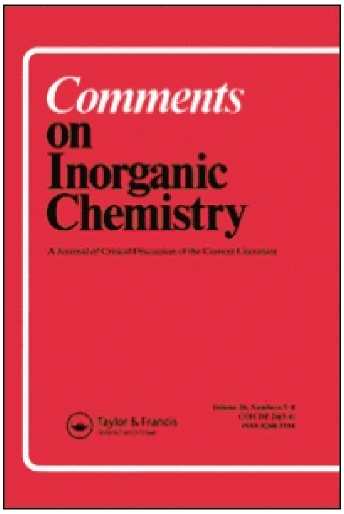

Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

The One-Electron Outer-Sphere Oxidation of Iodide and of Thiocyanide Ions by Transition Metal Complexes: Linear Free-Energy Relationships

Gwyneth Nord[a]
[a] Department of Inorganic Chemistry, The University of Copenhagen, Copenhagen 0, Denmark

To cite this Article Nord, Gwyneth(1992) 'The One-Electron Outer-Sphere Oxidation of Iodide and of Thiocyanide Ions by Transition Metal Complexes: Linear Free-Energy Relationships', Comments on Inorganic Chemistry, 13: 3, 221 — 239

To link to this Article: DOI: 10.1080/02603599208052196

URL: http://dx.doi.org/10.1080/02603599208052196

The One-Electron Outer-Sphere Oxidation of Iodide and of Thiocyanide Ions by Transition Metal Complexes: Linear Free-Energy Relationships

GWYNETH NORD
Department of Inorganic Chemistry,
The University of Copenhagen,
Universitetsparken 5,
DK-2100 Copenhagen 0, Denmark

Received February 12, 1992

The title reactions involve parallel and consecutive one-electron oxidations giving I, I_2^- and SCN, $(SCN)_2^-$ as radical intermediates. In most cases the rates of the individual steps can be well predicted using linear free-energy relationships. The necessary reduction-potentials of the non-metal couples are derived from kinetic data for complexes of very different charge and ligand type.

Key Words: *radical intermediates, linear free-energy relationships, one-electron outer-sphere oxidation*

INTRODUCTION

The oxidation of I^- and of SCN^- has been studied for many complexes under conditions where the reverse reaction is negligible. The stoichiometry is

$$2M_{ox} + 2X^- \rightarrow 2M_{red} + X_2 \qquad (1)$$

Comments Inorg. Chem.
1992, Vol. 13, Nos. 3 & 4, pp. 221-239
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where M_{ox} and M_{red} are the oxidising complex and the one-electron reduced product complex, respectively. X is either I or SCN. The rate law is

$$-d[M_{ox}]/dt = 2k_1[M_{ox}][X^-] + 2k_2[M_{ox}][X^-]^2. \qquad (2)$$

The stoichiometry and rate law conform with the stoichiometric mechanism given in Scheme I.

Since the reverse reaction (k_{-3} path) is negligible it is not necessary to include the equilibrium $X_2 + X^- \rightleftarrows X_3^-$. The general rate law is

$$-d[M_{ox}]/dt = 2k_3[M_{ox}]^2[X^-]^2\,[F]$$

where

$$[F] = k_1k_1 + k_2(k_{-1}[M_{red}] + k_4[X^-]) \times \{k_{-1}[M_{red}](k_{-4} + k_3[M_{ox}] + k_{-2}[M_{red}]) + k_4[X^-](k_3[M_{ox}] + k_{-2}[M_{red}])\}^{-1}.$$

From the experimental data,[1a,b] $k_{-1}[M_{red}] \ll k_4[X^-]$; $k_{-2}[M_{red}] \ll k_3[M_{ox}]$ and $k_{-1}k_{-4}[M_{red}] \ll k_4k_3[X^-][M_{ox}]$ so that this reduces to the experimental rate law.

The oxidation of iodide by the hexacyanoferrate(III) anion is a

SCHEME I

$$M_{ox} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_{red} + X$$

$$M_{ox} + 2X^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M_{red} + X_2^-$$

$$M_{ox} + X_2^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M_{red} + X_2$$

$$X + X^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X_2^-$$

classic example of a system where the reverse reactions cannot be neglected. The publications on this system are myriad and are briefly summarised in the Appendix to this review.

The pioneering pulse-radiolysis work of Baxendale[2a,b] on the measurement of k_4, k_{-4} and $K_4 = k_4/k_{-4}$ over a range of temperature and ionic strength has been confirmed by us and other later workers. It is of particular interest (see Table I) that K_4 for both $I + I^- \rightleftarrows I_2^-$ and for $SCN + SCN^- \rightleftarrows (SCN)_2^-$ is known at a temperature (22°C) and an ionic strength (0.1 M) where not only k_1 and k_2 are known for the oxidation of I^- by tris-2,2′-bipyridine Osmium(III), $Os(bpy)_3^{3+}$, but also the rates of the fast subsequent reactions of I_2^- and $(SCN)_2^-$ (k_{-2} and k_3 in Scheme I) are also known and are given in Scheme II; it is relevant that the metal complex competes efficiently for X_2^- so that the disproportionation of this can be ignored and also that no adducts were detected. Combining these data with k_2 from stopped flow measurements[1a] gives $K_2 = k_2/k_{-2}$ for both I_2^- and SCN_2^- and, since the reduction potential of the $Os(bpy)_3^{3+/2+}$ couple (ionic strength 0.1 M and 22°C) was 0.837 V, the reduction potentials of the $I_2^-/2I^-$ and $(SCN)_2^-/2SCN^-$ couples could be deduced. These are included in the potential diagrams (Fig. 1).

k_1 and k_{-1} are both known for the $Os(bpy)_3^{3+} + I^-$ reaction (see Table I) and have been used to calculate the reduction potential of the I/I^- couple given in Fig. 1.

For the $Fe(bpy)_3^{3+} + SCN^-$reaction, but not for the $Os(bpy)_3^{3+} + SCN^-$ system, k_1 has been measured at the appropriate temperature and ionic strength and this is used (see Table

TABLE I

Equilibrium and rate constants: see Schemes I and II

Reactants	$k_1/M^{-1}\,s^{-1}$	K_2/M^{-1}	K_4/M^{-1}	$k_{-1}/M^{-1}\,s^{-1}$
$Os(bpy)_3^{3+} + I^-$	61.71	3.03×10^{-4}	1.13×10^5	2.3×10^{10}
$Os(bpy)_3^{3+} + SCN^-$	—	3.93×10^{-9}	2.06×10^5	
$Fe(bpy)_3^{3+} + SCN^-$	5.25	(6.23×10^{-5})[a]	2.06×10^5	1.74×10^{10}

All values are for an ionic strength of 0.1 M and 22°C. $K_1 = k_1/k_{-1}$; $K_2 = k_2/k_{-2}$; $K_4 = k_4/k_{-4} = K_2/K_1$.

[a] Calculated from $E^\circ_{Fe(bpy)_3^{3+/2+}} = 1.085$ V and $E^\circ_{(SCN)_2^-/2SCN^-} = 1.331$ V derived from K_2 for $Os(bpy)_3^{3+} + SCN^-$ with $E^\circ_{Os(bpy)_3^{3+/2+}} = 0.857$ V.

SCHEME II

$$\mathrm{Os(bpy)_3^{2+} + I_2^-} \underset{(3.33 \pm 0.17) \times 10^4\ \mathrm{M^{-2}\,s^{-1}}}{\overset{(1.1 \pm 0.3) \times 10^8\ \mathrm{M^{-1}\,s^{-1}}}{\rightleftharpoons}} \mathrm{Os(bpy)_3^{3+} + 2I^-}$$

$$\mathrm{Os(bpy)_3^{3+} + I_2^-} \xrightarrow{(1.2 \pm 0.3) \times 10^{10}\ \mathrm{M^{-1}\,s^{-1}}} \mathrm{Os(bpy)_3^{2+} + I_2}$$

$$\mathrm{I_2^- + I_2^-} \xrightarrow{(4.5 \pm 1) \times 10^9\ \mathrm{M^{-1}\,s^{-1}}} \mathrm{2I^- + I_2}$$

$$\mathrm{Os(bpy)_3^{2+} + SCN_2^-} \underset{25 \pm 5\ \mathrm{M^{-2}\,s^{-1}}}{\overset{(2.8 \pm 0.2) \times 10^9\ \mathrm{M^{-1}\,s^{-1}}}{\rightleftharpoons}} \mathrm{Os(bpy)_3^{3+} + 2SCN^-}$$

$$\mathrm{Os(bpy)_3^{3+} + SCN_2^-} \xrightarrow{(1.0 \pm 0.1) \times 10^{10}\ \mathrm{M^{-1}\,s^{-1}}} \mathrm{Os(bpy)_3^{2+} + (SCN)_2}$$

$$\mathrm{SCN_2^- + SCN_2^-} \xrightarrow{(1.2 \pm 0.2) \times 10^9\ \mathrm{M^{-1}\,s^{-1}}} \mathrm{2SCN^- + (SCN)_2}$$

Results from pulse-radiolysis spectrophotometry, ionic strength 0.1 M, 22°C.

I) to calculate k_{-1} and the reduction potential of the SCN/SCN$^-$couple. k_{-1} was previously[1a] estimated as 2.2×10^{10} M^{-1} s^{-1} for both I and SCN. The reduction potentials for the X/X$^-$ with $X_2^-/2X^-$ couples included in Fig. 1 are in good agreement with those deduced by other workers using different methods[3] and are used throughout the present article.

Most kinetic data for these and other complexes are for 25°C and a range of ionic strength, and it is these which are further discussed in the next sections of this review, using the equilibrium constants K_1 and K_2 calculated from the data in Fig. 1 together with the reduction potentials of the metal couples at 25°C and the appropriate ionic strength.

Since theory relates the rates of outer-sphere electron-transfer reactions with the overall free energy changes it is now possible to meanfully discuss the mechanisms for both the k_1 and k_2 steps (Eq. (2)) for the reactions of the many complexes which have been used as one electron oxidants for iodide and for thiocyanide.

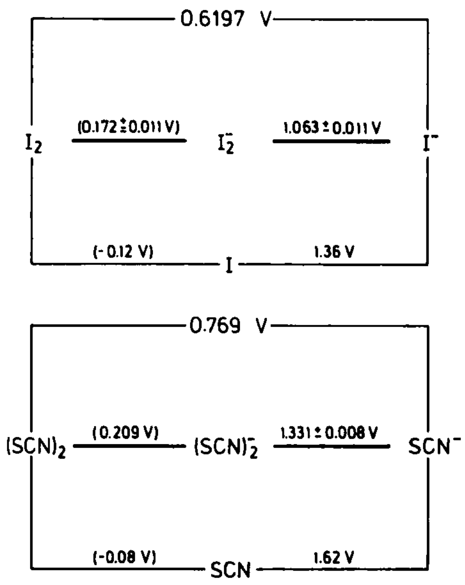

FIGURE 1 Potential diagrams for the non-metal couples (see text).

LFER AND INTIMATE MECHANISMS

(a) The one electron oxidation rate constants giving I and SCN as products (the k_1 path) give excellent LFER plots as illustrated in Figs. 2 and 3: the slope of the lines drawn is 1.0. The good correlation for complexes of different charge type and in different salt media has been attributed[4] to the fact that k_1 and K_1 involve an uncharged species and therefore would be affected to about the same extent.

There is some scatter for the Cu(III) peptides[5] and for the Ni(III) macrocycles[6] and the data for these are given in Tables II and III. The fact that the reverse reaction would be faster than the diffusion controlled rate with K_1 calculated using $E^\circ_{I/I^-} = 1.36$ V was attributed by Margerum[5] to association of the product I radical with the metal center of the Cu(II), thus decreasing the reducing power of the I/I$^-$ couple. The deviation from the LFER is only appreciable for two of these complexes which are therefore probably inner sphere, i.e., the coordination shell of the complex is not intact in the transition state. The authors of Ref. 6 believe that

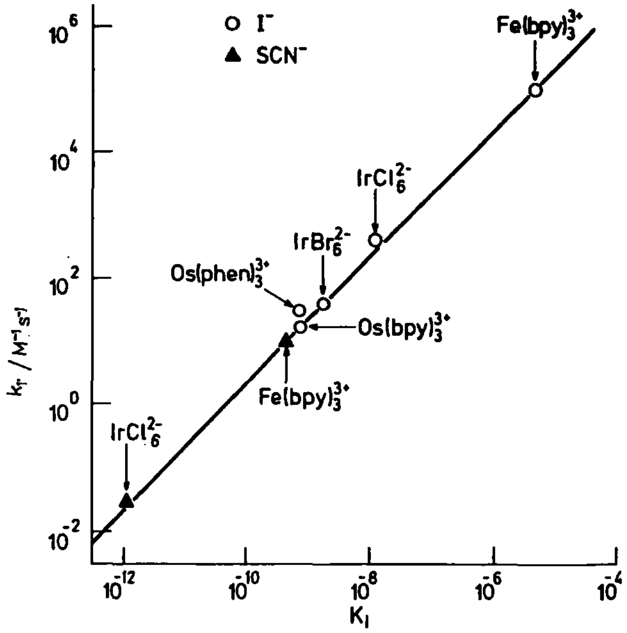

FIGURE 2 LFER (k_1 vs. K_1) plot. K_1 is calculated using E°_{I/I^-} and E°_{SCN/SCN^-} from Fig. 1. k_1 and $E^\circ_{M_{ox}/M_{red}}$ are from Ref. 1a. The line drawn gives $k_{-1} = 2.2 \times 10^{10}$ $M^{-1} s^{-1}$.

association of I^- with the Ni(III) center occurs and that this therefore would decrease the oxidising power of the Ni(III)/Ni(II) couple as given in Table III.

An extreme example of reactions which presumably have a yet different type of inner-sphere mechanism is the oxidation of iodide by gold(III) complexes. The reduction-potentials of the Au(III)/Au(II) couples are of course not known but, at least for the $AuCl_4^-$ + I^- reaction, it can be shown that in order to fit the LFER plot in Fig. 3, this would be much larger than that which can be approximated as an upper limit using the $AuCl_4^-/Au^0$ and $AuCl_2^-/Au^0$ reduction potentials given by the authors[7] who postulate bonding of the iodine radical to a ligand of a Au(II) complex.

With these exceptions the rate constants deviate from the LFER plot by less than a factor of four, i.e., the reactions can be presumed to be outer sphere. The intimate mechanism has been suggested[4]

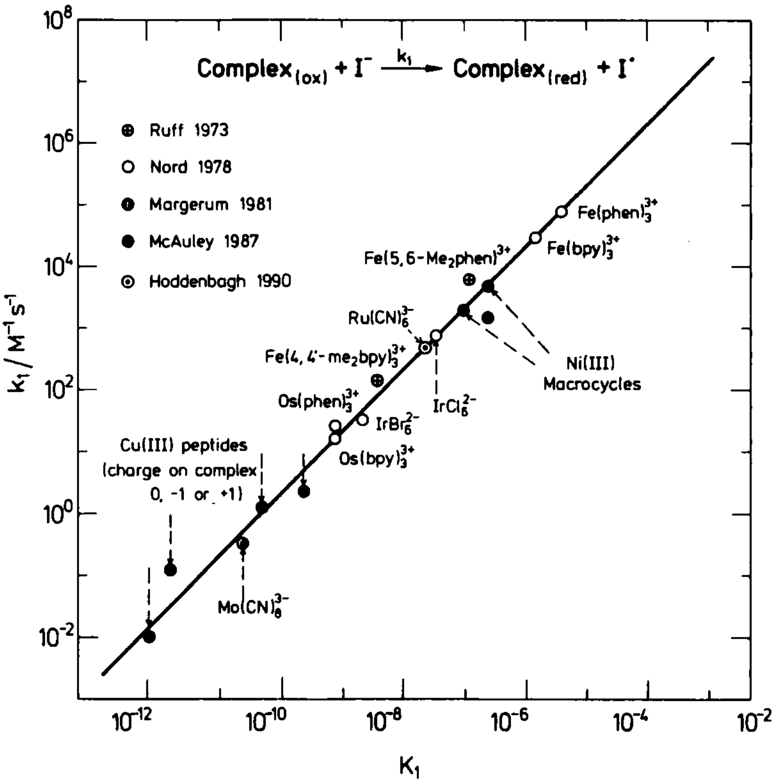

FIGURE 3 Extended LFER for the k_1 path with iodide. K_1 calculated as for Fig. 2. Rate data from Refs. 1a, 4, 5, 6, and 9. The line drawn gives $k_{-1} = 2.3 \times 10^{10}$ $M^{-1}\, s^{-1}$ (cf. Table I).

to be that given in Scheme III: rapid electron transfer in an ion-pair is followed by dissociation of the product as the slow step.

The title reactions were first studied[8a,b] in order to ascertain whether the Marcus Cross Relationship (MCR) as illustrated in Scheme IV could also be applied to outer-sphere electron-transfer from small non-metal molecules to metal complexes. The authors found that both the k_1 and k_2 terms in the rate law could be approximately correlated for a series of complexes using Eq. (2) in Scheme IV. Later[4] the limitations of this for the k_1 path were clearly stated; not only can the simplified cross relation not be

TABLE II

Cu(III) deprotonated peptide complexes, $(CuP)^z$

Nr.	Peptide (P)	z	$E^{\circ}_{(Cu(III)P)/(CuIIP)}$/V	$k_1/M^{-1}\,s^{-1}$	$k_{-1}/M^{-1}\,s^{-1a}$
1.	tri-L-alanine	0	0.81	4.5 ± 0.4	$\approx 9 \times 10^9$
2.	N,N′-diglycyl-1,2-diaminoethane	+1	0.81	4.5 ± 0.02	$\approx 9 \times 10^9$
3.	tri-L-leucine	0	0.77	2.6 ± 0.2	$\approx 2 \times 10^{10}$
4.	tetraglycinamide	0	0.68	0.23 ± 0.01	(7.1×10^{10})
5.	tri-α-aminoiso butyric acid	0	0.66	$2 \pm 1 \times 10^{-2}$	6.7×10^9
6.	tetraglycine	−1	0.63	0.10 ± 0.01	(2.1×10^{11})

[a]Calculated with $E^{\circ}_{I^{\cdot}/I^-} = 1.36$ V. Experimental data from Ref. 5.

TABLE III

Ni(III) macrocycles $(Ni(III)M)^{3+}$

Ligand	$E^{\circ}_{Ni(III)/Ni(II)}$/V	$k_1/M^{-1}\,s^{-1}$	$E^{\circ}_{Ni(III)/Ni(II)}$/V[a]
1,4,8,11-tetra-azacyclotetra-decane (cyclam)	0.990	1.55×10^3	0.935
α-c-meso-5,12-dimethyl-(cyclam)	0.995	2.0×10^3	0.942
c-meso-5,12-diethyl-(cyclam)	0.990	4.90×10^3	0.965
$(9\ ane\ N_3)_2$	0.947	9.55×10	0.864

[a]Calculated with $k_{-1} = 2.3 \times 10^{10}\ M^{-1}\,s^{-1}$ and $E^{\circ}_{I^{\cdot}/I^-} = 1.36$ V. (NB Neither of the extra two complexes listed by the authors[6] has a simple rate law.)

expected to hold for large free energy changes but there is a lack of sensitivity to the changes in the exchange rate constants k_{11} and k_{22}. The exchange rate of the reaction $X + X^-$, taken here as k_{11}, cannot be measured because the reaction $X + X^- \rightarrow X_2^-$ is too fast and the derived values differ greatly: for example, k_{11} derived from the data for oxidation of I^- by $IrBr_6^{2-}$ would be calculated to be $1.8 \times 10^5\ M^{-1}\,s^{-1}$ and for $Mo(CN)_8^{3-}$ would be $2.7 \times 10^7\ M^{-1}\,s^{-1}$; both systems, however, lie on the line of Fig. 3. The rate constants are of course composite but the excellent LFER correlation would not accord with an appreciable contribution from the electron transfer step. In spite of this, considerable effort has recently been expended in attempts to apply the MCR to the

SCHEME III

INTIMATE MECHANISM OF THE k_1 PATH

$$\mathrm{Ox} + \mathrm{X}^- \rightleftharpoons \mathrm{Ox}, \mathrm{X}^- \quad K_{1IP}$$

$$\mathrm{Ox}, \mathrm{X}^- \rightleftharpoons \mathrm{Red}, \mathrm{X} \quad k_{1et}, k_{-1et}$$

$$\mathrm{Red}, \mathrm{X} \xrightleftharpoons{\qquad} \mathrm{Red} + \mathrm{X} \quad k_{1s}, k_{-1d}$$

Applying the steady state approximation to the ion pair gives k_1 as a function of prior rapid ion pair formation (K_{1IP}), intra-ion pair electron transfer (k_{1et}, k_{-1et}) and product separation k_{1s}

$$k_1 = K_{1IP}k_{1et}k_{1s}/(k_{-1et} + k_{1s})$$

Two limiting forms,

$$k_{-1et} >> k_{1s}; \quad k_1 = K_{1IP}\frac{k_{1et}}{k_{-1et}}k_{1s} = K_{1eq}k_{-1d}$$

$$k_{-1et} << k_{1s}; \quad k_1 = K_{1IP}k_{1et}$$

reactions depicted in Fig. 3 with the object of dividing the systems into inner-sphere and outer-sphere reactions with electron transfer as the slow step.[6,9]

(b) The one electron oxidations giving I_2^- and $(SCN)_2^-$ as first products (k_2 path) are formally third order. This has been envisaged as reaction of X^- with an ion-pair $M_{ox}X^-$ or of M_{ox} with an X^-, X^- ion pair.[10] The bond distance in $[I-I]^-$ has been estimated to be 3.10 Å[4] and comparison with $I^- + I^- = 4.08$ Å shows that for this path activation energy is required for compression of the bond. There is considerable disagreement as to whether this occurs as the slowest step after electron transfer has been accomplished[5] leading to an LFER or whether bond compression and electron transfer is best considered as a concerned process to which an MCR can be applied.[4] Tests of both these relationships suffer from the lack of knowledge of ionic strength effects on the rates, e.g., reactions 1 and 10 in Table IV were measured at an ionic strength of 0.1 M, for 2, 3, 8, 9 the medium was 1 M sodium chloride, while reactions 4–7 were followed in 1 M perchloric acid. The formal potentials of the metal couples were measured in the medium used for the kinetic studies but the application of the MCR

SCHEME IV

Outer Sphere Electron Transfer

Example of the Marcus Cross Relation

$$\mathrm{Os(bpy)_3^{3+}} + \mathrm{I^-} \underset{k_{-12}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Os(bpy)_3^{2+}} + \mathrm{I} \tag{1}$$

$$\boxed{k_{12}^2 = k_{11}k_{22}K_{12}f} \tag{2}$$

$$\mathrm{I^*} + \mathrm{I^-} \underset{k_{11}}{\overset{k_{11}}{\rightleftharpoons}} \mathrm{I} + \mathrm{I^{*-}} \tag{3}$$

$$\mathrm{Os^*(bpy)_3^{3+}} + \mathrm{Os(bpy)_3^{2+}} \underset{k_{22}}{\overset{k_{22}}{\rightleftharpoons}} \mathrm{Os(bpy)_3^{3+}} + \mathrm{Os^*(bpy)_3^{2+}} \tag{4}$$

$$K_{12} = k_{12}/k_{-12}$$

$$\log f = \frac{(\log K_{12})^2/4}{(\log k_{11}k_{22}/z^2)} \tag{5}$$

$$z = 10^{11}\ \mathrm{M^{-1}\,s^{-1}}$$

TABLE IV

$$\mathrm{M_{ox}} + 2\mathrm{SCN^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{M_{red}} + \mathrm{(SCN)_2^-}$$

Nr.	Complex	$k_{22}/\mathrm{M^{-1}\,s^{-1}}$	$k_2/\mathrm{M^{-2}\,s^{-1}}$	$K_2/\mathrm{M^{-1}}$[a]
1	$\mathrm{IrBr_6^{2-}}$	2×10^8	1.53	5.75×10^{-9}
2	$\mathrm{Fe(bpy)_3^{3+}}$	5×10^8	7.5×10^3	2.63×10^{-5}
3	$\mathrm{Fe(phen)_3^{3+}}$	5×10^8	1.4×10^4	2.63×10^{-5}
4	$\mathrm{Fe(5\text{-}Cl(phen))_3^{3+}}$	5×10^8	1.87×10^5	2.75×10^{-4}
5	$\mathrm{Fe(5\text{-}Br(phen))_3^{3+}}$	5×10^8	1.75×10^5	4.0×10^{-4}
6	$\mathrm{Fe(5\text{-}Me(phen))_3^{3+}}$	5×10^8	7×10^3	5.62×10^{-6}
7	$\mathrm{Fe(4,7\text{-}Me_2(phen))_3^{3+}}$	5×10^8	50 ± 25	1.15×10^{-8}
8	$\mathrm{Os(bpy)_3^{3+}}$	1.8×10^8	4.9	4.57×10^{-9}
9	$\mathrm{Os(phen)_3^{3+}}$	3.1×10^8	10.8	5.13×10^{-9}
10	$\mathrm{IrCl_6^{2-}}$	2×10^5	0.466	3.80×10^{-8}

[a] From $E^\circ_{\mathrm{M_{ox}/M_{red}}}$ with $E^\circ_{\mathrm{(SCN)_2^-/2SCN^-}} = 1.331$ V; k_2, $E^\circ_{\mathrm{M_{ox}/M_{red}}}$ and k_{22} from Table V in Ref. 4.

is limited by the fact that coulombic work terms have been neglected.

However, Fig. 4 illustrates that, with one exception, the two sets of data given in Tables IV and V are accommodated rather well by the LFER plot, when allowance is made, according to Scheme II, for the rates of oxidation of $2SCN^-$ being twenty-five times as fast as those for $2I^-$. From the line drawn with slope 1.0 in Fig. 4, k_{-2} for the iodide systems would be 2.5×10^7 M^{-1} s^{-1} and for the SCN^- systems 6.3×10^8 M^{-1} s^{-1}. Both these values are much less than the diffusion-controlled rate and therefore could accord with the slowest step for the $X_2^- + M_{red}$ reactions (k_{-2} path) being the dissociation in an $[M_{ox}X_2]$ intermediate, the stretching of the X–X⁻ bond contributing to the activation energy.

Apart from the Cu(III) complexes the values of k_2 and k_{22} in

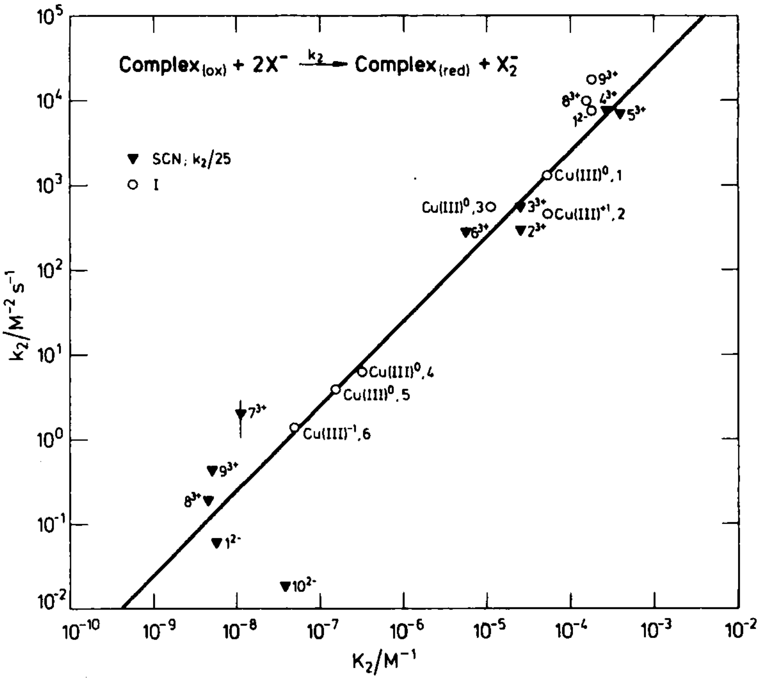

FIGURE 4 LFER for the k_2 path. Data from Tables IV and V. The line drawn gives $k_{-2} = 6.3 \times 10^8$ M^{-1} s^{-1} for the $M_{red} + (SCN)_2^-$ reaction and 2.5×10^7 M^{-1} s^{-1} for the $M_{red} + I_2^-$ reaction.

TABLE V

$$\mathrm{M_{ox}} + 2\mathrm{I^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{M_{red}} + \mathrm{I_2^-}$$

	Complex	$k_2/\mathrm{M^{-2}\,s^{-1}}$	$K_2/\mathrm{M^{-1}}$[a]	$k_{-2}/\mathrm{M^{-1}\,s^{-1}}$	$k_{22}/\mathrm{M^{-1}\,s^{-1}}$
a	$\mathrm{IrBr_6^{2-}}$	4.27×10^3	1.91×10^{-4}	2.2×10^7	2.0×10^8
b	$\mathrm{Os(phen)_3^{3+}}$	1.74×10^4	1.74×10^{-4}	1.0×10^8	3.1×10^8
c	$\mathrm{Os(bpy)_3^{3-}}$	9.12×10^3	1.51×10^{-4}	6.0×10^7	1.8×10^8
d	$\mathrm{(Cu(III)P)^0}$	1.29×10^3	5.37×10^{-5}	2.4×10^7	5.5×10^4
e	$\mathrm{(Cu(III)P)^{1+}}$	4.57×10^2	5.37×10^{-5}	0.84×10^7	5.5×10^4
f	$\mathrm{(Cu(III)P)^0}$	5.50×10^2	1.12×10^{-5}	4.8×10^7	5.5×10^4
g	$\mathrm{(Cu(III)P)^0}$	6.25	3.39×10^{-7}	1.9×10^7	2.0×10^4
h	$\mathrm{(Cu(III)P)^0}$	3.86	1.55×10^{-7}	2.4×10^7	5.5×10^4
i	$\mathrm{(Cu(III)P)^{-1}}$	1.40	4.90×10^{-8}	2.9×10^7	2.0×10^4

[a] Calculated from $E^\circ_{\mathrm{M_{ox}/M_{red}}}$ and $E^\circ_{\mathrm{I_2^-/2I^-}} = 1.063$ V. Cu(III) complexes d–i are those numbered 1–6 in Table II.

Tables IV and V are taken from Ref. 4 and reanalysed using the redox potentials given in Fig. 1. Both the LFER treatment and the MCR treatment reproduce many of the k_2 values equally well (see Fig. 5); this needs explanation.

The following division of the data in Tables IV and V is now made and explanation of the calculated results attempted.

(1) $\mathrm{IrCl_6^{2-}} + 2\mathrm{SCN^-}$ (reaction 10 in Fig. 4).

The forward and reverse reactions are both *slower* than that calculated by either method. Also the rate in sodium perchlorate[4] is rather slower than that in sodium chloride.[8] It seems likely that the dissociation of chloride from $\mathrm{IrCl_6^{2-}}$ is catalysed by the redox reaction, cf. earlier discussion of $\mathrm{AuCl_4^-}$, and that the product is $\mathrm{IrCl_5OH_2^{2-}}$, the reverse reaction requiring substitution of $\mathrm{SCN_2^-}$ in the iridium(III) coordination shell. This mechanism is analogous to that which was suggested[11] for the catalysis by iodide of substitution on ruthenium(III). The reaction would therefore be inner-sphere. It is also relevant that the lability of $\mathrm{IrCl_6^{3-}}$ was discussed as a complication by the authors[12] who first published the reduction potential of the $\mathrm{IrCl_6^{2-/3-}}$ couple.

(2) The Cu(III) peptide + $2\mathrm{I^-}$ reactions (see Table V).

The authors[5] consider that the Cu(III) complexes are planar but

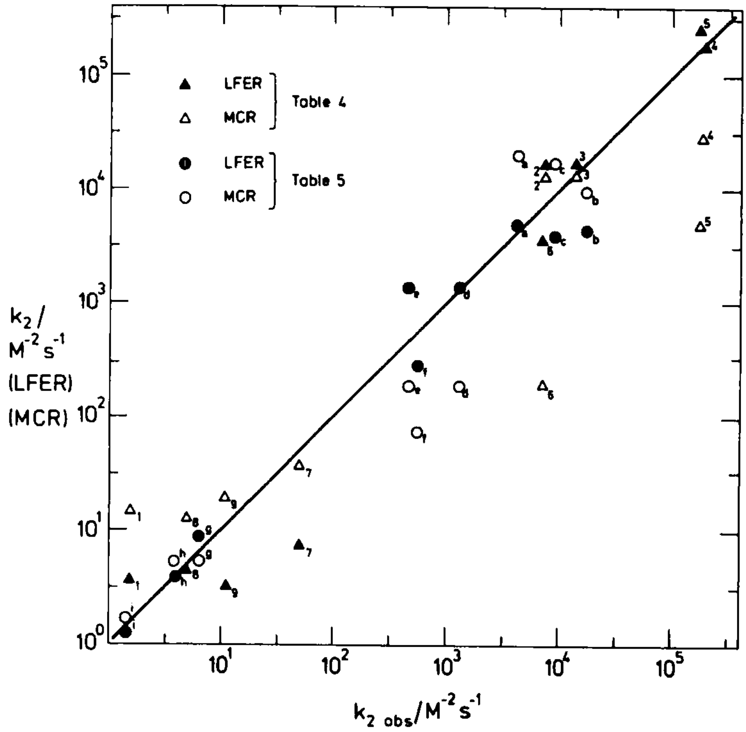

FIGURE 5 Calculated vs. observed values of k_2. k_2 (LFER) = K_2/k_{-2} (see Fig. 4 and Tables IV and V). k_2 (MCR) = k_2 outer-sphere electron transfer calculated from the Marcus Cross Relation given in Scheme IV and using k_{11} for $(SCN)_2^-$ + $2SCN^-$ = 1.26×10^4 M^{-1} s^{-1} and k_{11} for I_2^- + $2I^-$ = 2.5×10^4 M^{-2} s^{-1}. k_{22} and K_2 = K_{12} and k_2 = k_{12} are given in Tables IV and V.

that Cu(II) complexes have two axially coordinated water molecules. Both desolvation of the Cu(II) complex and the breaking of the I–I bond could therefore make significant contributions to the rate-limiting activation process for the k_{-2} path: if this is so then these reactions are *not* outer-sphere. The LFER fits these reactions very well.

(3) Tris-diimine complexes of iron(III) and osmium(III).

These have long been shown to be outer-sphere electron-transfer reagents and the rates of their cross reactions with other complexes have been compared with those predicted by Marcus theory.[13] Although the reaction $X^-,X^- + M_{ox} \rightarrow X_2^- + M_{red}$ does *not* conform with the basic assumption that the electron-transfer reagents may both be treated as spherical structureless reactants we nevertheless earlier believed that it was possible to correlate the rates with two parameters k_{22} and k_{11} which would represent the exchange rates of the metal and non-metal couples, respectively. The simplified MCR as illustrated in Scheme IV will in fact approximately reproduce the rate constants (see Refs. 1a and 4 and Tables IV and V). The rather good LFER in Fig. 4 was therefore unexpected and means that if the mechanism is *concerted* bond formation and electron transfer then the product $k_{11}k_{22}$ is required to increase strongly with K_{12}. It is known[14] for the homologous series of reactions 3 to 7 in Table IV that k_{22} does vary linearly with the reduction potential of the metal complex couple. However, not only does k_{22} *decrease* with increasing oxidising power of the complex but also the variation is small. The error introduced into the MCR calculations by taking a constant value of k_{22} for all the iron(III) complexes is therefore also small.

Reactions 4 to 7 were all measured in 1 M $HClO_4$[15] and when considered alone give a slope of only 0.76 for a log/log plot of k_2 and K_2. The general LFER plot is therefore useful for approximating the rates of the diimine complexes but is not compelling as mechanistic evidence. A two stage reaction with both slow electron transfer and bond formation contributing to the activation energy would seem to be required. Some support for a slow electron transfer contribution to the reverse reaction (k_{-2} path) is given by the rates measured by pulse radiolysis[16] for the reduction of $(SCN)_2^-$ by $Fe(CN)_6^{4-}$, $Mo(CN)_8^{4}$ and $W(CN)_8^{4-}$. These are given in Table VI.

Some support for the contribution of bond formation in decreasing the activation energy of the forward k_2 step is available from the rather scant activation parameters. These are available for both the k_1 and the k_2 paths only for $Os(phen)_3^{3+}$ with SCN^- and with I^- and for $IrBr_6^{2-}$ with I^-. In all cases[1a,4] the differences in enthalpy of activation for the two paths, $\Delta H_2^{\#} - \Delta H_1^{\#}$, is within the experimental error equal to ΔH° for the reaction $X + X^- \rightleftarrows X_2^-$; ΔH° is -5.6 ± 1 Kcal mol^{-1} for X = I and is -6.4 Kcal mol^{-1} for X = SCN.[2b]

TABLE VI

$$M_{red} + (SCN)_2^- \xrightarrow{k_{-2}} M_{ox} + 2SCN^-$$

M_{red}	$E^o_{M_{ox}/M_{red}}$/V	K_2^{-1}/M[a]	k_{-2}/M^{-1} s^{-1}[b]	k_{22}/M^{-1} s^{-1}[d]	k_{-2}/M^{-1} s^{-1} MCR[e]
$Fe(CN)_6^{4-}$	0.46	5.1×10^{14}	4.3×10^{7}[c]	3×10^{2}	4.4×10^{7}
$Mo(CN)_8^{4-}$	0.84	2.0×10^{8}	3.5×10^{6}	3×10^{4}	2.3×10^{6}
$W(CN)_8^{4-}$	0.57	7.1×10^{12}	7.1×10^{7}	7×10^{4}	1.3×10^{8}

[a] $E^o_{(SCN)_2^-/2SCN^-}$ taken as 1.331 V.

[b] 25°C, ionic strength adjusted with KSCN to 0.7 M, Ref. 16.

[c] $k_{-2} = 2.4 \times 10^7$ M^{-1} s^{-1} in 0.1 M KSCN.

[d] Accord with the MCR for oxidation by Ce(IV) and also by $IrCl_6^{2-}$ in 0.5 M H_2SO_4, Ref. 17.

[e] Calculated with k_{11}, the exchange rate constant for $(SCN)_2^- + 2SCN^-$, taken as 10 M^{-1}, s^{-1}.

The authors of Ref. 4 include data for the $2SCN^-$ + $Fe(5\text{-}NO_2phen)_3^{3+}$ reaction (phen = 1,10-phenanthroline); we find, however, that this highly oxidising complex is reduced in the kinetic medium (1 M $HClO_4$) at an appreciable rate without the addition of thiocyanide. Also the "Fe(III)" data in Table VI in Ref. 4 have been omitted. This is because the oxidation of $2SCN^-$ and of $2I^-$ by the hexaquo-iron(III) cation is generally accepted to be *inner sphere* and in accordance with this we find that the reverse reaction (k_{-2} path) probably does represent the limiting rates at which I_2^- or $(SCN)_2^-$ may enter the inner coordination shell of $Fe(OH_2)_6^{2+}$. k_{-2} for iodide is 6.8×10^5 M^{-1} s^{-1}[13] and for thiocyanide is 6.2×10^6 M^{-1} s^{-1}.[14] These rates are comparable with the rates of one electron reduction of *iodine* (k_{-3} path in Scheme I) by $FeEDTA^{2-}$ ($k_{-3} = 1.60 \times 10^6$ M^{-1} s^{-1}) and by trans-1,2-diaminocyclohexanetetraacetate-ferrate(II) ($k_{-3} = 1.24 \times 10^6$ M^{-1} s^{-1}) which were also attributed[15] to a rate controlling substitution on the Fe(II) center.

Since the outer-sphere *reduction* of iodine is of general interest we conclude this section with Table VII. This includes data for the only two systems we can find which are clearly outer sphere and also for which k_{22} for the metal couples has been measured. The MCR treatment is very successful, suggesting that the activation energy includes a much larger contribution from the slow electron

TABLE VII

$$I_2 + M_{red} \xrightarrow{k_{-3}} I_2^- + M_{ox}$$

Complex	$E^o_{M_{ox}/M_{red}}$/V	k_{-3}/M^{-1} s^{-1}	k_{22}/M^{-1} s^{-1}	K_3^{-1}[a]	k_{-3} MCR
$Co(sep)^{2+}$	−0.3	5.9×10^4[b]	5.13[c]	9.5×10^7	(5.9×10^4)
V^{2+} aqu	−0.255	7.5×10^3[d]	1×10^{-2}[c]	1.6×10^7	1.4×10^3[f]

[a] $E^o_{I_2/I_2^-}$ taken as 0.172 V.

[b] Ref. 21.

[c] Ref. 22.

[d] Ref. 23.

[e] Ref. 24.

[f] k_{11} from $Co(sep)^{2+}$ reaction is 46 M^{-1} s^{-1}; sep = 1, 3, 6, 8, 10, 13, 16, 19-octaazabicyclo[6.6.6.]icosane.

transfer than from stretching of the I–I bond. This also receives some support from the data for $Os(bpy)_3^{2+}$ derived from Scheme II, k_{-3} = 0.074 M^{-1} s^{-1}, k_{-3} MCR = 0.011 M^{-1} s^{-1}.

CONCLUSION

The outer-sphere oxidation of I^- and of SCN^-, by transition metal complexes, involves parallel paths both of which are first order in metal complex but which are first order and second order in I^- or SCN^-.

When measured under pseudo-first-order conditions $[X^-] >> [M_{ox}]$, where X^- is I^- or SCN^- and M_{ox} one of many transition metal complexes, the rate law for the outer-sphere oxidation reaction, $2M_{ox} + 2X^- \rightarrow 2M_{red} + X_2$, is:

$$-d[M_{ox}]/dt \times 1/[M_{ox}] = 2k_1[X^-] + 2k_2[X^-]^2.$$

In all cases the dependence of the rate on the overall free energy changes predominates so that the reverse rates for many metal complexes are approximately constant. It is therefore only necessary to know the reduction potential of the metal complex couple (E_o') in order to predict rate constants for each path within a factor of five, using the following LFER:

At 25°C and for both I^- and SCN^-, $k_1 = 2.3 \times 10^{10} K_1$

$K_1 = 10^{(E_0' - 1.36)/0.0592}$ for I^-

and $K_1 = 10^{(E_0' - 1.62)/0.0592}$ for SCN^-.

For I^-, $k_2 = 2.5 \times 10^7 K_2$ and $K_2 = 10^{(E_0' - 1.063)/0.0592}$.

For SCN^-, $k_2 = 6.3 \times 10^8 K_2$ and $K_2 = 10^{(E_0' - 1.331)/0.0592}$.

APPENDIX

On the Oxidation of Iodide by Hexacyanoferrate(III)

Since 1903, when the first kinetic measurements of the $Fe(CN)_6^{3-}$–I^- system were reported, most work has been carried out in concentrated iodide solutions where the forward reaction is second order in iodide concentration and, as early as 1924, was attributed to the formation of I_2^-. Particular interest has been aroused by the detection of specific cation catalysis and during this century discussion arose as to whether a special stoichiometric mechanism was required for $Fe(CN)_6^{3-}$, and presumably for the other cyano-metal anions treated in the present article. In 1983, however (Ref. 25 which includes references to earlier work), the rate of the reaction

$$Fe(CN)_6^{3-} + 2I^- \xrightarrow{k} Fe(CN)_6^{4-} + I_2^-$$

was reported in a series of concentrated salt solutions, 0.5 M to ≈ 4 M for the 1:1 electrolytes and 0.5 M to ≈ 1.75 M for the 1:2 electrolytes. The aim of the authors was to explore ion–solvent interactions (and their data treated accordingly); we find, however, that the new results allow the specific cation effects to be interpreted as arising from the lowering of the free energy of activation by electrostatic interaction in the transition state formed from the negatively charged reactants. Thus the authors[25] found for a series of nitrate solutions, concentrations c, that the rates were represented by the linear relation: $\log k = Sc$. We illustrate in Fig. 6 that for the same contribution from changes in ionic strength with increasing c, and from increasing nitrate concentration with in-

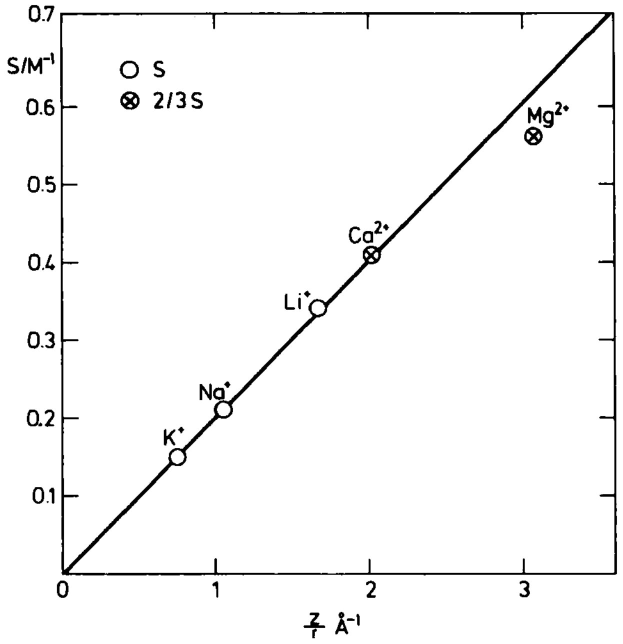

FIGURE 6 Plot of the slopes (S) of plots of log k vs. concentration of nitrate salts as a function of the ionic potential of the cations.

creasing c, the slope S is proportional to the charge/radius of the cations. It is therefore not surprising that $Fe(CN)_6^{4-}$, $Mo(CN)_8^{3-}$, $Ru(CN)_6^{3-}$ and $W(CN)_8^{4-}$ can be adequately included in the correlations with the other complexes treated in this review.

References

1. (a) G. Nord, B. Pedersen and O. Farver, Inorg. Chem. **17**, 2233 (1978); (b) G. Nord, B. Pedersen, E. Floryan-Løvberg and P. Padsberg, Inorg. Chem. **21**, 2327 (1982).
2. (a) J. H. Baxendale and P. L. T. Bevan, Trans. Faraday Soc. **64**, 2389 (1968); (b) J. Chem. Soc. A 2240 (1969).
3. D. M. Stanbury, Adv. Inorg. Chem. **33**, 69 (1989).
4. D. M. Stanbury, W. K. Wilmarth, S. Khalaf, H. N. Po and J. E. Byrd, Inorg. Chem. **19**, 2715 (1980).
5. J. M. T. Raycheba and D. W. Margerum, Inorg. Chem. **20**, 45 (1981).
6. M. C. Fairbank and A. McAuley, Inorg. Chem. **26**, 2844 (1987).

7. S. Elmroth, L. H. Skibsted and L. I. Elding, Inorg. Chem. **28**, 2703 (1989).
8. (a) J. E. Byrd, J. Y. Chen and W. K. Wilmarth, Proc. XV ICCC Moscow, U.S.S.R. (1973); (b) J. E. Byrd, J. Y. Chen, H. Po, C. P. Chua and W. K. Wilmarth, Abstracts No. INOR 102, 167th National Meeting of the American Chemical Society, Los Angeles, CA (1974).
9. J. M. A. Hoddenbagh and D. M. Macartny, Inorg. Chem. **29**, 245 (1990).
10. D. M. Stanbury, Inorg. Chem. **23**, 2914 (1984).
11. D. E. Richardson and H. Taube, Inorg. Chem. **18**, 549 (1979).
12. F. P. Dwyer, H. A. McKenzie and R. S. Nyholm, J. Proc. Roy. Soc. N. S. Wales **81**, 216 (1947).
13. M. Chou, C. Creutz and N. Sutin, J. Am. Chem. Soc. **99**, 5615 (1977).
14. (a) M.-S. Chan, Ph.D. Thesis, Washington University, St. Louis, Mo. (1974); (b) M.-S. Chan and A. C. Wahl, J. Phys. Chem. **82**, 2542 (1978).
15. F. T. T. Ng and P. M. Henry, Canadian J. Chem. **53**, 3319 (1975).
16. L. C. T. Shoute, Z. B. Alfassi, P. Neta and R. E. Huie, J. Phys. Chem. **95**, 3238 (1991).
17. R. J. Campion, N. Purdie and N. Sutin, Inorg. Chem. **3**, 1091 (1964).
18. G. S. Laurence and K. J. Ellis, J. Chem. Soc. Dalton 2229 (1972).
19. R. H. Betts and F. Dainton, J. Am. Chem. Soc. **75**, 5721 (1953).
20. W. H. Woodruff and D. W. Margerum, Inorg. Chem. **13**, 2578 (1974).
21. N. Rudgewick-Brown and R. D. Cannon, J. Chem. Soc. Dalton 479 (1984).
22. I. I. Creaser, J. MacB Harrowfield, A. J. Herlt, A. M. Sargeson, J. Springborg, R. J. Geue and M. R. Snow, J. Am. Chem. Soc. **99**, 3181 (1977).
23. J. M. Molin and J. H. Swinehart, Inorg. Chem. **8**, 1407 (1969).
24. K. V. Krishnamurthy and A. C. Wahl, J. Am. Chem. Soc. **80**, 5921 (1958).
25. P. P. Tejeda, J. R. Velasco and F. S. Burgos, Chem. Soc. Dalton 2679 (1983).