Electron Transfer. 40. Reactivity Patterns in the Reductions of Nitrile Complexes of Cobalt(III)[1]

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The specific rates of reduction of nine pentaamminecobalt(III) derivatives of nitriles, using Cr^{2+}, V^{2+}, Eu^{2+}, and $Ru(NH_3)_6^{2+}$, are compared. In some cases, nitrile groups are bound directly to Co(III); in others they are uncoordinated and may, in principle, act as lead-in groups. Three of the oxidants feature nitrile functions of both types. Specific rates for $Ru(NH_3)_6^{2+}$ (k_{Ru} values) exceed by 10^1–10^4 those reported for $(NH_3)_5Co^{III}$ derivatives of a wide variety of organic ligands. The great effectiveness of bound nitriles as outer-sphere mediators may be taken to reflect the high electronegativities of triply bonded carbon and nitrogen, and this effectiveness is further increased by replacement of aliphatic nitriles by aromatic nitriles and, beyond that, by incorporation of additional electron-withdrawing substituents. For oxidants which must react via outer-sphere paths the ratios k_{Ru}/k_{Cr}, k_V/k_{Eu}, and k_{Ru}/k_V conform to values previously reported for outer-sphere series. These ratios persist for the 1,2- and 1,3-dicyanobenzene derivatives, indicating the absence of redox-bridging action by the uncoordinated cyano group in these cases. Marked departures from these ratios are observed for reductions of the complexes of 1,4-dicyanobenzene, 4-cyanoacetophenone (III), and 4-cyanopyridine (ring-bound, IV), pointing to large inner-sphere components, not only in the Cr^{2+} reductions but also in the V^{2+} reductions and in two of the Eu^{2+} reductions. Values of k_{Ru}, in conjunction with linear free energy relationships which apply to related outer-sphere series, have been used to estimate the distribution between paths for those oxidants exhibiting evidence of an inner-sphere contribution. Although the cyano group is seen to function both as a "lead-in" group and, when coordinated, as a "conducting" group, it is much less effective than carbonyl in the first of these roles and somewhat less effective than the pyridine ring in the second. Autocatalysis, observed in the Eu^{2+} reduction of the complexes of 4-cyanopyridine and 1,2-dicyanobenzene, is attributed to catalysis by the aromatic ligands released in the primary reactions. These appear to be the first examples of catalysis of electron transfer by unbound nitriles, 1,2-dicyanobenzene being, in addition, the first example of such a catalyst having no nitrogen ring system.

Earlier investigations demonstrated that nitrilic cyano units, when appropriately positioned, could function effectively as lead-in substituents in inner-sphere redox reactions,[3] but such studies dealt solely with reductions by chromium(II). Since the lead-in properties of unsaturated groups are known to be sensitive to the identity of the reductant,[4] an extension of this work to include additional reducing centers was considered of interest.

Attempts to assign mechanisms for reduction by V^{2+} and Eu^{2+} encounter the difficulty that substitutions about vanadium(III) and europium(III) are rapid. Hence, a primary product in which the bridging ligand is bound to either of these centers cannot generally be characterized by methods applicable to chromium(III) products. However, the patterns of relative rates for outer-sphere reductions by dipositive metal centers have been found[5] to be sufficiently diagnostic to allow substantial deviations to be attributed, with some confidence, to the intervention of inner-sphere processes.[4,6]

In the present communication, we describe evidence that those coordinated nitriles which function most successfully as bridges in reductions of Cr^{2+} may also serve as inner-sphere mediators with V^{2+} and Eu^{2+}. As with a number of bound carboxylato groups and ligated pyridine derivatives,[4,6,7] however, bridging effects are subdued with the latter two reductants.

Experimental Section

Materials. Solutions of chromium(II),[8] europium(II),[4] vanadium(II),[9] and hexaammineruthenium(II)[5] were prepared by published procedures. Nitriles used in ligation (Aldrich products) were used as received.

Those cobalt–nitrile derivatives not available from previous studies[10] were prepared by published procedures[3,10] or by treatment of aquopentaamminecobalt(III) perchlorate[8] with the nitrile in *N,N*-diethylacetamide.[6] The desired complexes were purified by ion-exchange chromatography on Rexyn 102(H) in its Na$^+$ form (eluting with aqueous NaCl at 5 °C)[10] or Biogel P-2 (eluting with water at 25 °C) and then precipitated and recrystallized as their perchlorates.

Attempts to prepare the $(NH_3)_5Co^{III}$ complex of fumaronitrile were unsuccessful. Elemental analyses (C, H, Co) of all other complexes were consistent with the assigned structures.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[4,5] Measurements were made at the low-energy maxima of the Co(III) complexes near 470 nm. Reductions with $Ru(NH_3)_6^{2+}$ were carried out in 0.030 M HCl under argon using LiCl as the supporting electrolyte ($\mu = 0.5$). Other reductions were run under nitrogen in 1.0 M HClO$_4$. Reductions were first order each in Co(III) and reductant but were generally carried out under pseudo-first-order conditions with at least a fivefold excess of reductant. Since the reacting species do not partake in protonation equilibria in dilute acid, [H$^+$] was not systematically varied. Reactions were followed for at least 5 half-lives. Rate constants evaluated from successive half-life periods within a single run agreed to within 4%. Except as noted below, no trends indicative of systematic errors were evident, and average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. In general, specific rates obtained from replicate runs checked to within 7%. Satisfactory rate constants could not be obtained for the reaction of the acetonitrile complex with $Ru(NH_3)_6^{2+}$ nor for the benzonitrile complex with Eu^{2+}; individual runs for both of these combinations yielded reasonable pseudo-first-order curves, but agreement between runs was poor. The source of difficulty, which persisted despite several modifications in procedure, is not clear in these cases. Autocatalysis, similar to that observed for reductions of several complexes of 4-substituted pyridines,[4,7,11] was encountered in the Eu^{2+} reductions of the complexes of 1,2-dicyanobenzene and 4-cyanopyridine (Table I). Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Results and Discussion

Kinetic data are summarized in Table I. The substitution-inert character of the Ru(II) center ensures that the specific rates for reduction by $Ru(NH_3)_6^{2+}$ (k_{Ru} values) refer to outer-sphere processes. Moreover, since the complexes of acetonitrile, benzonitrile, and cinnamonitrile (II) are devoid of "lead-in" donor groups, reductions of each of these with all four oxidants may likewise be assigned outer-sphere paths.

Table I. Reductions of Pentaamminecobalt(III) Derivatives of Nitriles with $Ru(NH_3)_6{}^{2+}$, V^{2+}, Eu^{2+}, and Cr^{2+} [a]

oxidant	$k_{Ru}{}^b$	$k_V{}^c$	$k_{Eu}{}^c$	$k_{Cr}{}^c$
$(NH_3)_5CoN≡CCH_3{}^{3+}$	~6	1.18	0.41	0.020
$(NH_3)_5CoN≡C-⟨◯⟩{}^{3+}$	13.4	2.3		0.043[e]
$(NH_3)_5CoN≡C-⟨◯⟩{}^{3+}$ (I), NC	26	6.1	2[d]	0.142
$(NH_3)_5CoN≡C-⟨◯⟩{}^{3+}$, CN	30	4.1	0.99	0.059[f]
$(NH_3)_5CoN≡C-⟨◯⟩-CN{}^{3+}$	34	5.3	1.21	0.93[f]
$(NH_3)_5CoN≡CCH=CH-⟨◯⟩{}^{3+}$ (II)	11.7	2.0	0.39	0.033
$(NH_3)_5CoN≡C-⟨◯⟩-CCH_3{}^{3+}$ (III), O	22	17.3	11.2	$6 × 10^3$ [f]
$(NH_3)_5CoN⟨◯⟩-CN{}^{3+}$ (IV)	9.4	7.7	2[d]	124[g]

[a] Specific rates in M^{-1} s^{-1} at 25 °C. [b] $[H^+] = 0.030$ M, $[Ru^{II}] = 0.0015-0.006$ M, $[Co^{III}]_0 = 3 × 10^{-4}$ M, $\mu = 0.50$; supporting electrolyte LiCl. [c] $[H^+] = 1.0$ M, [reductant] = 0.002-0.03 M, $[Co^{III}]_0 = 2 × 10^{-4}-2 × 10^{-3}$ M, $\mu = 1.0$; supporting electrolyte $HClO_4$. [d] Autocatalytic reaction; value estimated from initial rate. [e] Reference 3a. [f] Reference 16. [g] Reference 3b.

Note that the k_{Ru} values in the present series exceed, by one to four powers of ten, those reported earlier[5] for $(NH_3)_5Co^{III}$ derivatives of a wide variety of organic ligands under similar conditions. Hence, coordinated nitriles, as a group, should be considered to be among the most powerful unidentate organic outer-sphere mediators.[12] Linck[13] has pointed out that the ease of outer-sphere electron transfer is enhanced by attachment of electron-withdrawing sites to the oxidizing center. Thus, the mediating effectiveness of bound nitriles may be taken to reflect the high electronegativities of triply bonded carbon and nitrogen,[14] and this effectiveness is further increased by replacement of aliphatic by aromatic nitriles and, beyond that, by incorporation of a second electron-withdrawing group (acetyl or cyano).

For those oxidants having structures which dictate outer-sphere redox paths, the ratios k_{Ru}/k_{Cr} (300–350) and k_V/k_{Eu} (3–5) conform closely to relative specific rates reported for an earlier series of outer-sphere reactions,[5] whereas values of

k_{Ru}/k_V (5–6) lie near the corresponding ratio observed for Co(III) oxidants having reactivities falling within this range.[9a] Moreover, the persistence of these ratios with the 1,2- and 1,3-dicyanobenzene derivatives indicates that the uncoordinated cyano group has assumed a negligible lead-in role in the latter two cases.[15] As expected, the k_{Ru}/k_{Cr} ratio changes dramatically for the 1,4-dicyano-, the 4-acetyl- (III), and the 4-cyanopyridine (IV) complexes, for these have been shown to be reduced by Cr^{2+} mainly through a bridged transition state, yielding, in each case, a primary product in which Cr(III) is bound to the remote "lead-in" group.[3b,16]

The k_{Ru} values for these oxidants, in conjuction with linear free energy relationships which have been found to apply to related outer-sphere series,[5,7,17,18] may be used to estimate specific rates that would apply to reactions of these complexes with Eu^{2+} and V^{2+} if these reactions were to proceed wholly by outer-sphere paths. Such calculated outer-sphere rates (k^{OS} values) are listed in Table II, as is the estimated fraction of each reaction proceeding by the bridged path. Calculated distributions based on previous studies[5,6] are also incuded for the complex of 4-benzoylpyridine and for $(NH_3)_5CoOAc^{2+}$, a typical carboxylato derivative.

Although the very approximate nature of the relationships used in these calculations has been emphasized,[5] it seems clear that V^{2+} and Eu^{2+}, like Cr^{2+}, reduce the 4-acetyl complex (III) and the 4-cyanopyridine derivative (IV) mainly by inner-sphere routes. For the V^{2+} reduction of the 1,4-dicyano complex, the two routes appear to be of comparable importance, whereas k_{Eu} for this oxidant indicates a negligible inner-sphere component here.[19] As in earlier investigations,[4–7] Cr^{2+}, among the dipositive reductants, exhibits the strongest preference for the inner-sphere route. These data also remind us that although the cyano group can function both as a lead-in group and, when coordinated, as a "conducting" group, it is considerably less effective than carbonyl in the first of these roles and slightly less effective than the pyridine ring in the second. Attempts to relate these functions quantitatively to the structure of the bridging substituent,[3b,20] although interesting, are not general enough to be considered convincing.

Autocatalysis in Eu^{2+} reductions of the complexes of 1,2-dicyanobenzene and 4-cyanopyridine doubtless arises from catalysis by ligand which is released as the primary reaction proceeds. Catalysis of electron transfer between metal centers by external conjugated organic species has been demonstrated in a number of systems[4,7,11,21] and has been shown to proceed via preliminary reduction of the aromatic to a radical, which then quickly reduces Co(III). Preliminary examination of the catalytic systems derived from the present study indicates that 4-cyanopyridine, the first nitrile described as having catalytic

Table II. Estimated Distribution between Reaction Paths for Reductions of Pentaamminecobalt(III) Derivatives with V^{2+}, Eu^{2+}, and Cr^{2+}

oxidant	k^{OS}(calcd)			k(obsd)[d]			fraction IS		
	V^{2+} [a]	Eu^{2+} [b]	Cr^{2+} [c]	V^{2+}	Eu^{2+}	Cr^{2+}	V^{2+}	Eu^{2+}	Cr^{2+}
$(NH_3)_5CoN≡C-⟨◯⟩-CN{}^{3+}$	2.9	~1	0.19	5.3	1.21	0.93	0.45	~0	0.81
$(NH_3)_5CoN≡C-⟨◯⟩-CCH_3{}^{3+}$ (III), O	2.1	0.7	0.12	17.3	11.2	$6 × 10^3$	0.88	0.93	1.00
$(NH_3)_5CoN⟨◯⟩-CN{}^{3+}$ (IV)	1.2	0.4	0.055	7.7	~2	124	0.85	0.80	1.00
$(NH_3)_5CoN⟨◯⟩-C-⟨◯⟩{}^{[e]}$, O	0.70	0.23	0.05	3.0	$2 × 10^3$	$4.8 × 10^4$	0.76	1.00	1.00
$(NH_3)_5CoOAc{}^{2+}$ [f]							0.99	1.00	1.00

[a] Calculated from the cross relationship: $\log k_V = 0.71 \log k_{Ru} - 0.617$ (see ref 17). [b] Estimated as $1/3 k^{OS}$ for V^{2+} (see ref 5). [c] Calculated from the equation: $\log k_{Cr} = 0.95 \log k_{Ru} - 2.19$ (see ref 17). [d] Specific rates in M^{-1} s^{-1}; 25 °C, $\mu = 1.0$ (this study and ref 17). [e] See ref 6. [f] Distribution between paths calculated by Fan.[5]

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properties, is somewhat more effective than either isonicotinamide or *N*-methylisonicotinic acid, the prototype electron-transfer catalysts of this sort. Catalytic action by 1,2-dicyanobenzene appears to be somewhat less pronounced but is nevertheless of interest since no other electron-transfer catalyst of this type has been reported which features a structure devoid of a nitrogen ring system.

Questions remain as to why 4-cyanopyridine and 1,2-dicyanobenzene exhibit catalytic action in electron-transfer reactions whereas 1,3- and 1,4-dicyanobenzene do not and whether these differences are related to the electrochemical potentials of these nitriles in the medium at hand. These points are being pursued.

Registry No. I, 53739-00-7; II, 68128-57-4; III, 53127-38-1; IV, 46247-07-8; (NH$_3$)$_5$CoN≡CCH$_3^{3+}$, 44819-13-8; (NH$_3$)$_5$CoN≡C-Ph^{3+}, 46343-53-7; (NH$_3$)$_5$CoN≡C-*m*-C$_6$H$_4$-CN^{3+}, 53127-37-0; (NH$_3$)$_5$CoN≡C-*p*-C$_6$H$_4$-CN^{3+}, 48162-76-1; Ru(NH$_3$)$_6^{2+}$, 19052-44-9; V^{2+}, 15121-26-3; Eu^{2+}, 16910-54-6; Cr^{2+}, 22541-79-3.

References and Notes

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(3) (a) R. J. Balahura, G. B. Wright, and R. B. Jordan, *J. Am. Chem. Soc.*, **95**, 1137 (1973); (b) R. J. Balahura, *ibid.*, **98**, 1487 (1976).

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(12) The coordinated nitriles in the present series are somewhat less effective mediators than the 2,5-dinitrophenylato group, but reactions involving the latter are complicated by the possibility of preliminary electron transfer to one or both of the nitro substituents: see R. Reid, F.-R. F. Fan, Y.-T. Fanchiang, and E. S. Gould, *Inorg. Chem.*, **17**, 2766 (1978).

(13) R. G. Linck, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One, 1972*, **9**, 903 (1972).

(14) See, for example, J. E. Huheey, "Inorganic Chemistry", 2nd ed., Harper and Row, New York, 1978, p 164.

(15) Note that the cyano groups in the 1,3 derivative are not in conjugation. We cannot, however, reasonably account for the apparent lack of interaction in the 1,2 complex. Examination of scale molecular models of the latter indicates negligible steric interference between the uncoordinated cyano substituent and the Co(NH$_3$)$_5$ group.

(16) (a) R. J. Balahura and W. L. Purcell, *Inorg. Chem.*, **14**, 1469 (1975); (b) *J. Am. Chem. Soc.*, **98**, 4457 (1976).

(17) Although Fan[5] has found k_{Ru}/k_V to be very nearly constant (in accord with the model of Marcus[18]) for reductions of Co(III) derivatives that react slowly via outer-sphere paths, Guenther and Linck[9a] have noted that this ratio increases markedly for very reactive oxidants. We find that data from both studies conform closely to the equation log k_V = 0.71 log k_{Ru} − 0.62 with a correlation coefficient of 0.991 for 13 entries.

(18) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

(19) In an earlier report[3] it was suggested that the relatively high k_{Cr} value for the 1,4-dicyano complex could be accommodated by a two-step outer-sphere process, in which preliminary reduction of the ligand preceded reduction of Co(III). Evidence against such a mechanism was subsequently presented.[16b] Our finding that k_{Eu} for this complex is not similarly enhanced likewise weighs against an outer-sphere process for Cr^{2+}, for one cannot reasonably explain why such a two-step path would be denied to Eu^{2+}, the formal potential of which is very nearly the same as that of Cr^{2+}.

(20) R. T. M. Fraser, *J. Am. Chem. Soc.*, **83**, 4920 (1961).

(21) (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, J. C. Thomas, V. D. Neff, J. C.-K. Heh, and E. S. Gould, *Inorg. Chem.* **16**, 1942 (1977); (c) Y.-T. Fanchiang and E. S. Gould., *ibid.*, **16**, 2516 (1977).