Electron Transfer. 141. Reactions of Indium(I) with Transition Metal Center Oxidants[1]

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Aqueous solutions of the hypovalent state In(I) reduce a series of complexes of Fe(III) and selected derivatives of Ir(IV), Cr(V), Pt(IV), Ag(III), and Ni(IV). All reactions yield In(III). Ions derived from Fe(III) and Ir(IV) undergo net le$^-$ conversions, whereas the other oxidants change by two units. Reductions of Fe(III) are strongly promoted by increasing pH or by adding Cl$^-$, Br$^-$, NCS$^-$, or N_3^-. Reaction appears to proceed through monoligated complexes, $Fe^{III}(Lig^-)^{2+}$, and the kinetic response to alteration of added ligand indicates initiation mainly via a bridged transition state $Fe^{III}-Lig-In^I$. Oxidations by $Fe(CN)_6^{3-}$ are exceptionally rapid, those by Fe^{III}(EDTA) are unusually slow, and redox is blocked by addition of excess F$^-$. Reduction of $IrCl_6^{2-}$ proceeds somewhat more slowly than predicted by the Marcus model for outer-sphere reactions. Conversions of the 2e$^-$ oxidants are rapid. For these, multistep routes initiated by le$^-$ changes are reasonable, but direct 2e$^-$ paths involving oxygen transfer (from Cr^VO) or Cl$^+$ transfer (from $PtCl_6^{2-}$) cannot be ruled out. Whether inner-sphere 2e$^-$ transactions without transfer of atomic species can be competitive remains an open question.

Introduction

It has long been conceded that reductants customarily taken to be 2e$^-$ donors can be induced to partake in single-electron transactions, given adequate driving force and the absence or indolence of complementary oxidants.[2] Moreover, Ghosh[3] and Chandra[4] have demonstrated that even with facile two-unit routes at hand, U(IV), $(Mo^V)_2$, and H_3PO_2 utilize minor, but detectable, single-electron paths in their reactions with Cr(VI).

The generation, in 1996, of long-lived aqueous In(I) solutions[5] added a strongly reducing[6] s^2 center to the array of available reagents, and this state was shown to react with le$^-$ oxidants derived from Co(III) and Ru(III),[5,7] necessarily by single-electron steps. In virtually all such instances, the initial transfer from In(I) was found to be much slower than the follow-up reaction with the more powerful reductant, In(II),[8] which was therefore kinetically silent. Evidence has recently been presented that the oxidation of In(I) by riboflavin proceeds predominantly by le$^-$ steps,[9] although both coreagents, in principle, offer possible two-unit routes.

The present report deals with the reactions of $In(I)_{aq}$ with oxidizing transition metal centers in aqueous acid. Reactions with a number of such oxidants, both le$^-$ and 2e$^-$ reagents, proceed readily, and single-electron transactions appear to be favored throughout. We find no evidence as yet for a predominant reaction path involving simultaneous transfer of two units.

Experimental Section

Materials. Solutions were prepared using Millipore water that had been boiled for 2 h and then sparged with N_2 for 2 h more to remove dissolved oxygen. Sodium perchlorate (used as a supporting electrolyte) was prepared in solution from concentrated $HClO_4$ and $NaHCO_3$. Iron(III) perchlorate, (EDTA)iron(III) sodium salt dihydrate, sodium hexachloroiridate(IV) ($Na_2IrCl_6\cdot 6H_2O$), sodium hexachoroplatinate(IV) ($Na_2PtCl_6\cdot 6H_2O$), sodium hexachloropalladate(IV) ($Na_2PdCl_6\cdot 6H_2O$), uranium trioxide (Alfa products), sodium thiocyanate (Mallinckrodt), sodium bromide (Allied Chemical), sodium fluoride, potassium hexacyanoferrate(III), anhydrous acetonitrile, indium metal powder, 2-ethyl-2-hydroxybutanoic acid, sodium dichromate (Aldrich products), and nickel chloride (Fisher) were used as received.

Concentrations of iron(III) in $Fe(ClO_4)_3$ solutions were determined iodometrically. Indium(I) solutions were prepared as described[5] and were used within 1 week of preparation. Ethylenebis(biguanide)silver(III) perchlorate, (ebbg)$Ag(ClO_4)_3$[10] (**I**), and sodium bis(2-ethyl-2-hydroxybutanoato)oxochromate(V), $[Cr^VO(EHB)_2^-]$[11] (**II**), were prepared by known procedures. Solutions of $UO_2(ClO_4)_2$ were prepared by dissolving UO_3 in 1.0 M $HClO_4$ at 60 °C and were analyzed spectrophotometrically.[12]

The nickel(IV) complex of 2,6-diacetylpyridine dioxime, Ni^{IV}(DAPD)$_2$ (**III**), was prepared by a modification of the method of Baucom.[13] Supersaturated solutions of this complex, which is nearly insoluble in water, were prepared by refluxing the crystalline product in 50:50 methanol/water for 2 h with stirring, cooling, and then diluting with distilled water. Solutions of this complex ($(2-3) \times 10^{-5}$ M) for kinetic runs were obtained by dilution and were analyzed at 575 nm[13b] ($\epsilon = 1.28 \times 10^4$ M^{-1} cm^{-1}); these were made fresh for each day's experiments.

Stoichiometric Studies. Stoichiometric determinations were carried out under argon at pH 1−2 and monitored at or near the low-energy

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[1] Sponsorship of this work by the National Science Foundation (Grant CHE-9714981) is gratefully acknowledged.

[2] See, for example: (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley: New York, 1968; p 497. (b) Lappin, G. *Redox Mechanisms in Inorganic Chemistry*; Ellis Horwood: New York, 1994; Chapters 2 and 5.

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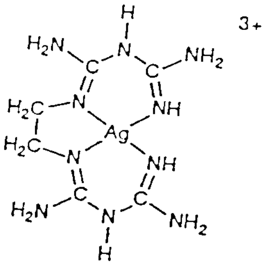

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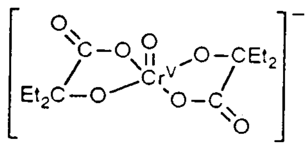

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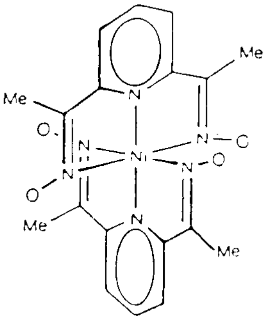

III

maximum of each oxidant. Measured deficient quantities of In(I) were added to a known excess of the oxidant. After 2−15 min reaction time, decreases in absorbance were compared with those resulting from addition of excess reductant. This procedure was not successful for the very slowly reacting oxidants; with these, decomposition of In(I) competed significantly with the principal redox reactions. Results are summarized in Table 1.

Kinetic Studies. Reactions, under argon, were examined at or near λ_{max} of the oxidant, using a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer system. All reactions were run at 24.0 ± 0.5 °C. To minimize the loss of In(I) in acidic media,[5] reactions were initiated by mixing In(I) solutions in 0.1 M aqueous $LiClO_4$ with oxidant solutions of appropriate acidity. Ionic strength was regulated by addition of ($NaClO_4 + HClO_4$) or (HCl + NaCl). Reactions were most often run under pseudo-first-order conditions with no more than 10% of the reagent in excess consumed by the redox transformation. The resulting exponential profiles were followed for at least four half-life periods, and rate constants were evaluated by nonlinear least-squares fittings to the relationship describing first-order decay.

Reductions of $PtCl_6^{2-}$ and $Cr^VO(EHB)_2^-$ were too rapid to measure ($k > 5 \times 10^5$ M^{-1} s^{-1}), even under second-order conditions. In contrast, reductions $Fe^{III}-F^-$ ($[F^-] = 0.005$ M) and the Fe^{III}(EDTA) systems were so slow that decomposition of In(I) in the acid media[5] became competitive with its oxidation. Only an approximate rate for Fe^{III}-(EDTA) and no meaningful value for the fluoride reaction could be obtained. No reactions were observed with either VO^{2+} or UO_2^{2+} in ClO_4^- media. Oxidations with Ag^{III}(ebbg) at pH > 1.0 and with $PdCl_6^{2-}$ were complicated by the rapid formation of black precipitates, presumably the parent noble metal. The reduction of $IrCl_6^{2-}$ was so rapid that only the last 20% of reaction could be observed using stopped-flow under second-order conditions; a rate constant $(1.4 \pm 0.5) \times 10^5$ M^{-1} s^{-1} was estimated, but a precise study of pH dependence was not feasible.

Table 1. Stoichiometry of Reactions of Indium(I) with Transition Metal Center Oxidants[a]

oxidant (Ox)	$[H^+]$, M	λ, nm	$\Delta[Ox]/\Delta[In^I]$
$Fe^{III}(Cl^-)$	0.05	280	1.91
$Fe^{III}(Br^-)$	0.05	280	1.95
Fe^{III}(HF)	0.05	240	*b*
$Fe(CN)_6^{3-}$	0.05	416	2.01
$Fe(NCS)^{2+}$	0.05	460	2.05
$Fe(N_3)^{2+}$	0.05	260	1.95
Fe^{III}(EDTA)	0.05	340	*b*
$Ir^{IV}Cl_6^{2-}$	0.01	490	1.99
$Cr^VO(EHB)_2^-$ (**II**)	0.01	510	1.05
$PtCl_6^{2-}$	0.01	370	1.09
Ag^{III}(ebbg) (**I**)	0.10	380	1.04
$Ni^{IV}(DAPD)_2$ (**III**)	0.10	575	1.06

[a] For reaction conditions, see Experimental Section. [b] Very slow reaction; decomposition of In(I) competed with the reduction of Fe(III).

Results and Discussion

Those reactions for which stoichiometric determinations could be carried out (Table 1) yield values confirming very nearly complete conversion to In(III) with both one- and two-electron acceptors, e.g., Fe^{III} and Pt^{IV}.

$$In^I + 2Fe^{III} \rightarrow In^{III} + 2Fe^{II} \tag{1}$$

$$In^I + Pt^{IV} \rightarrow In^{III} + Pt^{II} \tag{2}$$

Transformations for which kinetic measurements could be made were first-order in In(I) in each case. No spectral irregularities appeared that were attributable to the intervention of In(II) on a time scale comparable to the primary conversions.

Oxidations by Fe(III). Representative data for oxidation of In(I) by Fe(III)−halide systems appear in Table 2, and rates for systems having added NCS^- and N_3^- are listed in Table 3. Oxidations are seen to be strongly promoted by addition of each of these anions, and the halide (but not the thiocyanate) data show rate decreases with added H^+. The patterns for all three sets are consistent with partition of Fe(III) into three cations, Fe^{3+}(aq), $Fe(OH)^{2+}$, and $Fe(Lig)^{2+}$ in rapid equilibrium. If second-order rate constants (k_{aq}, k_{OH}, and k_{Lig}) are assigned to each species, observed rates may be expressed as

$$\text{rate} = \frac{(k_{aq}[H^+] + k_{OH}K_A + k_{Lig}K_{Lig}[Lig][H^+])[In][Fe]_T}{[H^+] + K_A + K_{Lig}[Lig][H^+]} \tag{3}$$

where K_A is the acidity constant for Fe^{3+}(aq), K_{Lig} is the association quotient for monoligation of Fe(III), and $[Fe]_T$ is the total added Fe(III). Refinement of rates in accordance with eq 3 yields the parameters in Table 5. Note that the Fe^{3+}(aq) path (k_{aq}) is found to be negligible for the chloro and bromo systems but is observed in the $Fe^{III}(NCS^-)$ experiments, which were carried out at much higher acidities.

A modified expression (eq 4, Table 4) is needed for the $Fe^{III}N_3$ system to take into account the partial conversion of the added azide to the weak acid, HN_3. Here, only the FeN_3^{2+} path is kinetically significant.

Rate enhancements of outer-sphere redox reactions by added halides and thiocyanate have been described,[14] but such effects are much less marked than those seen here for the Fe(III)−In(I) reactions. If, as implied in eq 3, we attribute these increases to partial conversion of Fe(III) to more reactive monoligated complexes, the trends in reactivity may be taken to indicate that halide and hydroxide have furnished bridging paths resembling those proposed for Fe(III)−Cr(II) and Fe(III)−Eu(II) reactions[14a] and for the corresponding oxidations of vitamin B_{12r} by Fe(III) systems.[15] In addition, the trend in rates for the cations $FeLig^{2+}$ toward In(I) (where Lig = Br, Cl, N_3, and F) calls to

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Table 2. Representative Kinetic Data for Oxidation of Indium(I) with Iron(III) in Chloride- and Bromide-Containing Media[a]

A. $In^I{-}Fe^{III}{-}Cl^-$				B. $In^I{-}Fe^{III}{-}Br^-$			
$10^4[In^I]$, M	$[H^+]$, M	$10^3[Cl^-]$, M	k, $s^{-1\,b}$	$10^4\,[In^I]$, M	$[H^+]$, M	$10^3[Br^-]$, M	k, $s^{-1\,b}$
6.0	0.010	2.4	0.31 (0.27)	6.0	0.010	2.4	0.24 (0.29)
12.0	0.010	2.4	0.58 (0.54)	12.0	0.010	2.4	0.56 (0.58)
36.0	0.010	2.4	1.41 (1.60)	24.0	0.010	2.4	1.13 (1.15)
48.0	0.010	2.4	2.3 (2.1)	36.0	0.010	2.4	1.65 (1.73)
12.0	0.010	1.2	0.45 (0.40)	12.0	0.010	1.20	0.47 (0.41)
12.0	0.010	3.6	0.74 (0.67)	12.0	0.010	3.6	0.76 (0.74)
12.0	0.010	4.8	0.82 (0.80)	12.0	0.010	4.8	0.91 (0.91)
12.0	0.010	6.0	0.92 (0.94)	12.0	0.010	6.0	1.08 (1.07)
12.0	0.020	2.4	0.41 (0.34)	12.0	0.020	2.4	0.37 (0.35)
12.0	0.050	2.4	0.21 (0.21)	12.0	0.050	2.4	0.21 (0.20)
12.0	0.100	2.4	0.122 (0.162)	12.0	0.100	2.4	0.125 (0.145)

[a] Reactions were run at 24 °C, $\mu = 0.50$ M (ClO_4^-), $\lambda = 280$ nm, $[Fe^{III}] = 1.2 \times 10^{-4}$ M. [b] Pseudo-first-order rate constants; parenthetical values were calculated from rate laws in Table 4, using kinetic parameters in Table 5.

Table 3. Kinetic Data for the Oxidation of In(I) with Fe(III) in Thiocyanate- and Azide-Containing Media[a]

A. $In^I{-}Fe^{III}{-}NCS^-$				B. $In^I{-}Fe^{III}{-}N_3^-$			
$10^4[In^I]$, M	$[H^+]$, M	$10^3[NCS^-]$, M	k, $s^{-1\,b}$	$10^4\,[In^I]$, M	$[H^+]$, M	$10^3[N_3^-]$, M	k, $s^{-1\,b}$
3.0	0.50	1.20	2.4 (2.2)	6.0	0.010	1.20	0.30 (0.30)
6.0	0.50	1.20	4.3 (4.3)	20.0	0.010	1.20	0.90 (1.00)
12.0	0.50	1.20	7.6 (8.6)	25.0	0.010	1.20	1.20 (1.25)
18.0	0.50	1.20	12.9 (13.0)	30.0	0.010	1.20	1.46 (1.49)
24.0	0.50	1.20	17.7 (17.3)	35.0	0.010	1.20	1.88 (1.74)
6.0	0.50	0.60	3.7 (3.6)	6.0	0.010	1.50	0.44 (0.59)
6.0	0.50	2.40	5.0 (5.5)	6.0	0.010	2.4	0.67 (0.74)
6.0	0.50	3.60	5.7 (6.4)	6.0	0.010	3.0	0.97 (0.83)
6.0	0.50	6.0	8.4 (7.8)	6.0	0.020	1.20	0.20 (0.25)
6.0	0.10	1.20	4.8 (4.3)	6.0	0.050	1.20	0.120 (0.110)
6.0	0.20	1.20	4.6 (4.3)				
6.0	0.30	1.20	4.7 (4.3)				

[a] Reactions were carried out at 24 °C, $\mu = 0.50$ (ClO_4^-), $\lambda = 260$ nm (N_3), 460 nm (NCS), $[Fe^{III}] = 6.0 \times 10^{-5}$ M. [b] Pseudo-first-order rate constants; parenthetical values were calculated from rate laws in Table 4, using kinetic parameters in Table 5.

Table 4. Rate Laws for Oxidations of Indium(I)

oxidant	rate law	eq no.
$Fe^{III}Cl^-$	$[In^I][Ox](k_{OH}K_A + k_{Hal}K_{Hal}[Hal][H^+])/([H^+] + K_A + K_{Hal}[Hal][H^+])$	4[a]
$Fe^{III}Br^-$		4
$Fe^{III}(NCS^-)$	$[In^I][Ox](k_{aq}[H^+] + k_{NCS}K_{NCS}[NCS][H^+])/([H^+] + K_A + K_{NCS}[NCS][H^+])$	5[a]
$Fe^{III}(N_3^-)$	$[In^I][Ox]k_{N_3}\,K_{N_3}[N_3]_T/([H^+]K_{HN_3} + K_AK_{HN_3} + K_{N_3}[N_3]_T)$	6[b]
$Fe(CN)_6^{3-}$	$[In^I][Ox]$	7
Fe^{III}(EDTA)		7[c]
Ag^{III}(ebbg) (**I**)		7
$Ni^{IV}(DAPD)_2$ (**III**)	$[In^I][Ox](k + k'[H'])$	8

[a] Eqs 4 and 5 are adaptations of eq 3 in text, with nonsignificant kinetic terms omitted. k's are second-order rate constants; K_A is the acidity constant for Fe^{3+}(aq), and K_{Hal}'s are association quotients for monoligated complexes. [b] K_{HN_3} is the acidity constant for HN_3. $[N_3]_T$ is the total concentration of added azide. [c] Reactions studied only at 0.01 M H^+.

mind the relative values for In(I) oxidations by the analogous $(NH_3)_5Co^{III}X$ complexes[5] (in both series, the fluoro derivative is negligibly active). The low value for Fe^{III}(EDTA) is in accord with the reported[5] reluctance of In^+ to utilize carboxyl-bridged redox paths.

The very high rate for $Fe(CN)_6^{3-}$ strongly implicates operation of a cyano-bridged route. Using the simplified relationship of Marcus, eq 9,[2,16] we may employ the proposed self-exchange

$$\log k_{FeCN,In} = 1/2(\log k_{In} + \log k_{FeCN} + \Delta E°/0.059) \quad (9)$$

rate (k_{In}, 10^{-9} M^{-1} s^{-1})[7a] and formal potential (−0.21 V)[8] associated with the In(II,I) system and the corresponding parameters for the $Fe(CN)_6^{3-,4-}$ system ($10^{4.9}$ M^{-1} s^{-1} and 0.36 V)[17] to estimate an outer-sphere kinetic component $k_{FeCN,In}$ for this reaction as $10^{2.6}$ M^{-1} s^{-1}, i.e., 4 orders of magnitude below the observed rate, thus implying a preponderant inner-sphere contribution in this instance as well.

Reactions with Nonferrous Oxidants. Among the non-iron coreagents listed in Table 5, only $IrCl_6^{2-}$ undergoes a net single-unit change. Marcus-related treatment analogous to eq 9 ($k_{Ir(4,3)}$, $10^{5.4}$ M^{-1} s^{-1}; $E° = 0.87$ V)[18] yields an estimated outer-sphere rate ($k_{Ir,In}$, 10^7 M^{-1} s^{-1}) perceptibly greater than the observed value. For this oxidant, evidence for a rate-enhancing bridged path has disappeared.

For each of the remaining $2e^-$ acceptors, routes initiated by le^- changes and proceding through recognized intermediate states (Ag^{II}, Ni^{III}, Cr^{IV}, and Pt^{III})[19] are, in principle, accessible; however, for the Cr(V) and Pt(IV) oxidants direct $2e^-$ paths involving oxygen or Cl^+ transfer cannot be ruled out. The high

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(16) The approximate nature of this calculation does not justify a more elaborate treatment.

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Table 5. Kinetic Parameters for Oxidations of Indium(I) by Transition Metal Center Oxidants[a]

oxidant	parameters[b]
$Fe^{III}Cl^-$	$k_{FeCl} = (2.5 \pm 0.6) \times 10^4$; $k_{FeOH} = (3.4 \pm 0.7) \times 10^3$ $K_A = 1.2 \times 10^{-3}$; $K_{FeCl} = 4.3\ M^{-1}$
$Fe^{III}Br^-$	$k_{FeBr} = (2.0 \pm 0.1) \times 10^5$; $k_{FeOH} = (3.8 \pm 0.2) \times 10^3$ $K_{FeBr} = 0.9\ M^{-1}$
$Fe^{III}NCS^-$	$k_{FeNCS} = (2.4 \pm 0.2) \times 10^4$ $k_{aq} = (4.6 \pm 0.4) \times 10^3$; $K_{FeNCS} = 130\ M^{-1}$
$Fe^{III}N_3^-$	$k_{FeN_3} = (2.0 \pm 0.2) \times 10^3$; $K_{FeN_3} = 1.6 \times 10^4\ M^{-1}$
$Fe(CN)_6^{3-}$	$k = (4.0 \pm 0.2) \times 10^6$
Fe(EDTA)[c]	$k = 46 \pm 2$
$IrCl_6^{2-}$	$k = (1.4 \pm 0.5) \times 10^5$
Ag^{III}(ebbg) (**I**)	$k = (5.3 \pm 0.1) \times 10^3$
$Ni^{IV}(DAPD)_2$ (**III**)	$k = (5.3 \pm 0.2) \times 10^5$; $k' = (1.49 \pm 0.03) \times 10^8\ M^{-2}\ s^{-1}$
$Cr^VO(EHB)_2^-$ (**II**)	$k > 5 \times 10^5$[d]
$PtCl_6^{2-}$	$k > 1 \times 10^6$[d]

[a] Reactions were run at 24 °C; μ was generally 0.50 M (ClO_4^-). [b] Parameters are those in the rate laws listed in Table 4. Rate constants (except k' for Ni^{IV}) are in $M^{-1}\ s^{-1}$; equilibrium constants for Fe(III) systems have been assembled by: Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum; New York, 1989; Vol. 6, pp 436−459. [c] Reaction in 0.01 M H^+. [d] Lower limits estimated assuming that reactions are first-order in both In(I) and oxidant.

rates prevailing throughout this group and the absence of distinctive differences in behavior prevent our drawing mechanistic inferences based upon the data at hand.

In sum, our experiments indicate that In^I(aq), in most, if not all, of its reactions with the metal-center oxidants examined, conforms to the pattern seen[5,7] for oxidations by complexes of Co(III) and Ru(III). In the preferred route, reaction is initiated by a le$^-$ reductions yielding In(II), which is then consumed much more rapidly. Evidence abounds, here and elsewhere, for single-electron redox paths, even when the oxidant, the reductant, or both are formally 2e$^-$ reagents. In contrast, direct single-step outer-sphere transactions of two electrons, if they occur at all, are recognized as being unusually slow, reflecting characteristically high Franck−Condon barriers.[2b] Analogous restrictions may apply to inner-sphere two-unit events, aside from those entailing concerted transfers of atomic species (oxo, halonium, or hydride). This point remains unsettled.

Acknowledgment. We are grateful to Mrs. Arla McPherson for technical assistance.

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(19) See, for example: (a) Levason, W.; Spicer, M. D. *Coord. Chem. Rev.* **1987**, *76*, 45. (b) Pappernhagen, T. L.; Kennedy, W. R.; Bowers, C. P.; Margerum, D. W. *Inorg. Chem.* **1985**, *24*, 4356. (c) Gould, E. S. *Coord. Chem. Rev.* **1994**, *135/136*, 651. (d) Glennon, C. S.; Hand, T. D.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, *19*.