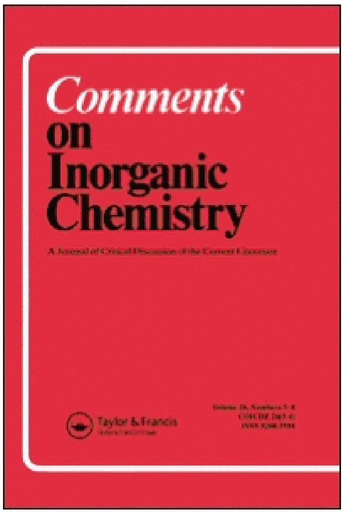

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

On the Mechanism of Octahedral Substitution

T. W. Swaddle[a]
[a] Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada

To cite this Article Swaddle, T. W.(1991) 'On the Mechanism of Octahedral Substitution', Comments on Inorganic Chemistry, 12: 4, 237 — 258

To link to this Article: DOI: 10.1080/02603599108053476

URL: http://dx.doi.org/10.1080/02603599108053476

On the Mechanism of Octahedral Substitution

T. W. SWADDLE
Department of Chemistry,
The University of Calgary,
Calgary, Alberta, Canada T2N 1N4

In terms of the Langford–Gray mechanistic classification, simple ligand substitution in octahedral complexes in donor solvents may be described as an **I** process in all cases; it is doubtful whether the criteria for **D** or **A** mechanisms could ever be met. It is argued, however, that no meaningful, unequivocal assignments along the **D**/$\mathbf{D_l}$/$\mathbf{I_d}$/$\mathbf{I_a}$/**A** lines can be made for octahedral substitution, and that attempts to make them are actually counterproductive. Instead, we should seek means of expressing the selectivity shown by various substrates towards nucleophiles, and also the lifetimes of putative intermediates, at least semi-quantitatively. Computer modelling can provide important insights into the mechanism of reaction, particularly into the key role played by the solvent in the activation process. Certain complexes of metals of the second transition series show anomalous lability; the effect requires experimental and theoretical clarification, but appears to have relativistic origins.

Key Words: *reaction mechanisms, ligand substitution, octahedral complexes, second transition series*

Lay has recently presented in these pages[1] a thoughtful review of the existing information on the kinetics and mechanism of both spontaneous and base-catalyzed substitution in pseudo-octahedral metal amine complexes. He draws several conclusions, some of which have antecedents while others are new but should find ready acceptance. Inevitably, there are some assertions which may benefit from further consideration. I present here an update, stimulated at least in part by Lay's proposals, of earlier viewpoints[2,3]

Comments Inorg. Chem.
1991, Vol. 12, No. 4, pp. 237–258
Reprints available directly from the publisher
Photocopying permitted by license only

regarding the mechanism(s) of simple octahedral substitution processes in water and other coordinating solvents, and attempt to identify directions for constructive future work. The thrust of this article, which is not intended to be a comprehensive review, is that the traditional preoccupation with mechanistic classification of reactions has outlived its usefulness, and is actually hindering progress.

MECHANISTIC DEFINITIONS

Much of the debate that has taken place regarding the intimate mechanism of simple octahedral substitution has, in the last analysis, been semantic, inasmuch as operational definitions of mechanism[4] are technique-specific.[3,5] Thus, a mechanistic assignment made on the basis of a pressure effect may differ from one inferred from free-energy relationships or scavenger competition ratios, simply because the criteria for mechanistic assignment are necessarily different. Furthermore, the criteria themselves may be less decisive than is generally supposed.

For example, the widely used scheme of Langford and Gray[4] defines three classes of "stoichiometric" mechanism based upon the *kinetic detectability of intermediates* (dissociative, "**D**": detectable intermediate of reduced coordination number; associative, "**A**": detectable intermediate of expanded coordination number; interchange, "**I**": no kinetically detectable intermediates). It further proposes to distinguish two categories of "intimate" mechanism within the **I** class depending on whether the reaction rate is at least as sensitive to the nature of the entering group as to that of the leaving group ($\mathbf{I}_a$) or not ($\mathbf{I}_d$). This latter distinction is generally impractical for substitution of a leaving group X by a nucleophile Y in octahedral complexes ML_5X in donor solvents, since X is often replaced by solvent as a first step, and so one is driven to propose various alternative criteria for the intimate mechanism. Yet, even for the ostensibly simpler exercise of distinguishing *kinetically* between the alternative "stoichiometric" mechanisms, a definitive answer may be elusive because the basic mathematical form of the dependence of the pseudo-first-order rate constants k_{obsd} on the concentration of entering ligand Y (in large excess) can be the same for **D**, **I**, and **A**:

$$k_{\mathrm{obsd}} = a[\mathrm{Y}]/(b + [\mathrm{Y}]). \tag{1}$$

For the **D** mechanism,

$$\mathrm{ML_5X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_5} + \mathrm{X} \xrightarrow{+\,\mathrm{Y},\ k_2} \mathrm{ML_5Y} + \mathrm{X}, \tag{2}$$

$$k_{\mathrm{obsd}} = k_1k_2[\mathrm{Y}]/(k_2[\mathrm{Y}] + k_{-1}[\mathrm{X}]) \tag{3}$$

so that, if X is the solvent, [X] is effectively constant and we have Eq. (1) in which $a = k_1$ and $b = k_{-1}[\mathrm{X}]/k_2$. For an **I** process, an encounter complex[4] such as an ion pair is considered to form (equilibrium constant K_{ec}) and to undergo internal ligand exchange (first order rate constant k_1):

$$\mathrm{ML_5X} + \mathrm{Y} \overset{K_{\mathrm{ec}}}{\rightleftharpoons} \{\mathrm{ML_5X, Y}\} \xrightarrow{k_i} \mathrm{ML_5Y} + \mathrm{X}, \tag{4}$$

$$k_{\mathrm{obsd}} = k_iK_{\mathrm{ec}}[\mathrm{Y}]/(1 + K_{\mathrm{ec}}[\mathrm{Y}]) \tag{5}$$

which again has the form of Eq. (1) with $a = k_i$ and $b = K_{\mathrm{ec}}^{-1}$. Similarly, as Langford and Gray pointed out,[4] k_{obsd} for an **A** mechanism will start to show a non-linear dependence on [Y] as in Eq. (1) if the intermediate of expanded coordination number accumulates to the point at which it forms a significant fraction of the total metal complex concentration. Thus, the empirical rate law will be the same (Eq. (1)) regardless of mechanism, but the significance of the parameters a (in effect, a limiting first-order rate constant, rarely reached in practice) and b will be mechanism-dependent—for a **D** mechanism, a is the rate constant for M–X bond breaking, whereas for an **I** process it is the rate constant for the replacement of X by Y within the encounter complex, and for **A** it represents the rate of breakup of an intermediate of expanded coordination number.

For the replacement of X = solvent in $\mathrm{ML_5X}$ by Y, a **D** mechanism may be said to be demonstrated kinetically if, on fitting the data to Eq. (1), a is the same for all Y *including Y = solvent.* It has recently been shown[6] that the reactions of $\mathrm{Co(CN)_5OH_2^{2-}}$ with various Y (the classic Haim–Wilmarth series,[7] long held to constitute the benchmark example of the **D** mechanism) fail to meet this criterion, and that these substitution reactions are better described as $\mathbf{I}_d$ processes.[6,8-10] The Haim–Wilmarth reactions were considered to be particularly likely candidates for the **D** mechanism, as anionic complexes should be less vulnerable to nucleophilic attack than are neutral or, especially, cationic species, and so it is probable that many other supposed examples of the **D** mechanism will, on close scrutiny, turn out to meet the $\mathbf{I}_d$ criteria more closely. As for the **A** mechanism, it seems that this is extremely rare for ionic octahedral species; we have previously argued[11] that it operates in the substitution of aqueous $Ru(NH_3)_5OH_2^{3+}$ by Cl^- and the reverse process, but this now seems unlikely (see below). The unusually fast reaction of NO with aqueous $Ru(NH_3)_6^{3+}$ [12,13] at pH < 7 remains a possible candidate for an **A** mechanism in octahedral substitution, but an initial electron transfer followed by a dissociatively activated reaction of labile $Ru(NH_3)_6^{2+}$ with NO^+ is a feasible alternative (indeed, redox occurs at higher pH, giving $Ru(NH_3)_5N_2^{2+}$). The **A** mechanism is, of course, well established for ligand substitution in d^8 square planar complexes,[4,14] for which intermediates of expanded coordination number are relatively easily accessible, both sterically and electronically, and have been unambiguously detected in reactions of certain Pt^{II},[14] Pd^{II} [15] and Au^{III} [16] species.

Thus, it appears that, for octahedral substitution in coordinating solvents such as water, only the **I** mechanism need be considered. This is not hard to understand. Associative processes are inhibited sterically. On the other hand, the essential feature of a **D** mechanism is that the complex should have lost all "memory" of the departing ligand X before the M–Y bond forms, which implies that the lifetime of the putative intermediate of reduced coordination number is longer than the relaxation time of the surroundings of the complex (second and successive coordination spheres, solvation sheath, paired counter-ions, etc.), i.e., that the intermediate survives on the nanosecond or longer timescale.[3] In octahedral substitution, it is unlikely that a high-energy five-coordinate intermediate would survive on the nanosecond timescale in the presence of a large number of donor solvent molecules—particularly if the complex is cationic, in which case the solvent molecules will be preferentially oriented with donor atoms toward the complex, and other nucleophiles such as anions will tend to be concentrated in the outer coordination spheres. This is not to say that species of reduced coordination number cannot have long lifetimes in coordinating solvents, but rather that the high-energy intermediates invoked in mechanistic studies will have lifetimes that are short relative to the relaxation of their immediate surroundings. For example, there is evidence[17] that the tetrahedral species $Co(H_2O)_4^{2+}$ coexists with the familiar $Co(H_2O)_6^{2+}$ in aqueous solution (ca. 0.1% at 298 K, 7% at 625 K, at 16–25 MPa), but the enthalpy change for the octahedral–tetrahedral equilibrium is only some 17 kJ mol^{-1}, whereas the enthalpy of activation ΔH^* for water exchange on $Co(H_2O)_6^{2+}$ is 47 kJ mol^{-1}.[18] Thus, although the octahedral–tetrahedral equilibrium obviously presents a potential path for water exchange, the actual exchange is carried almost entirely by a higher-energy path of the **I** type.[18]

SELECTIVITY PARAMETERS VERSUS MECHANISTIC LABELS

As Lay[1] has remarked, the **I** mechanism is properly regarded as a continuum in which the degree of bond-making by the incoming ligand Y to a complex ML_5X in the transition state ranges from very substantial ($\mathbf{I}_a$) to negligible ($\mathbf{I}_d$). Lay[1] is also correct in stressing that factors such as the nature of the spectator ligands L and solvational influences, as well as the commonly invoked size and electronic configuration of the central metal ion M, can determine the location of the reaction pathway (or, more accurately, pathways—see below) within this continuum. In this sense, the substitution reactions of complex ions in solution undoubtedly do follow a single mechanism—the **I** mechanism.

Problems arise, however, when one tries to lump together certain reactions as "$\mathbf{I}_a$", others as "$\mathbf{I}_d$", when in fact *there can be no universally satisfactory demarcation between these categories*. Looking back to the original Langford–Gray definition, it is apparent that what is wanted is a means of expressing the fact that the range of rates of reaction of aqueous anions Y^- with $Cr(H_2O)_6^{3+}$ spans at least four orders of magnitude, whereas the range for Y^- with $Co(NH_3)_5OH_2^{3+}$ is about two-fold, and that with $Cr(NH_3)_5OH_2^{3+}$

is somewhere in between. The tendency has been to place the $Co(NH_3)_5OH_2^{3+}$ reactions in the $\mathbf{I}_d$ category, the $Cr(H_2O)_6^{3+}$ series in the $\mathbf{I}_a$, and to argue interminably about what to do with the $Cr(NH_3)_5OH_2^{3+}$ substitutions (cf. the history of this controversy given by the Mønsteds[19]). What is required is a means of expressing the *selectivity* of each of these substrates towards a range of attacking ligands Y.[3] The selectivity S of a substrate A relative to another, B, may be defined as

$$S = (\delta \ln k^A)/(\delta \ln k^B) \qquad (6)$$

in which $\delta \ln k$ represents the change in ln(rate constant) as X is varied. Since S is a relative quantity, it would be convenient to choose a particular substrate B to be a universal reference series; then, the slopes of plots of $\ln k^A$ against $\ln k^B$ will give S. A suitable B might be $Cr(H_2O)_6^{3+}$, and Table I lists some selectivities S calculated on this basis for the reactions of mononegative anions with some typical substrates.

This approach is similar to that taken in defining nucleophilicity towards Pt^{II} in its square planar complexes.[20] It has not found widespread application in octahedral substitution, however, partly because truly strong discrimination between nucleophiles requires the **A** mechanism, but mainly because there is a surprising lack of data for any consistent set of reference nucleophiles from one substrate to the next. Part of the problem is that, for substrates

TABLE I

Selectivity parameters S relative to hexaaquachromium(III) for the reactions of some cationic substrates with mononegative anions in aqueous solutions.

Substrate	S^a	Source of Data
$Mo(H_2O)_6^{3+}$	1.1[b]	21
$Cr(H_2O)_6^{3+}$	1.0	22
$Fe(H_2O)_6^{3+}$	0.7	22
$Cr(H_2O)_5OH^{2+}$	0.4	22
$Cr(NH_3)_5OH_2^{3+}$	0.3	3
$Fe(H_2O)_5OH^{2+}$	0.1	22
$Co(NH_3)_5OH_2^{3+}$	−0.1	23

[a] ±0.1; rate constants have dimensions L mol^{-1} s^{-1}.
[b] Only two data points.

that contain ionizable protons, the choice of nucleophiles is limited to those with negligible Brønsted basicity, because of the "proton ambiguity".[2] Furthermore, the rate constants used in Eq. (6) should be the first-order k_i's of Eqs. (4) and (5), to allow for any preassociation (e.g., ion pairing) by the nucleophile, but an accurate resolution of k_{obsd} into k_i and K_{ec} is only rarely possible for aqueous systems (solvent exchange data cannot be included, since K_{ec} is then indeterminate). Second-order k_{obsd} values may be used instead if attention is confined to reactions of a particular charge-type, as in Table I, since K_{ec} will then vary relatively little. Despite these limitations, effort might be better directed towards attempts to identify selectivity sequences, such as that which is apparent in Table I, than in force-fitting results to the arbitrary and uninformative I_a/I_d dichotomy. As a case in point, few accurate rate data exist for the replacement of coordinated solvent in octahedral complexes of metal ions of the second and third transition series.

INSIGHTS FROM COMPUTER MODELLING

As the speed and capabilities of electronic computers improve, it is becoming feasible to simulate ligand substitution processes in condensed phases in a fairly realistic manner. Inevitably, some approximations and simplifying assumptions have to be made, and there is the danger that some features of the results may be artifacts of the particular model, but several important insights have already emerged that represent significant departures from the traditional pictures of substitution mechanisms.

For example, Wilson, Hynes and co-workers[24] have carried out molecular dynamics calculations on the exchange of Cl^- with aqueous CH_3Cl to elucidate the manner in which the reactants accumulate sufficient energy to surmount the potential energy barrier to reaction. They show that the reagents acquire energy to climb the barrier primarily at the expense of the *intermolecular potential energy* of the water molecules, with a 50% smaller contribution from their kinetic energy—thus, the mode of activation in aqueous solution involves strong coupling to the solvent. The final ascent of the remainder of the barrier, which occurs in a mere 50 fs, involves a sharp rise in the potential energy of the reactants at the expense of their kinetic energy. The solvent must also reorganize to solvate the transition state, and the calculations confirm that this must take place *before* any change in the charge distribution of the reagents occurs. The interaction of the solvent with the reagents involves large numbers of water molecules and consists of both "helping work" and "hindering work", with only a small balance remaining between these very large contributions to provide a net facilitation of the reaction; thus, of the large number of water molecules involved, about 20 provide more than 4 kJ mol^{-1} each of helping work (centered mainly around the Cl of the CH_3Cl), but a similar number provide over 4 kJ mol^{-1} of hindering work (centered mainly on the chloride ion) in "violent and rapid competition".[24] The overall timescale of vibrational excitation is on the order of 1–10 μs; the kinetic energy of the reagents increases steadily until 50 fs before the barrier is crossed in a final, very rapid ascent, while the potential energy rises significantly only over the last 100 (and particularly the last 50) fs, but it is important to note that *a successful climb of the barrier can only occur if solvent reorganization is completed first.*

These computations refer, of course, to a particular model of the aqueous Cl^-–CH_3Cl reaction, which in any case differs from ligand substitution reactions of transition metal complexes in several respects, but they lend support to the views advanced by Lay[1] and others[3,25,26] concerning the importance of considering the whole assemblage, reactants *plus solvent*, when discussing the mechanism of reaction. In particular, simplistic pictures of purported mechanistic alternatives, such as in Fig. 1 in Ref. 1, may hinder the quest to understand of what actually happens in the activation process.

To my knowledge, the only serious attempt to date to model a ligand substitution process in solution by computer methods has been that of Connick and Alder,[27] who considered the case of "rare" solvent exchange—rare in the sense that a barrier of only a few kJ mol^{-1} will ensure that, although solvent exchange may be quite rapid on the timescale of chemical kinetics, it will occur extremely rarely relative to the frequency of collision of solvent particles, of which the mean free path is an order of magnitude smaller than their effective radii. For this reason, Connick and Alder[27] restricted their model to two dimensions, and constrained their system of 90 particles (including one metal ion around which, at equilibrium, four solvent molecules would be close-packed) to evolve along a successful reaction trajectory. Their results can be summarized as follows.

(a) The three bound, non-reacting (spectator) solvent molecules undergo angular displacements but little radial movement during the exchange process.

(b) A particle will undergo several hundred collisions in the time it takes to move a small fraction of its radius.

(c) Many collisions occur in the system while the incoming and outgoing solvent molecules (which are invariably separated in the first coordination sphere by one spectator ligand on one side and two on the other) remain at about the same distance from the metal ion, between the first and second coordination spheres. During this time, which of the two exchanging solvent molecules is nearest to the metal ion changes several times, but eventually one molecule settles into the first coordination sphere and the other migrates to the second in a series of small, correlated angular and radial displacements.

(d) The exchange pathway involves a highly correlated collective motion of *all* the solvent and reactant molecules in the assemblage, such that no large voids are created. Thus, the movement of a given particle is dependent upon the movement of all the others to make way for it.

(e) The configuration corresponding to the activated complex persists for a relatively long period on the collisional timescale (though still only briefly relative to relaxation of the solvation sheath, ion pairs, etc.). This may seem to be at variance with the usual picture of a transition state that decays in a single vibration, and also with the final 50 fs climb noted for the methyl chloride system (above), but in effect it says simply that the system could cross and recross the activation barrier several times before settling towards a re-equilibrated state.

The Connick–Alder results make it easy to understand why the transition states for solvent exchange within a series of octahedral complexes show less variability in volume than do the ions themselves[3,25,28]; the space required for cooperative movements of a large assemblage of solvent molecules around a central metal ion will be much the same regardless of the nature of that metal ion, whereas the molar volume of the static system will reflect specific properties of the ion. It is also clear that, for aqueous hexaaqua complexes in general, the smallest metal ions (i.e., those with essentially close-packed ligands) will require an expansion of the assemblage to reach the transition state, while for the larger ions, with more free space between the ligands, the activation process may entail some degree of collapse of the assemblage as a whole.

However, since we are concerned with the *whole* assemblage, we must consider not only the *size* of the central ion but also its structure-making effect on the solvent. For water, this will be related to the hydrogen-bonding ability and hence should be reflected by the acidity (K_a) of the hydrated metal ion (there is, however, no correlation between K_a for hexaaqua complexes[29] and $M-OH_2$ bond lengths,[1] so that Lay's claim[1,30] that hydrogen bond strengths increase with decreasing M-ligand distances in ammine complexes may have no general validity). Thus, ΔV^* for water exchange on $Cr(H_2O)_6^{3+}$ (-9.6 cm^3 mol^{-1}),[22] which is considered by Lay[1] and Merbach[31] to be anomalously strongly negative, is matched by an unusually large pK_a (4.0 at infinite dilution, cf. about 2 for most comparable 3+ ions) as well as a very slow exchange rate ($k^{298} = 2.4 \times 10^{-6}$ s^{-1},[22] cf. ms or μs timescales for most high-spin 3+ transition-metal aqua complexes) and a low ligand field splitting parameter Dq (1740 cm^{-1}, cf. ca. 2000 cm^{-1} for other comparable 3+ hexaaqua complexes). The connection between all these properties is not obvious. Ligand field effects are usually invoked to explain the slow rates of substitution in $Cr(H_2O)_6^{3+}$,[20] but then why is substitution on Cr^{III} slower than on Mo^{III}, for which Dq is at least 50% larger?[21] A qualitative explanation[3] of this slowness invokes the higher t_{2g} electron density encountered by a nucleophile attacking Cr^{III} relative to Mo^{III}, but clearly there are many details of the quantitative chemistry of even the simplest transition metal complexes that are eluding us at present, and such necessarily naive models as that of Connick and Alder[27] cannot be expected to do much more than to provide new perspectives on old and persistent problems.

The essential point of this discourse is that computer simulations and molecular mechanics calculations make it clear that solvent dynamics must be included in any model of the intimate mechanism of substitution processes in solution. Furthermore, they show that there can be no clear-cut mechanistic classification of the $\mathbf{I}_a/\mathbf{I}_d$ type; for octahedral substitution at least, there is just one mechanism (interchange, in effect) which spans an essentially infinite number of microscopic pathways. For a particular reaction, some broad manifold of such pathways will be more important than others, leading to a distinctive set of parameters such as S, ΔV^*, etc., and it is these parameters which should be used to characterize that reaction rather than some arbitrary label such as $\mathbf{I}_a$ or $\mathbf{I}_d$. Modifications made to the reactants, such as the introduction of methyl groups on the ammine ligands in complexes of the type $M(NH_3)_5OH_2^{3+}$, may cause a shift in the selection of pathways followed, much as Lay[1] has suggested, and the characteristic parameters will change accordingly, but there is really no change of mechanism.

AM(M)INE COMPLEXES OF COBALT(III) AND CHROMIUM(III)

Lay's review[1] deals specifically with ammine and amine complexes of transition metals, i.e., those which exist in solution by virtue of their large ligand field stabilization energy. This limits the field somewhat (there is, for example, no comparable chemistry of titanium, vanadium, manganese or iron), and so some of the conclusions reached may lack generality. There are, in any event, some assertions which require comment.

For example, it is argued[1] that "the fact that ΔV^* for the [aquation of] $M(NH_3)_5Cl^{2+}$ ions (M = Co, Cr) are the same within the experimental error supports a common mechanism", yet this overlooks the fact that ΔV^* values for Cr and Co *are different* for the aquations of $M(NH_3)_5X^{(3-n)+}$ where X^{n-} is Br^-, $N\mathrm{CS}^-$, or H_2O.[32] Similarly, much is made of the observation that the M–Cl bond length in $M(NH_2R)_5Cl^{2+}$ is shorter when R = CH_3 than when R = H, for M = Cr or Rh; this does not *disprove* the suggestion[33] (made without knowledge of these particular bond lengths) that the lower rate of aquation when R = CH_3 reflects steric hindrance to associative attack by water, but simply provides an alternative (and not necessarily exclusive) explanation of the phenomenon. In fact, House[34] has shown that there is no clear correlation between chloride aquation rate and Cr–Cl bond length in a number of related chromium(III) chloroa(m)mine complexes. Furthermore, the high pressure studies of Curtis, Lawrance, and van Eldik[35,36] on the aquation of chromium(III) and cobalt(III) ammines with neutral leaving groups has confirmed that the two series behave differently, and the same might still prove true for corresponding aquations with charged leaving groups if solvational effects could be unambiguously separated.

Thus, there is nothing that contradicts the notion that increased steric congestion in the chromium(III) ammines contributes to the reduction of aquation rates through suppression of associative attack, leaving pathways closer to the dissociative end of the range to carry the reaction as they do for cobalt(III) ammines. M–Cl bond strengths are obviously another factor in the overall picture, but are not necessarily dominant.[34] Debate on the question of the comparative chemistry of Co^{III}, Cr^{III} and Rh^{III} a(m)mines has arisen largely as a result of the insistence of authors upon classifying the reaction mechanisms as *either* I_a *or* I_d; it is contended here that this categorization is a meaningless exercise.

PI BONDING

Lay[1] invokes π-bonding to account for the shortening of the M–Cl bond in d^3 and d^5 complexes as we go from R = H to R = CH_3. The ligand-field spectra of these complexes, however, suggest a different explanation. Certainly, simple ligand-field concepts predict that increased π electron donation from Cl to M should cause a decrease in the d orbital splitting and hence a shift of the ligand field bands to the red. For $M(NH_2R)_5X^{(3-n)+}$ in general, however, replacement of R = H by R = CH_3 results in a red shift of all ligand-field bands to much the same extent *whether or not X is a π-donor such as Cl^-*—indeed, it occurs even for the homoleptic complexes (X = RNH_2)[33,37] in which π-bonding is impossible. Rather, this red-shift is evidently due to loss of ligand-field strength arising from increased M–N distances when R is CH_3, which in turn can be ascribed to steric crowding. (This same loss of ligand σ-electron-donating power explains the higher acidity of $X = H_2O$ for $R = CH_3$ relative to $R = H$ for $M = Cr, Co, Rh$.[33]) The shorter M–Cl bond lengths with $R = CH_3$ for the larger M (i.e., M other than Co) can then be attributed to a stronger σ interaction of Cl with M in partial compensation for the weakened interaction with the N ligands.

RUTHENIUM(III) AMMINES

The case of the formation and aquation of $Ru(NH_3)_5Cl^{2+}$,

$$Ru(NH_3)_5OH_2^{3+} + Cl^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Ru(NH_3)_5Cl^{2+} + H_2O, \quad (7)$$

has presented interpretational difficulties because of the unusually strongly negative volumes of activation found for the forward (-20 cm^3 mol^{-1}) and reverse (-27 to -30 cm^3 mol^{-1}) directions of reaction (7).[11] The problem is compounded by the recent finding[25] that ΔV^* for solvent exchange on aqueous $Ru(NH_3)_5OH_2^{3+}$ is not particularly strongly negative (-4 cm^3 mol^{-1}), and is well within the range found for other aquapentammine complexes; there is nothing particularly unusual about the solvent exchange reaction (although it turns out to be the fastest reaction of its type to be investigated to date—see below). Thus, the earlier suggestion,[11] that the ΔV^* values for reaction (7) indicate a full-blown **A** mechanism, now seems to be untenable. One might naturally suspect the data, but these were obtained by three different procedures, the difference between the volumes of activation for the forward and backward reactions agrees with the measured volume of reaction, and the rate constants at 0.1 MPa are in good agreement with literature values.[11]

Lay[1] suggests that the mechanism of aquation (and therefore also that of formation) of $Ru(NH_3)_5Cl^{2+}$ is predominantly $\mathbf{I_d}$ at ambient pressure, but that a minor path involving a seven-coordinate intermediate $Ru(NH_3)_5(OH)_2Cl^{2+}$ (effectively, an **A** mechanism with a late transition state) becomes important as the pressure is increased. If this were so, however, the rate constant for the *anation* reaction, k_f, would first decrease and then increase with rising pressure (cf. water exchange on Fe^{3+} (aq) at $[H^+] \simeq 1$ mol kg^{-1} [38]), and this is not at all the case.[11] Homolytic pathways have also been considered, and ruled out.[25]

One possibility that would give a strongly negative ΔV^* for the aquation of $Ru(NH_3)_5Cl^{2+}$ and be essentially unique to Ru(III) ammines is that the reaction could proceed via electron transfer between $Ru(NH_3)_5Cl^{2+}$ and $Ru(NH_3)_5OH_2^{2+}$ to give the labile $Ru(NH_3)_5Cl^+$ which rapidly ($k_{Cl} = 6 \pm 1\ s^{-1}$ at 25°C[39]) aquates to regenerate the catalyst $Ru(NH_3)_5OH_2^{2+}$:

$$Ru(NH_3)_5Cl^{2+} + Ru(NH_3)_5OH_2^{2+} \xrightarrow{k_{red}} Ru(NH_3)_5Cl^+ + Ru(NH_3)_5OH_2^{3+}, \quad (8)$$

$$Ru(NH_3)_5Cl^+ + H_2O \xrightarrow{k_{Cl}} Ru(NH_3)_5OH_2^{2+} + Cl^-. \quad (9)$$

Cycles of this sort are commonly used to prepare Ru^{III} complexes,[40] and indeed both Ru^{II} and Ru^{IV} are known to catalyze reaction (7).[41] Ohyoshi *et al.*[42] have shown reaction (8) to be a rather rapid ($k_{red} = 1.47 \times 10^2\ L\ mol^{-1}\ s^{-1}$ at 25°C) outer-sphere process. Thus, reactions (8) and (9) could carry the aquation of $Ru(NH_3)_5Cl^{2+}$ ($k_r = 8.8 \times 10^{-7}\ s^{-1}$ at 25°C[43]) if concentrations of $Ru(NH_3)_5OH_2^{2+}$ as low as 6 nmol L^{-1} were present.

Where might this $Ru(NH_3)_5OH_2^{2+}$ (or, equivalently, $Ru(NH_3)_5Cl^+$) come from? It is apparently not simply an impurity carried over from the preparation, since both k_f and k_r are readily reproducible from sample to sample and between different laboratories.[11,41,43,44] The most likely source is a slight disproportionation of $Ru(NH_3)_5Cl^{2+}$ (cf. Lay's proposal for the base hydrolysis of Ru^{III} ammines[1]):

$$2Ru(NH_3)_5Cl^{2+} \xrightleftharpoons{K_{disp}} Ru(NH_3)_5Cl^+ + Ru(NH_3)_5Cl^{3+}. \quad (10)$$

Disproportionation of Ru^{III} ammines seems to require the presence of π-donor ligands such as NH_2^-, and indeed Cl^- is a weak

π-donor. Theory gives a volume of activation of -11 cm^3 mol^{-1} for an adiabatic reaction (8), or around -16 cm^3 mol^{-1} if it is non-adiabatic; to this may be added -2 to -3 cm^3 mol^{-1} for a pre-equilibrium (10) and -5 to -10 cm^3 mol^{-1} for reaction (9). Thus, the above scheme would account for the measured ΔV^* for reaction (7). Unfortunately, the rate equation for the aquation reaction, according to this sequence, does not reduce cleanly to the first-order dependence on $[Ru(NH_3)_5Cl^{2+}]$ that is observed. There is a particular need for further experimental work, as well as new ideas, on the kinetics of substitution in Ru^{III} complexes of all kinds, but it will be apparent from the foregoing discussion that redox and other side-reactions make precise measurements of substitution rates, and even the preparation of pure materials, maddeningly difficult in many cases.

ANOMALOUS SECOND-TRANSITION-PERIOD LABILITY

Basolo has long recognized[20,45–48] that, in the substitution of CO in metal carbonyls by ligands such as organophosphines, complexes of metals of the second transition series are frequently more labile than those of the corresponding metals of the first or third transition series (Table II; the vanadium case is an exception). A similar trend is found in the rates of replacement of triethylphosphite in $\{(C_2H_5O)_3P\}_4M^0$ by cyclohexyl isonitrile (Ni < Pd > Pt).[49] The effect seems to be independent of the reaction mechanism. The origin of the phenomenon is as yet unclear, but density func-

TABLE II

Relative reactivities of metal carbonyls toward CO replacement.[a]

Complex	Relative Rate of CO Substitution
$(\eta^5\text{-}C_5H_5)_2M(CO)_2$	Ti < Zr > Hf
$(\eta^5\text{-}C_5H_5)M(CO)_4$	V > Nb > Ta
$M(CO)_6$	Cr < Mo > W
$M_2(CO)_{10}$	Mn < Tc > Re
$M(CO)_5$	Fe <<< Ru >> Os
$(\eta^5\text{-}C_5H_5)M(CO)_2$	Co < Rh > Ir

[a] Ref. 48.

tion molecular orbital calculations by Ziegler *et al.*[50] have shown that relativistic quantum-mechanical effects become increasingly important as one descends the Periodic Table and should lead to minima in typical M–CO bond dissociation energies in the second transition series.

These examples all involve transition metals in a low (often zero) oxidation state. It now appears[25] that a similar phenomenon occurs with some, but by no means all, series of reactions of Werner complexes of metals in more "normal" oxidation states. Thus, it was noted above that aqueous $Mo(H_2O)_6^{3+}$ reacts markedly faster in substitution reactions than does $Cr(H_2O)_6^{3+}$,[21] and that this runs counter to conventional wisdom which would predict a marked slowing of substitution as one descend a periodic group because of the steady increase in the ligand field splitting parameter *Dq*. The same effect can be seen in the exchange of acetylacetone (Hacac) between M^{III} $(acac)_3$ and Hacac solvent, a bimolecular reaction (according to the effect of added acetonitrile diluent) which is some 10^4-fold faster when M = Mo than when M = Cr.[51]

It was further remarked above that water exchange in aqueous $M(NH_3)_5OH_2^{3+}$ (M = Ru, Cr, Co, Rh, Ir) is fastest for M = Ru,[25] contrary to the widespread perception that Ru^{III} ammines are less kinetically labile than, say, their Cr^{III} analogues (Table III). This perception, however, comes from observations on the aquations of $M(NH_3)_5Cl^{2+}$, and reflects the preference of the relatively "soft" acid Ru^{III} for Cl over the "harder" H_2O; the chloride anation data

TABLE III

Kinetic parameters for water exchange (k_{ex}) and chloride anation (k_{Cl}) on $M(NH_3)_5OH_2^{3+}$ in aqueous solution at 25°C.[a]

M	k_{ex} $/10^{-5}\,s^{-1}$	ΔH^*_{ex} /kJ mol^{-1}	k_{Cl}[b] $/10^{-5}$ L $mol^{-1}\,s^{-1}$	k_{aq} $/10^{-6}\,s^{-1}$
Ru	23.0	91.5	12.0 (0.10)	0.88
Cr	5.2	97.1	0.35 (0.10)	6.8
Co	0.57	111.3	0.28 (0.10)	1.7
Rh	0.87	102.9	0.68 (0.20)	0.042
Ir	0.00061	117.6	230.[c] (0.03)	0.64[c]

[a] Ref. 25.
[b] Ionic strength/mol L^{-1} in parenthesis.
[c] At 95°C (at which k_{ex} = $5.9 \times 10^{-4}\,s^{-1}$).

show that it has no generality (Table III).[25,52] Table III also reveals that $Rh(NH_3)_5OH_2^{3+}$ is somewhat more labile than its Co analogue in both water exchange (this is more clearly shown in the enthalpies of activation) and chloride anation, despite a 46% higher *Dq*, although $Rh(NH_3)_5Cl^{2+}$ is much less reactive than the cobalt(III) complex in chloride aquation. Evidently, "soft" Rh^{III} shows anomalous second-transition-series lability when a "hard" ligand is being displaced, but a "hard" nucleophile (water) has difficulty in displacing a "softer" ligand (chloride). The Ir complexes are much more inert than the Co or Rh species in all such reactions, just as expected.

It is difficult to document the phenomenon of second-transition-series lability clearly because of problems in finding complete sets of truly comparable complexes; often, the first-transition-series member of a d^4–d^7 set differs in being high-spin and may not even exist in solution (e.g., the Ru or Os ammines have no Fe analogues that are stable in aqueous solution), while the third-series member may be too strongly reducing (e.g., no $W(H_2O)_6^{3+}$ is known, or is even likely to survive oxidation by water long enough for kinetic measurements to complete the Cr–Mo–W set). Furthermore, there is evidence that not all second-series complexes are anomalously labile; thus, Hoddenbagh and Macartney[53] found that the substitution of water in $Ru(CN)_5OH_2^{3-}$ is some 10–30 times slower than in $Fe(CN)_5OH_2^{3-}$ (both are low-spin). These complexes are unselective in their (predominantly dissociatively activated) substitution reactions, whereas substantial selectivity (i.e., a significant associative contribution to activation) characterizes the Cr^{III}/Mo^{III} pairs discussed above; therein may lie a clue to the nature of second-series lability and where to look for it.

LIFETIMES OF INTERMEDIATES

Lawrance has recently provided an excellent review[54] of the numerous studies made over the past three decades of substitution-inert octahedral complexes containing ligands with strong leaving tendencies, either inherent or induced. Although these complexes have turned out to be of particular interest because of their synthetic possibilities, the objective of many such investigations was to attempt to generate and characterize intermediates of reduced coordination number. Such intermediates have also been inferred to be involved in the base hydrolysis of complexes containing spectator ligands with ionizable protons, in particular cobalt(III) ammines.[55] It has been commonly supposed that the lifetimes of these intermediates would in general be relatively long, corresponding to the Langford–Gray **D** mechanism. There is an emerging consensus, however, that the lifetimes of most such intermediates must be *short* on the timescale of the reorganization of solvent, ion pairs, etc.[56–61] Once again, mechanistic labels (here, **D** vs. $\mathbf{I}_d$) are unhelpful in characterizing inferred differences in the behavior of the various putative intermediates, and probably serve only to compound the confusion.

It has therefore been argued[3] that attempts should be made to place such differences in the framework of their estimated (or at least relative) lifetimes. Obviously, this is not a simple task, but recently Rotzinger[61] has used the Debye equation to estimate lower limits for the lifetimes τ for the intermediates $\{Co(NH_3)_4NH_2^{2+} \ldots X^{n-}\}$ produced in the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ ($\tau >$ 72, 190, and 1600 ps for X^{n-} = NO_3^-, $(CH_3)_2SO$, and SO_4^{2-}, respectively); it will be noted that "memory" of the departing group persists for substantial periods. Similarly, Rotzinger[62] has estimated $\tau \simeq 1$ ns for the intermediate $Co(NH_2CH_3)_4(NHCH_3)^{2+}$ formed during the base hydrolysis of $Co(NH_2CH_3)_5X^{(3-n)+}$ (X = Cl^- or dimethylformamide). The rapidity of the hydrolysis and the relatively long lifetime of the five-coordinate intermediate result from steric compression in the $Co(NH_2CH_3)_5$ unit. For base hydrolyses or induced substitutions in cobalt(III) a(m)mines without this compression, a considerably shorter τ is expected. In the base hydrolysis and Hg^{2+}- and NO^+-induced aquations of Co(Metren) $(NH_3)X^{(3-n)+}$ isomers, τ has been estimated to be about 10 ps.[59]

The widespread preoccupation with mechanistic stereotypes can lead to significant information being overlooked. For example, in their study of pressure effects on the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ (X^{n-} = F^-, Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, and $(CH_3)_2SO$), Kitamura *et al.*[63] calculate a quantity $\overline{V}_R$ which, it is asserted, corresponds to the molar volume of the intermediate $Co(NH_3)_4NH_2^{2+}$, and they claim that it is the same (average =

71.1 ± 3.9 $cm^3 mol^{-1}$) for all these X^{n-}, as required by the traditional concept of the conjugate-base **D** mechanism in which $Co(NH_3)_4NH_2^{2+}$ is long-lived relative to the departure of X^{n-} into bulk solution. In fact, $\overline{V}_R$ ranges from 66.0 $cm^3 mol^{-1}$ for X^{n-} = $(CH_3)_2SO$ to 76.6 $cm^3 mol^{-1}$ for Cl^- and 76.2 for SO_4^{2-}, with the other values scattered in between—a wide range in terms of both the uncertainties (typically < 1.0 $cm^3 mol^{-1}$) and spread (22.2 for X^{n-} = SO_4^{2-} to 40.2 for $(CH_3)_2SO$, with the mononegative X^- other than F^- clustered around 33 $cm^3 mol^{-1}$) of the actual measured volumes of activation. Thus, the $\overline{V}_R$ values, so far from conforming with the **D** model, show a distinct dependence on the nature of X^{n-} and actually support the growing consensus that the putative intermediate $Co(NH_3)_4NH_2^{2+}$ does *not* lose memory of the departing group before picking up a sixth ligand to complete the reaction. Lay[1] suggests that a new mechanistic class, $\mathbf{D_I}$, be introduced to cover this type of situation, but undoubtedly further debate will then arise over the assignment of individual reactions to **D** vs. $\mathbf{D_I}$, or $\mathbf{D_I}$ vs. $\mathbf{I_d}$; would any useful purpose be served?

FUTURE DIRECTIONS

As noted above, there is still a need for reliable kinetic data on several ostensibly simple substitution reaction series—Lay[1] mentions iridium(III) ammines, but we can add ammine and/or aqua complexes of molybdenum(III), ruthenium(III), and other second- and third-period metals. The catch is, of course, that redox phenomena and other side reactions may make the required measurements exceptionally difficult. The objective should be to collect sets of comparable data for various reaction series in a systematic way, so that clearly defined scales of selectivity can replace the traditional but very limited notions of definite mechanistic classes. The selectivity displayed by octahedral complexes may not be as spectacular as that shown by square-planar platinum(II) species, but neither is it always trivial.

The question of anomalous lability in certain complexes of second-transition-period metals needs to be examined in the light of current ideas on the relativistic quantum mechanics of atoms and molecules. Clearly, traditional approaches based on ligand field parameters are inadequate. On the experimental front, we need to determine just which types of complexes and which kinds of reactions exhibit anomalous second-period lability.

In the more distant future, it should prove to be possible to combine calculations of the electronic and steric properties of the reactants with a statistical mechanical treatment of solvent dynamics to achieve a realistic representation of the activation process that will reproduce the observed kinetic parameters with acceptable accuracy. Molecular mechanics calculations such as those carried out by Lay's group[1] and molecular orbital calculations such as those of Ziegler[50] need to be combined with simulations of the actual dynamic substitution process along the lines pioneered by Connick and Alder.[27] Clearly, the reactants undergo a tremendous high-frequency battering from solvent and other particles on their relatively slow and haphazard journey to the transition state, and so the need to include the participation of the solvent on a statistical molecular basis, i.e., other than as a continuous dielectric, is particularly pressing. Indeed, much of the paraphernalia of classical solution chemistry in general, such as dielectric constants and the concept of ionic strength, may fall into disuse if package programmes (and sufficiently fast computers) for the realistic simulation of solution phenomena become generally available. The task of the kineticist or solution chemist will then be to adjust the models so as to reproduce the experimental data as closely as possible. It is in this direction that progress lies.

References

1. P. A. Lay, Comments Inorg. Chem. **9**, 235 (1991).
2. T. W. Swaddle, Coord. Chem. Rev. **14**, 217 (1974).
3. T. W. Swaddle, Adv. Inorg. Bioinorg. Mech. **2**, 95 (1983).
4. C. H. Langford and H. B. Gray, *Ligand Substitution Processes* (W. A. Benjamin, New York, 1965); Chem. Eng. News **46**, 68 (April 1, 1968).
5. T. W. Swaddle, Rev. Phys. Chem. Japan **50**, 230 (1980).
6. S. M. Bradley, H. Doine, H. R. Krouse, M. J. Sisley and T. W. Swaddle, Aust. J. Chem. **41**, 1323 (1988).
7. A. Haim and W. K. Wilmarth, Inorg. Chem. **1**, 573, 583 (1962).
8. M. G. Burnett and W. M. Gilfillan, J. Chem. Soc. Chem. Commun. **1981**, 1578.
9. M. H. M. Abou-El-Wafa, M. G. Burnett and J. F. McCullagh, J. Chem. Soc. Dalton Trans. **1986**, 2083; **1987**, 1059, 2311.

10. A. Haim, Inorg. Chem. **21**, 2887 (1982).
11. M. T. Fairhurst and T. W. Swaddle, Inorg. Chem. **18**, 3241 (1979).
12. J. N. Armor, H. Scheidegger and H. Taube, J. Am. Chem. Soc. **90**, 5928 (1968).
13. S. D. Pell and J. N. Armor, J. Am. Chem. Soc. **95**, 7625 (1973).
14. R. J. Cross, Chem. Soc. Rev. **14**, 197 (1985); Adv. Inorg. Chem. **34**, 219 (1989).
15. L. Canovese, L. Cattalini, P. Uguagliatti and M. L. Tobe, J. Chem. Soc. Dalton Trans. **1990**, 3271.
16. A. J. Hall and D. P. N. Satchell, J. Chem. Soc. Chem. Commun. **1976**, 163.
17. T. W. Swaddle and L. Fabes, Can. J. Chem. **58**, 1418 (1980).
18. Y. Ducommun, K. E. Newman and A. E. Merbach, Inorg. Chem. **19**, 3696 (1980).
19. L. Mønsted and O. Mønsted, Coord. Chem. Rev. **94**, 109 (1989).
20. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd. Edition (J. Wiley, New York, 1967).
21. Y. Sasaki and A. G. Sykes, J. Chem. Soc. Dalton Trans. **1975**, 1048.
22. F.-C. Xu, H. R. Krouse and T. W. Swaddle, Inorg. Chem. **24**, 267 (1985).
23. T. W. Swaddle and G. Guastalla, Inorg. Chem. **8**, 1604 (1969).
24. B. J. Gertner, R. M. Whitnell, K. R. Wilson and J. T. Hynes, J. Am. Chem. Soc. **113**, 74 (1991).
25. H. Doine, K. Ishihara, H. R. Krouse and T. W. Swaddle, Inorg. Chem. **26**, 3240 (1987).
26. D. W. Watts, Pure Appl. Chem. **51**, 1713 (1979).
27. R. E. Connick and B. J. Alder, J. Phys. Chem. **87**, 2764 (1983).
28. T. W. Swaddle, J. Chem. Soc. Chem. Commun. **1982**, 832.
29. C. F. Baes and A. E. Mesmer, *The Hydrolysis of Cations* (J. Wiley, New York, 1976).
30. T. W. Hambley and P. A. Lay, Inorg. Chem. **25**, 4553 (1986).
31. A. E. Merbach, Pure Appl. Chem. **59**, 161 (1987).
32. G. Guastalla and T. W. Swaddle, Can. J. Chem. **51**, 821 (1973).
33. T. W. Swaddle, Can. J. Chem. **55**, 3166 (1977).
34. D. A. House, in *Mechanisms of Inorganic and Organometallic Reactions*, Vol. 6, ed. M. V. Twigg (Plenum, London, 1989), Ch. 6.
35. G. A. Lawrance and R. van Eldik, J. Chem. Soc. Chem. Commun. **1987**, 1105.
36. N. J. Curtis, G. A. Lawrance and R. van Eldik, Inorg. Chem. **28**, 329 (1989).
37. P. A. Lay, Inorg. Chem **26**, 2144 (1987).
38. T. W. Swaddle and A. E. Merbach, Inorg. Chem. **20**, 4212 (1981).
39. J. A. Marchant, T. Matsubara and P. C. Ford, Inorg. Chem. **16**, 2160 (1977); G. N. Coleman, J. W. Gesler, F. A. Shirley and J. R. Kuempel, Inorg. Chem. **12**, 1036 (1973).
40. E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium* (Elsevier, Amsterdam, 1984).
41. J. F. Endicott and H. Taube, J. Am. Chem. Soc. **84**, 4984 (1962).
42. A. Ohyoshi, K. Yoshitani, H. Ohtsuyama, T. Yamashita and S. Sasaki, Bull. Chem. Soc. Japan **50**, 666 (1977).
43. J. A. Broomhead, F. Basolo and R. G. Pearson, Inorg. Chem. **3**, 826 (1964).
44. J. A. Broomhead and L. Kane-Maguire, Inorg. Chem. **10**, 85 (1971).
45. H. G. Schuster-Woldan and F. Basolo, J. Am. Chem. Soc. **88**, 1657 (1966).
46. F. Basolo, Isr. J. Chem. **27**, 233 (1986).
47. F. Basolo, J. Organomet. Chem. **383**, 579 (1989).

48. F. Basolo, Polyhedron **9**, 1503 (1990).
49. M. Meier, F. Basolo and R. G. Pearson, Inorg. Chem. **8**, 795 (1969).
50. T. Ziegler, V. Tschinke and C. Ursenbach, J. Am. Chem. Soc. **109**, 4825 (1987).
51. H. Kido and Y. Hatakayama, Inorg. Chem. **27**, 3623 (1988).
52. D. P. Fairlie and H. Taube, Inorg. Chem. **24**, 3199 (1985).
53. J. M. A. Hoddenbagh and D. H. Macartney, Inorg. Chem. **25**, 380, 2099 (1986).
54. G. A. Lawrance, Adv. Inorg. Chem. **34**, 145 (1989).
55. M. L. Tobe, Adv. Inorg. Bioinorg. Mech. **2**, 1 (1983).
56. W. L. Reynolds, M. Glavaš and Y. Yuan, Polyhedron **6**, 1337 (1987).
57. W. G. Jackson, B. C. McGregor and S. S. Jurisson, Inorg. Chem. **26**, 1286 (1987); **29**, 4677 (1990).
58. W. G. Jackson and B. H. Dutton, Inorg. Chem. **28**, 525 (1989).
59. D. A. Buckingham, J. D. Edwards and G. M. McLaughlin, Inorg. Chem. **21**, 2770 (1982).
60. N. E. Brasch, D. A. Buckingham, C. R. Clark and K. S. Finnie, Inorg. Chem. **28**, 4567 (1989).
61. F. P. Rotzinger, Inorg. Chem. **27**, 768, 772 (1988).
62. F. P. Rotzinger, Inorg. Chem. **30**, 2763 (1991).
63. Y. Kitamura, R. van Eldik and H. Kelm, Inorg. Chem. **23**, 2038 (1984).