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Kinetics and mechanisms of the electron transfer reactions of oxo-centred carboxylate bridged complexes, $[Fe_3(\mu_3\text{-}O)(O_2CR)_6L_3]ClO_4$, with verdazyl radicals in acetonitrile solution†

Lynette Keeney and Michael J. Hynes*
Department of Chemistry, National University of Ireland, Galway, Ireland

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A range of oxo-centred, carboxylate bridged tri-iron complexes of general formula $[Fe_3(\mu_3\text{-}O)(O_2CR)_6L_3]ClO_4$ (R = CH_2CN, CH_2F, CH_2Cl, CH_2Br, $p\text{-}NO_2C_6H_4$; L = pyridine, 3-methylpyridine, 4-methylpyridine, 3,5-dimethylpyridine, 3-cyanopyridine and 3-fluoropyridine) have been prepared and characterised. The choice of R and L was dictated by the requirement that the complexes undergo a one-electron reduction when reacted with verdazyl radicals. All except the complexes where L = pyridine and R = CH_2CN, CH_2Cl and $p\text{-}NO_2C_6H_4$ have not been previously reported. The redox behaviour of these compounds has been investigated using cyclic voltammetry in acetonitrile in the absence and in the presence of free L. In general, all complexes exhibited reversible one-electron reductions. Electrochemical behaviour improved in the presence of an excess of L. The kinetics of the electron transfer reaction observed when acetonitrile solutions of the complexes were reacted with a range of verdazyl radicals were monitored using stopped-flow spectrophotometry. Under the experimental conditions, the reactions were quite rapid and were monitored under second-order conditions. Marcus linear free energy plots indicated that the outer-sphere electron transfer reactions were non-adiabatic in nature. Nevertheless, application of the self-exchange rate constants of the verdazyl radicals, k_{11}, and the tri-iron complexes, k_{22}, to the Marcus cross-relation resulted in calculated values of the cross-reaction rate constant, k_{12}, that were within a factor of five of the experimentally determined value.

Introduction

Complexes in which carboxylate ligands serve as a bridge between metal atoms in oxo-centred, carboxylate-bridged trinuclear complexes of general formula $[M_3(\mu_3\text{-}O)(O_2CR)_6L_3]^{0/1+}$ have evoked considerable interest.[1] The three metal ions are bound to a central oxygen ion ($\mu_3\text{-}O^{2-}$) and adjacent metal ions are bridged by two carboxylate moieties. The neutral monodentate ligands (*e.g.*, H_2O, pyridine, or substituted pyridine) occupy the remaining coordination sites on each metal centre (*trans* to the bridging oxo-ligand), thereby completing the approximately octahedral coordination sphere, Fig. 1.

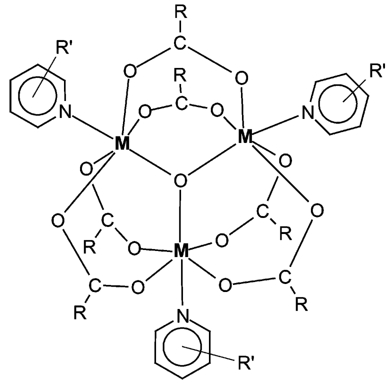

Fig. 1 Structure of oxo-centred, carboxylate-bridged, tri-nuclear complexes of general formula, $[M_3(\mu_3\text{-}O)(O_2CR)_6L_3]^{0/1+}$.

The relatively large metal–metal distances preclude the possibility of direct metal–metal bonding and the complexes are particularly interesting and are useful models for systematically studying weak metal–metal interactions in multi-nuclear metal complexes. Mixed-valence derivatives, $[M^{III}{}_2M^{II}(\mu_3\text{-}O)(O_2CR)_6L_3]$, may be prepared and it is therefore possible to obtain direct information on the dynamics of *intra*molecular electron transfer processes.[1–6] Whereas the mixed-valence ruthenium complex, $[Ru^{III}{}_2Ru^{II}(\mu_3\text{-}O)(O_2CCH_3)_6(py)_3]$, is thought to be fully delocalised (D_{3h} symmetry),[7–9] it is clear that even at room temperature electron delocalisation in the tri-iron complexes remains a dynamic process.[2,10] The process is an *intra*molecular electron transfer reaction since the Fe(II) and Fe(III) valence states remain distinguishable on the vibrational time scale (intermediate between D_{3h} and C_{2v} symmetry).[1,3,11–14]

Much of the work to date on oxo-centred tri-nuclear complexes has centred on investigations of these complexes in the solid state. With the exception of cyclic voltammetry studies, their solution chemistry has been relatively unexplored. Triruthenium complexes can exhibit reversible multistep redox nature, for example, the cyclic voltammogram of $[Ru_3(\mu_3\text{-}O)(O_2CCH_3)_6(py)_3]^n$ revealed a series of one-electron reversible redox waves where $n = +3, +2, +1, 0, -1, -2$.[7] Hence, the majority of the electrochemical studies of the $[M_3(\mu_3\text{-}O)(O_2CR)_6L_3]^n$ complexes focus on the ruthenium analogs.[7,15–20] Variations in the bridging carboxylates and the monodentate ligands were found to influence the magnetic, structural and electronic properties of the complexes.[21] Studies on the role of substituents and their effect on electron transfer in these complexes were carried out by Manchanda,[22] who investigated the effect of altering the carboxylate bridge ($\text{–}O_2CCH_3$, $\text{–}O_2CC_6H_5$ and $\text{–}O_2CCCl_3$) on the electrochemical behaviour of basic iron acetates. Bond *et al.*[23] prepared a series of $[Fe_3(\mu_3\text{-}O)(O_2CR)_6L_3]X$ complexes (L = pyridine or substituted pyridine, R = alkyl or aryl group, X = ClO_4^- or NO_3^-) and investigated their electrochemistry in dichloromethane in the presence and absence of free L. It was found that $E°$ for $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(py)_3]^{0/1+}$ was strongly dependent on the identity of the bridging carboxylate ligand and both the identity and the location of the substituent on the pyridine ring.[23]

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† Electronic supplementary information (ESI) available: Kinetic and electrochemical data for $[Fe_3(\mu_3\text{-}O)(O_2CR)_6L_3]ClO_4$ (Figs. S1–S9, Table S1). See http://www.rsc.org/suppdata/dt/b4/b418809h/

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To date, kinetic investigations of the electron transfer of the complexes in solution have involved self-exchange studies of $[Ru_3(\mu_3\text{-}O)(O_2CCH_3)_6(py)_3]^{0/1+}$ and $[Fe_3(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]^{0/1+}$ by ^{1}H NMR line broadening; the calculated second-order rate constants are 1.1 × 10^8 dm^3 mol^{-1} s^{-1} (at 24 °C) and (3.7 ± 0.1) × 10^4 dm^3 mol^{-1} s^{-1} (at 23 °C), respectively.[9,24] However, no reports of any cross-reaction studies of these metal complexes were sourced. Preliminary cyclic voltammetry studies of the heterogeneous electron transfer rate constants for $[M^{III}{}_2Mn^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_2C_2H_5)_6(py)_3]$ complexes (where M = Fe or Mn) were conducted previous to this work[25] and it was shown that the heterogeneous rate constant for the mixed-metal complex ($k_s \sim 4.3 \times 10^{-3}$ cm s^{-1}) was similar to that of the homonuclear complex ($k_s \sim 3.7 \times 10^{-3}$ cm s^{-1}).

The *inter*molecular electron transfer reactions of $[M_3(\mu_3\text{-}O)(O_2CR)_6L_3]^{0/1+}$ species remain relatively unexplored. While the complexes are soluble in organic solvents, many of the inorganic reducing agents available are insoluble in these or are charged complexes such that the interpretation of much of the kinetic data has been plagued by ion-pairing considerations. Verdazyl radicals, Fig. 2, discovered by Kuhn and Trischmann in 1964,[26] are ideal candidates as reducing agents of the fully oxidised tri-iron complexes, $[Fe^{III}{}_3(\mu_3\text{-}O)(O_2CCR)_6L_3]^{1+}$. They are a class of stable organic free radicals in which the stability is enhanced by extensive delocalisation of the unpaired electron over the four nitrogen atoms.[26,27] That their electron transfer reactions are outer-sphere was demonstrated by reacting them with tris(polypyridine)cobalt(III) complexes.[28] The results were shown to be consistent with Marcus theory.[29] As one of the reactants (the verdazyl radical) and one of the products (the mixed-valence tri-iron complex) are uncharged, the individual work terms, w_{ij}, of the self-exchange and cross-reactions are zero. In this paper we report the results of our stopped-flow investigations of the kinetics and mechanism of the one-electron reduction of a series of triangular iron(III) complexes by verdazyl radicals (X-TPV$^\bullet$), eqn. (1).

$$[Fe^{III}{}_3(\mu_3\text{-}O)(O_2CR)_6L_3]^{1+} + \text{X-TPV}^\bullet = [Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CR)_6L_3] + \text{X-TPV}^+ \qquad (1)$$

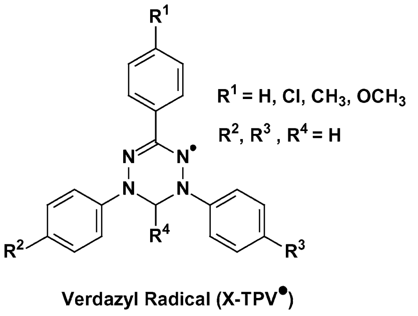

Fig. 2 Structure of verdazyl radicals.

Results

Cyclic voltammetry studies

In general, in the absence of free ligand, the tri-iron complexes, $[Fe^{III}{}_3(\mu_3\text{-}O)(O_2CR)_6L_3]^{1+}$, exhibited chemically reversible one-electron reductions at low scan rates (10 mV s^{-1}) in the region +0.7 to 0.0 V (*vs.* Ag/AgCl). This was attributed to a one-electron reduction to the neutral mixed-valence form, $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CR)_6L_3]$. Table 1 summarises the cyclic voltammetric data for the complexes in acetonitrile solution in the presence of a ten-fold excess of free ligand, L. Unlike the corresponding manganese complexes,[25] addition of an excess of L did not have a very significant effect on the shape of the cyclic voltammogram or the position of the peaks, Fig. S1 (see ESI).† A ten-fold excess of free ligand generally resulted in a lowering of $E°$ by ≤15 mV. The largest effect was observed for 4-methylpyridine. Higher excesses of free ligand had no further effect on the shape of the cyclic voltammograms, indicating that ten-fold excess free ligand was sufficient to prevent dissociation of these particular complexes. The verdazyl radicals (X-TPV$^\bullet$) show a chemically reversible one-electron oxidation to their corresponding verdazylium cations (X-TPV$^+$) at low scan rates (10 mV s^{-1}) in acetonitrile in the region +0.5 to −0.1 V (*vs.* Ag/AgCl), Table 2. By comparing the inductive influence of the different substituents on L in the complexes or the different X groups on the verdazyls, the variations in $E°$ can be readily rationalised. Electron withdrawing groups promote $E°$ to more positive potentials, while electron donating groups have the opposite effect. The magnitude of this effect in the tri-iron complexes can be related to the pK_a of the respective ligands, Table S1 (see ESI).† The reduction potentials of the $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(L)_3]^{1+}$ complexes vary linearly with the pK_a of L, as illustrated by the plot in Fig. S2 (see ESI).† In general, the stronger the acid, the more positive the $E°$ value. As the electronegativity of the halogen substituent of the carboxylic acid (R), increases, $E°$ of $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(py)_3]^+$ decreases in the sequence:

$$R = CH_2Br > CH_2Cl > CH_2F$$

Table 1 Electrochemical data for 5.0 × 10^{-4} mol dm^{-3} $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^{0/1+}$ in 0.2 mol dm^{-3} $(^nC_4H_9)_4NPF_6$–acetonitrile in the presence of a ten-fold excess of free ligand, L

R	L	$E°$/V	ΔE_p/mV	I_{pa}/I_{pc}
CH_2CN	py	0.347	68	1.08
CH_2CN	3-Mepy	0.310	66	1.13
CH_2CN	4-Mepy	0.297	67	0.86
CH_2CN	3,5-dimepy	0.290	66	1.23
CH_2CN	3-CNpy	0.428	61	1.08
CH_2CN	3-Fpy	0.448	69	1.11
CH_2F	py	0.228	69	1.08
CH_2Cl	py	0.243	69	1.31
CH_2Br	py	0.282	75	1.12
p-$NO_2C_6H_4$	py	0.234	63	1.07

Table 2 Electrochemical data for 3-(4-X-phenyl)-1,5-diphenyl verdazyl radicals in 0.2 mol dm^{-3} $(^nC_4H_9)_4NPF_6$–acetonitrile

X	$E°$/V	ΔE_p/mV	I_{pa}/I_{pc}
CH_3O	0.168	59	1.04
CH_3	0.180	60	1.03
H	0.215	61	0.88
Cl	0.239	59	0.718

This is opposite to what might be expected from arguments based on the inductive effect (Table 1). However, the electron transfer rate constants correlate in the expected manner with the $E°$ values for the complexes (*vide infra*). The $E°$ values for the complexes where R = CH_2CN, CH_2Cl and p-$NO_2C_6H_4$ follow the same pattern as was previously observed for these complexes in 0.2 mol dm^{-3} $(^nC_4H_9)_4NPF_6$-dichloromethane between +0.5 and −0.2 V (*vs.* Ag/AgCl).[23]

Kinetic studies of the reactions of $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ with verdazyl radicals

The kinetics of electron transfer between 3-(4-X-phenyl)-1,5-diphenyl-verdazyl radicals, X-TPV$^\bullet$, and the fully oxidised oxo-centred carboxylate bridged tri-iron complexes, $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$, were studied using X-TPV$^\bullet$ (X = Cl, H, CH_3 and CH_3O) as the electron donor by stopped-flow spectrophotometry at 25 °C. For the complexes, R = CH_2CN, CH_2F, CH_2Cl, CH_2Br and L = py (pyridine), 3-mepy (3-methylpyridine) and 3,5-dimepy (3,5-dimethylpyridine). An absorbance decrease was observed between 720–730 nm, which corresponded to the disappearance of X-TPV$^•$. A larger absorbance increase, which occurred at the same rate as the decrease, was observed between 560–600 nm, where most of the kinetic measurements were made. This absorbance increase corresponded to the formation of the verdazylium cation, X-TPV$^+$. Thus, it was clear that an electron transfer reaction was occurring. Reactions of X-TPV$^•$ with $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ were conducted in argon saturated, dried and distilled acetonitrile. Addition of 0.2 mol dm^{-3} $(^nC_4H_9)_4NPF_6$ to the reactant solutions had no effect on the rate of electron transfer. It was therefore assumed that ion-pairing was not an important consideration in these reactions. This result was not unexpected, as the reactant, X-TPV$^•$, and the product, $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]$, are uncharged. Subsequently, no additional electrolyte was used to control the ionic strength. The stoichiometry of the reactions of X-TPV$^•$ with $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ was investigated by comparing the final absorbance obtained when the radical and the complex were reacted in a 1 : 1 ratio with that obtained when a solution of verdazyl radical having the same concentration was reacted with an excess of $Cu(NO_3)_2$ which is known to undergo a one-electron transfer with verdazyl radicals. In all cases, a 1 : 1 stoichiometry was observed confirming the fact that the verdazyl radical acts as a one-electron reducing agent.

The solution chemistry of the tri-nuclear complexes was more complicated than originally envisaged. This arises from the fact that there is some dissociation of one or more of the coordinated pyridine or substituted pyridines in solvents such as acetonitrile and dichloromethane.[23–25] When acetonitrile solutions of the tri-iron complexes and verdazyl radicals were reacted together in the absence of free terminal ligand, two absorbance increases were observed in the stopped-flow trace indicating the presence of a rapid ($t_{1/2} < 0.1$ s) and slow ($t_{1/2} > 1$ s) reaction. The amplitude of the faster of the two absorbance changes accounted for most of the total absorbance change, this was followed by a relatively small slower absorbance change. Upon addition of a small excess (ten-fold) of either pyridine or substituted pyridine to the reacting solutions, the slow absorbance change disappeared. Pre-trigger experiments confirmed that only a single reaction was involved when the reactions were conducted in the presence of a ten-fold excess of free terminal ligand.

These observations are readily explained in terms of eqn. (2)

$$[Fe^{III}{}_3(\mu_3\text{-}O)(O_2CR)_6L_3]^{1+} + S = [Fe^{III}{}_3(\mu_3\text{-}O)(O_2CR)_6L_2S]^{1+} + L \quad (2)$$

where S represents asolvent molecule and L represents pyridine or substituted pyridine. Partial dissociation of L takes place and it appears that the rate constant for reaction of the solvent species with the verdazyl radical is less than that of its reaction with the parent complex, eqn. (1). This was confirmed by the cyclic voltammetry experiments where addition of an excess of L improved the shape of voltammograms and resulted in a small shift in the potentials, Fig. S1 (see ESI).† Subsequently, all reactions of $[Fe_3(\mu_3\text{-}O)(O_2CR)_6L_3]^+$ with X-TPV$^•$ were conducted in the presence of an excess of L. Ten-fold excess of free L was sufficient to suppress dissociation of the complex and increased concentrations of L had no further effect on the kinetics.

The reactions were too rapid to allow measurement of rate constants under pseudo-first-order conditions using the stopped-flow technique. The rate constants were measured under second-order conditions and the reactions were repeated at several equivalent concentrations in the reactant concentration range 1.0×10^{-5} – 1.25×10^{-4} mol dm^{-3} in the presence of a ten-fold excess of free terminal ligand. Tables 3 and 4 summarise the kinetic and thermodynamic data for the reactions studied.

Table 3 Kinetic and thermodynamic data for reduction of $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(L)_3]^+$ by X-TPV$^•$ in the presence of 10-fold excess of terminal ligand in acetonitrile at 25 °C

L	X-TPV$^•$	$10^{-6}k_{12}$/dm^3 mol^{-1} s^{-1}	$\Delta E°$/V	K_{12}	logK_{12}	logk_{12}
py	$X = CH_3O$	5.05(±0.56)	0.179	1081	3.03	6.70
3-Mepy	$X = CH_3O$	4.33(±0.28)	0.142	255	2.41	6.64
3,5-dimepy	$X = CH_3O$	2.42(±0.22)	0.122	117	2.07	6.38
py	$X = CH_3$	4.20(±0.16)	0.167	677	2.83	6.62
3-Mepy	$X = CH_3$	3.16(±0.14)	0.130	160	2.20	6.50
3,5-dimepy	$X = CH_3$	1.94(±0.14)	0.110	73	1.86	6.29
py	$X = H$	2.99(±0.15)	0.132	173	2.24	6.48
3-Mepy	$X = H$	2.36(±0.07)	0.095	41	1.61	6.37
3,5-dimepy	$X = H$	1.80(±0.01)	0.075	19	1.27	6.26
py	$X = Cl$	2.28(±0.08)	0.108	68	1.83	6.36
3-Mepy	$X = Cl$	2.00(±0.12)	0.071	16	1.20	6.30
3,5-dimepy	$X = Cl$	1.48(±0.01)	0.051	7.3	0.86	6.17

Table 4 Kinetic and thermodynamic data for reduction of $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(py)_3]^+$ by X-TPV$^•$ in the presence of 10-fold excess of pyridine in acetonitrile at 25 °C

R	X-TPV$^•$	$10^{-6}k_{12}$/dm^3 mol^{-1} s^{-1}	$\Delta E°$/V	K_{12}	logK_{12}	logk_{12}
CH_2CN	$X = CH_3O$	5.05(±0.56)	0.179	1081	3.03	6.70
CH_2Br	$X = CH_3O$	3.18(±0.11)	0.114	85.6	1.93	6.50
CH_2Cl	$X = CH_3O$	2.14(±0.01)	0.075	18.7	1.27	6.33
CH_2F	$X = CH_3O$	1.30(±0.07)	0.060	10.4	1.02	6.11
CH_2CN	$X = CH_3$	4.20(±0.16)	0.167	677	2.83	6.62
CH_2Br	$X = CH_3$	2.28(±0.12)	0.102	53.6	1.73	6.36
CH_2Cl	$X = CH_3$	1.84(±0.05)	0.063	11.7	1.07	6.27
CH_2F	$X = CH_3$	1.20(±0.14)	0.048	6.51	0.814	6.08
CH_2CN	$X = H$	2.99(±0.15)	0.132	172	2.24	6.48
CH_2Br	$X = H$	2.05(±0.16)	0.067	13.7	1.14	6.31
CH_2Cl	$X = H$	1.39(±0.09)	0.028	2.98	0.475	6.14
CH_2F	$X = H$	0.887(±0.172)	0.013	1.66	0.220	5.94
CH_2CN	$X = Cl$	2.28(±0.08)	0.108	67.7	1.83	6.36
CH_2Br	$X = Cl$	1.44(±0.01)	0.043	5.36	0.729	6.16
CH_2Cl	$X = Cl$	1.08(±0.12)	0.004	1.17	0.068	6.03
CH_2F	$X = Cl$	0.687(±0.011)	−0.011	0.651	−0.186	5.84

Table 5 Kinetic and thermodynamic data for reaction of $[Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ with $[Co(N\text{–}N)_3]^{3+}$ in the presence of 100-fold excess of pyridine in acetonitrile at 25 °C and $I = 0.05$ mol dm^3 $(^nC_4H_9)_4PF_6$

N–N	$E°[Co(N\text{–}N)_3]^{3+}/V$	$10^{-5}k_{12}$/dm^3 mol^{-1} s^{-1}	$(2\log k_{AB} - \log f_{AB} - 2\log W_{AB} - \log k_{AA})$	$\log K_{AB}$	k_{AA}/dm^3 mol^{-1} s^{-1}	$10^{-3}k_{BB}$/dm^3 mol^{-1} s^{-1}
bpy	0.345	46.4(±0.2)	13.0	9.42	5.7[33]	4.0
4,7-Me$_2$bpy	0.218	2.21(±0.15)	9.89	7.27	4.5[28]	0.45
4,4′-(MeO)$_2$bpy	0.168	0.260(±0.281)	7.31	6.42	—	—

Kinetic studies of the reactions of $[Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ with $[Co(N\text{–}N)_3]^{3+}$ complexes

The self-exchange rate constant of the tri-iron pivalate complex, $[Fe_3(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]^{0/1+}$, was investigated using an approach whereby the complex was reacted with complexes whose self-exchange rate constants were already known and applying the cross-reaction rate constants determined by stopped-flow spectrophotometry to the Marcus relationships. The kinetic and thermodynamic data are shown in Table 5.

According to the Marcus cross-relationship[29] the rate constant for the cross-reaction, k_{AB}, is given by eqns (3) and (4) where K_{AB} is the equilibrium constant for the cross-reaction and k_{AA} and k_{BB} are the self-exchange rate constants.

$$k_{AB} = \left[\frac{(k_{AA}\,k_{BB}\,K_{AB}f_{AB})}{\kappa_{AA}\,\kappa_{BB}}\right]^{1/2}\kappa_{AB}\,W_{AB} \qquad (3)$$

where

$$\log f_{AB} = \frac{(\log K_{AB})^2}{4\log(k_{AA}k_{BB}/Z^2)} \qquad (4)$$

and

$$W_{AB} = \exp\left[\frac{-(w_{AB}+w_{BA}-w_{AA}-w_{BB})}{2RT}\right] \qquad (5)$$

The individual electric work terms, w_{ij}, can be determined using eqn. (6) where a is the contact distance of the ions ($a = r_1 + r_2$ where r is the radius of a reactant), z_i and z_j are the charges on the reacting species, ε_o is the permittivity of a vacuum and ε is the bulk dielectric constant. $\chi = (2e_0{}^2N_AI/\varepsilon_0\varepsilon k_BT)^{1/2}$ where e_0 is the charge on a electron (1.602×10^{-19} C), N_A is Avogadro's constant, k_B is Boltzmann's constant, I is the ionic strength and T is the absolute temperature. In eqn. (3), Z is the collision frequency $\approx 10^{11}$ dm^3 mol^{-1} s^{-1}.

$$w_{ij} = {}^{z_iz_je_0{}^2N_A}\!\big/_{4\pi\varepsilon_0\varepsilon a(1+\chi a)} \qquad (6)$$

Assuming that the reaction approaches adiabaticity such that the electronic transmission coefficient, κ_{ij} is approximately equal to 1, eqn. (3) can be written as eqn. (7).

$$2\log k_{AB} - \log f_{AB} - 2\log W_{AB} - \log k_{AA} = \log k_{BB} + \log K_{AB} \qquad (7)$$

Eqn. (7) predicts that a plot of the left hand side against $\log K_{AB}$ for a series of related electron transfer reactions should be linear with a slope 1.0 and intercept equal to $\log k_{BB}$ if the Marcus theory is obeyed. When the work terms can be neglected and when f_{AB} is ~ 1 (that is when $(\log K_{AB})^2$ and/or $\log k_{AA}k_{BB}$ are sufficiently small), eqn. (3) can be written in the form of eqn. (8) in the case of an adiabatic electron transfer reaction.

$$\log k_{AB} = \frac{1}{2}\log(k_{AA}k_{BB}) + \frac{1}{2}\log K_{AB} \qquad (8)$$

If a series of related reactions is studied as a function of the driving force, a plot of $\log k_{AB}$ *vs.* $\log K_{AB}$ should be linear, with a slope 0.5 and intercept $0.5\log k_{AA}k_{BB}$.

With ionic radii of 0.7 nm for the cobalt complexes,[30] 0.9 nm for $[Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ (calculated from the volume of its crystal structure),[31] $I = 0.05$ mol dm^{-3} and $\varepsilon = 37.5$ for acetonitrile at 25 °C,[32] the work terms for the reactions were calculated using eqn. (6) to be: $w_{AB} = 0$, $w_{BA} = 1.71$ kJ mol^{-1}, $w_{AA} = 6.38$ kJ mol^{-1} and $w_{BB} = 0$. $E°$ for $[Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ is −0.211 V (in 0.2 mol dm^{-3} $(^nC_4H_9)_4NPF_6$-acetonitrile in the presence of a fifty-fold excess of free pyridine *vs.* Ag/AgCl) and the $E°$ values for the $[Co(N\text{–}N)_3]^{3+}$ complexes (in 0.2 mol dm^{-3} $(^nC_4H_9)_4NPF_6$-acetonitrile *vs.* Ag/AgCl) are presented in Table 5. Fig. S3 (see ESI)† shows a plot of $(2\log k_{AB} - \log f_{AB} - 2\log W_{AB} - \log k_{AA})$ against $\log K_{AB}$ (eqn. (7)) using the data in Table 5. Although the self-exchange rate constant of $[Co(4,4'\text{-}(MeO)_2bpy)_3]^{3+/2+}$ is unknown, this plot can be constructed as it is assumed that the self-exchange rate constant of $[Co(4,4'\text{-}(MeO)_2bpy)_3]^{3+/2+}$ will not differ by much from the self-exchange rate constants of $[Co(bpy)_3]^{3+/2+}$ (5.7 dm^3 mol^{-1} s^{-1})[33] and $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$ (4.5 dm^3 mol^{-1} s^{-1}).[28] This assumption is supported by the fact that a linear relationship between $E°([Co(N\text{–}N)_3]^{3+})$ and $\log k_{AB}$ and also between $\log k_{AB}$ and $\log K_{AB}$ was obtained for reaction of the $[Co(N\text{–}N)_3]^{3+}$ complexes with $[Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$.[34] Arising from this, the k_{AA} value used in the construction of the plot in Fig. S3 (see ESI)† was 5.1 dm^3 mol^{-1} s^{-1}, the averaged value of the self-exchange rate constants of $[Co(bpy)_3]^{3+/2+}$ and $[Co(4,7\text{-}Me_2phen)_3]^{3+/2+}$. f_{AB} for $[Co(4,4'\text{-}(MeO)_2bpy)_3]^{3+}$ was assumed to be equal to 1. A linear relationship is observed in Fig. S3 (see ESI)† for the plot of $(2\log k_{AB} - \log f_{AB} - 2\log W_{AB} - \log k_{AA})$ *vs.* $\log K_{AB}$ for the reactions. This supports the operation of an outer-sphere electron transfer process. However, this plot yielded a slope of 1.81(±0.35), significantly greater than the theoretically predicted value of 1.0, eqn. (7). Nevertheless, application of the cross-reaction data for the reaction of $[Co(bpy)_3]^{3+}$ ($k_{AA} = 5.7$ dm^3 mol^{-1} s^{-1})[33] and $[Co(4,7\text{-}Me_2phen)]^{3+}$ ($k_{AA} = 4.5$ dm^3 mol^{-1} s^{-1})[28] with $[Fe^{III}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ to the Marcus cross-relation (eqn. (3)) yielded self-exchange rate constants for the complex, k_{BB}, that were within a factor of ten of each other, 4.0×10^3 and 4.5×10^2 dm^3 mol^{-1} s^{-1}, respectively (Table 5). In the case of the reaction with $[Co(bpy)_3]^{3+}$ a self-exchange rate constant was obtained for the complex that was within a factor of ten of the previously reported value determined by NMR line-broadening methods of 3.7×10^4 dm^3 mol^{-1} s^{-1}.[24] Therefore, it appears that even in the case where Marcus linear free energy plots of reactants yield slopes that are different to those predicted, the Marcus cross-relation is useful in the estimation of approximate values for rate constants.

Discussion

Most of the previous investigations of the oxidation of organic radicals by inorganic species have involved systems where the radical is generated *in situ* by techniques such as pulse radiolysis.[35–37] In their investigation of the reduction of $[M(phen)_3]^{3+}$ (M = Fe, Ru, Os) by alkyl radicals Rollick and Kochi identified two different types of mechanism.[36] Generation of the cation occurred by an outer-sphere mechanism while an inner-sphere mechanism was proposed for the oxidative process leading to phenanthroline substitution. While stereochemical effects were absent in the former, the rate constants for phenanthroline substitution were subject to stereochemical influence.[36] Rate constants for the formation of the cation were shown to increase monotonically with increase in the reduction potential, $E°$, of the phenanthroline complexes. Since outer-sphere electron transfer reactions are insensitive to steric effects and also give a linear correlation between the rate constant and driving force (according to Marcus theory), oxidation of alkyl radicals leading to cation formation was assumed to proceed *via* an outer-sphere mechanism.

In the present investigation, only formation of the verdazylium cation was observed and no ligand substitution products were formed. Reactions of the verdazyl radicals with tris(polypyridine)cobalt(III) and ruthenium(III) complexes were shown to undergo electron-transfer *via* outer-sphere mechanisms.[28] It is therefore reasonable to suggest that formation of the verdazylium cation from electron transfer between X-TPV$^•$ and $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ proceeds *via* an outer-sphere mechanism. Linear correlations between the driving force of the reactions, $E°$, and the cross-reaction rate constants, k_{12}, as observed in Figs. S4–S7 (see ESI),† further support the assertion that these reactions proceed by an outer-sphere electron transfer pathway.

In view of the fact that the reactions appear to be of the outer-sphere nature, it is useful to consider the reactions of X-TPV$^•$ and $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ in the framework of Marcus theory for outer-sphere electron transfer reactions, eqn (3). The work term, W_{12}, eqns. (5) and (6), is equal to 1 as one of the reactants, X-TPV$^•$ and one of the products, $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]$, of the cross-reaction are uncharged. This also applies to the self-exchange reactions.

A linear correlation of cross-reaction rate constants, $\log k_{12}$ with driving force, $\log K_{12}$ is observed for the above systems as shown in Fig. S8 (see ESI)† for reaction of X-TPV$^•$ with $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(L)_3]ClO_4$, in Fig. S9 (see ESI)† for reaction of X-TPV$^•$ with $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(py)_3]ClO_4$ and in Fig. 3 for reaction of X-TPV$^•$ with $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]ClO_4$. These plots were constructed using eqn. (8) and the data in Tables 3 and 4. It has been shown previously[28] that the self-exchange rate constants within the verdazyl radical series used here do not vary greatly and it is reasonably assumed that the self-exchange rate constants within the complex series would not vary greatly either. However, despite the linearity of the plots, the slopes are equal to 0.24(± 0.03), 0.25(± 0.02) and 0.244(± 0.015) for Figs. S8 and S9 (see ESI)† and Fig. 3, respectively. These values are considerably lower than the theoretical slope of 0.5 predicted by eqn. (8).

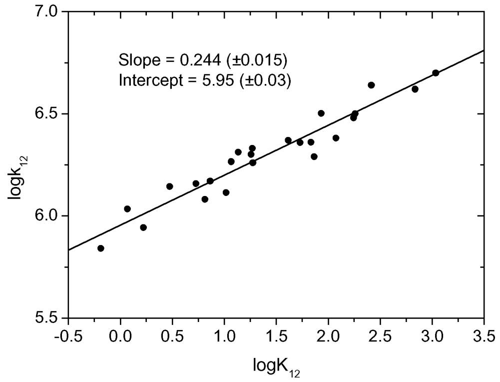

Fig. 3 Marcus plot of $\log k_{12}$ against $\log K_{12}$ for reaction of X-TPV$^•$ and $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ in the presence of ten-fold excess L in acetonitrile at 25 °C—data for variation of both terminal ligand and carboxylate bridge of the tri-iron complex are included.

It is suggested that the systems operating here are somewhat non-adiabatic, *i.e.* the electron transfer distance significantly exceeds the structural extension of the donor and acceptor groups and the electronic coupling between the two, H_{AB}, becomes too weak to allow adiabatic electron transfer. As a result, κ_{el}, the electronic transmission coefficient, will be less than unity. In general, electronic coupling results from overlap of the HOMO (highest occupied molecular orbital) donor and LUMO (lowest unoccupied molecular orbital) of the acceptor. In view of the fact that wave functions decay exponentially with distance, it follows that H_{AB} will also decay with distance, eqn. (9) where a is the contact distance of the reactants and is approximated by the sum of the reactant radii ($a = r_1 + r_2$, where r is the radius of a reactant) and d is some critical distance so that $H_{AB}°$ is the value of H_{AB} when $d = a$ and the reaction is defined as adiabatic.

$$H_{AB} = H_{AB}° \exp(-\alpha(d - a)) \tag{9}$$

A comprehensive treatment of the inner-sphere reorganization energy, λ_i, requires a detailed vibrational analysis of the individual complexes and verdazyl radicals and recognition of the quantum mechanical nature of the problem. However, due to the large size of both the iron complex and the verdazyl radicals, it is to be expected that both the inner- and outer-sphere reorganisation energies for both will be relatively small and that the structural differences between the oxidised and reduced forms are slight. The partially electron delocalised nature of the mixed-valence neutral iron complex at room temperature[2,38] is consistent with this. Similar arguments have been proposed for the fully delocalised ruthenium complexes.[9] Deriving the radii from the crystal structure volume data gives a value of *ca.* 0.9 nm for the tri-iron complexes[31,38–41] and *ca.* 0.85 nm for the verdazyl radicals.[42,43] Thus $(r_1 + r_2)$ is of the order of 1.75 nm. At this distance between the reacting centres, the electron transfer reaction is expected to be electronically non-adiabatic. Electronically non-adiabatic electron rate expressions have been found for iron hexa-aquo complexes[44] and iron bi-imidazoline complexes[45] at distances of *ca.* 0.7 nm and 1.03 nm, respectively. However given that $(r_1 + r_2)$ is *ca.* 1.55 nm for $[Co(N\text{–}N)_3]^{3+}$ and X-TPV$^•$ and that their electron transfer reactions were found to be adiabatic in nature,[28] the bulk of the tri-iron complexes may be a major factor in contributing to the inefficient orbital overlap of the LUMO of the complex and the HOMO of the verdazyl radicals. While $[Co(N\text{–}N)_3]^{3+}$, X-TPV$^•$ and the $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ are non-spherical molecules and averaged radii are quoted, due to the fact that the complexes are large bulky molecules, the effective radius may vary considerably at different parts of the complex molecule. Hence a poor approximation of the contact distance between the complexes and the verdazyl radicals may be obtained by assuming $a = r_1 + r_2$.

Marcus theory is based on the assumption that the reactions are adiabatic in nature. Furthermore, the reagents are supposed to be spherical, structureless reactants and the motions of the inner coordination shells are assumed to be harmonic. In terms of gross structure, the complexes are non-spherical bulky molecules and it is difficult to envisage that these complexes would engage in efficient orbital overlap such as to allow completely adiabatic electron transfer with the verdazyl radicals. The inconsistency of the data obtained in this work with Marcus theory, as reflected in the slopes of the lines shown in Figs S8 and S9 (see ESI) and Fig. 3, may arise from inefficient orbital overlap of the reacting molecules due to the distance between the reacting centres and the bulky nature of the complexes.

Although there is clearly some element of non-adiabaticity in the electron transfer reactions of the complexes and the verdazyl radicals, nevertheless it was decided to apply the values of the self-exchange rate constants of the verdazyl radicals and tri-iron complexes to the Marcus cross-relation, eqn. (3),[29,46] and compare the predicted rate constant for the cross-reaction with that of the value determined experimentally by the stopped-flow technique. Using a value of 3.4×10^7 dm^3 mol^{-1} s^{-1} for the verdazyl radical-verdazylium cation self-exchange rate constant, k_{11},[28] and a self-exchange rate of 4.0×10^3 dm^3 mol^{-1} s^{-1} for the tri-iron complexes, k_{22}, (calculated by applying the cross-reaction data for reaction of $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ with $[Co(bpy)_3]^{3+}$ to the Marcus cross-relation, above), the rate constant for the cross-reaction, k_{12}, for TPV$^{\bullet}$ with $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(py)_3]^+$ ($\Delta E^\circ = 0.132$ V) was calculated using eqn. (3) to be equal to 4.2×10^6 dm^3 mol^{-1} s^{-1}. There is less than a factor of two between this calculated value and 2.99×10^6 dm^3 mol^{-1} s^{-1}, the experimentally determined value. The agreement between theory and experiment for these systems is clearly well within the accepted uncertainty in the treatment of Marcus theory.[47,48] It is generally found that the experimentally determined rate constant is smaller than that calculated from the Marcus equations, as is also observed here. However, the self-exchange rate constant of the tri-iron complexes was determined using a cross-reaction that did not strictly obey Marcus theory, therefore the correspondence between the calculated and observed cross-reaction rate constant for the tri-iron complex and the verdazyl radical reaction may be fortuitous. Applying the self-exchange rate constant for the tri-iron complexes, 3.7×10^4 dm^3 mol^{-1} s^{-1}, determined experimentally by Sowrey *et al.*[24] using NMR line-broadening techniques, gives a calculated value of 1.3×10^7 dm^3 mol^{-1} s^{-1} for the cross-reaction rate constant, k_{12}, for TPV$^{\bullet}$ with $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(py)_3]^+$. This value is within a factor of five of the observed rate constant for the reaction, also well within the accepted uncertainty[47,48] when using the Marcus cross-relation and complies with the general observation that calculated rate constants are higher than experimentally determined rate constants. It therefore appears that application of the Marcus cross-relation gives calculated rate constants that agree reasonably well with the experimentally determined values for the reactions of the verdazyl radicals with the tri-iron complexes, even though the electron-transfer process is not completely adiabatic. The similarity between predicted and observed rate constants supports the proposal of an outer-sphere electron transfer mechanism for the reactions. The reverse reaction, whereby the verdazylium cation, X-TPV$^+$, oxidised the mixed-valence tri-iron complex, $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$, was found to be rapid on the stopped-flow time scale, as predicted by the self-exchange rate constants of the reactants and the thermodynamic data ($\Delta E^\circ \approx 0.4$ V) for the cross-reaction.

In conclusion, there is strong evidence that the electron transfer reactions of X-TPV$^{\bullet}$ with $[Fe_3(\mu_3\text{-}O)(O_2CR)_6(L)_3]^+$ are outer-sphere in nature and a linear relationship between the driving force and rate of electron transfer is obtained. However, as is indicated by the slope of $\log k_{12}$ *vs.* $\log K_{12}$ being significantly smaller than that expected for adiabatic reactions, it is assumed that the electron transfer does not occur *via* an efficient, adiabatic pathway. Nonetheless, treatment of the thermodynamic data and the self-exchange rate constants of the reactants to the Marcus cross-relation provides a correlation between the calculated and observed rate constants for the cross-reaction, k_{12}, that are well within the accepted uncertainty. It is therefore demonstrated that application of the Marcus cross-relation provides a useful means for the theoretical prediction of rate constants for outer-sphere electron transfer reactions, even in the case of the systems explored in this work where it was demonstrated that there is some element of non-adiabaticity in the electron-transfer process. Marcus theory greatly simplifies the theoretical treatment of outer-sphere electron transfer reactions, excluding the need for the evaluation of complex factors associated with the motion of atoms in the reactant complexes when computing electron transfer rates. However, this work highlights that although agreement between calculated and experimentally determined rate constants may indicate that an electron transfer reaction is adiabatic, it is wise to construct a Marcus free energy plot for a series of closely related reactants to determine whether their electron transfer reactions are consistently adiabatic and to provide more comprehensive descriptions of electron transfer processes. The data provide information about complex- and stable radical-based electron transfer processes of which few examples are available in the chemical literature and are of value in the context of a discussion based on electron-transfer theory.

Experimental

Materials

The compounds $Fe(ClO_4)_3 \cdot 6H_2O$, cyanoacetic acid, sodium fluoroacetate, chloroacetic acid, bromoacetic acid, 4-nitrobenzoic acid, trimethylacetic acid, pyridine, 3-cyanopyridine, 3-methyl pyridine, 4-methyl pyridine, 3,5-dimethylpyridine, and 3-fluoropyridine were obtained from Aldrich and used to prepare the oxo-centred, carboxylate-bridged tri-iron complexes. Distilled phenylhydrazine, *p*-tolubenzaldehyde, *p*-methoxybenzaldehyde, 4-chlorobenzaldehyde, distilled aniline, pyridine, DMF, KBr, 37% aqueous formaldehyde, obtained from Aldrich and sodium nitrite from RDH were used in preparation of the 3-(4-X-phenyl)-1,5-diphenyl-verdazyl radicals. Solvents were of standard laboratory grade except for acetonitrile (Rathburn Chemicals Ltd.), which was HPLC grade and was dried by refluxing with CaH_2 for several hours and distilled.

Synthesis

CAUTION: perchlorate salts of metal complexes are potentially explosive, as are the verdazyl radicals, which contain a ring of four nitrogen atoms in their structure. Therefore, these compounds were prepared in small quantities (<1 g) in a fume cupboard equipped with a safety screen.

1,3,5-Triphenyl verdazyl radical (TPV$^{\bullet}$), 3-(4-Cl-phenyl)-1,5-diphenyl-verdazyl radical (Cl-TPV$^{\bullet}$), 3-(4-CH$_3$-phenyl)-1,5-diphenyl-verdazyl radical (CH$_3$-TPV$^{\bullet}$) and 3-(4-CH$_3$O-phenyl)-1,5-diphenyl-verdazyl radical (CH$_3$O-TPV$^{\bullet}$). These radicals were prepared from their corresponding formazans by reaction with 37% aqueous formaldehyde and $KHSO_4$, following the procedure of Kuhn and Trischmann.[26] The analyses were satisfactory and are described elsewhere.[28]

Verdazylium cations (X-TPV$^+$). The verdazylium salts were synthesised from their corresponding formazans according to the procedure of Katritzky *et al.*[49,50] Their authenticity was confirmed by elemental analysis and visible spectroscopy.[34]

$[Fe_3O(O_2CCH_2CN)_6(py)_3]ClO_4$. This complex was prepared following the procedure of Bond *et al.*[23] (1.01 g, 75% based on $[Fe_3O(O_2CCH_2CN)_6(H_2O)_3]$) (Found: C, 38.43, H, 2.60, N, 12.14. Calc for $C_{33}H_{27}Cl_1Fe_3N_9O_{17}$: C, 38.68, H, 2.66, N, 12.30%)

$[Fe_3O(O_2CCH_2CN)_6(3\text{-mepy})_3]ClO_4$. This complex was prepared by an adaptation of the procedure of Bond *et al.*[23] for the synthesis of the pyridine analogue. The previously prepared complex,[23] $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4 \cdot 6H_2O$ (1.25 g, 1.32 mmol), was dissolved with warming (*ca.* 40–50 °C) in absolute ethanol (40 cm^3). Dropwise addition of 3-methylpyridine (3-Mepy) (13 cm^3, 0.134 mol) led to the immediate formation of a fine light green precipitate. The mixture was cooled to room temperature and after stirring continuously for 3 h; the product was collected by filtration on a sintered glass crucible. It was washed thoroughly with ethanol and diethyl ether and dried over silica gel in a vacuum dessicator connected to a vacuum pump. (1.23 g, 87% based on $[Fe_3O(O_2CCH_2CN)_6(H_2O)_3]$. Found: C, 40.78, H, 2.92, N, 11.43. Calc for $C_{36}H_{33}Cl_1Fe_3N_9O_{17}$: C, 40.54, H, 3.12, N, 11.82%)

$[Fe_3O(O_2CCH_2CN)_6(4\text{-mepy})_3]ClO_4$. The synthesis of this compound from $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4 \cdot 6H_2O$ is identical to that of $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(3\text{-Mepy})_3]ClO_4$ except that 13 cm^3 (0.134 mol) of 4-methylpyridine (4-Mepy) was added instead of 3-methylpyridine. The purity, as indicated by C, H, N analysis and the percentage yield of this complex are lower than that of the complex where L = 3-Mepy. This indicates that the replacement of water by a 4-methylpyridine ligand is more difficult than in the case of a 3-methylpyridine ligand. (Yield = 0.14 g. 0.131 mmol, 10% based on $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4 \cdot 6H_2O$. Found: C, 41.45, H, 2.53, N, 10.67. Calc for $C_{36}H_{33}Cl_1Fe_3N_9O_{17}$: C, 40.54, H, 3.12, N, 11.82%)

$[Fe_3O(O_2CCH_2CN)_6(3,5\text{-dimepy})_3]ClO_4$. The synthesis of this compound from $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4\cdot 6H_2O$ is identical to that of $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(3\text{-Mepy})_3]ClO_4$ except that 15.50 cm^3 (0.133 mol) of 3,5-dimethylpyridine (3,5-dimepy) was used in place of 3-methylpyridine. (Yield = 0.82 g. 0.740 mmol, 56% based on $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4\cdot 6H_2O$. Found: C, 41.73, H, 3.64, N, 11.77. Calc $C_{39}H_{39}Cl_1Fe_3N_9O_{17}$: C, 42.25, H, 3.55, N, 11.37%)

$[Fe_3O(O_2CCH_2CN)_6(3\text{-CNpy})_3]ClO_4$. The synthesis of this compound from $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4\cdot 6H_2O$ is identical to that of $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(3\text{-Mepy})_3]ClO_4$ using 2.75 g (0.026 mol) of 3-cyanopyridine (3-CNpy) in place of 3-methylpyridine. For ligands that are solids the complex : ligand ratio was 1 : 20. (Yield = 0.75 g. 0.682 mmol, 52% based on $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4\cdot 6H_2O$. Found: C, 38.22, H, 2.19, N, 14.64. Calc for $C_{36}H_{24}Cl_1Fe_3N_{12}O_{17}$: C, 39.32, H, 2.2, N, 15.29%)

$[Fe_3O(O_2CCH_2CN)_6(3\text{-Fpy})_3]ClO_4$. The synthesis of this compound from $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4\cdot 6H_2O$ is identical to that of $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(3\text{-Mepy})_3]ClO_4$ except that 11.5 cm^3 (0.134 mol) of 3-fluoropyridine (3-Fpy) was added instead of 3-methylpyridine. (Yield = 0.81 g. 0.751 mmol, 57% based on $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(H_2O)_3]ClO_4\cdot 6H_2O$. Found: C, 35.73, H, 1.94, N, 11.40. Calc for $C_{33}H_{24}Cl_1F_3Fe_3N_9O_{17}$: C, 36.75, H, 2.24, N, 11.69%)

$[Fe_3(\mu_3\text{-}O)(O_2CCH_2F)_6(py)_3]ClO_4$. $[Fe_3(\mu_3\text{-}O)(O_2CCH_2F)_6(H_2O)_3]ClO_4\cdot 6H_2O$ was prepared from CH_2FCO_2Na and $Fe(ClO_4)_3\cdot 6H_2O$ in the same manner as for other complexes,[23,51,52] except the solvent (H_2O) was removed under vacuum to yield the dark red product. 1 g (1.10 mmol) of $[Fe_3(\mu_3\text{-}O)(O_2CCH_2F)_6(H_2O)_3]ClO_4\cdot 6H_2O$ was dissolved with warming in 20 cm^3 absolute ethanol. The solution was cooled in a beaker over ice and sufficient pyridine (*ca.* 0.5 cm^3, 6.2 mmol) was added dropwise to form a green precipitate. Care was required in the addition of pyridine, as too much could re-dissolve the precipitate and may result in the formation of white crystalline pyridinium perchlorate. Excess solution was decanted off and the green powder was collected on a grade four porosity sintered glass crucible, washed with diethyl ether then dried over silica in a dessicator connected to a vacuum pump. (Yield = 0.95 g. 0.97 mmol, 75% based on $[Fe_3(\mu_3\text{-}O)(O_2CCH_2F)_6(H_2O)_3]ClO_4\cdot 6H_2O$. Found: C, 31.98, H, 2.57, N, 4.03. Calc for $C_{27}H_{27}Cl_1F_6Fe_3N_3O_{17}$: C, 33.01, H, 2.77, N, 4.28%)

$[Fe_3(\mu_3\text{-}O)(O_2CCH_2Cl)_6(py)_3]ClO_4\cdot 0.5py$. This complex was prepared using $[Fe_3(\mu_3\text{-}O)(O_2CCH_2Cl)_6(H_2O)_3]ClO_4\cdot 6H_2O$ and pyridine in a complex : ligand ratio of 1 : 100 according to published methods.[23,51,52] Slow addition of pyridine to an ice-cold mixture of the complex was required to precipitate the complex as the green product is soluble in pyridine. (Yield = 0.42 g. 0.375 mmol, 28% based on $[Fe_3(\mu_3\text{-}O)(O_2CCH_2Cl)_6(H_2O)_3]ClO_4\cdot 6H_2O$. Found: C, 32.59, H, 2.48, N, 4.44. Calc for $C_{29.5}H_{29.5}Cl_7Fe_3N_{3.5}O_{17}$: C, 31.61, H, 2.65, N, 4.38%)

$[Fe_3(\mu_3\text{-}O)(O_2CCH_2Br)_6(py)_3]ClO_4$. $[Fe_3(\mu_3\text{-}O)(O_2CCH_2Br)_6(H_2O)_3]ClO_4\cdot 6H_2O$ was prepared from $BrCH_2CO_2H$, $NaHCO_3$ and $Fe(ClO_4)_3\cdot 6H_2O$ in the same manner as for other complexes,[23,51,52] however, when the red precipitate formed, it was filtered immediately to prevent it from re-dissolving. 1 g (0.79 mmol) of $[Fe_3(\mu_3\text{-}O)(O_2CCH_2Br)_6(H_2O)_3]ClO_4\cdot 6H_2O$ was dissolved in 20 cm^3 absolute ethanol with warming. The solution was cooled in an ice bath, to which *ca.* 0.5 cm^3 (6.2 mmol) of pyridine was added. In the case of this complex the replacement of a water ligand by a pyridine ligand was an especially delicate procedure. Care was taken not to add too much pyridine as the precipitate could re-dissolve; it is quite soluble in pyridine. When the green precipitate formed, the solution was stirred gently then left to cool in a beaker over ice for 5 min. The fine green powder was collected on a grade four porosity sintered glass-crucible and dried over silica gel in a vacuum desiccator connected to a vacuum pump. (Yield = 0.62 g. 0.460 mmol, 58% based on $[Fe_3(\mu_3\text{-}O)(O_2CCH_2Br)_6(H_2O)_3]ClO_4\cdot 6H_2O$. Found: C, 23.78, H, 1.89, N, 2.89. Calc for $C_{27}H_{27}Br_6Cl_1Fe_3N_3O_{17}$: C, 24.06, H, 2.02, N, 3.12%)

$[Fe_3(\mu_3\text{-}O)(p\text{-}NO_2C_6H_4CO_2)_6(py)_3]ClO_4$. This complex was prepared using $[Fe_3(\mu_3\text{-}O)(p\text{-}NO_2C_6H_4CO_2)_6(H_2O)_3]ClO_4\cdot 6H_2O$ and pyridine in a complex : ligand ratio of 1 : 100 in acetone as the reaction solvent according to published methods.[23,51,52] Slow addition of pyridine to an ice-cold mixture of the complex was required to precipitate the complex as the green product is soluble in pyridine. (Yield = 0.99 g. 0.65 mmol, 82% based on $[Fe_3O(p\text{-}NO_2C_6H_4CO_2)_6(H_2O)_3]ClO_4\cdot 6H_2O$. Found: C, 45.54, H, 2.27, N, 7.71. Calc for $C_{57}H_{39}Cl_1Fe_3N_9O_{29}$: C, 45.13, H, 2.59, N, 8.31%)

Mixed-valence $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$. This complex was prepared from $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(O_2CC(CH_3)_3)_3]$ and pyridine according to the method of Wilson.[53] Shiny black crystals formed under an argon atmosphere and were filtered, dried by vacuum and stored under argon. (Yield = 1.92 g. 1.87 mmol, 47% based on $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(O_2CC(CH_3)_3)_3]$. Found: C, 52.45, H, 6.55, N, 3.79. Calc for $C_{45}H_{69}Fe_3N_3O_{13}$: C, 52.60, H, 6.77, N, 4.09%).

$[Co(bpy)_3](ClO_4)_3\cdot 3H_2O$ and $[Co(4,7\text{-}Me_2phen)_3](ClO_4)_3\cdot 3H_2O$. These complexes were prepared as previously described.[28,54]

$[Co(4,4'\text{-}(MeO)_2bpy)_3]ClO_4\cdot 3H_2O$. This compound was synthesised in the same fashion as the published method[54] for $[Co(bpy)_3](ClO_4)_3\cdot 3H_2O$ using 4,4′-dimethoxy-2,2′-bipyridine (6.49 g, 0.030 mol) in place of 2,2′-dipyridyl. (Yield = 6.42 g. 6.06 mmol, 61% based on $CoCl_2\cdot 6H_2O$. Found: C, 40.80, H, 4.04, N, 7.57. Calc for $C_{36}H_{42}Cl_3Co_1N_6O_{21}$: C, 40.79, H, 3.99, N, 7.93%)

Cyclic voltammetry studies

Solutions of the complexes (5×10^{-4} mol dm^{-3}) were analysed by cyclic voltammetry in acetonitrile containing 0.2 mol dm^{-3} $(^nC_4H_9)_4NPF_6$ using apparatus as described previously.[28] Ag/AgCl was the reference electrode against which ferrocene was oxidised at +0.43 V. The electrochemistry of the metal complexes was studied in the absence of and in the presence of an excess of the terminal ligand at a scan rate of 10 mV s^{-1} in the region +0.7 to −0.45 V. The electrochemical behaviour of the verdazyl radicals was investigated at a scan rate of 10 mV s^{-1} in acetonitrile in the region +0.5 to −0.1 V. Cyclic voltammograms of the $[Co(N\text{-}N)_3]^{3+}$ complexes were obtained at a scan rate of 10 mV s^{-1} in the region of +0.7 to −0.1 V.

Kinetic studies

The electron transfer reactions were studied at 25(±0.1) °C using a Hi-Tech SF-20 stopped flow apparatus interfaced to a PC as described previously.[28] The electron transfer reactions were quite rapid with half lives of the order of 5 ms when one of the reactants was present at a 5-fold excess (1×10^{-4} mol dm^{-3}). Arising from this it did not prove possible to carry out the kinetic studies under pseudo-first-order conditions with either an excess of the complex or the radical. Due to this, the kinetics were studied under second-order conditions with equal concentrations of the fully oxidised complex and verdazyl radical in acetonitrile solution. Rate constants were evaluated using a computer program based on published methods.[55,56] A number of different concentrations (at a range of 1.0×10^{-5} – 1.25×10^{-4} mol dm^{-3}) of verdazyl and complex were used for each system. Within experimental error, similar second-order rate constants were obtained for a particular reaction over the concentration range investigated, consistent with a second-order rate law. Errors in individual rate constants as reported by the program were of the order of 1%. The thermodynamic driving force for the reaction between the verdazyl radicals and $[Fe_3(\mu_3\text{-}O)(O_2CCH_2CN)_6(L)_3]^+$ where L = 3-CNpy or 3-Fpy is very large and the reaction is too fast to study on the stopped-flow apparatus.

Kinetic studies of the reactions of $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ with $[Co(N–N)_3]^{3+}$ complexes were conducted in deoxygenated acetonitrile solution at an ionic strength of 0.05 mol dm^{-3} $(^nC_4H_9)_4NPF_6$ and were monitored using stopped-flow spectrophotometry. The kinetics of electron transfer of $[Fe^{III}{}_2Fe^{II}(\mu_3\text{-}O)(O_2CC(CH_3)_3)_6(py)_3]$ with $[Co(bpy)_3]^{3+}$, $[Co(4,7\text{-}Me_2phen)_3]^{3+}$ and $[Co(4,4\text{-}(MeO)_2bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine, 4,7-Me$_2$phen = 4,7-dimethylphenanthroline and 4,4′-(MeO)$_2$bpy = 4,4′-dimethoxy-2,2′-bipyridine) were investigated by monitoring absorbance decreases at wavelengths of 319, 358 and 305 nm, respectively. One hundred-fold excess of free pyridine was used in the acetonitrile solutions to prevent dissociation of the terminal ligand of the mixed-valence complexes. The cross-reactions were too rapid to allow measurement under pseudo-first-order conditions and the kinetic measurements were therefore conducted under second-order conditions as described above using equivalent concentrations of reactants over a concentration range of 1×10^{-5} to 1×10^{-4} mol dm^{-3}. Ion-pairing did not appear to affect the reaction over the range of concentrations used, as rate constants for experiments carried out in the absence of ionic strength control did not differ from those obtained in the presence of 0.05 mol dm^{-3} $(^nC_4H_9)_4NPF_6$. The kinetic data reported are those obtained when the ionic strength was controlled. A single absorbance decrease was observed in each reaction corresponding to the reduction of the cobalt(III) complex and oxidation of the tri-iron complex. This was confirmed by carrying out pre-trigger experiments where it was seen that there was no evidence of any preceding or succeeding reactions.

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