# Mixed-valence cyano-bridged complexes containing $[M^{II}(CN)_6]^{4-}$ (M = Fe, Ru or Os) and $[Ru^{III}(edta)]^{-}$ (edta = ethylenedinitrilotetraacetate): synthesis, spectroscopic and kinetic characterization

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The mixed-valence, cyanide-bridged complexes $K_5[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]$ (M = Fe, Ru or Os; edta = ethylenedinitrilotetraacetate) were prepared by mixing the hexacyanide species with a solution of $[Ru(edta)(H_2O)]^-$. The complexes were characterized by chemical analysis, IR, Raman and VIS/NIR spectroscopy. They show an intense band in the 600–1000 nm region (dependent on M), associated with an intervalence (i.v.) transition from $M^{II}$ to $Ru^{III}$, as confirmed by electrochemical measurements of the redox potentials at both metal centres. The equilibrium constants for the formation of the binuclear species were similar for the three complexes, $(1.5 \pm 0.1) \times 10^3$ dm$^3$ mol$^{-1}$. These complexes were the predominant species in excess of free hexacyanide, but tri- and poly-nuclear species were obtained by increasing the concentration of $[Ru(edta)(H_2O)]^-$, as demonstrated through the electronic spectral shifts of the i.v. band and the redox potentials of the $M^{III/II}$ couples, which were indicative of Ru(edta) co-ordination to the exposed nitrogen ends of cyanides in the precursor binuclear complexes. The kinetics of formation and dissociation of the binuclear complexes were also measured, with $k_f$ and $k_d$ showing values nearly independent of $M^{II}$ (*ca.* 10 dm$^3$ mol$^{-1}$ s$^{-1}$ and $8 \times 10^{-3}$ s$^{-1}$ respectively, at 25.0 °C, $I = 0.1$ mol dm$^{-3}$), suggesting the onset of associative mechanisms. The Hush model showed the three complexes to adopt a valence-trapped behaviour, with a moderate coupling between the metal centres.

Cyano-bridged mixed-valence compounds have been known for a long time, as Prussian Blue type polymeric solids, but the interest in discrete complexes of well defined nuclearity (bi- and tri-nuclear species) has emerged more recently.[1] Cyanide provides a substantial amount of metal–metal electronic coupling, as shown by detailed electrochemical and spectroscopic studies.[1–7] Potential applications in the field of solar energy conversion and molecular electronics were proposed, associated with the optical charge-transfer properties. Cyanide complexes can be attached to surfaces and derivatized onto electrodes, providing new insights into electro-chromic and -catalytic phenomena, linked to the build-up of display and memory devices and sensors.[8] More recently, bimetallic complexes of this family were presented as promising chromophoric materials with large second-order electric susceptibilities, relevant to the construction of new non-linear optical devices.[9]

The $Ru^{II/III}$(edta) pentadentate moiety (edta = ethylenedinitrilotetraacetate) has been useful for systematic studies in co-ordination chemistry, due to the easy redox interconversion of the $d^6$–$d^5$ low-spin configurations and the large variety of ligands able to bind to ruthenium.[10] Like the pentacyanide species, this moiety can also be attached to electrodes.[11] Recently, the co-ordination of $[Fe(CN)_6]^{4-}$ to $[Ru^{III}(edta)(H_2O)]^-$ has been achieved, thus characterizing the first member of the $[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]^{5-}$ series.[12] We have extended this preparative work to the ruthenium and osmium analogues and present a spectroscopic and electrochemical characterization of the mixed-valence species, together with equilibrium and kinetic studies of the formation and dissociation reactions. The onset of bi-, tri-nuclear and probably higher oligomers is highlighted.

## Experimental

### Materials

The complexes $K[Ru^{III}(Hedta)Cl]\cdot 2H_2O$ and $[Ru^{III}(Hedta)(H_2O)]\cdot 2H_2O$ were prepared as described.[13] By dissolving any of them in aqueous solution, pH 5–6, the $[Ru^{III}(edta)(H_2O)]^-$ ion becomes the predominant species. The salt $K_4[Os(CN)_6]$ was prepared using $OsO_4$ (Johnson-Matthey) as a starting reagent;[14] $K_4[Ru(CN)_6]$ (Johnson-Matthey) was used as received and $K_4[Fe(CN)_6]$ (Merck) was previously recrystallized from water. All other chemicals were AR grade and water was doubly distilled before use.

### Synthesis of $K_5[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]\cdot nH_2O$

The complexes were prepared as described earlier for the iron compound,[12] by mixing solutions of $K[Ru(Hedta)Cl]\cdot 2H_2O$ or $[Ru(Hedta)(H_2O)]\cdot 3H_2O$ and the corresponding $K_4[M(CN)_6]$ {Found: C, 22.0; H, 2.3; N, 13.2. Calc. for $K_5[(NC)_5Fe^{II}{-}CN{-}Ru^{III}(edta)]\cdot 4H_2O$: C, 22.1; H, 2.3; N, 12.9. Found: C, 20.4; H, 2.4; N, 11.75. $K_5[(NC)_5Ru^{II}{-}CN{-}Ru^{III}(edta)]\cdot 6H_2O$ requires C, 20.25; H, 2.55; N, 11.8. Found: C, 18.95; H, 2.3; N, 10.95. $K_5[(NC)_5Os^{II}{-}CN{-}Ru^{III}(edta)]\cdot 5H_2O$ requires C, 18.75; H, 2.15; N, 10.95%}.

### Instrumentation and techniques

Microanalyses were carried out in a Carlo Erba elemental analyser model EA 1108, at INQUIMAE. Infrared spectra were measured on a Nicolet 1508 FTIR spectrophotometer, in KBr pellets, UV/VIS/NIR spectra in aqueous solutions with a Hewlett-Packard 8452A diode-array instrument or with a Shimadzu UV-3101 PC spectrophotometer. The Raman-resonance experiments were performed at LASIR-CNRS, with a Dilor RTI 30 spectrometer, equipped with a triple monochromator, as

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**Table 1** Intervalence band results and formation equilibrium constants for compounds $[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]^{5-}$ **I** and $[(edta)Ru^{III}{-}NC{-}M^{II}(CN)_4{-}CN{-}Ru^{III}(edta)]^{6-}$ **II**

| M | $\lambda_{max}$/nm ($\varepsilon/10^{-3}$ dm$^3$ mol$^{-1}$ cm$^{-1}$) | | | $10^{-3}$ $K_{eq.1}$[a]/ dm$^3$ mol$^{-1}$ | $10^{-3}$ $K_{eq.2}$[b]/ dm$^3$ mol$^{-1}$ |
|---|---|---|---|---|---|
| Fe | 940 (2.7)[c] | 969 ± 10 (3.20 ± 0.35)[d] | 801 ± 7 (2.60 ± 0.3)[e] | 1.4 ± 0.2 | 2.30 ± 0.25 |
| Ru | 674 (2.8)[c] | 678 ± 6 (2.70 ± 0.3)[d] | 615 ± 5 (2.50 ± 0.25)[e] | 1.5 ± 0.2 | 3.00 ± 0.30 |
| Os | 762 (2.9)[c] | 792 ± 8 (3.40 ± 0.34)[d] | 693 ± 4 (3.70 ± 0.40)[e] | 1.6 ± 0.2 | 2.80 ± 0.30 |

[a] Corresponds to equation (1). [b] Corresponds to equation (2). [c] Equilibrated solutions obtained from the solids. [d] Obtained by factor analysis of a set of solutions, $I = 0.1$ mol dm$^{-3}$ (KCl), pH 5.5; 25.0 °C for compound **I**. Method of calculation: SPECFIT. [e] Obtained for compound **II** as in footnote *d*.

well as with a micro-Raman Dilor XY instrument containing a CCD Wright detector refrigerated with liquid $N_2$. The measurements were carried out in aqueous solutions, after reaction of the mononuclear species at different concentrations, pH 5.0 (buffer acetic acid–acetate), by using $CH_3CN$ (0.5%) as a reference for intensity. Powder spectra were recorded on the XY spectrometer in the micro-configuration.

The electrochemical experiments (cyclic voltammetry, CV) in aqueous solution were performed with a PAR model 273 potentiostat, using KCl as supporting electrolyte. A vitreous carbon disc, a Ag–AgCl (saturated KCl) and a platinum net were used as working, reference and counter electrodes, respectively.

For studying the solution equilibria after mixing the mononuclear reactants two spectrophotometric methods were employed, namely the continuous variation and molar-ratio techniques.[15] The conditions were pH 5.5, $I = 0.1$ mol dm$^{-3}$ (KCl), 25.0 °C. An adequate characterization of the different species present in the solution equilibria was achieved by using the SPECFIT‡ software package; this is a global least-squares fitting routine for equilibrium and kinetics studies which uses factor-analysis decomposition methods.[16] This program also allows one to obtain the spectra of the individual species present in the equilibrium. The concentration of $[M(CN)_6]^{4-}$ was kept constant ($3 \times 10^{-4}$ mol dm$^{-3}$) and that of $[Ru^{III}(edta)(H_2O)]^-$ was varied in the range $3 \times 10^{-5}$–$3 \times 10^{-3}$ mol dm$^{-3}$. For diluted samples, cells of different path lengths were used. The substitution kinetic experiments were performed spectrophotometrically. In the case of the formation reaction of the mixed-valence complexes a PQ/SF-5B HI-TECH stopped-flow instrument was used, interfaced with a laboratory-made data-acquisition system. Rate constants, $k_{obs}$, were obtained under pseudo-first-order conditions, either in excess of $[M(CN)_6]^{4-}$ or $[Ru^{III}(edta)(H_2O)]^-$. The minor species was at $10^{-4}$ mol dm$^{-3}$ and the concentration of the other was varied in the range $2.5 \times 10^{-3}$–$12.5 \times 10^{-3}$ mol dm$^{-3}$. The experiments were done at pH 5.5 ($10^{-2}$ mol dm$^{-3}$ acetic acid–acetate buffer), $I = 0.5$ mol dm$^{-3}$ (KCl), 25.0 °C, by measuring the increase at the maximum of the intense VIS/NIR bands of the binuclear complexes. The formation rate constants, $k_f$, were calculated from the slope of plots of $k_{obs}$ against the concentration of the reactant in excess. To obtain the dissociation kinetic rate constants, $k_d$, of the mixed-valence complexes, a rapid kinetics accessory (Applied Photophysics RX 1000) was attached to the diode-array spectrophotometer. By mixing the reactants under equimolar conditions $\{[M(CN)_6{}^{4-}] = [Ru^{III}(edta)(H_2O)^-] = 2 \times 10^{-4}$ mol dm$^{-3}\}$ the complete spectra were scanned successively at increasing times. Values of $k_f$ and $k_d$ were calculated using SPECFIT. The factorized data were fitted using an adequate model which takes into account both the formation of bi- and tri-nuclear species and the spectra obtained from the equilibrium experiments. The solution of the differential equations was achieved using a numerical integration (Bülirsh–Stoer). The fit was improved by using a Marquardt iteration procedure. We estimated the constants as the dispersion in the values obtained from the fitting of several experiments.

## Results and Discussion

### (a) Spectral and electrochemical characterization of the mixed-valence complexes

On mixing a solution of each of the $[M(CN)_6]^{4-}$ ions (M = Fe, Ru or Os) with $[Ru^{III}(edta)(H_2O)]^-$ an intense band appears between 600 and 1000 nm, depending on M (Table 1). As the spectra of the reactants are featureless in that region, and considering previous evidence with the iron binuclear complex[12] and the spectral shifts observed upon changing the $[M(CN)_6]^{4-}$ ion, we conclude that mixed-valence species are formed according to equation (1). Several pieces of evidence (see below) show

$$[M^{II}(CN)_6]^{4-} + [Ru^{III}(edta)(H_2O)]^- \rightleftharpoons \underset{\textbf{I}}{[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]^{5-}} + H_2O \quad (1)$$

that the solution equilibria contain a mixture of **I** and the trinuclear complex, which forms according to equation (2). The

$$[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]^{5-} + [Ru^{III}(edta)(H_2O)]^- \rightleftharpoons \underset{\textbf{II}}{[(edta)Ru^{III}{-}NC{-}M^{II}(CN)_4{-}CN{-}Ru^{III}(edta)]^{6-}} + H_2O \quad (2)$$

molar-ratio procedure was applied to the ruthenium cyanide compound. A plot of absorbance against the ratio $r = [Ru(edta)(H_2O)^-]:[Ru(CN)_6{}^{4-}]$ shows three different linear regions. The first two lines cross at $r \approx 1$ while a second cross-point appears at $r = 2$. On the other hand, the continuous-variation method also exhibits a flat maximum for $r' = [Ru(CN)_6{}^{4-}]:\{[Ru(edta)(H_2O)^-] + [Ru(CN)_6{}^{4-}]\} = 0.3$–$0.5:1$. Both methods indicate the formation of bi- and tri-nuclear species. In order to obtain quantitative information (not accessible in a straightforward way through both previous approaches in the presence of coupled equilibria), we used factor-analysis procedures with the compounds of Fe, Ru and Os. The equilibrium constants thus obtained for equations (1) and (2) are shown in Table 1, which also includes the spectral results. From the above analysis it can be seen that the binuclear species is predominant at low values of $[Ru(edta)(H_2O)]^-:[M(CN)_6]^{4-}$ (*ca.* 0.1 : 1), while higher values of the same quotient (*ca.* 10 : 1) favour the formation of trinuclear species. Also, for a given quotient, the more concentrated solutions favour even more the formation of trimers.

The electronic spectral results support this explanation. The trinuclear species containing $[Ru(CN)_6]^{4-}$ as the central moiety shows intervalence absorption at 615 nm; this is significantly shifted to the blue compared to that of the binuclear ion (678 nm); the co-ordination of $Ru^{III}$(edta) to the exposed terminal cyanide induces stabilization of the highest occupied molecular orbital (HOMO) and thus the charge-transfer transition shifts to higher energy, as observed upon protonation of cyanides.[17]

From analytical data obtained for the solid compounds, we infer that they contain the corresponding binuclear species.

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‡ Provided by Robert A. Binstead of Spectrum Software Associates, Chapel Hill, NC.

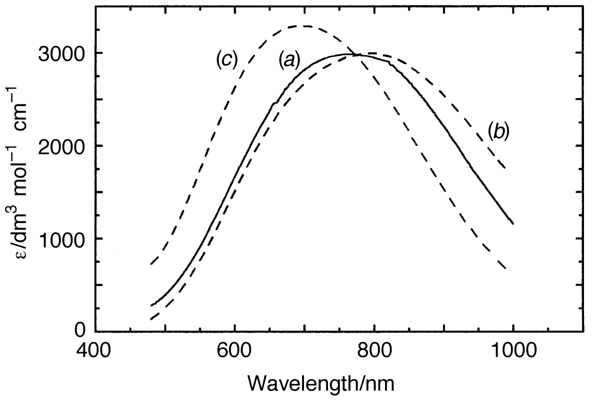

**Fig. 1** The VIS/NIR spectra: ($a$, ——) $K_5[(NC)_5Os^{II}–CN–Ru^{III}(edta)]$ solid in water; ($b$ and $c$, – – –) **I** and **II** respectively, calculated by factor analysis

Table 1 shows that the absorption maxima obtained upon dissolution of the solids are similar to the values calculated by factor analysis for the binuclear species; however, the shift of the maximum suggests that some trinuclear species exists in the equilibrium mixture (see Fig. 1).

From the IR spectra of the solids, a group of bands in the 600–1600 cm$^{-1}$ region appear characteristic of the $Ru^{III}$(edta) moiety, and bands associated with water are seen at *ca.* 3440 and 1610 cm$^{-1}$ (the latter also relate to carboxylate groups). In the C–N stretching region the most intense peaks are found at 2060, 2068 and 2060 cm$^{-1}$ for the cyanide compounds of Fe, Ru and Os respectively. In each case these values are shifted to higher energies by *ca.* 30 cm$^{-1}$ compared to those of the potassium salts of the corresponding mononuclear anions.[18] This is consistent with the electron-withdrawing ability of the $Ru^{III}$(edta) moiety, which diminishes the $\pi^*$(CN) electron density at cyanides. Finally, a very weak shoulder at *ca.* 2100 cm$^{-1}$ for the three binuclear compounds suggests that bridging C–N stretching is present.

Raman spectroscopy clearly shows the presence of a bridging cyanide. Indeed, equimolar mixtures of $[Ru(CN)_6]^{4-}$ and $[Ru(edta)]^-$ exhibit a third band at 2121 cm$^{-1}$, in addition to the bands at 2070 and 2108 cm$^{-1}$ also observed in the spectrum of $[Ru(CN)_6]^{4-}$ {$[Ru(edta)]^-$ is silent in this spectral region}. The band at 2121 cm$^{-1}$ is enhanced by resonance in the spectrum excited at 632.8 nm relative to the 457.9 and 514.5 nm spectra (see Fig. 2), as expected for the stretching of a $CN^-$ bridge ($\nu_{CN}{}^{br}$) in a dimer where the metal–metal charge-transfer (m.m.c.t.) band appears at 615 nm. Consistently, the bands at 2070 and 2108 cm$^{-1}$ corresponding to the stretching of the terminal cyanides do not show this resonance effect. Solid (powder) samples exhibit the same behaviour, with $\nu_{CN}{}^{br}$ at 2127 cm$^{-1}$ being red-enhanced; there are minor differences in the position of the non-enhanced bands between solid and solution spectra.

Similar results were obtained for the iron and osmium derivatives: $\nu_{CN}{}^{br}$ at 2103 (Fe) or 2122 cm$^{-1}$ (Os) is in resonance with the corresponding intervalence absorptions. Two additional bands at 2056, 2092 (Fe) and 2063, 2114 cm$^{-1}$ (Os) were also observed, similar to those found for the respective monomers. These bands (as well as those at 2070 and 2108 cm$^{-1}$ for the ruthenium derivative) certainly correspond to the stretching of equatorial ($\nu_{CN}{}^{eq}$) and axial ($\nu_{CN}{}^{ax}$) cyanides respectively. Higher-frequency values for axial than for equatorial cyanides were found for several $[M^{II}(CN)_5L]^{n-}$ species with a stronger $\pi$ acceptor L than cyanide.[19]

An increase in the frequency of $\nu^{br}$ compared with the $\nu^{eq}$ and $\nu^{ax}$ stretching modes for $CN^-$ has also been observed for several closely related cyanide-bridged binuclear complexes.[20–22] The same was found for Prussian Blue type compounds[23] and for $[M(CN)_6]^{4-}$ adsorbed onto $TiO_2$ surfaces (where a $M^{II}–CN–Ti^{IV}$ unit is likely formed).[24] With other $L_nM^{II}$ donor fragments, however, a decrease in $\nu^{br}$ has been detected when cyanide bridges to a Lewis-acid $M^{III}L'_n$ moiety.[2] A discussion on the reasons for upward or downward shifts of $\nu_{CN}$ compared to terminal ones can be found elsewhere.[2,3,20]

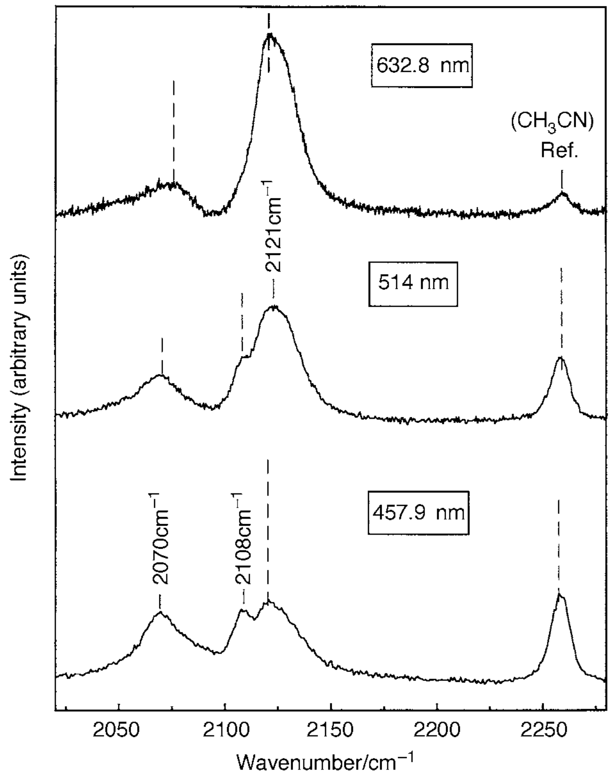

**Fig. 2** Raman spectra of $[(NC)_5Ru^{II}–NC–Ru^{III}(edta)]^{5-}$ in water solution, pH 5.0 (acetic acid–acetate buffer), 0.5% $CH_3CN$ at three different excitation wavelengths

As stated above, non-negligible amounts of trimer **II** could be present under these experimental conditions. In order to assess whether or not our spectra were spoiled by the presence of trimers, we compared the Raman spectra of solutions spanning a wide range of $[Ru(CN)_6{}^{4-}]:[Ru(edta)^-]$ concentration ratios ($R$). Solutions containing either dimer **I** or $[Ru(CN)_6]^{4-}$ monomer as the predominant species ($R < 1$) confirm that the spectra presented in Fig. 2 correspond to the dimeric species. The frequency $\nu_{CN}{}^{br}$ starts to shift to higher values for $R > 1.5$, reaching 2149 cm$^{-1}$ for $R = 8$. This shift is continuous with $R$, suggesting that not only trimers but also higher oligomers might exist if the concentration of $[Ru(edta)]^-$ is sufficiently high: the greater the number of $[R(edta)]^-$ units co-ordinated to a central $[Ru(CN)_6]^{4-}$, the lesser the $\pi^*$(CN) electron density at each of the bridging cyanides. This hypothesis also finds support in the electrochemical results (see below).

The cyclic voltammetric results show two well defined reversible waves for the three binuclear complexes. We assign the peaks at the more positive potentials to the reduction processes at the M centre [Table 2, equation (3)]. The values are shifted

$$[(NC)_5M^{III}–CN–Ru^{III}(edta)]^{4-} + e^- \rightleftharpoons [(NC)_5M^{II}–CN–Ru^{III}(edta)]^{5-} \quad (3)$$

positively by *ca.* 30 mV compared to the values for the corresponding $[M^{III/II}(CN)_6]^{3/4-}$ couples, as expected from the presence of the electron-withdrawing $Ru^{III}$(edta) moiety.[28] The shift is, however, only modest compared to values of *ca.* 0.3 V obtained for the $[(NC)_5Os^{II}–CN–Ru^{III}(NH_3)_5]^-$ complex.[22] The great positive shifts in the redox potentials of the $M^{III/II}(CN)_5$ couples in these complexes could be related to the strong intermolecular (donor–acceptor) interactions between cyanide and

**Table 2** Electrochemical results for $[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]^{5-}$ **I** and theoretical parameters derived from the intervalence band (Hush model)[a]

| Parameter | M = Fe | Ru | Os |
|---|---|---|---|
| $E°(M^{III/II})$ (**I**)/V | 0.43 | 0.97 | 0.67 |
| $E°[Ru^{III/II}(edta)]$ (**I**)/V | −0.08 | 0.00 | −0.01 |
| $\Delta E°_{calc}{}^{b}/cm^{-1}$ | −2173 | −6439 | −3944 |
| $\bar{\nu}_{max}/cm^{-1}$ | 10 320 | 14 881 | 12 626 |
| $\Delta\bar{\nu}_{\frac{1}{2}}/cm^{-1}$ | 4434 (5050)[c] | 5172 (6843)[c] | 6892 (5926)[c] |
| $10^2\alpha^{2\,d}$ | 2.2 ± 0.3 | 1.5 ± 0.2 | 2.3 ± 0.3 |
| $10^{-3}H_{ab}{}^{e}/cm^{-1}$ | 1.87 ± 0.02 | 1.82 ± 0.02 | 1.78 ± 0.02 |

[a] All potentials *vs.* normal hydrogen electrode (NHE), $I = 0.1$ mol dm$^{-3}$ (KCl), 25.0 °C. [b] Corresponds to the conversion of **I** into its electronic isomer, $[(NC)_5M^{III}{-}CN{-}Ru^{II}(edta)]^{5-}$, obtained through a thermodynamic cycle, *cf.* ref. 25. [c] Calculated from $\Delta\bar{\nu}_{\frac{1}{2}} = [2310(E_{op} - \Delta E°)]^{\frac{1}{2}}$, see ref. 26; experimental with calculated values in parentheses. [d] Delocalization factor, calculated from the spectra obtained by factor analysis. The value of the distance between the metal centres was assumed to be the same as in $[(NC)_5M^{II}{-}CN{-}Ru^{III}(NH_3)_5]^-$ (ref. 27 for M = Fe; appropriate corrections were done for the compounds of Ru and Os). $E°\{[Ru(edta)(H_2O)]^{-/2-}\} = 0.010$ V. [e] Electronic coupling between metal centres.

amine ligands, which are absent when $Ru^{III}(NH_3)_5$ is replaced by $Ru^{III}$(edta). On the other hand, the values for the reduction at the $Ru^{III}$(edta) fragment [equation (4)] are little influenced

$$[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]^{5-} + e^- \rightleftharpoons [(NC)_5M^{II}{-}CN{-}Ru^{II}(edta)]^{6-} \quad (4)$$

by the metal–cyanide moiety, showing a similar value to that obtained for the mononuclear $[Ru^{III/II}(edta)(H_2O)]^{-/2-}$ complex, *ca.* 0.0 V (Table 2).

When the measurements are performed under conditions of a significant formation of tri(poly)nuclear species, the waves associated with the metal(III)–metal(II) couples show a displacement toward more positive potentials (*ca.* 250 mV). As also shown by the electronic spectral changes (see above), a positive shift is expected for the reduction potential in equation (3) when another $Ru^{III}$(edta) fragment is bound to cyanide.§

### (b) Theoretical treatment of the i.v. band

Table 2 shows the parameters obtained by application of the Hush model[26] to the intervalence band data for the three asymmetric binuclear complexes. The results for $\Delta\bar{\nu}_{\frac{1}{2}}$, $\alpha^2$ and $H_{ab}$ are consistent with those obtained for other cyanide-bridged complexes, showing a valence-trapped behaviour, with a weak-to-moderate coupling between the metal centres.[27,29,30] In contrast to the behaviour found for symmetric systems,[31] the experimental $\Delta\bar{\nu}_{\frac{1}{2}}$ values for Fe and Ru are lower than the calculated ones; this was also found for related cyanopyridine-bridged complexes.[32] The greatest value of experimental $\Delta\bar{\nu}_{\frac{1}{2}}$ for the osmium complex reflects the influence of spin–orbit coupling through the broadening of the i.v. band. If a correction for this factor is performed, a similar value to those for iron and ruthenium is found.

In addition to the previous Raman assignments, structural information was obtained from the post-resonance spectra of the dimers of Fe and Ru (excitation wavelength = 514.5 nm) according to time-dependent resonance methods.[33] The calculated values of absolute distortions, $|\Delta a|$ for the bridging, axial and equatorial modes were 0.036, 0.034, 0.012 (Fe) and 0.056, 0.038, 0.017 Å (Ru). From these bond-distortion data individual contributions to vibrational reorganization energies ($\chi_i$) were also calculated. The values are 580, 489, 240 (Fe) and 1410, 631, 482 cm$^{-1}$ (Ru) for the bridging, axial and equatorial modes respectively. These results indicate that a great part of the reorganization energy comes from modes assigned to the bridging ligand. Although Raman-based Δ values could be in error by as much as 20%, the values obtained show similar trends to those for the $[(NC)_5M^{II}{-}CN{-}Ru^{III}(NH_3)_5]^-$ (M = Fe or Ru) dimers.[21]

**Table 3** Kinetics of formation and dissociation of $[(NC)_5M^{II}{-}CN{-}Ru^{III}(edta)]^{5-}$

| M | $k_f/dm^3\ mol^{-1}\ s^{-1}$ | | | $10^3k_d/s^{-1}$ |
|---|---|---|---|---|
| Fe | 99 ± 5[a] | 18 ± 2[b] | — | — |
| Ru | 86 ± 4[a] | 17 ± 2[b] | 11 ± 4[c] | 8 ± 3[c] |
| Os | 120 ± 6[a] | 24 ± 2[b] | 10 ± 4[c] | 8 ± 3[c] |

[a] See Experimental section, $I = 0.5$ mol dm$^{-3}$. [b] Calculated values at $I = 0.1$ mol dm$^{-3}$, obtained by extrapolation, *cf.* ref. 12. [c] Obtained by factor analysis, after mixing the mononuclear reactants in equimolar conditions, $I = 0.1$ mol dm$^{-3}$.

### (c) Kinetics of formation and dissociation of binuclear complexes

The rate law for the formation of the mixed-valence complexes was as in equation (5). By working under pseudo-first-order

$$v = d(M{-}CN{-}Ru)/dt = k[M(CN)_6{}^{4-}][Ru(edta)(H_2O)^-] \quad (5)$$

conditions, either in excess of $[M(CN)_6]^{4-}$ or $[Ru(edta)(H_2O)]^-$, $k_{obs}$ values were obtained through a least-squares fitting, up to 2–3 half-lives. For longer times, deviations from the rate law were observed, suggesting the formation of polynuclear species. Table 3 shows the second-order rate constants [equation (1)] for the three binuclear complexes. The value for the iron complex is the same as previously reported,[12] similar to that for ruthenium and slightly lower than for osmium. By comparing with formation rate constants found for a variety of ligands binding to $[Ru^{III}(edta)(H_2O)]^-$,[10] it appears that the changes among the hexacyanide ligands are poorly significant. The rates of substitution of $[Ru^{III}(edta)(H_2O)]^-$ have been discussed in terms of an associative mechanism, in view of the high discrimination observed for different ligands as well as from the values of the activation parameters.[10] The nucleophilicity of ligands is expected to depend on basicity as well as on polarizability factors. As the p$K_a$ for the hexacyanide species decrease in the sense Fe (2.5) > Ru (*ca.* 2.0) ⩾ Os (1.9) ($I = 1$ mol dm$^{-3}$),[28] the similar values for Fe and Ru could arise as a consequence of a compensation of the lower basicity at Ru by the greater polarizability of the latter centre. For the osmium complex, the polarizability influence seems to be determinant for the higher rate of formation, leading to a stronger covalent bond. The $k_f$ values are reasonably similar to that found with $CH_3CN$,[10a] 30 dm$^3$ mol$^{-1}$ s$^{-1}$.

The values of the dissociation rate constants (Table 3) were very similar for the complexes of Ru and Os (that for Fe could not be measured because no instrument was available to obtain the complete successive spectra). By calculating $K_{eq}$ for reaction (1) using $k_f$ and $k_d$, similar values are obtained compared to those found through the equilibrium measurements (Table 1). The $k_d$ values for other $[Ru^{III}(edta)L]^{n-}$ complexes span a range from[10a] *ca.* $10^{-5}$ to 3.2 s$^{-1}$. The $k_d$ value for cleavage of the $Ru^{III}$(edta)–NC bond for the binuclear complexes is significantly lower than that found for $[Ru^{III}(edta)(CH_3CN)]^-$, 3.2 s$^{-1}$, probably because of the greater basicity of the hexacyanide ligands, leading to stronger covalent bonds with the $[Ru^{III}$-(edta)$]^-$ moiety.

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§ The continuous increase in the redox potential for the $[Ru^{III/II}(CN)_5]$ couple, as well as the similar shift to greater energies of the intervalence band when the relative concentration of $[Ru^{III}(edta)]^-$ increases with respect to that of $[M(CN)_6]^{4-}$, suggests that equations (1) and (2) describe the behaviour of the solutions when the concentrations of both mononuclear species are of comparable magnitude, with only a moderate excess of either. For high $[Ru^{III}(edta)^-]$, compounds of higher nuclearity seem to be formed through co-ordination to the exposed cyanides.

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## References

1 F. Scandola, R. Argazzi, C. A. Bignozzi, C. Chiorboli, M. T. Indelli and M. A. Rampi, *Coord. Chem. Rev.*, 1993, **125**, 283.
2 C. A. Bignozzi, R. Argazzi, J. R. Schoonover, K. C. Gordon, R. B. Dyer and F. Scandola, *Inorg. Chem.*, 1992, **31**, 5260.
3 M. A. Watzky, J. F. Endicott, X. Song, Y. Lei and A. Macatangay, *Inorg. Chem.*, 1996, **35**, 3463.
4 A. Vogler, A. H. Osman and H. Kunkely, *Inorg. Chem.*, 1987, **26**, 2337.
5 A. Vogler, A. H. Osman and H. Kunkely, *Coord. Chem. Rev.*, 1985, **64**, 159.
6 S. K. Doorn, R. B. Dyer, P. O. Stontland and W. H. Woodruff, *J. Am. Chem. Soc.*, 1993, **115**, 6398.
7 J. R. Schoonover, C. J. Timpson, T. J. Meyer and C. A. Bignozzi, *Inorg. Chem.*, 1992, **31**, 3185; J. R. Schoonover, K. C. Gordon, R. Argazzi, W. C. Woodruff, K. A. Peterson, C. A. Bignozzi, R. B. Dyer and T. J. Meyer, *J. Am. Chem. Soc.*, 1993, **115**, 10 996; B. J. Coe, T. J. Meyer and P. S. White, *Inorg. Chem.*, 1995, **34**, 3600.
8 Y. Wu, B. W. Pfenning, A. B. Bocarsly and E. P. Vicenzi, *Inorg. Chem.*, 1995, **34**, 4262; D. Rong, H. G. Hong, Y. I. Kim, J. S. Krueger, J. E. Mayer and T. E. Mallouk, *Coord. Chem. Rev.*, 1990, **97**, 237; K. Itaya, I. Uchida and V. D. Neff, *Acc. Chem. Res.*, 1986, **19**, 162.
9 W. M. Laidlaw, R. G. Denning, T. Verbiest, E. Chauchard and A. Persoons, *Nature* (*London*), 1993, **363**, 58.
10 (*a*) T. Matsubara and C. Creutz, *Inorg. Chem.*, 1979, **18**, 1956; (*b*) H. C. Bajaj and R. van Eldik, *Inorg. Chem.*, 1988, **27**, 4052; (*c*) H. E. Toma, P. S. Santos, M. P. D. Mattioli and L. A. Oliveira, *Polyhedron*, 1987, **6**, 603.
11 N. Oyama and F. C. Anson, *J. Am. Chem. Soc.*, 1979, **101**, 1634; 3450.
12 D. Chatterjee, H. C. Bajaj and A. Das, *Inorg. Chem.*, 1993, **32**, 4049.
13 A. A. Diamantis and J. V. Dubrawsky, *Inorg. Chem.*, 1981, **20**, 1142; H. Okuno, M. Mukaida and T. Ishimori, *Nippon Kagaku Zasshi*, 1965, **86**, 56.
14 L. M. Baraldo, M. S. Bessega, G. E. Rigotti and J. A. Olabe, *Inorg. Chem.*, 1994, **33**, 5890.
15 C. N. Reilley and D. T. Sawyer, *Experiments for Instrumental Methods*, McGraw-Hill, New York, 1961, pp. 176–184.
16 E. R. Malinowski, *Factor Analysis in Chemistry*, Wiley-Interscience, New York, 2nd edn., 1991; A. R. Parise, S. Pollak, L. D. Slep and J. A. Olabe, *An. Asoc. Quim. Argent.*, 1995, **83**, 211.
17 H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.
18 Y. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1962, **18**, 101.
19 G. Paliani, A. Poletti and A. Santucci, *J. Mol. Struct.*, 1971, **8**, 63; L. D. Slep, L. M. Baraldo and J. A. Olabe, *Inorg. Chem.*, 1996, **35**, 6327.
20 R. E. Hester and E. M. Nour, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 939.
21 S. K. Doorn and J. T. Hupp, *J. Am. Chem. Soc.*, 1989, **11**, 1142; G. C. Walker, P. F. Barbara, S. K. Doorn, Y. Dong and J. T. Hupp, *J. Phys. Chem.*, 1991, **95**, 5712.
22 P. Forlano, L. M. Baraldo, J. A. Olabe and C. O. Della Védova, *Inorg. Chim. Acta*, 1994, **223**, 37.
23 A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, New York, 1976, ch. 7.
24 R. L. Blackbourn, S. K. Doorn, C. S. Johnson and J. T. Hupp, *J. Am. Chem. Soc.*, 1991, **113**, 1060.
25 H. Huang, W. Chen, C. Yang and A. Yeh, *Inorg. Chem.*, 1991, **30**, 1862.
26 N. S. Hush, *Prog. Inorg. Chem.*, 1967, **8**, 391.
27 A. Burewicz and A. Haim, *Inorg. Chem.*, 1988, **27**, 1611.
28 D. M. Macartney, *Inorg. Chem.*, 1991, **30**, 3337.
29 A. Vogler, A. H. Osman and H. Kunkely, *Coord. Chem. Rev.*, 1985, **64**, 159.
30 A. Vogler, A. H. Osman and H. Kunkely, *Inorg. Chem.*, 1987, **26**, 2337.
31 C. Creutz, *Prog. Inorg. Chem.*, 1983, **30**, 1.
32 A. E. Almaraz, L. A. Gentil, L. M. Baraldo and J. A. Olabe, *Inorg. Chem.*, 1996, **35**, 7718.
33 S. K. Doorn, R. L. Blackbourn, C. S. Johnson and J. T. Hupp, *Electrochim. Acta*, 1991, **36**, 1775.

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