^{II}(CN)_5L]^{n-}$ complexes with L = *N*-heterocyclic ligands show an interesting contrast with the results for the iron and ruthenium analogs, as well as with the related $[Os^{II}(NH_3)_5L]^{n-}$ series. Ongoing work affords the subject of the energies and intensities of the electronic bands being dependent on the metal, X and L ligands, as well as on the solvent for the $\{MX_5L\}$ systems [20b].

The mechanism of the ligand interchange reactions seems to be a reasonably well-understood problem, based on the important contribution of high-pressure studies for the Fe(II) and Fe(III) complexes. However, volumes of activation have not been measured for the ruthenium complexes, and a distinction between D and I_d mechanisms cannot be made as in the case of iron complexes. An extension to osmium is underway [27], and, besides the dramatic drop in substitution rates, the mechanisms can be anticipated to be similar. The information available on the $[Os^{II}(CN)_5pz]^{n-}$ complex points to the robust nature of this species, as well as of other Os(II) and Os(III) complexes. A broad range of tunable redox potentials can be obtained (0.4–1.2 V) by selecting adequately the nature of M or L. Here again, the mechanism of the redox reactions for the osmium systems should be similar to the related analogs, as already found with the hexacyanides.

The influence of the solvent on the electronic structure and properties of the $[M^{II}(CN)_5L]^{n-}$ compounds has been greatly explored, and is well understood qualitatively in terms of Gutmann's view of solvent–solute interactions; however, theoretical advances should be desirable in modeling the cyanide environment in the different solvents. The reviewed work shows that the great sensitivity of cyanide-complexes to medium effects makes them attractive for derivatization on surfaces, electrodes, as well as for forming polynuclear aggregates with novel physical properties relevant to material's performance. From the chemical viewpoint, development of synthetic procedures would be welcome, particularly through the design of supramolecular species where the ligand reactivity could be controlled systematically, as shown with nitrosyl complexes. It is feasible that the enhanced back-bonding toward the L ligands in aprotic solvents compared to water could reveal new chemistry for the bound L ligand, namely redox chemistry, stabilization of otherwise reactive intermediates and the like.

The borderline situations found in the pz-bridged CT analogs (related to the transition from Class II to Class III delocalized systems) drives attention to the problem of electronic coupling in polymetallic bridged-complexes. It suggests the convenience of exploring the electronic communicating abilities of new complexes. Given the wide use of cyanide as a bridge, the synthesis of solid compounds with symmetric pentacyanide-fragments seems to be particularly challenging and attractive, as a finely tuned electronic coupling between the metallic centers could be achieved upon solvent variations. Modern techniques are needed for the relevant spectroscopic studies, namely low-temperature IR, resonance Raman and electroabsorption (Stark) effects. The latter measurements would be crucial for disclosing the true charge-transfer distances, with a consequent revision of the coupling energies currently used [118]. This should be done in parallel with efforts for improving the theoretical methods, as with current studies with the pentaammine analogs [87,153].

Acknowledgements

The authors gratefully acknowledge main financial support from the University of Buenos Aires, ANPCyT (grant 01703), CONICET (grant 4653), UBACyT (grant TW 62), as well as a complementary aid from Fundación Antorchas. L.M.B and J.A.O are members of the research staff of CONICET.

References

[1] A.G. Sharpe, The Chemistry of Cyano Complexes of the Transition Metals, Academic Press, New York, 1976.
[2] D.H. Macartney, Rev. Inorg. Chem. 9 (1988) 101.
[3] (a) W. Kaim, A. Klein, M. Glöckle, Acc. Chem. Res. 33 (2000) 755;
(b) C. Creutz, Prog. Inorg. Chem. 30 (1983) 1.
[4] (a) H. Vahrenkamp, A. Geiß, G.N. Richardson, J. Chem. Soc. Dalton Trans. (1997) 3643;
(b) Y. Wu, B.W. Pfennig, S.L. Sharp, D.R. Ludwig, C.J. Warren, E.P. Vicenzi, A.B. Bocarsly, Coord. Chem. Rev. 159 (1997) 245;
(c) F. Scandola, R. Argazzi, C.A. Bignozzi, C. Chiorboli, M.T. Indelli, M.A. Rampi, Coord. Chem. Rev. 125 (1993) 283.
[5] (a) B.L. Westcott, J.H. Enemark, in: E.I. Solomon, A.B.P. Lever (Eds.), Inorganic Electronic Spectroscopy, vol. II, Wiley, New York, 1999, p. 403;
(b) P. Coppens, D.V. Formitchev, M.D. Carducci, K. Culp, J. Chem. Soc. Dalton Trans. (1998) 865.
[6] (a) G. Stochel, Coord. Chem. Rev. 114 (1992) 269;
(b) G. Stochel, R. van Eldik, Coord. Chem. Rev. 159 (1997) 153;
(c) Z. Stasicka, E. Wasiliewska, Coord. Chem. Rev. 159 (1997) 294.
[7] K.R. Dunbar, R.A. Heintz, Prog. Inorg. Chem. 45 (1997) 283.
[8] L.A. Gentil, A. Navaza, J.A. Olabe, G.E. Rigotti, Inorg. Chim. Acta 179 (1991) 89.
[9] (a) J.A. Olabe, L.A. Gentil, G.E. Rigotti, A. Navaza, Inorg. Chem. 23 (1984) 4297;
(b) L.M. Baraldo, M.S. Bessega, G.E. Rigotti, J.A. Olabe, Inorg. Chem. 33 (1994) 5890.
[10] A.R. Parise, O. Piro, E.E. Castellano, J.A. Olabe, Inorg. Chim. Acta 319 (2001) 199.
[11] A. Tullberg, N.G. Vannerberg, Acta Chem. Scand. A 28 (1974) 340.
[12] M. Holzbecher, O. Knop, M. Falk, Can. J. Chem. 49 (1971) 1413.
[13] B.J. Coe, S.J. Glenwright, Coord. Chem. Rev. 203 (2000) 5.
[14] D.B. Soria, O.E. Piro, E.L. Varetti, P.J. Aymonino, submitted for publication.
[15] R.L. De Kock, A.C. Sarapu, R.F. Fenske, Inorg. Chem. 10 (1971) 38.
[16] (a) M.M. Vergara, E.L. Varetti, Spectrochim. Acta A 49 (1993) 527;
(b) L.A. Gentil, J.A. Olabe, E.J. Baran, P.J. Aymonino, J. Thermal Anal. 7 (1975) 279;

(c) J.I. Amalvy, E.L. Varetti, P.J. Aymonino, E.E. Castellano, O.E. Piro, G. Punte, J. Crystallogr. Spectrosc. Res. 16 (1986) 537;
(d) J.I. Amalvy, E.L. Varetti, P.J. Aymonino, J. Phys. Chem. Solids 46 (1985) 1153;
(e) D.B. Soria, J.I. Amalvy, O.E. Piro, E.E. Castellano, P.J. Aymonino, J. Chem. Crystallogr. 26 (1996) 325;
(f) M.M. Vergara, E.L. Varetti, J. Phys. Chem. Solids 48 (1987) 13;
(g) M.M. Vergara, E.L. Varetti, G. Rigotti, A. Navaza, J. Phys. Chem. Solids 50 (1989) 951;
(h) J.I. Amalvy, E.L. Varetti, P.J. Aymonino, An. Asoc. Quím. Argent. 74 (1986) 437;
(i) G. Rigotti, P.J. Aymonino, E.L. Varetti, J. Crystallogr. Spectrosc. Res. 14 (1984) 517;
(j) A.G. Alvarez, P.J. Aymonino, E.J. Baran, L.A. Gentil, A.H. Lanfranconi, E.L. Varetti, J. Inorg. Nucl. Chem. 38 (1976) 221;
(k) C.O. Della Vedova, J.H. Lesk, E.L. Varetti, P.J. Aymonino, O.E. Piro, B.E. Rivero, E.E. Castellano, J. Mol. Struct. 70 (1981) 241;
(l) E.E. Castellano, O.E. Piro, A.D. Podjarny, B.E. Rivero, P.J. Aymonino, J.H. Lesk, E.L. Varetti, Acta Crystallogr. B 34 (1978) 2673;
(m) E.L. Varetti, P.J. Aymonino, Inorg. Chim. Acta 7 (1973) 597.
[17] (a) G. Stochel, R. van Eldik, Inorg. Chim. Acta 174 (1990) 217;
(b) C.H. Hung, H.Y. Huang, J.Y. Liao, A. Yeh, Inorg. Chem. 29 (1990) 2940;
(c) C.N. Chen, M.C. Wu, A. Yeh, T.Y.R. Tsai, Inorg. Chim. Acta 267 (1998) 81;
(d) C.S. Lin, A. Yeh, T.Y. Liu, K.S. Kwan, D.J. Hodgson, H.J. Tien, Inorg. Chim. Acta 192 (1992) 81;
(e) F.H. Chao, B.K. Sun, A. Juang, A. Yeh, J. Chin. Chem. Soc. 37 (1990) 327;
(f) P.R. Norris, J.M. Pratt, J. Chem. Soc. Dalton Trans. (1995) 3643;
(g) E.M. Sabo, R.E. Shepherd, M.S. Rau, M.G. Elliott, Inorg. Chem. 26 (1987) 2897;
(h) H.E. Toma, M.N. Takayasu, An. Acad. Bras. Ci. 61 (1989) 131;
(i) L.C.G. Vasconcellos, K.S.M. Ferreira, L.M.A. Plicas, A.A. Batista, I.D. Moreira, E. Tfouni, D.W. Franco, Inorg. Chim. Acta 214 (1993) 23;
(j) M.M. Monzyk, R.A. Holwerda, Polyhedron 9 (1990) 2433;
(k) S.D.S. Borges, A.L. Coelho, I.S. Moreira, M.A.B. Dearaujo, Polyhedron 13 (1994) 1015;
(l) L.D. Slep, S. Pollak, J.A. Olabe, Inorg. Chem. 38 (1999) 4369;
(m) H.E. Toma, E. Stadler, Inorg. Chem. 24 (1985) 3085.
[18] (a) C.R. Johnson, R.E. Shepherd, Inorg. Chem. 22 (1983) 1117;
(b) C.R. Johnson, R.E. Shepherd, Inorg. Chem. 22 (1983) 2439.
[19] (a) J.M.A. Hoddenbagh, D.H. Macartney, Inorg. Chem. 25 (1986) 380;
(b) L.A. Gentil, H.O. Zerga, J.A. Olabe, J. Chem. Soc. Dalton Trans. (1986) 2731;
(c) A.A. Chevalier, L.A. Gentil, J.A. Olabe, J. Chem. Soc. Dalton Trans. (1991) 1959.
[20] (a) L.D. Slep, L.M. Baraldo, J.A. Olabe, Inorg. Chem. 35 (1996) 6327;
(b) L.D. Slep, J.A. Olabe, J. Am. Soc. Chem. 123 (2001) 7186.
[21] H.E. Toma, J.M. Malin, Inorg. Chem. 12 (1973) 1039.
[22] (a) A.E. Almaraz, L.A. Gentil, J.A. Olabe, J. Chem. Soc. Dalton Trans. (1989) 1973;
(b) J.M.A. Hoddenbagh, D.H. Macartney, Inorg. Chem. 25 (1986) 2099.
[23] A.P. Szecsy, S.S. Miller, A. Haim, Inorg. Chim. Acta 28 (1987) 189.
[24] (a) A.A. Chevalier, L.A. Gentil, J.A. Olabe, Polyhedron 11 (1992) 1229;
(b) A.L. Tokman, L.A. Gentil, J.A. Olabe, Polyhedron 8 (1989) 2091;
(c) L.A. Gentil, A.M. Rabino, J.A. Olabe, An. Asoc. Quim. Argent. 75 (1987) 419.
[25] J.A. Olabe, H.O. Zerga, L.A. Gentil, J. Chem. Soc. Dalton Trans. (1987) 1267.
[26] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier Science, Amsterdam, 1984.
[27] L.D. Slep, P. Alborés, L.M. Baraldo, J.A. Olabe, submitted.
[28] B.A. Goodman, J.B. Raynor, Adv. Inorg. Radiochem. 13 (1970) 192.
[29] (a) C. Creutz, M.H. Chou, Inorg. Chem. 26 (1987) 2995;
(b) R.H. Magnuson, H. Taube, J. Am. Chem. Soc. 97 (1975) 5129.
[30] D.A. Foucher, D.H. Macartney, L.J. Warrack, J.P. Wilson, Inorg. Chem. 32 (1993) 3425.
[31] (a) G. Stochel, J. Chatlas, P. Martinez, R. van Eldik, Inorg. Chem. 31 (1992) 5480;
(b) M.I. Finston, H.G. Drickamer, J. Phys. Chem. 85 (1981) 50;

(c) I. Maciejowska, R. van Eldik, G. Stochel, Z. Stasicka, Inorg. Chem. 36 (1997) 5409.
[32] (a) G. Stochel, R. van Eldik, E. Hejmo, Z. Stasicka, Inorg. Chem. 27 (1988) 2767;
(b) G. Stochel, R. van Eldik, Inorg. Chim. Acta 190 (1991) 55.
[33] J.C. Curtis, T.J. Meyer, Inorg. Chem. 21 (1982) 1562.
[34] H.W. Kang, G. Moran, E. Krausz, Inorg. Chim. Acta 249 (1996) 231.
[35] (a) A.B.P. Lever, E.S. Dodsworth, in: E.I. Solomon, A.B.P. Lever (Eds.), Inorganic Electronic Structure and Spectroscopy, vol. II, Wiley, New York, 1999, p. 227;
(b) E.S. Dodsworth, A.B.P. Lever, Chem. Phys. Lett. 119 (1985) 61;
(c) E.S. Dodsworth, A.B.P. Lever, Chem. Phys. Lett. 124 (1986) 152.
[36] E. Waldhör, W. Kaim, J.A. Olabe, L.D. Slep, J. Fiedler, Inorg. Chem. 36 (1997) 2969.
[37] P.A. Bott, K.A.K. Lott, Inorg. Chim. Acta 111 (1986) L33.
[38] (a) J.M.A. Hoddenbagh, D.H. Macartney, Inorg. Chem. 29 (1990) 245;
(b) D.H. Macartney, Inorg. Chem. 30 (1991) 3337.
[39] N. Sutin, Prog. Inorg. Chem. 30 (1983) 441.
[40] R.A. Marcus, N. Sutin, Biochim. Biophys. Acta 811 (1995) 265.
[41] (a) J.M.A. Hoddenbagh, D.H. Macartney, J. Chem. Soc. Dalton Trans. (1990) 615;
(b) A. Wanat, R. van Eldik, G. Stochel, J. Chem. Soc. Dalton Trans. (1998) 2497;
(c) N. Kagayama, M. Sekiguchi, Y. Inada, H.D. Takagi, S. Funahashi, Inorg. Chem. 33 (1994) 1881.
[42] (a) D.R. Stranks, Pure Appl. Chem. 38 (1974) 303;
(b) R.A. Marcus, J. Phys. Chem. 24 (1956) 966;
(c) R.A. Marcus, J. Phys. Chem. 26 (1957) 867;
(d) R.A. Marcus, J. Phys. Chem. 72 (1963) 891;
(e) N.S. Hush, Trans. Faraday Soc. 57 (1961) 557.
[43] P.D. Metelski, T.W. Swaddle, Inorg. Chem. 38 (1999) 301.
[44] Y. Fu, T.W. Swaddle, Inorg. Chem. 38 (1999) 876.
[45] Y. Fu, T.W. Swaddle, J. Am. Chem. Soc. 119 (1997) 7137.
[46] E. Ilkowska, K. Lewinski, R. van Eldik, G. Stochel, J. Biol. Inorg. Chem. 4 (1999) 302.
[47] (a) I. Krack, R. van Eldik, Inorg. Chem. 25 (1986) 1743;
(b) M. Kanesato, M. Ebihara, Y. Sasaki, K. Saito, J. Am. Chem. Soc. 105 (1983) 5711;
(c) M. Martinez, M.A. Pitarque, R. van Eldik, J. Chem. Soc. Dalton Trans. (1994) 3159.
[48] M.D. Johnson, K.D. Sharma, Inorg. Chim. Acta 293 (1999) 229.
[49] T.E. Mallouk, J.S. Krueger, J.E. Mayer, C.M.G. Dymond, Inorg. Chem. 28 (1989) 3507.
[50] (a) D.G. Bray, R.C. Thompson, Inorg. Chem. 33 (1994) 905;
(b) V. Vanag, J. Phys. Chem. A 102 (1998) 601;
(c) V. Vanag, Y. Mori, I. Hanazaki, J. Phys. Chem. 98 (1994) 8392;
(d) G. Rabai, I.R. Epstein, Inorg. Chem. 28 (1989) 732.
[51] H.E. Toma, Inorg. Chim. Acta 15 (1975) 205.
[52] M.H. Chen, S. Lee, S. Liu, A. Yeh, Inorg. Chem. 35 (1996) 2627.
[53] P. Forlano, A.R. Parise, M. Videla, J.A. Olabe, Inorg. Chem. 36 (1997) 5642.
[54] S.K. Wei, A. Yeh, J. Chin. Chem. Soc. 46 (1999) 905.
[55] A. Haim, Adv. Chem. Ser. 253 (1997) 239.
[56] (a) A.E. Almaraz, L.A. Gentil, L.M. Baraldo, J.A. Olabe, Inorg. Chem. 35 (1996) 7718;
(b) A.R. Parise, L.M. Baraldo, J.A. Olabe, Inorg. Chem. 35 (1996) 5080;
(c) J.A. Olabe, A. Haim, Inorg. Chem. 28 (1989) 3277.
[57] A.E. Almaraz, L.A. Gentil, L.M. Baraldo, J.A. Olabe, Inorg. Chem. 36 (1997) 1517.
[58] P. Chen, T.J. Meyer, Chem. Rev. 98 (1998) 1439.
[59] (a) J. Burgess, Spectrochim. Acta A 26 (1970) 1369;
(b) J. Burgess, Spectrochim. Acta A 26 (1970) 1957.
[60] (a) H.E. Toma, M.S. Takasugi, J. Solut. Chem. 12 (1983) 547;
(b) H.E. Toma, M.S. Takasugi, J. Solut. Chem. 18 (1989) 575;
(c) C.J. Timpson, C.A. Bignozzi, B.P. Sullivan, E.M. Kober, T.J. Meyer, J. Phys. Chem. 100 (1996) 2915.

[61] V. Gutmann, The Donor–Acceptor Approach to Molecular Interactions, Plenum, New York, 1980.
[62] A.R. Parise, PhD Thesis, University of Buenos Aires, 2000.
[63] L.D. Slep, PhD Thesis, University of Buenos Aires, 1999.
[64] L.M. Baraldo, PhD Thesis, University of Buenos Aires, 1994.
[65] H.E. Toma, M.S. Takasugi, Polyhedron 8 (1989) 941.
[66] D.A. Estrin, L.M. Baraldo, L.D. Slep, B.C. Barja, J.A. Olabe, L. Paglieri, G. Corongiu, Inorg. Chem. 35 (1996) 3897.
[67] M. Wanner, T. Scheiring, W. Kaim, L.D. Slep, L.M. Baraldo, J.A. Olabe, S. Zális, E.J. Baerends, Inorg. Chem., in press.
[68] F. Baumann, W. Kaim, L.M. Baraldo, L.D. Slep, J.A. Olabe, J. Fiedler, Inorg. Chim. Acta 285 (1999) 129.
[69] (a) F. Armand, H. Sakuragi, K. Tokumaru, S. Okada, K. Yase, H. Matsuda, H. Nakanishi, T. Yamada, K. Kajikawa, H. Takezoe, Thin Solid Films 245 (1994) 202;
(b) F. Armand, H. Sakuragi, K. Tokumaru, New J. Chem. 17 (1993) 351;
(c) F. Armand, H. Sakuragi, K. Tokumaru, J. Chem. Soc. Faraday Trans. 89 (1993) 1021.
[70] J.C. Curtis, B.P. Sullivan, T.J. Meyer, Inorg. Chem. (1983) 4369.
[71] L.W. Warner, M.F. Hoq, T.K. Myser, W.W. Henderson, R.E. Shepherd, Inorg. Chem. 25 (1986) 1911.
[72] P.K. Mascharak, Inorg. Chem. 25 (1986) 245.
[73] O.Y. Hamra, L.D. Slep, J.A. Olabe, D.A. Estrin, Inorg. Chem. 37 (1998) 2033.
[74] J. Burgess, E. Pelizzetti, Gazz. Chim. Ital. 118 (1988) 803.
[75] A.R. Parise, S. Pollak, L.D. Slep, J.A. Olabe, An. Asoc. Quim. Argent. 83 (1995) 211.
[76] (a) G. Fernández, M.D. Graciani, A. Rodríguez, M. Muñoz, M.L. Moyá, J. Colloid Interface Sci. 225 (2000) 47;
(b) R. Prado-Gotor, R. Jimenez, P. López, P. Pérez, C. Gomez-Herrera, F. Sánchez, Langmuir 14 (1998) 1539;
(c) M.D. Graciani, M.A. Rodríguez, M.L. Moyá, Int. J. Chem. Kinet. 29 (1997) 377;
(d) M.L. Moyá, J. Burgess, F. Sánchez, Int. J. Chem. Kinet. 25 (1993) 469;
(e) A. Alalousy, S. Alshehri, J. Burgess, M.D. Graciani, M.L. Moyá, E. Muñoz, A. Rodríguez, F. Sánchez, Transit. Met. Chem. 18 (1993) 179;
(f) J. Burgess, M.S. Patel, J. Chem. Soc. Faraday Trans. 89 (1993) 783;
(g) I. Tejera, A. Rodríguez, F. Sánchez, M.L. Moyá, J. Burgess, J. Chem. Soc. Faraday Trans. 87 (1991) 2573;
(h) M.D. Graciani, A. Rodríguez, G. Fernández, M.L. Moyá, Langmuir 13 (1997) 4329.
[77] P. Lopez, A. Rodríguez, C. Gomez-Herrera, F. Sánchez, M.L. Moyá, J. Chem. Soc. Dalton Trans. 88 (1992) 2701.
[78] (a) G. Fernández, M.D. Graciani, A. Rodríguez, M. Muñoz, M.L. Moyá, Int. J. Chem. Kinet. 31 (1999) 229;
(b) M.L. Moyá, F. Sánchez, J. Burgess, Int. J. Chem. Kinet. 25 (1993) 891.
[79] A. Rodríguez, M.D. Graciani, R. Balahura, M.L. Moyá, J. Phys. Chem. 100 (1996) 16978.
[80] F. Pina, A.J. Parola, A. Saint-Maurice, M.F. Manfrin, L. Moggi, T. Indelli, F. Scandola, J. Chem. Soc. Dalton Trans. (1997) 2327.
[81] N.S. Hush, Prog. Inorg. Chem. 8 (1967) 391.
[82] F. Felix, A. Ludi, Inorg. Chem. 17 (1978) 1782.
[83] M. Ketterle, W. Kaim, J.A. Olabe, A.R. Parise, J. Fiedler, Inorg. Chim. Acta 291 (1999) 66.
[84] F.M. Hornung, F. Baumann, W. Kaim, J.A. Olabe, L.D. Slep, J. Fiedler, Inorg. Chem. 37 (1998) 31.
[85] T. Scheiring, W. Kaim, J.A. Olabe, A.R. Parise, J. Fiedler, Inorg. Chim. Acta 300–302 (2000) 125.
[86] T. Ito, T. Hamaguchi, H. Nagino, T. Yamaguchi, J. Washington, C.P. Kubiak, Science 277 (1997) 660.
[87] R.J. Crutchley, Adv. Inorg. Chem. 41 (1993) 273.
[88] (a) W. Kaim, W. Bruns, S. Kohlmann, M. Krejcik, Inorg. Chim. Acta 229 (1995) 143;
(b) D.T. Pierce, W.E. Geiger, Inorg. Chem. 33 (1994) 373;

(c) W. Bruns, W. Kaim, E. Waldhör, M. Krejcik, Inorg. Chem. 34 (1995) 663;
(d) K.D. Demaddis, G.A. Neyhart, E.M. Kober, T.J. Meyer, J. Am. Chem. Soc. 120 (1998) 7121.
[89] M. Glöckle, W. Kaim, Angew. Chem. Int. Ed. Engl. 38 (1999) 3072.
[90] P.A.M. Williams, P.J. Aymonino, Inorg. Chim. Acta 113 (1986) L17.
[91] R.L. Blackbourn, Y. Dong, A. Lyon, J.T. Hupp, Inorg. Chem. 33 (1994) 4446.
[92] (a) J.C. Rubim, M.L.A. Temperini, P. Corio, O. Sala, A.H. Jubert, M.E. Chacon Villalba, P.J. Aymonino, J. Phys. Chem. 99 (1995) 345;
(b) P.A.M. Williams, P.J. Aymonino, Inorg. Chim. Acta 113 (1986) 37;
(c) E.H. Cutin, N.E. Katz, P.A.M. Williams, P.J. Aymonino, Transition Met. Chem. 16 (1991) 155;
(d) V. Palaniappan, R.M. Singru, U.C. Agarwala, Inorg. Chem. 27 (1988) 181.
[93] (a) I.D. Moreira, D.W. Franco, Inorg. Chem. 33 (1994) 1607;
(b) I.D. Moreira, D.W. Franco, Adv. Chem. Ser. 253 (1997) 255;
(c) I.D. Moreira, E.C. Lima, D.W. Franco, Inorg. Chim. Acta 267 (1998) 93;
(d) I.D. Moreira, J.B. de Lima, D.W. Franco, Coord. Chem. Rev. 196 (2000) 197.
[94] (a) C.L. Lin, K. Hung, A. Yeh, H.T. Tsen, C.C. Su, Inorg. Chem. 38 (1999) 411;
(b) G. Tsaur, M.C. Wu, A. Yeh, J. Chin. Chem. Soc. 41 (1994) 431;
(c) H.Y. Huang, W.J. Chen, C.C. Yang, A. Yeh, Inorg. Chem. 30 (1991) 1862;
(d) A. Yeh, A. Haim, J. Am. Chem. Soc. 107 (1985) 369.
[95] (a) S. Siddiqui, W.W. Henderson, R.E. Shepherd, Inorg. Chem. 26 (1987) 3101;
(b) W.W. Henderson, R.E. Shepherd, Inorg. Chem. 24 (1985) 2398.
[96] G.H. Lee, L. Dellaciana, A. Haim, J. Am. Chem. Soc. 111 (1989) 2535.
[97] (a) H.E. Toma, J. Coord. Chem. 7 (1978) 231;
(b) H.E. Toma, A.B.P. Lever, Inorg. Chem. 25 (1986) 176.
[98] (a) J.M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH, Weinheim, 1995;
(b) in: J.P. Sauvage, C. Dietrich-Buchecker (Eds.), Molecular Catenanes, Rotaxanes, and Knots, Wiley–VCH, Weinheim, 1999;
(c) R.S. Wylie, D.H. Macartney, J. Am. Chem. Soc. 114 (1992) 3136;
(d) D.H. Macartney, C.A. Waddling, Inorg. Chem. 33 (1994) 5912;
(e) A.P. Lyon, D.H. Macartney, Inorg. Chem. 36 (1997) 729;
(f) A.J. Baer, D.H. Macartney, Inorg. Chem. 39 (2000) 1410.
[99] (a) R. Glauser, U. Hauser, F. Herren, A. Ludi, P. Roder, E. Scmidt, H. Siegenthaler, F. Wenk, J. Am. Chem. Soc. 95 (1973) 8457;
(b) K.Z. Ismail, M.S. Tunuli, S.G. Weber, Inorg. Chem. 26 (1987) 1555.
[100] (a) D.E. Khostariya, A.M. Kjaer, T.A. Marsagishvili, J. Ulstrup, J. Phys. Chem. 95 (1991) 8798;
(b) D.E. Khostariya, A.M. Kjaer, T.A. Marsagishvili, J. Ulstrup, J. Phys. Chem. 96 (1992) 4154;
(c) R. Billing, D.E. Khostariya, Inorg. Chem. 33 (1994) 4038;
(d) R. Billing, Coord. Chem. Rev. 159 (1997) 257;
(e) D.E. Khostariya, R. Billing, M. Ackermann, R. van Eldik, J. Chem. Soc. Faraday Trans. 91 (1995) 1625.
[101] (a) A. Vogler, A.H. Osman, H. Kunkely, Inorg. Chem. 26 (1987) 2337;
(b) A. Vogler, H. Kunkely, Ber. Bunsen-Ges. Phys. Chem. 79 (1975) 301.
[102] (a) A. Burewicz, A. Haim, Inorg. Chem. 27 (1988) 1611;
(b) P. Forlano, L.M. Baraldo, J.A. Olabe, C.O. Della Vedova, Inorg. Chim. Acta 223 (1994) 37.
[103] D.R. do Carmo, Y. Gushikem, D.W. Franco, in: J.B. Blitz, C.B. Little (Eds.), Fundamental and Applied Aspects of Chemically Modified Surfaces, The Royal Society of Chemistry, London, 1999.
[104] F. Sanchez-Burgos, M. Galan, M. Dominguez, P. Perez-Tejeda, New J. Chem. (1998) 907.
[105] (a) D. Chatterjee, Polyhedron 18 (1999) 1767;
(b) P. Forlano, F.D. Cukiernik, O. Poizat, J.A. Olabe, J. Chem. Soc. Dalton Trans. (1997) 1595;
(c) D.E. Khostariya, H.C. Bajaj, P.A. Tregloan, R. van Eldik, J. Phys. Chem. A 104 (2000) 5535;
(d) D. Chatterjee, H.C. Bajaj, Inorg. Chem. 32 (1993) 4049.
[106] (a) P.V. Bernhardt, M. Martinez, Inorg. Chem. 38 (1999) 424;
(b) P.V. Bernhardt, B.P. Macpherson, M. Martínez, Inorg. Chem. 39 (2000) 5203.
[107] B.W. Pfennig, J.V. Lockard, A.B. Bocarsly, Inorg. Chem. 38 (1999) 2941.

[108] (a) G. Stochel, R. van Eldik, H. Kunkely, A. Vogler, Inorg. Chem. 28 (1989) 4314;
(b) H. Kunkely, A. Vogler, Z. Naturforsch. Teil B 51 (1996) 245.
[109] E.H. Cutin, N.E. Katz, Polyhedron 12 (1993) 955.
[110] G.N. Richardson, U. Brand, H. Vahrenkamp, Inorg. Chem. 38 (1999) 3070.
[111] B.W. Pfennig, J.L. Cohen, I. Sosnowski, N.M. Novotny, D.M. Ho, Inorg. Chem. 38 (1999) 606.
[112] (a) H. Kunkely, A. Vogler, Inorg. Chim. Acta 209 (1993) 93;
(b) H. Kunkely, V. Pawlowski, A. Vogler, Inorg. Chim. Acta 225 (1994) 327.
[113] H. Kunkely, A. Vogler, Inorg. Chim. Acta 254 (1997) 195.
[114] (a) B.W. Pfennig, A.B. Bocarsly, J. Phys. Chem. 96 (1992) 226;
(b) Y. Wu, C. Cohran, A.B. Bocarsly, Inorg. Chim. Acta 226 (1994) 251;
(c) D.F. Watson, A.B. Bocarsly, Coord. Chem. Rev. 211 (2001) 177.
[115] B.W. Pfennig, V.A. Fritchman, K.A. Hayman, Inorg. Chem. 40 (2001) 255.
[116] (a) Y. Wu, B.W. Pfennig, A.B. Bocarsly, Inorg. Chem. 34 (1995) 4262;
(b) B.W. Pfennig, A.B. Bocarsly, Comments Inorg. Chem. 13 (1992) 251.
[117] B.W. Pfennig, J.K. Goertz, D.W. Wolff, J.L. Cohen, Inorg. Chem. 37 (1998) 2608.
[118] (a) S.K. Doorn, R.L. Blackbourn, C.S. Johnson, J.T. Hupp, Electrochim. Acta 36 (1991) 1775;
(b) S.K. Doorn, J.T. Hupp, J. Am. Chem. Soc. 111 (1989) 1142;
(c) S.K. Doorn, J.T. Hupp, J. Am. Chem. Soc. 111 (1989) 4704;
(d) G.C. Walker, P.F. Barbara, S.K. Doorn, Y. Dong, J.T. Hupp, J. Phys. Chem. 95 (1991) 5712.
[119] R.L. Blackbourn, C.S. Johnson, J.T. Hupp, J. Am. Chem. Soc. 113 (1991) 1060.
[120] H. Lu, J.T. Hupp, J. Am. Chem. Soc. 115 (1993) 4927.
[121] Y. Dong, J.T. Hupp, Inorg. Chem. 31 (1992) 3170.
[122] C. Wang, B.K. Mohney, R.D. Williams, V. Petrov, J.T. Hupp, G.C. Walker, J. Am. Chem. Soc. 120 (1998) 5848.
[123] (a) L. Karki, J.T. Hupp, J. Am. Chem. Soc. 119 (1997) 4070;
(b) F.W. Vance, L. Karki, J.K. Reigle, J.T. Hupp, M.A. Ratner, J. Phys. Chem. A 102 (1998) 8320;
(c) G.U. Bublitz, W.M. Laidlaw, R.G. Denning, S.G. Boxer, J. Am. Chem. Soc. 120 (1998) 6068.
[124] M.A. Watzy, J.F. Endicott, Z. Song, Y. Lei, A.V. Macatangay, Inorg. Chem. 35 (1996) 3463.
[125] G.B. Richter-Addo, P. Legzdins, Metal Nitrosyls, Oxford University Press, New York, 1992.
[126] M. Feelisch, J.S. Stamler (Eds.), Methods in Nitric Oxide Research, Wiley, Chichester, 1996.
[127] J.H. Swinehart, Coord. Chem. Rev. 2 (1967) 385.
[128] (a) A.R. Butler, C. Glidewell, Chem. Soc. Rev. 16 (1987) 361;
(b) M.J. Clarke, J.B. Gaul, Struct. Bond. (Berlin) 81 (1993) 147.
[129] F. Bottomley, F. Grein, J. Chem. Soc. Dalton Trans. (1980) 1359.
[130] J. Masek, E. Maslova, Collect. Czech. Chem. Commun. 39 (1974) 2141.
[131] R.P. Cheney, M.G. Simic, M.Z. Hoffman, I.A. Taub, K.D. Asmus, Inorg. Chem. 16 (1977) 2187.
[132] (a) J.D.W. van Voorst, P. Hemmerich, J. Chem. Phys. 45 (1966) 3914;
(b) R. Nast, J. Schmidt, Angew. Chem. Int. Ed. Engl. 8 (1969) 383.
[133] (a) V. Sampath, J.T. Hazzard, L.M. Avery, FASEB J. 4 (1990) A1773;
(b) X.J. Zhao, V. Sampath, W.S. Caughey, FASEB J. 7 (1993) A1115.
[134] J. Schmidt, H. Köhr, W.I. Dorn, J. Köpf, Inorg. Nucl. Chem. Lett. 10 (1974) 55.
[135] J. Fiedler, Collect. Czech. Chem. Commun. 58 (1993) 461.
[136] (a) D.S. Bohle, C.H. Hung, J. Am. Chem. Soc. 117 (1995) 9584;
(b) L.E. Laverman, M. Hoshino, P.C. Ford, J. Am. Chem. Soc. 119 (1997) 12663;
(c) X.D. Ding, A. Weischel, J.F. Andersen, T.K. Shokireva, C. Balfour, A.J. Pierik, B.A. Averill, W.R. Montfort, F.A. Walker, J. Am. Chem. Soc. 121 (1999) 128.
[137] F. Bottomley, in: P.S. Braterman (Ed.), Reactions of Coordinated Ligands, vol. 2, Plenum, New York, 1985, p. 115.
[138] J.H. Swinehart, P.A. Rock, Inorg. Chem. 5 (1966) 573.
[139] F. Bottomley, Acc. Chem. Res. 11 (1978) 158.
[140] P. Forlano, A.R. Parise, J.A. Olabe, Inorg. Chem. 37 (1998) 6406.
[141] (a) P.A. Rock, J.H. Swinehart, Inorg. Chem. 5 (1966) 1078;
(b) M.D. Johnson, R.G. Wilkins, Inorg. Chem. 23 (1984) 231.

[142] (a) P.J. Morando, E.B. Borghi, L.M. de Steingart, M.A. Blesa, J. Chem. Soc. Dalton Trans. (1981) 435;
(b) A.R. Butler, A.M. Calsy-Harrison, C. Glidewell, Polyhedron 7 (1988) 1197.
[143] K. Szacilowski, G. Stochel, A. Stasicka, H. Kisch, New J. Chem. 21 (1997) 893.
[144] K. Szacilowski, J. Oszajca, G. Stochel, Z. Stasicka, J. Chem. Soc. Dalton Trans. (1999) 2353.
[145] M.J. Akhtar, F.T. Bonner, A. Borer, I. Cooke, M. Hughes, Inorg. Chem. 26 (1987) 4379.
[146] A.A. Chevalier, L.A. Gentil, M.M. Gutierrez, V.R. Amorebieta, J.A. Olabe, J. Am. Chem. Soc. 122 (2000) 11238.
[147] D. Stanbury, Prog. Inorg. Chem. 47 (1998) 511.
[148] (a) F. Doctorovich, N. Escola, C. Trapani, D.A. Estrin, M.C. Gonzalez Lebrero, A.G. Turjanski, Organometallics 19 (2000) 3810;
(b) F. Doctorovich, C. Trapani, Tetrahedron Lett. 40 (1999) 4635.
[149] I.A. Funai, M.A. Blesa, J.A. Olabe, Polyhedron 8 (1989) 419.
[150] V.G. Povse, J.A. Olabe, in preparation.
[151] (a) I. Maciejowska, A. Stasicka, G. Stochel, R. van Eldik, J. Chem. Soc. Dalton Trans. (1999) 3643;
(b) A. Katho, M.T. Beck, Inorg. Chim. Acta 154 (1988) 99;
(c) L. Dozsa, V. Kormos, M.T. Beck, Inorg. Chim. Acta 82 (1984) 69.
[152] (a) S.K. Wolfe, C. Andrade, J.H. Swinehart, Inorg. Chem. 13 (1974) 2567;
(b) I. Banyai, L. Dozsa, M.T. Beck, G. Gyemant, J. Coord. Chem. 37 (1996) 257.
[153] (a) A. Bencini, I. Ciofini, C.A. Daul, A. Ferretti, J. Am. Chem. Soc. 121 (1999) 11418;
(b) A. Ferretti, R. Improta, A. Lami, G. Villani, J. Phys. Chem. A 104 (2000) 9591;
(c) P.N. Schatz, in: E.I. Solomon, A.B.P. Lever (Eds.), Inorganic Electronic Structure and Spectroscopy, vol. II, Wiley, New York, 1999, p. 175.