(5.7×10^7 dpm), rose from 0.04 to 2.63% in the presence of unlabeled catharanthine (11 mg). These conditions have not been fully optimized but the incorporations are almost three orders of magnitude greater than those of **5** and **6** into VLB, which remain unchanged[1,3] ($\sim 10^{-3}$%) regardless of workup time and conditions.

On the other hand, the incorporation of **5** and **6** into the epoxide, leurosine (**3**), although positive (0.1–0.5%) must be regarded with caution in view of the inherent in vitro chemistry of the anhydro-VLB (**8**) → leurosine (**3**) conversion reported by Potier.[6] Since the epoxide of leurosine corresponds to the 4′-hydroxyl group of leurosidine (**4**) rather than that of VLB (**1**), the biosynthesis of the latter may proceed either by stereospecific hydration of the 3′,4′ double bond of **8** or by reduction to give the 4′ epimers of deoxy-VLB (**9, 10**) which are subsequently hydroxylated to **1** and **4,** respectively.

The availability of anhydro-VLB (**8**) both biosynthetically and by partial synthesis[8] would gain further significance if transformation to VLB could be effected. To this end administration of [*acetyl*-^{14}C]-**8** to *C. roseus* plants was examined and found to yield leurosine (**3,** 2.9% incorporation) almost exclusively. The corresponding blank (1.16%) indicates that some epoxide formation is enzyme catalyzed in a 2-day feeding experiment but also reveals that VLB (**1**) and leurosidine (**4**) are not formed under these feeding conditions owing to (a) the instability of the anhydro-VLB and/or (b) compartmentalization of the VLB synthesizing enzymes.

With the realization that the anhydro dimer **8** is formed in quite high yield in the in vivo condensation of vindoline and catharanthine but can suffer extensive in vitro degradation (e.g., to leurosine), the stage is now set for a rational experimental approach to the bioconversion of **8** to the deoxy- (**9, 10**) and VLB-leurosidine (**1, 4**) series under controlled conditions. The fascinating question remains, whether based on the isolation of **8** in *C. roseus,* the biologically active compounds **1–4** are *all* in vitro artefacts produced from the enzymically formed anhydro-VLB.

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(10) The term "natural product" herein is defined as any compound found in nature (with particular reference to secondary metabolites) whether formed by enzymatic catalysis or spontaneous reaction as favored by the in vivo environment. It is becoming clear that many "natural products" are formed *nonenzymatically* as the result of nonspecific reactions involving redox agents, radicals, localized pH variation, and so on. In other words, the subsequent reactivity of unstable enzyme-generated intermediates (e.g., **8**) in secondary metabolism may explain the origin of a host of structures whose formation is either entirely chemical in origin (see ref 6) or nonspecific in terms of subsequent enzymatic transformation(s).

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Inverted Redox Catalysis: Catalysis of Substitution on Ruthenium(II) by an Extraordinarily Labile Ruthenium(III) Metal Center

Sir:

Our attempts to study the kinetics of the substitution reactions of ruthenium(II) complex, $Ru(edta)(H_2O)^{2-}$

$$Ru(edta)(H_2O)^{2-} + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ru(edta)L^{2-} + H_2O \quad (1)$$

failed repeatedly. When slightly acidic solutions (typically 10^{-4} M) of the pentadentate EDTA complex of ruthenium(III), $Ru(edta)(H_2O)^-$ (from $Ru(edtaH)(H_2O)\cdot 4H_2O$)[1,2] were reduced over amalgamated zinc or Pt/H_2 and then mixed with deaerated ligand ($\geq 10^{-3}$ M isonicotinamide or pyrazine), the formation of the orange $Ru(edta)L^{2-}$ product followed zero-order kinetics (plots of absorbance vs. time were linear). With $Ru(edta)H_2O^{2-}$ in excess (2×10^{-4} to 2×10^{-3} M, [isonicotinamide] = 2×10^{-5} M), similar results were obtained. However, long reduction periods and extreme care in the exclusion of dioxygen gave slower, mixed first-order/zero-order decays. From the apparently exponential portions of these decays, $k_1 = 25 \pm 15$ M^{-1} s^{-1} was found for substitution by isonicotinamide. Preliminary studies of the reaction of $Ru(edta)H_2O^{2-}$ with O_2 indicated the reaction to be moderately rapid ($k \sim 10^1$ M^{-1} s^{-1}) and kinetically well behaved. As it seemed possible that Ru(III) produced by residual dioxygen might be responsible for the ill-behaved Ru(II) substitution kinetics, studies of the Ru(III) reactions were undertaken.

The kinetics of the substitution reactions of $Ru(edta)(H_2O)^-$ ($pK_a(-CO_2H) = 2.37$, $pK_a(-OH_2) = 7.5$) were studied in buffered aqueous solutions (0.1 M acetate buffer (pH 5.5), $\mu = 0.2$ M KCF_3SO_3, 25 °C) by the stopped-flow technique. Absorbance increases due to complexation by L which was 10^{-4}–10^{-1} M and in at least tenfold excess over Ru(III) were monitored in the 300–400 nm range. Absorbance change vs. time curves were exponential for at least two half-lives. (Depending on L, a second stage—probably the addition of a second molecule of L—was responsible for up to 20% of the total absorbance change. As the apparent rate for this process was, in all cases, at least ten times slower than the first process, the two stages were readily disentangled.) Data for the first stage were found to conform to the equation $k_{obsd} = a + b[L]$ which is compatible with the approach to equilibrium

$$Ru(edta)(H_2O)^- + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Ru(edta)L^- + H_2O \quad (2)$$

with $a = k_{-2}$, $b = k_2$ (see Figure 1). Values obtained for k_2/k_{-2} were in good agreement with K_2 determined from the magnitudes of the absorbance changes produced; that is, plots of ΔA^{-1} vs. $[L]^{-1}$, where ΔA is the absorbance increase accompanying the first stage of complexation by L, were linear with intercept/slope ratios which were within experimental error of the k_2/k_{-2} ratios. The rate constants k_2 were large and varied greatly with the nature of the entering ligand (ligand, k_2 (M^{-1} s^{-1})): CH_3CN, 30 ± 7; SCN^-, $(2.7 \pm 0.2) \times 10^2$; isonicotinamide, $(8.3 \pm 0.6) \times 10^3$; pyrazine, $(2.0 \pm 0.1) \times 10^4$.

In Figure 2 the rate constants k_2 obtained for substitution of L on $Ru(edta)H_2O^-$ are plotted vs. values for the ligand binding constant k_2/k_{-2}. The rate constants, which vary over three orders of magnitude, are seen to parallel the driving force for the substitution. The magnitude 0.95 of the slope of the plot (intercept 0.25) suggests a very high degree of bond making in the transition state[3] and so provides strong evidence for associative character in the substitution on Ru(III) in $Ru(edta)H_2O^-$. Although the displacement of NH_3 in $Ru(NH_3)_6^{3+}$ by nitric oxide also proceeds by an associative

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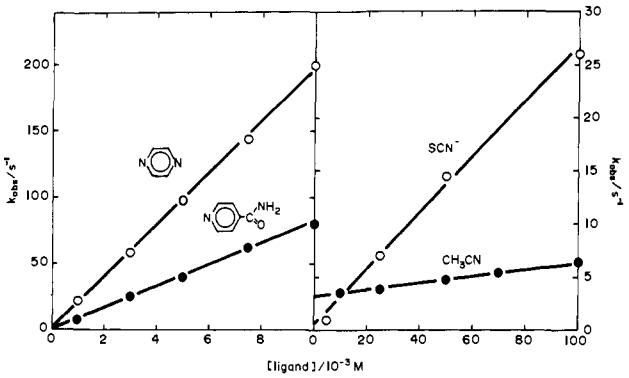

Figure 1. Plots of the observed pseudo-first-order rate constant (k_{obsd}) vs. incoming ligand concentration.

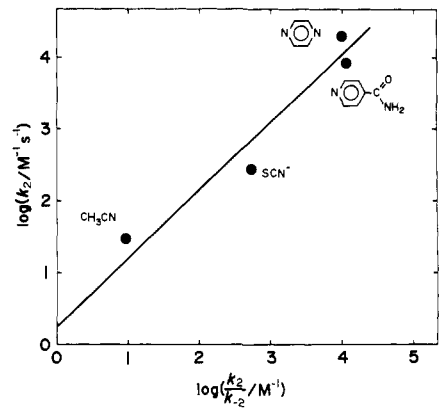

Figure 2. Plot of the logarithm of k_2, the second-order rate constant for substitution on $Ru^{III}(edta)(H_2O)^-$ vs. the logarithm of $k_2/k_{-2} = K_2$, the equilibrium constant for reaction 2.

mechanism,[4] the present system is so far unique in providing definitive evidence for *nucleophilic* substitution on Ru(III) by an associative pathway.

A further interesting feature of the Ru(III) substitution reactions is provided by the pH dependence of the substitution rates. The value of k_2 is maximal in the pH range 5–7 (e.g., $(2.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1}, L = pyrazine) and drops smoothly at both higher and lower pH. The behavior is quantitatively in accord with a model in which $Ru(edta)H_2O^-$ is the predominant reactive form over the pH range 0.7–10. An upper limit for the rate constants for substitution of pyrazine on the protonated and deprotonated species, $Ru(edtaH)H_2O$ and $Ru(edta)OH^{2-}$, is 1×10^2 M^{-1} s^{-1}. Observations of a similar nature have been reported for substitution on $Cr^{III}(edta)H_2O^-$ [5] and for conversion of $Co^{III}(edta)H_2O^-$ to $Co^{III}(edta)^-$.[6]

The large rates found for substitution on $Ru^{III}(edta)(H_2O)^-$ support the hypothesis that this species is responsible for the anomalies encountered in the $Ru^{II}(edta)(H_2O)^{2-}$ kinetics studies. Reactions 2 and 3 may provide a catalytic pathway for substitution on $Ru(edta)(H_2O)^{2-}$

$$Ru^{III}(edta)L^- + Ru^{II}(edta)(H_2O)^{2-} \underset{k_{-3}}{\overset{k_3,K_3}{\rightleftharpoons}} Ru^{II}(edta)L^{2-} + Ru^{III}(edta)(H_2O)^- \quad (3)$$

if they are thermodynamically favorable and sufficiently rapid.[7] Equilibrium constants for the outer-sphere oxidation–reduction reaction 3 have been calculated from the results of cyclic voltammetry studies: $K_3 = (6 \pm 1) \times 10^2$, $(1.7 \pm 0.3) \times 10^4$, and $(1.7 \pm 0.3) \times 10^4$ for isonicotinamide, pyrazine, and acetonitrile, respectively. ($E_{1/2}$ values for the reversible $Ru(edta)L^-/Ru(edta)L^{2-}$ couples at pH 5.5, μ = 0.2 M with KCF_3SO_3, 25 °C, are as follows: -0.01 ± 0.01,[8] 0.25 ± 0.01, 0.16 ± 0.01,[9] and 0.24 ± 0.01 V for L = H_2O, acetonitrile, isonicotinamide, and pyrazine, respectively.) Furthermore for both L = isonicotinamide and acetonitrile the rapidity of the electron-transfer reaction 3 has been verified. Solutions $1–5 \times 10^{-5}$ M in $Ru(edta)L^-$ were mixed in a stopped-flow spectrophotometer with solutions $0.1–1.0 \times 10^{-3}$ M in $Ru(edta)H_2O^{2-}$. Rate constants $k_3 = (2.8 \pm 0.5) \times 10^6$ M^{-1} s^{-1} and $(3.3 \pm 0.4) \times 10^5$ M^{-1} s^{-1} (25 °C, pH 5.5 acetate buffer, μ = 0.2 M with KCF_3SO_3) were obtained for isonicotinamide and acetonitrile, respectively. It is thus possible to detail all of the parameters for eq 1–3. For isonicotinamide $k_1 = 25 \pm 15$ M^{-1} s^{-1}, $k_{-1} = (1.2 \pm 0.8) \times 10^{-3}$ s^{-1} (from k_1/K_3K_2), $k_2 = (8.3 \pm 0.6) \times 10^3$ M^{-1} s^{-1}, $k_{-2} = 0.7 \pm 0.2$ s^{-1}, $k_3 = (2.8 \pm 0.5) \times 10^6$ M^{-1} s^{-1}, and $K_3 = (6 \pm 1) \times 10^2$. With acetonitrile the catalytic pathway was more easily suppressed and a better value for k_1 was obtained: $k_1 = 13 \pm 1$ M^{-1} s^{-1}, k_{-1} (calculated from k_1/K_3K_2) $= (8 \pm 4) \times 10^{-5}$ s^{-1}, $k_2 = 30 \pm 7$ M^{-1} s^{-1}, $k_{-2} = 3.2 \pm 0.2$ s^{-1}, $k_3 = (3.3 \pm 0.4) \times 10^5$ M^{-1} s^{-1}, $K_3 = (1.7 \pm 0.3) \times 10^4$. Despite the fact that the electron-transfer reaction 3 is more favorable and rapid with L = CH_3CN, the catalytic pathway is more difficult to suppress with L = isonicotinamide. This evidently arises because substitution by isonicotinamide on $Ru(edta)H_2O^-$ is 10^2 more rapid than when L = CH_3CN.

Labilization of metal–water bonds in EDTA complexes may be a rather general phenomenon,[5,6,10,11] but the behavior observed in these ruthenium–EDTA substitution reactions is remarkable on several accounts. While substitution reactions of Ru(II) complexes are often moderately rapid,[12–15] those of comparable Ru(III) complexes are usually several orders of magnitude *slower*.[16–20] (Thus Ru(II) catalysis of Ru(III) substitution is useful for synthetic purposes.[15,21,22]) Typical of this reactivity pattern are the reactions of $Ru(NH_3)_5OH_2^{2+}$ and $Ru(NH_3)_5OH_2^{3+}$ with Cl^- for which second-order rate constants of 4.4 M^{-1} s^{-1} (μ = 0.2 M, 25 °C)[14] and 4.7×10^{-4} M^{-1} s^{-1} (μ = 0.1 M, 35 °C)[16] have been reported. Comparison of data for the present system with those of other complexes indicates that the lability of Ru(II) is not altered markedly by complexation to EDTA.[13] By contrast, when Ru(III) is bound to EDTA as $Ru(edta)(H_2O)^-$, its lability is increased by *at least seven orders of magnitude*[23]—to such an extent that the usual order of labilities is inverted: Ru(III) undergoes substitution more rapidly than Ru(II).

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$$\frac{d[Ru^{II}L]}{dt} = [Ru^{II}H_2O][L]\left(k_1 + \frac{k_3k_2[Ru^{III}H_2O]}{k_{-2} + k_3[Ru^{II}H_2O]}\right)$$

when the reverse of reactions 1 and 3 are neglected. Kinetics pseudo first order in Ru(II) will only be encountered when $[Ru^{III}H_2O]$ is zero or the rate of Ru(II) substitution is very rapid compared with reactions 2 and 3. The condition $k_3[Ru^{II}H_2O] \gg k_{-2}$ gives rise to a decay zero order in $[Ru^{II}H_2O]$ when the second term in parentheses is much greater than k_1.
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The Molybdenum Iodide Cluster Anion $Mo_4I_{11}^{2-}$. A New Cluster Type Structurally Related to the $Mo_6I_8^{4+}$ Octahedral Cluster

Sir:

Recently interest in metal cluster compounds has been stimulated by their potential participation in important catalytic processes where discrete cluster species may to some degree serve as models for reactions which take place at surfaces of metals.[1,2] The progress of work in this area will depend heavily on the success of synthetic methods which must be developed in order to efficiently construct cluster species having the desired structural and chemical properties.

We earlier reported[3] the preparation of a new compound $[(C_4H_9)_4N]_2Mo_4I_{10}Cl$ whose formulation was based on composition and magnetic susceptibility information, but whose structure was not determined because of lack of success in obtaining suitable single crystals. This compound, however, was obtained in good yields as a result of our efforts to develop the approach shown below as a useful method for preparing metal cluster compounds:

$$M(CO)_4X_3^- \xrightarrow[\Delta]{\text{solvent}} [MX_3^-] + 4CO \qquad (1)$$

$$MX_3^- \longrightarrow M_nX_{3n}^{n-} \qquad (2)$$

When applied to the thermal decomposition of $[(n\text{-Bu})_4N]Mo(CO)_4I_3$ in refluxing chlorobenzene, a product of uncertain composition near $[(n\text{-Bu})_4N]_2Mo_4I_{10}$ was obtained, which provided the salt of $Mo_4I_{10}Cl^{2-}$ after crystallization from 1,2-dichloroethane.

Based upon this observation that the initial product easily abstracted chlorine from 1,2-dichloroethane, subsequent work demonstrated that addition of iodine sufficient for the required oxidation, according to

$$4[(n\text{-Bu})_4N]Mo(CO)_4I_3 + \tfrac{1}{2}I_2 = [(n\text{-Bu})_4N]_2Mo_4I_{11} + 16CO + 2(n\text{-Bu})_4N^+I^- \qquad (3)$$

provided crystalline $[(n\text{-Bu})_4N]_2Mo_4I_{11}$ in high yield.[4] After slow recrystallization from acetonitrile, crystals suitable for structure determination were obtained.[5] Full details of the structure determination, which presented some unusual problems, will be reported at a later date.

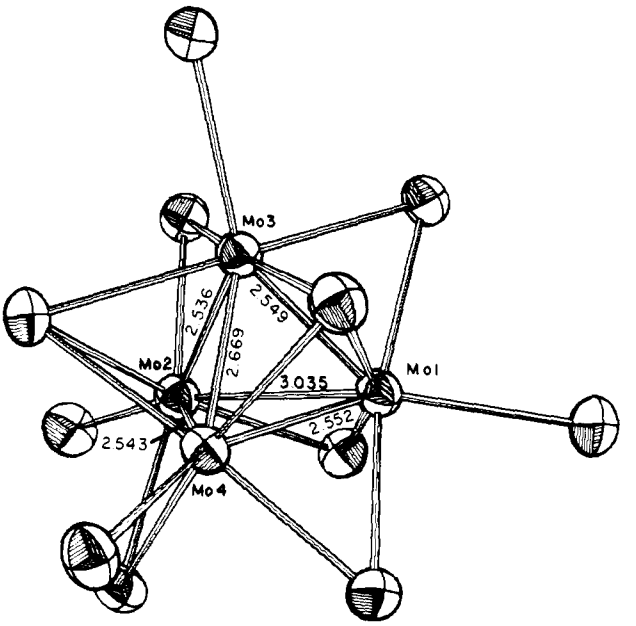

Figure 1. Structure of the $Mo_4I_{11}^{2-}$ anion with numbering scheme for the molybdenum atoms. Atoms are represented by thermal ellipsoids scaled to enclose 50% of the electron density.

From data taken at −75 °C with Mo Kα radiation (λ = 0.70954 Å) the cell parameters are a = 19.99 (3), b = 12.49 (3), c = 23.67 (2) Å; α = 89.89 (6), β = 105.80 (5), and γ = 90.27 (8)°; z = 4, $P\bar{1}$. Using 6791 reflections with $I > 3\sigma_I$, the structure has been refined with anisotropic thermal parameters for all nonhydrogen atoms to the final conventional discrepancy factors R = 0.090 and R_w = 0.122. The novel structure of the $Mo_4I_{11}^{2-}$ anion thus revealed is shown in Figure 1.

On one hand this structure may be viewed as a severely distorted tetrahedral cluster of Mo atoms bridged on two faces by triply bridging I atoms and on five edges by doubly bridging I atoms. The coordination sphere of each Mo atom is completed by one bond to a terminal I atom such that each metal atom attains coordination number 8, viz., by bonding to five I atoms and three Mo atoms. The anion has approximate C_{2v} symmetry with the C_2 axis passing through the unique atom I(1) and the midpoint of the bonds Mo(1)–Mo(2) and Mo(3)–Mo(4) of length 3.035 (5) and 2.669 (5) Å, respectively. All other atoms and bonds related by the C_2 axis have average distances as follows: d(Mo–Mo) = 2.542 (5), d(Mo–I_t) = 2.848 (5), d(Mo–I_{db}) = 2.758 (5), and d(Mo–I_{tb}) = 2.826 (5) Å (where t = terminal, db = doubly bridging, tb = triply bridging). The very acute Mo–I_{db}–Mo and Mo–I_{tb}–Mo bond angles, which average 57.3 (1) and 54.5 (1)°, respectively, testify to strong Mo–Mo bonding between all Mo–Mo pairs; even in the case of the "long bond" between Mo(1)–Mo(2), the Mo(1)–I(1)–Mo(2) angle is very acute, 66.8 (1)°. The average of all six Mo–Mo bond distances of 2.645 Å may be compared with the Mo–Mo distance in the metal, 2.73 Å.[6]

On the other hand this structure is more fruitfully viewed as a fragment of the well-known octahedral clusters $Mo_6X_8^{4+}$. As shown in Figure 2 the structure of $Mo_4I_7^{2+}$ (terminal I atoms omitted) can be derived from that of $Mo_6I_8^{4+}$ by removing two adjacent Mo atoms from the Mo_6 octahedron and one I atom from the I_8 cube. The I atom remaining on the cube edge adjacent to the positions of the two removed Mo atoms then is shifted to the midpoint of that edge and becomes the unique atom I(1) which bridges the long bond Mo(1)–Mo(2). From the standpoint of Mo–I bonding and net charge on the cluster, the fragment $Mo_4I_8^+$ also would seem quite reason-

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