CCl_4 gave white crystals of triphenylphosphine oxide, mp 153.5–154.5°. The proton nmr spectrum (shown in ref 1b) in C_6D_6 solution at 60 MHz showed an intensity ratio of the *meta* + *para* signal at τ 2.9 to the *ortho* signal at τ 2.2 of 9.8, *vs.* a ratio of 1.5 for undeuterated triphenylphosphine oxide. The observed ratio corresponds to 85% deuteration of the *ortho* positions.

Deuteration of $[(C_6H_5)_3P]_3Ru(N_2)H_2$. A solution of 0.50 g of dihydridonitrogentris(triphenylphosphine)ruthenium(II)[1c] in 50 ml of *m*-xylene was stirred and heated at 65° for 24 hr with deuterium (9 mmoles) at 631 mm. Oxidation of the complex with hydrogen peroxide gave triphenylphosphine oxide with 75% deuteration of the *ortho* positions.

Temperature Effects on Charge-Transfer Luminescence Intensity of Some Transition Metal Ion Chelates

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Contribution from the Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015. *Received February 2, 1969*

Abstract: The unusually large temperature effect on the luminescence intensity of some imine chelates of d^6 ions of certain group VIII metals can be attributed to the effect on the intersystem crossing rate of a temperature-dependent equilibrium between high- and low-spin states established during the lifetime of the charge-transfer excited state of the chelate. The absence of luminescence from Fe(II)–imine chelates may result from complete crossover to the high-spin state upon excitation.

Most complexes of transition metal ions are paramagnetic by virtue of the partly filled outer d subshell. Because the rate of intersystem crossing in most paramagnetic species is quite rapid, very few of these species are luminescent in fluid solution.[1,2]

Brandt and coworkers reported an intense red-orange luminescence at room temperature upon ultraviolet irradiation of dilute aqueous solutions of several Ru(II)–imine chelates.[3,4] They assigned the luminescence to a radiative ligand-to-metal charge-transfer transition ($\pi^* \rightarrow$ d). Recent work[5,6] has confirmed that this luminescence probably originates from a ligand triplet ($^3\pi^*$); thus, it is a phosphorescence.[7] Some imine chelates of Ir(III) and Os(II) also show a charge-transfer luminescence;[8,9] in some cases this radiation is emitted by samples in fluid solution at room temperature.[10,11] These species have several structural characteristics in common: the chelates have octahedral microsymmetry, metal ions with d^6 electron configuration, and ligands which produce strong ligand fields; these species all show charge-transfer excited states at lowest energies, *i.e.*, below ligand field (d*,d) and ligand (π^*,π) excited states. Also of interest is the very striking temperature dependence of the luminescence intensity in fluid solution near room temperature.[5,11]

However, all transition metal ion chelates that might be expected to show charge-transfer luminescence of the kind just described do not do so. In particular none of the Fe(II)–imines luminesces (even in rigid media); neither does the Ru(II)–ter chelate (ter = 2,2′,2′′-terpyridine) at room temperature, although the red-orange phosphorescence characteristic of Ru(II)–imines is seen upon exposure of rigid solutions of $[Ru^{II}(ter)_2]^{2+}$ to near-ultraviolet radiation.[4,7,12] In the present work the unusual temperature effect is studied in more detail, and a simple general explanation for this remarkable phenomenon is proposed. Moreover, the same considerations can also account for the absence of luminescence from these imine chelates of Fe(II) and certain imines formed by Ru(II) and Ir(III).

Results

Absolute ethanol solutions of the chelates shown in Table I were examined at and within *ca.* 50° of room temperature as well as in the form of rigid glasses at *ca.* 80°K (the temperature of liquid nitrogen). Solutions of most of these chelates were prepared by dissolving the solid compounds which were obtained as indicated in Table I. The chelates were also synthesized directly in solution by mixing the metal ion (as ruthenium(III) chloride, iridium(III) chloride, or iron(II) sulfate) and a large amount (5 to 10 molar excess) of the ligand in aqueous solution; solutions containing iridium or ruthenium ions were heated for *ca.* 2 hr at gentle boil and hydroxylamine hydrochloride was also added to the ruthenium solutions. Most of the excess ligand was removed from a nearly neutral aqueous phase (25 ml) by two extractions with 10-ml portions of chloroform. Absolute ethanol was added to the residual aqueous extract after heating to evaporate nearly all of the water (the final solution was at least 95% in ethanol). No differences believed to be of consequence for the present work were detected in the optical properties determined on solutions of the chelates prepared by dissolving the solid or by mixing the metal ion and the ligand. There were small differ-

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[1] R. S. Becker in "Technique of Organic Chemistry," Vol. IX, 2nd ed, W. West, Ed., Interscience Publishers, New York, N. Y., 1968, Chapter 4.

[2] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 14.

[3] J. P. Paris and W. W. Brandt, *J. Am. Chem. Soc.*, **81**, 5001 (1959).

[4] H. Veening and W. W. Brandt, *Anal. Chem.*, 32, 1426 (1960).

[5] F. E. Lytle and D. M. Hercules, *J. Am. Chem. Soc.*, **91**, 253 (1969).

[6] J. N. Demas and G. Crosby, *J. Mol. Spectry.*, **26**, 72 (1968).

[7] J. P. Paris, Ph.D. Thesis, Purdue University, 1960, University Microfilms, Inc., Ann Arbor, Mich., Mic 60-4199, pp XIV, 99, 101.

[8] G. A. Crosby, *J. Chim. Phys.*, **64**, 160 (1967).

[9] F. Zuloaga and M. Kasha, *Photochem. Photobiol.*, 7, 549 (1968).

[10] K. R. Wunschel, Jr., and W. E. Ohnesorge, *J. Am. Chem. Soc.*, **89**, 2777 (1967).

[11] D. W. Fink and W. E. Ohnesorge, *Anal. Chem.*, **41**, 39 (1969).

[12] D. M. Klassen and G. A. Crosby, *J. Chem. Phys.*, **48**, 1853 (1968).

Table I. Luminescence Properties of Some Imine Chelates of Fe(II), Ru(II), and Ir(III)[a]

Chelates luminescent in absolute EtOH soln at room temp and at ~80 °K	Chelates nonluminescent in absolute EtOH soln at room temp but do luminesce in EtOH glasses at ~80 °K	Chelates nonluminescent in absolute EtOH soln at room temp and at ~80 °K
$[Ir^{III}(bipy)]^{3+}$ [b]	$[Ir^{III}(2\text{-Me-phen})]^{3+}$	$[Fe^{II}(bipy)_3]^{2+}$ [d]
$[Ir^{III}(phen)]^{3+}$ [b]	$[Ru^{II}(2\text{-Me-phen})_3]^{2+}$ [e]	$[Fe^{II}(phen)_3]^{2+}$ [d]
$[Ir^{III}(ter)]^{3+}$ [c]	$[Ru^{II}(ter)_2]^{2+}$ [f]	$[Fe^{II}(ter)_2]^{2+}$
$[Ru^{II}(bipy)_3]^{2+}$ [d]		$[Fe^{II}(2\text{-Me-phen})_3]^{2+}$
$[Ru^{II}(phen)_3]^{2+}$ [d]		
$[Ru^{II}(5\text{-Me-phen})_3]^{2+}$ [e]		
$[Ru^{II}(4,7\text{-DiMe-phen})_3]^{2+}$ [e]		

[a] bipy is 2,2′-bipyridine; phen is 1,10-phenanthroline; ter is 2,2′,2′′-terpyridine; others are methyl-substituted 1,10-phenanthrolines. [b] Preparation described in ref 10. [c] Preparation described in ref 11. [d] Solid obtained and used as received from G. F. Smith Chemical Co., Columbus, Ohio. [e] Solid prepared by appropriately modified method described by F. H. Burstall, *J. Chem. Soc.*, 173 (1936). 2-Methyl-1,10-phenanthroline was prepared and kindly provided by Professor N. D. Heindel and Dr. C. J. Ohnmacht: N. D. Heindel and C. J. Ohnmacht, *J. Heterocyclic Chem.*, **5**, 869 (1968). [f] Preparation described by G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).

Table II. Temperature Effects on Luminescence Intensity

Species	Wavelength, nm Excitn	Wavelength, nm Emission	Average % increase in luminescence intensity 30–20°	20–10°	10–0°	Factor increase in I_L; room temp to ~80 °K
$[Ir^{III}(ter)]^{3+}$	365	520	33	35	40	×27
$[Ir^{III}(phen)]^{3+}$	365	530	39	56	55	×50
$[Ru^{II}(5\text{-Me-phen})_3]^{2+}$	436	580	66	62	56	×50
$[Ru^{II}(phen)_3]^{2+}$	436	580	33	36	46	×10
$[Ru(bipy)_3]^{2+}$	365	590	57	40	26	×5
$[In^{III}Q_3]$[a]	365	530	11	13	19	×8
QSO_4[b]	365	450	2.5	3.9	...	...

[a] Tris(8-quinolinolato)indium(III) in absolute ethanol. [b] 1 ppm of quinine sulfate in 0.1 *N* H_2SO_4(aq).

ences in the positions of the charge-transfer absorption or emission maxima and in the relative intensities of these bands; these are very probably due to the presence of appreciable quantities of lower imine chelates in the solutions prepared by mixing the reactants (based on evidence from molar ratio studies).

In addition to the intense ligand $\pi^* \leftarrow \pi$ bands in the ultraviolet, all Ru(II) chelates show intense and rather broad absorption bands near 450 nm.[3,4,13] These latter bands arise from metal to ligand charge-transfer ($\pi^* \leftarrow$ d) transitions analogous to those shown by the Fe(II)–imines.[13,14] In some cases the components of the charge-transfer bands are sufficiently separated and a shoulder is discernible. The Ir(III)–imines show no well-defined charge-transfer absorption peaks; the molar absorptivity decreases gradually and irregularly with increasing wavelength above *ca.* 400 nm; however, the absorbance in the visible is also due to metal to ligand ($\pi^* \leftarrow$ d) charge-transfer transitions.[10,11,14]

The emission (365- or 436-nm excitation, low-pressure mercury arc) of the Ru(II) chelates that luminesce at room temperature is red-organge; the spectrum is a broad band with a peak at *ca.* 580 nm.[3,4] The Ir(III) chelates that luminesce under these conditions show a green emission; again the spectrum is a broad band, but the emission maximum appears at somewhat shorter wavelengths, *ca.* 530 nm.[10,11] Emission at lower temperatures is similar in color, but the spectral band widths are smaller (with adequate resolution vibrational structure is also revealed) compared to the room-temperature luminescence.[3,5,8,12]

The first column of Table I lists the chelates emitting luminescence detectable on the spectrofluorometer at room and at lower temperatures (for 0.01 m*M* solutions this luminescence is readily visible to the eye). The chelates in column 2 did not emit luminescence that could be seen or detected from solutions at room temperature or from those cooled with Dry Ice; however, glassy solutions of these chelates did emit the characteristic red-orange or green phosphorescence when exposed to 365- or 436-nm radiation. When these glassy solutions were allowed to warm, it was observed that the emission ceased before the solution was fluid; similar effects were observed when these solutions were cooled to form the glasses. The third column of Table I lists those chelates that did not luminesce in solution either at room temperature or from glasses at the temperature of liquid nitrogen.

Figure 1 and Table II show variation of the luminescence intensity of some of these chelates with temperature. For comparison the much smaller, but typical, temperature effects on the luminescence intensity of some other species ($\pi^* \rightarrow \pi$ radiative transition) are also included.

Discussion

Intersystem crossing rates have very important effects on luminescence characteristics of excited species. An increase in the rate of intersystem crossing results in decreased fluorescence intensity and perhaps increased phosphorescence intensity if the sample is examined in a rigid matrix. However, when the intersystem crossing rate becomes very large, the phosphorescence may be quenched also.[1,2,15,16] The intersystem crossing rate constant is large for diamagnetic species containing heavy atoms (due to the strong spin–orbit coupling) and is very large for species that are paramagnetic. Hoijtink has attributed this effect of paramagnetic species to an exchange interaction between the excited and the para-

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(13) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

(14) C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 166 (1957).

(15) R. S. Becker and J. B. Allison, *J. Phys. Chem.*, **67**, 2662 (1963).

(16) D. C. Bhatnagar and L. S. Forster, *Spectrochim. Acta*, **21**, 1803 (1965).

magnetic species;[17a] Murrell and others considered mixing of the singlets and triplets with charge-transfer states involving the paramagnetic species.[2,17b] Thus, paramagnetic species are usually nonfluorescent, *e.g.*, transition metal ion complexes, and may also be very efficient quenchers of the luminescence of other species, *e.g.*, O_2 and NO.

Of the d^6 metal ion species investigated in the present work, the magnetic characteristics of only the Fe(II) complexes have been extensively studied. However, most complexes of Ru(II) and Ir(III) are low spin and, thus, diamagnetic.[18] For complexes of these metal ions with a given ligand the order of the ligand field splitting increases in the order Fe(II) < Ru(II) < Ir(III).[19]

The magnetic properties of some Fe(II)–imines are summarized in Table III. All of the lower complexes are high spin and paramagnetic, but the highest complexes (tris species of bipy, phen, 5-Me-phen, and the bis species of ter) are diamagnetic. These spin-state changes are reflected (in those cases where data are available) by an abnormally large stepwise formation constant for those chelates whose formation accompanies the conversion from a high- to a low-spin species (Table III). It is of particular interest to note that none of the Fe(II) chelates with 2-Me-phen is of the low-spin kind at room temperature.

Table III. Magnetic Properties and Formation Constants for Some $[Fe^{II}(imine)]^{2+}$ Chelates

		Mono chelate		Bis chelate		Tris chelate	
Ligand	Source	Spin state	Log K_1	Spin state	Log K_2	Spin state	Log K_3
bipy	*a*	High	4.3	High	3.7	Low	9.5
phen	*a*	High	5.8	High	5.2	Low	10.0
5-Me-phen	*b*	High	6.5	?	7.0	Low	8.4
2-Me-phen	*c*	High	4.2	High	3.6	High	3.0
ter	*d*, *e*	High	7.1	Low	13.8		

[a] H. Irving and D. H. Mellor, *J. Chem. Soc.*, 5222 (1962). [b] W. A. E. McBryde, D. A. Brisbin, and H. Irving, *ibid.*, 5245 (1962). [c] H. Irving and D. H. Mellor, *ibid.*, 5237 (1962). [d] R. Hogg and R. G. Wilkens, *ibid.*, 341 (1962). [e] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

Considerable interest has recently been directed to studying the temperature dependence of magnetic properties and the identification of magnetic crossover points for complexes that are capable of existing both in high-spin and in low-spin configurations.[20–24] The low-spin state is favored at lower temperatures. For octahedral complexes of Fe(II) and Co(II) the energy difference between these states may be rather small compared to the energy supplied to the complex upon excitation by absorption of ultraviolet–visible radiation.

Goodwin and Sylva have recently summarized and studied the temperature dependence of the magnetic properties of the tris(2-Me-phen)–Fe(II) complex ion.[25] Steric hindrance due to the methyl group on the 2 position of the phenanthroline prevents the ligand from approaching the ferrous ion sufficiently closely to provide a ligand field strength of adequate magnitude to form a low-spin complex.

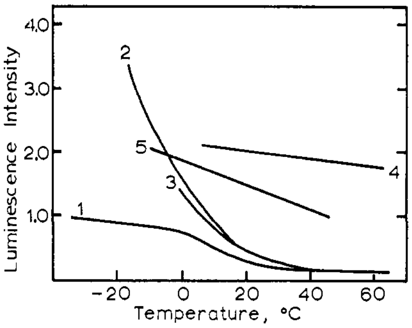

Figure 1. Temperature effects on luminescence intensity. For curves 1–5, the following data are given as species, wavelength (excited and luminiscent), concentration, and relative I_L at 80°K, respectively: (1) $[Ru^{II}(bipy)_3]^{2+}$, 365 and 590 nm, 0.015 m*M*, 1.25; (2) $[Ru^{II}(5\text{-Me-phen})_3]^{2+}$, 436 and 580 nm, 1.7 m*M*, 18; (3) $[(Ir^{III}(phen)]^{3+}$, 365 and 530 nm, 0.1 m*M*, 19; (4) quinine sulfate, 365 and 450 nm, 1 ppm in 0.1 *N* H_2SO_4, · · ·; (5) $[In^{III}Q_3]$ (absolute ethanol solution of tris(8-quinolinolato)indium(III); prepared by precipitation), 365 and 530 nm, 0.1 m*M*, 4.2.

Although *a priori* calculations of the ligand field strength, *Dq*, have not been particularly successful, it is nevertheless clear that the metal ion–ligand bond distance (*a*) is one of the parameters having important influence on the *Dq* value as suggested in the equations derived from perturbation theory by the inverse high-order dependence on *a*.[26]

$$Dq = \frac{(Ze^2)\bar{r}_2^{\,4}}{6a^5} = \frac{5\mu\bar{r}_2^{\,4}}{6a^6}$$

The magnetic moment of $[Fe^{II}(2\text{-Me-phen})_3]^{2+}$ at room temperature has the value expected for a high-spin d^6 species (*ca.* 5 BM). However, upon cooling the magnetic properties deviate from the Curie–Weiss law. The magnetic moment becomes smaller, approaching 3 BM at 100°K, and behaves as expected if an equilibrium between approximately equienergetic high-spin (t_{2g}^4, e_g^2) and low-spin (t_{2g}^6) configurations was shifting to favor increased population of the low-spin state as the temperature is lowered: $^1A_1 \rightleftarrows {}^5T_2$. Accompanying the change in spin states will be a decreased metal ion–ligand bond distance and an increase in the ligand field strength.[25] An additional observation consistent with these explanations reported by Goodwin and Sylva is a change in the color of solutions containing the $(2\text{-Me-phen})_3Fe^{II}$ ion upon cooling; this they attribute to the enhancement of the metal-to-ligand charge-transfer absorption transition probability with decreased ligand-to-metal ion bond distances in the low-spin complex.

The Ru(II) and the Ir(III) imines are probably in the low-spin configuration in the ground state at all temperatures used in this work. Chelates of these metal ions studied in the present work showed the characteristic metal-to-ligand charge-transfer absorption bands near 450 nm at room temperature. Furthermore no

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(17) (a) G. J. Hoijtink, *Mol. Phys.*, **3**, 67 (1960); (b) J. N. Murrell, *ibid.*, **3**, 319 (1960).

(18) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966.

(19) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding," Addison-Wesley Publishing Co., Reading, Mass., 1962.

(20) E. Konig and K. Madeja, *Inorg. Chem.*, **7**, 1848 (1968).

(21) E. Konig, K. Madeja, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 1146 (1968).

(22) G. A. Renovitch and W. A. Baker, Jr., *ibid.*, **89**, 6377 (1967).

(23) J. S. Judge and W. A. Baker, Jr., *Inorg. Chem. Acta*, **1**, 68 (1967).

(24) R. C. Stoufer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *Inorg. Chem.*, **5**, 1167 (1966).

(25) H. A. Goodwin and R. N. Sylva, *Aust. J. Chem.*, **21**, 83 (1968).

(26) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, New York, N. Y., 1966.

noticeable color changes were observed when absolute ethanol solutions containing these chelates were converted to glasses by cooling to liquid nitrogen temperatures.

Upon excitation to a charge-transfer excited state (π^*,d) there will be considerable redistribution of the electron density in the chelate because of transfer of the excited electron from an orbital centered at the metal ion to one largely delocalized on the ligands. Thus, it is anticipated that there are large and important increases in the metal ion–ligand bond distances when these chelates are excited to charge-transfer states; in consequence the ligand field splitting will be lower in this excited state of the chelate.

If the ligand field splitting is lowered sufficiently upon excitation and is then near the magnetic crossover point at room temperature, an excited-state equilibrium will be established between the diamagnetic (t_{2g}^5, π^*) and the paramagnetic (t_{2g}^3, e_g^2, π^*) configurations. The luminescence intensity will be decreased accordingly—approximately in proportion to the extent of crossover to the high-spin state. In this case not only is the intersystem crossing rate constant greatly enhanced by the formation of the high-spin paramagnetic species, a group of closely spaced energy levels, *e.g.*, ligand field states of the high-spin species, are also created; these are available to the excited species and their presence would enhance further the probability of nonradiative decay of the excitation energy.[1,9]

The extent of crossover will be governed by a Boltzmann-like distribution, and a very marked temperature dependence is anticipated. The smaller excited state ligand fields, Dq^*, that exist with the Fe(II)–imines and with the most hindered Ru(II) and Ir(III) chelates could result in nearly complete crossover to the high-spin forms at room temperature. Thus, luminescence would not be observed. Reducing the sample solution temperature to form a rigid glass might permit observation of the characteristic charge-transfer luminescence. The experimental facts are consistent with these explanations: the imine chelates of Fe(II), the metal ion which would show the smallest ligand field splittings, show no luminescence even at the lowest temperatures. The most hindered ligands, 2-Me-phen and ter, form chelates with Ru(II) that do not luminesce at room temperature but do emit the characteristic red-orange luminescence at the temperatures of liquid nitrogen. With Ir(III), the metal ion that would be subject to the largest ligand field splittings, only the most hindered ligand, 2-Me-phen, forms a chelate that fails to show charge-transfer luminescence in fluid solution although this chelate too emits in rigid media.

These considerations can account for the observed phenomena under discussion regardless of the kind of luminescence (fluorescence or phosphorescence) and the multiplicity (singlet or triplet) of the emitting excited state in the low-spin cases. Two alternatives should also be considered, particularly for the Fe(II)–imines. The existence of triplet ligand field excited state(s) ($^3T_{1g}$, $^3T_{2g}$) at energies below the lowest energy charge-transfer excited state (emission from such states might be in the near-infrared and not detectable in the present work) has been discussed by Palmer and Piper;[13] no firm conclusions were reached. Distortion of the excited chelate species from octahedral microsymmetry might cause a triplet ($^3T_{1g}$) to assume lowest energy among the ligand field states;[20] paramagnetic quenching of the luminescence would probably result in this event.

Acknowledgment. This work was supported by the National Science Foundation (Grant GP-8585).

Electron Transfer through Organic Structural Units. VI. Steric Assistance in the Outer-Sphere Reduction of Pyridinepentaamminecobalt(III) Derivatives[1]

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Contribution from the Department of Chemistry, Kent State University, Kent, Ohio 44240. *Received March 8, 1969*

Abstract: Pentaamminecobalt(III) complexes of pyridine, five alkyl-substituted pyridines, and quinoline have been prepared as their perchlorates, and their rates of reduction with Cr(II) at 25° have been measured. Reductions proceed *via* an outer-sphere mechanism with formation of $Cr(H_2O)_6^{3+}$ and release of the heterocyclic ligand. Specific rates for the 3- and 4-substituted pyridine complexes are comparable to that for the unsubstituted pyridine derivative, but the complexes of 2-methylpyridine and quinoline are reduced about 100 times as rapidly as are the other members of the series. These two complexes, for which molecular models show serious interference between the organic ligand and *cis* ammonias, also undergo aquation with loss of the heterocyclic base much more rapidly than do the 3- and 4-substituted complexes. This work reinforces an earlier suggestion, arising from the study of the reduction of carboxamidopentaamminecobalt(III) derivatives, that, for outer-sphere reductions of complexes of this sort, a major requirement for activation is the stretching of the Co(III)–N bonds.

The reductions, with Cr(II), of carboxylatopentaaminecobalt(III) complexes proceed with transfer of the carboxylate group from cobalt to chromium and are subject to steric retardation. The formato derivative (I, R = H) is reduced about 10,000 times as

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[1] From the M.Sc. thesis of Y. W. This work was supported in part by the Petroleum Research Fund of the American Chemical Society under Grant 2868-A3.