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Electron Transfer. 45. Measurements of Redox Rates Requiring Suppression of Autocatalysis

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The reductions, using Eu^{2+} and V^{2+}, of a number of Co(III) complexes of reducible ligands featuring pyridine ring systems exhibit autocatalysis, with the active intermediate in the catalytic path the radical, Lig·, derived from one-electron reduction of the ligand. It has been found that autocatalysis can be strongly suppressed by addition of excess Eu^{3+} or V^{3+}, which reverses the act of electron transfer to the unbound ligand. This suppression allows evaluation of the specific rate for the uncatalyzed reduction. Vanadium(III) is the more effective suppressant, reflecting its more positive potential and the more rapid $V^{3+/2+}$ self-exchange. The apparent specific rate for the uncatalyzed V^{2+} reduction of the $(NH_3)_5Co^{III}$ complex of 4-carbamoyl-2-pyridinecarboxylic acid (I) increases with acidity ($k_{obsd} = 5.0 + 2.8[H^+]$; $\mu = 1.0$), the first reported example of this type of rate law for a pyridine-derived oxidant. The $[H^+]$-dependent term, in conjuction with the known ease with which the parent acid is reduced, supports a mechanism in which electron transfer to the ligand precedes internal transfer to Co^{III} (the "chemical mechanism"). Aside from medium effects, uncatalyzed reductions by V^{2+} are not affected by added V^{3+}, the one exception being the oxidant derived from 2,6-pyridinedicarboxylic acid (III), which appears to be converted to a less reactive vanadium(III)–cobalt(III) complex (reaction 5). Vanadium(II) forms strongly absorbing complexes with the monoprotonated forms of the 2,3-, 2,4-, 2,5-, and 2,6-dicarboxylic acids. The specific rate at which the 2,3 complex is formed from $V(H_2O)_6^{2+}$ (4.9×10^2 M^{-1} s^{-1} at $\mu = 1.2$) is unexpectedly large for an anation reaction at this dipositive center, suggesting that the intervening ion pair $V(H_2O)_6^{2+}HL^-$ is unusually tight.

Earlier studies, dealing with the effects of structural variation in cobalt(III)-bound ligands on reductions by Eu^{2+} and V^{2+}, disclosed instances of marked autocatalysis.[2] The catalytically active species in such cases was the unbound ligand released during, or very shortly after, the primary reaction. Catalysis by such ligands has since been shown[3] to proceed via reduction to a ligand radical, Lig·, which reacts rapidly with the cobalt(III) center, regenerating the ligand and releasing an additional ligand molecule (see eq 1–3).

$$Co^{III}\text{–Lig} + M^{2+} \xrightarrow{k_u} Co^{2+} + \text{Lig} + M^{3+} \qquad (1)$$

$$M^{2+} + \text{Lig} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Lig}\cdot + M^{3+} \qquad (2)$$

$$\text{Lig}\cdot + Co^{III}\text{–Lig} \xrightarrow{k_2} 2\text{Lig} + Co^{2+} \qquad (3)$$

$$(M = Eu, V)$$

Intervention of the catalytic sequence (2) and (3) complicates attempts to obtain k_u, the specific rate of the uncatalyzed reaction (1); for although it is in priniciple possible to measure a reaction rate immediately after mixing (in the momentary absence of unbound ligand), such estimates of initial rates are significantly less precise than a specific rate evaluated from a series of data points taken throughout the course of a straightforward reaction.

In the present reexamination of some redox systems exhibiting autocatalysis, we have utilized the reversibility of the reduction of the ligand to its radical (reaction 2) to suppress the catalytic path and thus isolate the uncatalyzed component. Although we report no large scale surprises, we have encountered several minor points that might otherwise have escaped detection.

Experimental Section

Materials. Lithium perchlorate[4] and solutions of the perchlorates of Eu(III),[2a] Eu(II),[2a] and V(II)[5] were prepared as described. Solutions of V(III) were prepared by mixing equivalent quantities of $V(ClO_4)_2$ and $VO(ClO_4)_2$ in aqueous $HClO_4$. Cobalt(III) complexes, including pyridinedicarboxylato derivatives, in which ligation was directed specifically at one of the two nonequivalent carboxyl positions,[6a] were available from previous studies.[2a,6]

Rate Measurements. Rates were estimated from measurements of decreases in absorbance at the low-energy Co(III) maximum (475 or 502 nm), by using a Cary 14 or Beckman 5260 recording spectrophotometer or a Durrum-Gibson stop-flow spectrophotometer, as described.[2a,4,6c] Reactions were generally carried out at ionic strength near 1.0 M, by using combinations of $HClO_4$ and $LiClO_4$ as the supporting electrolyte. Those reactions not exhibiting autocatalysis were first order each in Co(III) and reductant but were generally run under pseudo-first-order conditions with at least a 10-fold excess of reductant. Reactions for which the bimolecular specific rate fell below 1.5 M^{-1} s^{-1} were carried out in a cell having an optical path length of 1.00 cm with $[Co^{III}]_0$ near 1×10^{-3} M, whereas faster reactions were monitored in a 10.0-cm cell with $[Co^{III}]_0$ near 1×10^{-4} M. Autocatalytic reactions yielded, instead of the usual logarithmic curves, decay curves which were more nearly linear. When such reactions were carried out with excess Eu^{3+} or V^{3+} to suppress catalysis (see the following section), very nearly normal first-order curves were obtained. Reactions were followed for at least 4 half-lives. Rate constants from successive half-life values within a single run agreed to within 6%, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction times. Specific rates obtained from replicate runs on the Cary or Beckman spectrophotometer checked to better than 7%, whereas successive reactions on the Durrum (with the same pair of master solutions) were superimposable. Specific rates obtained by stopped flow from different master solutions agreed to better than 6%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Reduction of the complex of 2,3-pyridinedicarboxylic acid with excess V^{2+} in the stop-flow system, as monitored at 502 nm, exhibited the expected absorbance decrease when it was carried out in 1.2 M H^+, practically no decrease in 0.4 M H^+, and marked increases at 0.24 and 0.12 M H^+, reflecting the formation, at lower acidities, of a strongly absorbing (λ_{max} 575 nm, $\epsilon = 370$) vanadium(II) complex of the ligand released in the primary reaction. The same complex may be prepared, in cobalt-free systems, by treatment of V^{2+} with an excess of the dicarboxylic acid; 50% conversion to the complex occurs at 0.0080 M diacid in 0.1 M $HClO_4$ and at 0.0137 M diacid in 0.2 M $HClO_4$. Estimated specific rates for formation of the complex (25 °C) are 4.0×10^2 M^{-1} s^{-1} at $\mu = 0.5$ M and 4.9×10^2

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(1) On leave from Vivekenada College, *mylapore*, Madras, India.

(2) See, for example: (a) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972); (b) C. Norris and F. Nordmeyer, *ibid.*, **93**, 4044 (1971); (c) J. C. Chen and E. S. Gould, *ibid.*, **95**, 5539 (1973); (d) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2369 (1974).

(3) See, for example: (a) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *J. Am. Chem. Soc.*, **99**, 1073 (1977); (b) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **16**, 2516 (1977).

(4) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 5661 (1971).

(5) (a) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 2769 (1971); (b) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

(6) (a) J. C.-K. Heh and E. S. Gould, *Inorg. Chem.*, **17**, 3138 (1978); (b) J. R. Barber, Jr., and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 4045 (1971); (c) E. S. Gould, *ibid.*, **96**, 2373 (1974); (d) E. S. Gould and H. Taube, *ibid.*, **86**, 1318 (1964).

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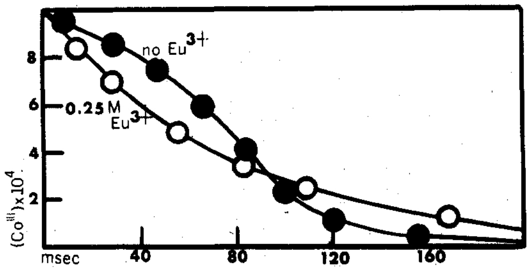


Figure 1. Kinetic curves for the Eu^{2+} reduction of the $(NH_3)_5Co^{III}$ complex of 4-carbamoyl-2-pyridinecarboxylic acid (I) in the absence (●) of added Eu^{3+} and with 0.25 M $Eu(ClO_4)_3$ added (○) to suppress the autocatalysis. Reactions were carried out at 25 °C in 1.2 M $HClO_4$; $[Eu^{2+}] = 0.0100$ M; $[Co^{III}]_0 = 1.0 \times 10^{-3}$ M. Note that the initial rate is much greater in the presence of excess Eu^{3+}, but that the unsuppressed reaction accelerates. The two rates become equal at 50 ms. The plot for the suppressed reaction closely approximates a first-order decay curve with a pseudo-first-order constant of 12.2 s^{-1}.

$M^{-1}\ s^{-1}$ at $\mu = 1.2$ M. This complex undergoes air oxidation much more readily than V^{2+}(aq).

Results and Discussion

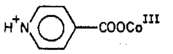
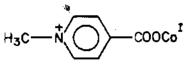
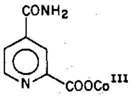
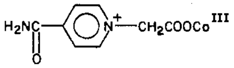
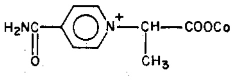
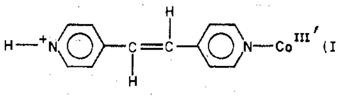
As in previous work,[3] the reaction sequence (1)–(3), leads, on application of the steady-state approximation to the radical intermediate, "Lig·", to rate law 4, with the k_u term, pertaining

$$\text{rate} = \frac{k_1k_2[Co^{III}][M^{2+}][Lig]}{k_{-1}[M^{3+}] + k_2[Co^{III}]} + k_u[Co^{III}][M^{2+}] \quad (4)$$

to the uncatalyzed electron transfer act, remaining predominant throughout the course of those reactions not exhibiting autocatalysis. When $k_2[Co^{III}]$ greatly exceeds $k_{-1}[M^{3+}]$, the kinetic character of autocatalytic reactions is determined by the relative magnitudes of the terms k_1[Lig] and $k_u[Co^{III}]$. Since the ligand is stoichiometrically released as Co(III) is consumed,[7] the relative importance of the catalyzed and uncatalyzed components cannot be regulated externally, although the partition between paths does change during the progress of the reaction. With the reductant M^{2+} in excess and with M^{3+} present, the kinetic behavior of the reaction depends upon the relative magnitudes of k_u and the quotient $k_1k_2[Lig]/k_{-1}[M^{3+}]$. Under these conditions, the catalytic component may be inhibited and, in favorable cases, suppressed, by addition of an external source of V^{3+} or Eu^{3+}.[8]

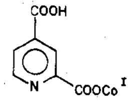
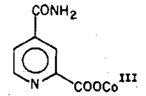
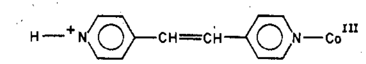
Figure 1 shows both the kinetic curve for the Eu^{2+} reduction of the $(NH_3)_5Co^{III}$ complex of 4-carbamoyl-2-pyridinecarboxylic acid (I) with no Eu^{3+} added and that for the same reduction in the presence of 0.25 M Eu^{3+} (both reactions at 25 °C in 1.2 M $HClO_4$). Although the initial rate is greater for the latter (suppressed) reaction, reflecting the higher ionic strength of the medium, the unsuppressed reaction is seen to accelerate during its early stages, indicating that k_1 exceeds k_u in this system. The two rates become equal at about 50 ms, after which the unsuppressed reaction remains the more rapid until very nearly all the oxidant is consumed. Note that the curve for the suppressed reaction is, in effect, a first-order decay curve.

Table I. Specific Rates for Europium(II) Reductions of Pentaamminecobalt(III) Complexes, Measured with Autocatalysis Suppressed[a]

oxidant	$[H^+]$, M	$[Eu^{3+}]$,[g] M	k_{Eu}
	1.0	0.013	2.4
	0.5	0.013	2.3
	0.1	0.013	1.85
	1.0	0.013	2.4
	0.1	0.013	2.1
 (I)	1.0	0.25[b]	1.22×10^3
	1.2	0.080	1.6×10^2 [e]
	1.2	0.080	97[e]
 (II)	1.25	0.21[c]	0.56
		0.45[d]	0.53

[a] Specific rates are in $M^{-1}\ s^{-1}$ at 25 °C. Reactions were carried out at $\mu = 1.0$ unless otherwise noted. Eu^{3+} was added to suppress autocatalysis. See Experimental Section for further details. [b] $\mu = 2.2$. [c] $\mu = 2.0$. [d] $\mu = 2.7$. [e] See ref 8. [f] For evidence that this ligand is a trans olefin, see T. Katsumoto, *Bull. Chem. Soc. Jpn.*, **33**, 1376 (1960). [g] $[Eu^{3+}]$ values given are near the minimum needed to obtain an undistorted exponential kinetic curve for the reductions listed.

Table II. Specific Rates for Vanadium(II) Reductions of Pentaamminecobalt(III) Complexes, Measured with Autocatalysis Suppressed[a]

oxidant	$[H^+]$, M	k_V
	1.0	8.0
	0.2	7.8
 (I)	1.0	7.8
	0.8	6.9
	0.6	6.8
	0.5	6.4
	0.3	6.0
	0.2	5.6
	1.0[b]	0.66

[a] Specific rates are in $M^{-1}\ s^{-1}$ at 25 °C. Reactions were carried out with μ near 1.0 ($LiClO_4$-$HClO_4$) in the presence of 0.007 M V^{3+} (as suppressant) unless otherwise noted. See Experimental Section for details. [b] $[V^{3+}] = 0.071$ M.

Kinetic data for Eu^{2+} reductions with autocatalysis suppressed are collected in Table I, and similar data for V^{2+} reductions appear in Table II. Table III lists rates for a number of structurally related oxidants not exhibiting autocatalysis. Comparing the concentrations of suppressants used in the europium(II) systems with those in the autocatalytic V(II) systems, we see that V^{3+} is considerably more effective in this role than is Eu^{3+}. This difference is a consequence not only of the greater ratio k_{-1}/k_1 (eq 4) associated with the vanadium system (reflecting the more strongly oxidizing potential for $V^{2+/3+}$)[3b] but also of the greater self-exchange rate[9] for this couple.

Particularly high concentrations of M^{3+} are needed to suppress the autocatalytic components in reductions of the complex of 4,4′-dipyridylethylene (II). Here, competition between Co(III) (k_2) and M^{3+} (k_{-1}) for the radical interme-

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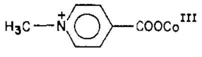
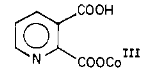
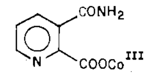
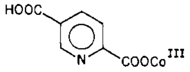
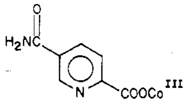
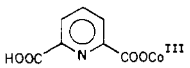
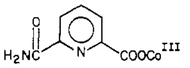
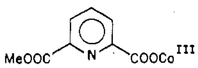
(7) Note that when k_1 is nearly equal to k_u, i.e., when the specific rate of direct reduction of bound Co(III) approaches that of 1e reduction of the unbound ligand, the overall loss of Co(III), by a combination of the catalyzed and uncatalyzed paths, proceeds at nearly a constant rate in the presence of excess reductant. This is in accord with kinetic behavior observed in a number of autocatalytic systems.[2]

(8) Isolated instances of suppression of autocatalysis of electron-transfer reactions have been described by C. A. Radlowski and E. S. Gould, *Inorg. Chem.*, **18**, 1289 (1979).

(9) K. V. Krishnamurthy and A. C. Wahl, *J. Am. Chem. Soc.*, **80**, 5921 (1958).

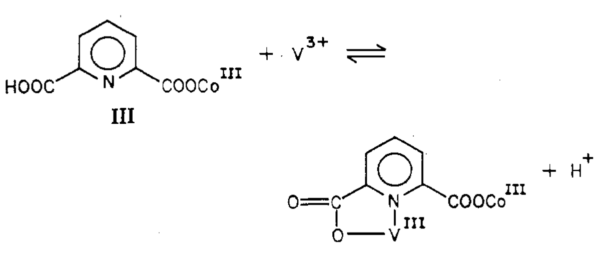
Table III. Vanadium(II) Reductions Not Exhibiting Autocatalysis[a]

oxidant	[H$^+$], M	10^3[V^{3+}], M	k_V
	1.0	0	0.82
	1.0	70	0.93
	0.20	0	0.87
	1.0	0	3.3
	0.20	0	4.1
	0.20	7	4.1
	1.0	0	1.22
	1.0	70	1.31
	0.20	70	1.22
	1.0	0	2.9
	1.0	7	2.8
	0.70	0	3.1
	0.50	0	3.6
	0.20	0	4.3
	1.0	0	4.4
	0.1	0	4.6
	0.1	7	3.6
	1.0	0	6.0
	1.0	0[b]	5.8
	1.0	1.8	4.2
	1.0	7.1	3.7
	0.20	3.5	3.2
	0.20	14.2	3.0
	1.0	0	4.6
	1.0	7	4.5
	1.0	0	3.9
	1.0	7	4.1

[a] Specific rates are in M^{-1} s^{-1} at 25 °C. Reactions were carried out with μ near 1.0 ($LiClO_4$). All oxidants are $(NH_3)_5Co^{III}$ complexes. [b] [Al^{3+}] = 0.0070 M.

diate Lig• has come into play. Values of k_{-1} for this ligand are known to be unusually low in strongly acidic media[3b] in which both nitrogen atoms are protonated. In the absence of "lead-in" functions (e.g., carbonyl or carboxyl groups with unshared pairs that can coordinate with an attacking metal center), electron transfers must occur via outer-sphere paths which, for aromatics of this type, have been shown[3b] to be sluggish, whereas with all other ligands in this study, bridged routes (involving oxygen coordination) for the initial catalytic step (k_1), and for its reversal, are at hand.

Data for noncatalytic systems (Table III) are included principally to demonstrate that vanadium(III), at the concentration levels used in the suppression experiments, exerts, in the absence of autocatalysis, no substantial effect on the reaction rate. In an exceptional instance, however, reduction of the complex of 2,6-pyridinedicarboxylic acid (III) is found to be inhibited by added V^{3+}, an effect which may be reasonably attributed to partial conversion of the oxidant to a chelated vanadium(III) complex, IV (see eq 5), which is reduced about half as rapidly as complex III. Conversion of the latter, at the 10^{-4} M level, to IV appears to be very nearly complete in the presence of 0.014 M V^{3+} at [H^+] = 0.20 M and is accompanied by a shift in the visible maximum from 502 to 496 nm, the development of a marked shoulder at 350 nm, and the appearance of a peak at 271 nm (ϵ = 880). Our data are not sufficiently precise to allow evaluation of an association constant for this V(III)–Co(III) complex. As expected, we find no evidence for formation of an analogous species from the 2,3 and 2,5 isomers of III nor from those 2,6 oxidants (final entries in Table III) in which the nonligated carboxyl is "blocked off" by conversion to an ester or amide function. Moreover, virtually no retardation is noted if Al^{3+}, rather than V^{3+}, is added.


III

IV

(5)

Variations of reduction rates with acidity, when detected in the present series, are seen to be modest. Retardation at high acidities, as noted for the V^{2+} reductions of the 2,3- and 2,5-pyridinedicarboxylato complexes, conforms to the pattern reported for the Cu^+ and Cr^{2+} reductions of these derivatives,[4,6a] doubtless by reflecting the [H^+]-dependent partition of the oxidant into a protonated and a somewhat more reactive nonprotonated form.

Acceleration with increasing [H^+], observed here in the V^{2+} reduction of the 4-carboxamide derivative (I) ($k_{obsd} = 5.0 + 2.8[H^+]$, $\mu = 1.0$), is less usual. This type of pattern has been described for several systems[2c,10] in which an unsaturated "lead-in" group lies in conjugation with $COOCo^{III}$ but, until now, has not been reported for oxidants featuring the pyridine ring. Others have suggested[10a,11] that an [H^+]-dependent term is diagnostic of reduction via a path in which electron transfer to the ligand precedes internal transfer to the bound acceptor metal center (the "chemical mechanism"). On this basis, it is reasonable to expect such a mechanism to operate in the present case, for the parent ligand has been shown to undergo one-electron reduction with unusual ease,[12] and this type of reduction is known further to be facilitated by protonation, both of the ring nitrogen and of donor atoms of substituents.[13]

Note finally that reduction of the Co(III) derivative of the 2,3-dicarboxylic acid with excess V^{2+} at low acidities is complicated by the appearance of a strongly absorbing (λ_{max} 575 nm, ϵ = 370) complex formed in this case by the rapid reaction of excess reductant with the ligand released by aquation of the primary V(III) product. The same species can be prepared from V(II) and the unbound ligand in systems containing neither Co(III) nor added V(III). Observed variation of the apparent association constant of this adduct with acidity (120 M^{-1} at [H^+] = 0.1 M; 73 M^{-1} at [H^+] = 0.2 M), considered in conjuction with the reported pK_1 value of the ligand (1.3 at 25 °C),[14] indicates this to be a 1:1 complex derived from the monoprotonated form of the ligand, HL^-, with a "limiting" formation constant, expressed in terms of [HL^-], of 360 M^{-1}. The specific rate at which this complex is formed from $V(H_2O)_6^{2+}$ (4.9×10^2 M^{-1} s^{-1} at μ = 1.2) may be considered remarkably great for a species of this charge type.[15] Since this rate constant is determined jointly by the specific rate of heterolysis of a V–O bond in the aquo cation (a process nearly independent of the incoming ligand) and the formation constant of the outer-sphere ion pair $V(H_2O)_6^{2+}HL^-$,[15,16] we may infer the latter aggregate to be unusually weakly dissociated.

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(10) See, for example: (a) J. K. Hurst and H. Taube, *J. Am. Chem. Soc.*, **90**, 1178 (1968); (b) A. Zanella and H. Taube, *ibid.*, **94**, 6403 (1972).

(11) See, for example, H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970).

(12) Y.-T. Fanchiang, J. C. Thomas, V. D. Neff, J. C.-K. Heh, and E. S. Gould, *Inorg. Chem.*, **16**, 1942 (1977).

(13) See, for example, U. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974).

(14) G. K. S. Ooi and R. J. Magee, *J. Inorg. Nucl. Chem.*, **32**, 3315 (1970).

(15) (a) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968), report, for example, a specific rate of 28 M^{-1} s^{-1} (μ = 0.84) for anation of $V(H_2O)_6^{2+}$ by NCS^-; (b) for additional data pertaining to substitution at V(II) centers, see N. Sutin, *Acc. Chem. Res.* **1**, 225 (1968).

(16) See, for example, N. Sutin, *Annu. Rev. Phys. Chem.*, **17**, 119 (1966).

Analogous V(II) complexes are formed from 2,4-, 2,5-, and 2,6-pyridinedicarboxylic acids.[17] Since, however, kinetic experiments involving the Co(III) derivatives of these acids were carried out in much more dilute solutions, formation of these complexes did not interfere with our measurements.

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Registry No. 1-H-4-COOCo(NH$_3$)$_5$-C$_5$H$_4$N^{3+}, 42532-70-7; 1-CH$_3$-4-COOCo(NH$_3$)$_5$-C$_5$H$_4$N^{3+}, 74911-56-1; 2-COOCo(NH$_3$)$_5$-4-CONH$_2$-C$_5$H$_3$N^{2+}, 67598-21-4; 1-CH$_2$COOCo(NH$_3$)$_5$-4-CONH$_2$-C$_5$H$_4$N^{3+}, 69421-18-7; 1-CH(CH$_3$)COOCo(NH$_3$)$_5$-4-CONH$_2$-C$_5$H$_4$N^{3+}, 69421-20-1; 1-H-4-(4-CH=CH-C$_5$H$_4$N)Co(NH$_3$)$_5$-C$_5$H$_4$N^{4+}, 74911-57-2; 2-COOCo(NH$_3$)$_5$-4-COOH-C$_5$H$_3$N^{2+}, 67662-33-3; 2-COOCo(NH$_3$)$_5$-3-COOH-C$_5$H$_3$N^{2+}, 67598-28-1; 2-COOCo(NH$_3$)$_5$-3-CONH$_2$-C$_5$H$_3$N^{2+}, 67598-20-3; 2-COOCo(NH$_3$)$_5$-5-COOH-C$_5$H$_3$N^{2+}, 67598-29-2; 2-COOCo(NH$_3$)$_5$-5-CONH$_2$-C$_5$H$_3$N^{2+}, 67598-23-6; 2-COOCo(NH$_3$)$_5$-6-COOH-C$_5$H$_3$N^{2+}, 67662-34-4; 2-COOCo(NH$_3$)$_5$-6-CONH$_2$-C$_5$H$_3$N^{2+}, 67632-51-3; 2-COOCo(NH$_3$)$_5$-6-COOCH$_3$-C$_5$H$_3$N^{2+}, 67598-24-7; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3.

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(17) Visible absorption maxima are at 610 nm ($\epsilon = 600$) for the 2,4 isomer, 572 nm ($\epsilon = 88$) for the 2,5 complex, and 600 nm ($\epsilon = 95$) for the 2,6 complex.

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Optical Activity Induced in Tris(4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione)europium(III) by Association with Chiral Amino Alcohols

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The optical activity induced in the title compound by complex formation with seven chiral amino alcohols was studied by means of circularly polarized luminescence (CPL) spectroscopy. The signs of the CPL peaks associated with the Eu(III) emission bands could be correlated with the absolute configuration of the added amino alcohol, and the magnitude of the CPL appeared to be dictated by steric considerations. It proved possible to calculate association constants for the chelate/substrate adducts from the enhancement of luminescence intensities that resulted from the formation of adduct species. For all substrates, the presence of 1:1 and 1:2 chelate/substrate adducts was noted, but the 1:2 adduct only formed at high concentrations of substrate. It was found that all log K_1 values were approximately 4.5, while the log K_2 values ranged from 1.1 to 1.8. The magnitude of the formation constants and of the induced optical activity appears to be a complicated function of steric and electronic effects.

Introduction

Complexes of lanthanide ions are finding increasing degrees of application in a wide variety of areas, and the solution-phase coordination chemistry of these ions is receiving a great deal of attention. While solutions of aquated metal ions have been investigated via diffraction techniques,[1] these methods cannot easily be applied to lanthanide complexes containing more complex ligands. Unlike transition metals, lanthanide ions can exhibit a wide range of coordination numbers,[2] and this situation greatly extends the range of available chemistry. Nevertheless, quantitative aspects of lanthanide chemistry require detailed knowledge of solution stereochemistries, and without this information the application of lanthanide ions as NMR shift reagents[3] or as probes of calcium-binding proteins[4] cannot hope to become more than qualitative.

A wide variety of physical methods have been brought to bear on solutions of lanthanide complexes in order to obtain the necessary stereochemical information. The most useful of these are chiroptical techniques, and circular dichroism studies have been used to probe solution stereochemistries.[5,6] Unfortunately, the intensity of lanthanide f–f absorptions are extremely weak and CD spectra are only obtained at relatively high concentrations of complex. Many of these complexes have been shown to associate into polynuclear species under these conditions, and this association is most extensive at alkaline pH where the CD signals are the strongest.[6,7]

A more recently developed technique that is better suited for the study of lanthanide complexes is that of circularly polarized luminescence (CPL) spectroscopy.[8] With this method, the differential emission of left and right circularly polarized light by a chiral luminescent molecule is detected, and this method has been shown to be extremely sensitive toward slight stereochemical changes. Lanthanide ions are best studied by emission methods such as CPL since the luminescence spectra are well characterized and the bands arising from various states are well separated. In addition, the f–f transitions are highly nonbonding in character, and one is then able to assume that any measurement of excited-state chirality must have its origin in the ground-state stereochemical effects.

The study of lanthanide complexes of β-diketones is very important due to the use of these chelates as NMR shift reagents.[3] These complexes are easily studied by CPL spectroscopy since the solution geometries can be reasonably well-defined, the Tb(III) and Eu(III) derivatives are often highly emissive, and most complexes are mononuclear. These features make this particular class of compounds especially useful in the development of spectra–structure correlations, and these in turn can be applied to new systems of unknown stereochemistry. When one prepares a lanthanide tris(β-diketone) complex, the compound that is produced is actually a racemic mixture of highly labile enantiomers. The observation of CPL therefore requires a stereoselective enrichment

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