1628 *Inorg. Chem.* **1988**, *27*, 1628–1633

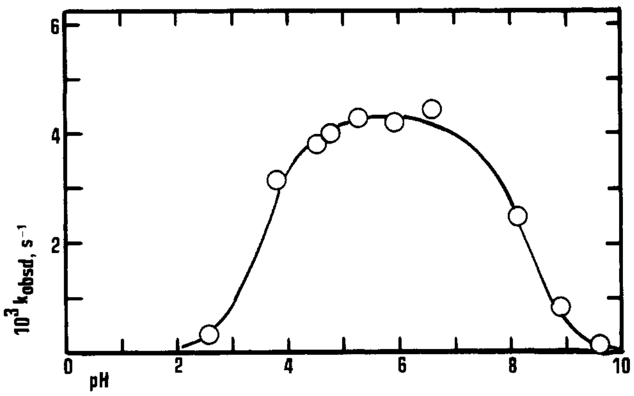
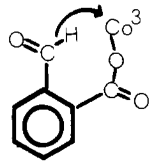


Figure 1. Variation, with pH, of the specific rate of reduction of vitamin B_{12a} (hydroxocobalamin) (2.7×10^{-4} M) with formate at 25 °C and $\mu = 1.0$ M ($LiClO_4$). Reactions were carried out under N_2 in solutions buffered by phthalate, acetate, phosphate, and borate (see Table III). The solid line represents pseudo-first-order rate constants, calculated from eq 4, with $[\text{formate}]_t$ taken as 0.0810 M, K_{Co} as 6.15×10^{-9} M, and K_A as 2.95×10^{-4} M; the circles represent experimental values.

Attempts to apply this reaction to other formyl species led to results summarized in Table V, which emphasize the unique effectiveness of formate. The other carboxylates would be expected to coordinate with B_{12a} in the same manner as formate and acetate, but the formyl group is generally not properly positioned for migration to Co^{III}. Modest activity is observed in the case of *o*-formylbenzoic acid, which may react through a somewhat strained transition state I (featuring a seven-membered ring). The



I

complex of glyoxylic acid, HC(=O)COOH, appears to offer a more favorable orientation for internal hydride migration, but reaction here may be inhibited by conversion of this acid by hydration to its *gem*-diol form ($>C{=}O + H_2O \rightarrow >C(OH)_2$), a transformation that is known to be very nearly complete under our conditions.[21]

Reduction of B_{12a} by ascorbic acid is found to be rapid, but the biphasic profiles observed for this reaction, in conjunction with the known ability of this reductant to undergo both 1e and 2e oxidations,[22] indicate the operation of a different, and more complex, mechanism for this process.

Acknowledgment. We thank Arla White for technical assistance.

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Contribution from the Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna,
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Electron- and Energy-Transfer Processes Involving Excited States of Lanthanide Complexes: Evidence for Inner-Sphere and Outer-Sphere Mechanisms

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The interaction of the luminescent excited states of the Eu_{aq}^{3+} and Tb_{aq}^{3+} ions, the $[Eu{\subset}2.2.1]^{3+}$ and $[Tb{\subset}2.2.1]^{3+}$ complexes, and the $[Eu{\subset}2.2.1]^{3+}$–$2F^-$ and $[Tb{\subset}2.2.1]^{3+}$–$2F^-$ ion pairs with $M(CN)_6^{z-}$ complexes (M = Cr(III), Fe(II), Co(III), Ru(II), Os(II)) has been studied in aqueous solution by luminescence lifetime measurements. Some measurements on solid samples precipitated from the aqueous solutions have also been performed. Depending on the specific lanthanide-species/cyanide-complex system, the lifetime of the luminescent lanthanide species is quenched (by an energy- or electron-transfer mechanism), unaffected, or enhanced. The enhancement is attributed to substitution of H_2O molecules in the coordination sphere of the lanthanide ion by cyanide complexes that are unable to cause energy- or electron-transfer quenching. The lower values obtained for the quenching constants of exergonic energy- and electron-transfer processes than those for diffusion are attributed to poor electronic factors (nonadiabatic behavior). The results can be accounted for by making the reasonable assumption that the precursor complex has a different structure depending on the lanthanide species involved: (i) for the aquo ions, water molecules can be replaced by the cyanide complex to yield an intimate ion pair; (ii) for the $[Ln{\subset}2.2.1]^{3+}$ complexes, a CN-bridged ion pair can be formed, as previously suggested on the basis of spectroscopic (intervalence-transfer band) results; (iii) for the $[Ln{\subset}2.2.1]^{3+}$–$2F^-/M(CN)_6^{z-}$ systems, only outer-sphere ion pairs can be involved in the quenching process.

Introduction

The study of processes involving electronically excited states can make an important contribution to elucidating reaction mechanisms and understanding the role played by nuclear and electronic factors in determining reaction rates. This is particularly true in the field of coordination chemistry, where the numerous studies carried out in the last few years on photoinduced electron-transfer processes[2–5] have strongly improved the original Marcus–Hush theory[6–7] and have focused on some important unresolved problems.[8–9]

Electronic energy transfer via an exchange mechanism[10] (eq 1, where an asterisk denotes electronic excitation) is a process quite

$$^*A + Q \rightleftarrows {}^*A{\cdots}Q \rightleftarrows A{\cdots}{}^*Q \rightleftarrows A + {}^*Q \qquad (1)$$

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(10) The Coulombic mechanism is generally not effective for coordination compounds, because in most cases Laporte- and/or spin-forbidden excited states are involved.[11,12]

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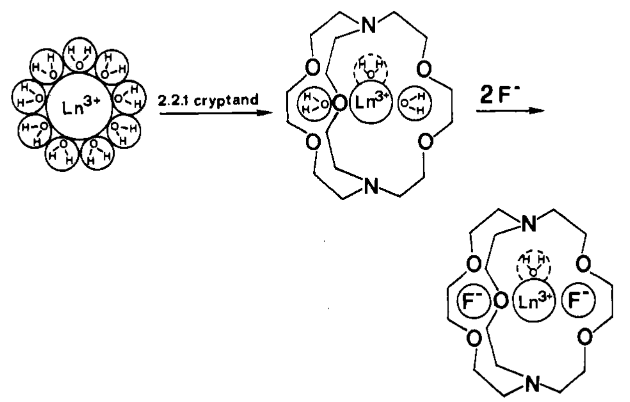

Figure 1. Pictorial representation of $\mathrm{Ln_{aq}}^{3+}$, $[\mathrm{Ln}\subset 2.2.1]^{3+}$, and $[\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$ species.

similar to (and in some way simpler than) electron transfer (eq 2).[11,12] Thus, information on the mechanisms of electron-transfer

$$^*\mathrm{A} + \mathrm{Q} \rightleftarrows {}^*\mathrm{A}\cdots\mathrm{Q} \rightleftarrows \mathrm{A}^-\cdots\mathrm{Q}^+ \rightleftarrows \mathrm{A}^- + \mathrm{Q}^+ \qquad (2)$$

processes can often be obtained from the study of energy-transfer processes, and vice versa.[13]

In the last few years we have been engaged in the study of the photophysical properties of lanthanide compounds,[14-20] and we have found that the $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and $[\mathrm{Tb}\subset 2.2.1]^{3+}$ cryptate complexes[21] possess suitable properties to play the role of excited-state reactants in electron- and energy-transfer processes. While the ligand (solvent) molecules that surround the lanthanide ions in aqueous solution are weakly bound[23] and can be easily replaced by the reaction partner in the precursor complex,[24,25] encapsulation of the lanthanide ions into the cryptand cages (Figure 1) yields inert complexes and substantially (although not completely) shields the metal ions from interaction with other species.[14-16] It has also been shown that in such cryptate complexes F^- ions can replace the solvent molecules coordinated to the metal ion through the cryptand holes (Figure 1).[17,26] Thus, we have at our disposal three well-defined lanthanide species (Figure 1) that, with suitable reaction partners, should give rise to precursor complexes exhibiting quite different intimate structures. We felt that a systematic and comparative study of electron- and energy-transfer processes involving the excited states of such lanthanide species and a homogeneous series of quenchers could yield interesting mechanistic information. The lanthanide ions chosen were the luminescent Eu^{3+} and Tb^{3+} ions, in view of their redox properties and excited-state energies, and the quenchers used were the hexacyano complexes of Cr(III), Fe(II), Co(III), Ru(II), and Os(II), since previous investigations[27,28] suggested an interesting structure for the $[\mathrm{Eu}\subset 2.2.1]^{3+}\text{–}\mathrm{M(CN)_6}^{4-}$ ion pairs.

Experimental Section

$\mathrm{EuCl_3{\cdot}6H_2O}$ and $\mathrm{TbCl_3{\cdot}6H_2O}$ were obtained from Alfa Ventron (purity 99.9%), and the 2.2.1 cryptand was a Merck product. The 2.2.1 cryptates of Eu^{3+} or Tb^{3+}, $[\mathrm{Ln}\subset 2.2.1]\mathrm{Cl_3{\cdot}2H_2O}$, were prepared as described elsewhere.[14,16] The $[\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$ ion pairs (Ln = Eu, Tb) were obtained in solutions containing 5.0×10^{-3} M $[\mathrm{Ln}\subset 2.2.1]^{3+}$ and 5.0×10^{-1} M F^-.[17,26] $\mathrm{K_4[Fe(CN)_6]{\cdot}3H_2O}$, $\mathrm{K_3[Co(CN)_6]}$, and $\mathrm{K_4[Ru(CN)_6]{\cdot}3H_2O}$ (Alfa Ventron) and $\mathrm{K_3[Cr(CN)_6]}$ and $\mathrm{K_4[Os(CN)_6]}$ (K&K) were purified by recrystallization from water. All the experiments were carried out in aqueous solutions containing 1 M KCl at natural pH (~6.5) and room temperature (~20 °C). The concentrations of the Eu^{3+} or Tb^{3+} species were on the order of 10^{-3} M and those of the cyanide complexes in the range 10^{-3}–10^{-6} M. In some cases, the addition of the cyanide complex to the Eu^{3+} or Tb^{3+} species caused the precipitation of insoluble salts. Luminescence decays were measured by a JK System 2000 neodymium YAG laser ($\lambda_{\mathrm{exc}} = 355$ nm), a Lambda Physik M 100 A nitrogen laser ($\lambda_{\mathrm{exc}} = 337$ nm), or a Perkin-Elmer LS 5 spectrofluorometer. The results obtained for the same solution by using the different lifetime equipment agreed within ~10%. With the same equipment, the reproducibility was within 3%. The luminescence emission was monitored at 615 nm for the Eu^{3+} species and at 544 nm for the Tb^{3+} species.

Results

Under all the experimental conditions used, the luminescence emission was found to decay with time according to a single exponential. Lifetime values in the absence (τ°) and in the presence (τ) of various quencher concentrations yielded linear Stern–Volmer plots. The values of the bimolecular quenching constants obtained from the slopes of the Stern–Volmer plots and the known excited-state lifetimes of the various species according to eq 3 are collected in Table I.[29] In the same table, the free

$$\frac{I^\circ}{I} = \frac{\tau^\circ}{\tau} = 1 + k_q\tau^\circ[\mathrm{Q}] \qquad (3)$$

energy changes for energy-transfer (eq 1) and reductive electron-transfer (eq 2) quenching processes via an outer-sphere mechanism are shown and the most likely quenching mechanisms (see later) are indicated. To facilitate discussion, the bimolecular quenching constants have been displayed in a more compact form in Table II. Note that $\mathrm{Os(CN)_6}^{4-}$ does not quench, but slightly increases, the emission lifetime of $[\mathrm{Tb}\subset 2.2.1]^{3+}$.

The precipitates obtained upon mixing $\mathrm{EuCl_3{\cdot}6H_2O}$ with $\mathrm{K_3Co(CN)_6}$ and $\mathrm{TbCl_3{\cdot}6H_2O}$ with $\mathrm{K_4Os(CN)_6}$ in $\mathrm{H_2O}$ solution showed luminescence emission with $\tau = 0.33$ and 0.60 ms, respectively. The luminescence lifetimes of the solid lanthanide chlorides precipitated from $\mathrm{H_2O}$ or $\mathrm{D_2O}$ solutions were also measured. The values obtained were as follows: $\tau = 0.12$ and 1.40 ms for $\mathrm{EuCl_3{\cdot}6H_2O}$ and $\mathrm{EuCl_3{\cdot}6D_2O}$, and $\tau = 0.50$ and 3.80 ms for $\mathrm{TbCl_3{\cdot}6H_2O}$ and $\mathrm{TbCl_3{\cdot}6D_2O}$.

When $[\mathrm{Eu}\subset 2.2.1]^{3+}$ was mixed with $\mathrm{Fe(CN)_6}^{4-}$, $\mathrm{Ru(CN)_6}^{4-}$, or $\mathrm{Os(CN)_6}^{4-}$ in $\mathrm{H_2O}$ solution, the previously reported[27,28] ion-pair charge-transfer (IPCT) bands were observed. For a solution containing 5.0×10^{-3} M $[\mathrm{Eu}\subset 2.2.1]^{3+}$ and 7.0×10^{-2} M $\mathrm{Fe(CN)_6}^{4-}$, addition of F^- caused a blue shift and a decrease of the IPCT band. This band completely disappeared for $[\mathrm{F}^-] > {\sim}10^{-1}$ M.

Discussion

The following discussion is a comparison of the behaviors of $\mathrm{Ln_{aq}}^{3+}$, $[\mathrm{Ln}\subset 2.2.1]^{3+}$, and $[\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$ (Figure 1) toward electron- and energy-transfer quenching. While $[\mathrm{Ln}\subset 2.2.1]^{3+}$

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Table I. Bimolecular Rate Constants, Thermodynamic Parameters, and Nature of the Quenching Mechanisms

excited species (lifetime)	quencher	k_q,[a] $M^{-1}\ s^{-1}$	$\Delta G_{el}°$,[b] eV	$\Delta G_{en}°$,[c] eV	quenching mechanism[d]
$\mathrm{Eu_{aq}}^{3+}$[e] (0.11 ms[f])	$\mathrm{Cr(CN)_6}^{3-}$	1.0×10^8	<0	−0.60	energy transfer
	$\mathrm{Fe(CN)_6}^{4-}$	6.0×10^8	−1.29	~0.0	electron transfer
	$\mathrm{Co(CN)_6}^{3-}$	$<7.0 \times 10^5$	>0	~+0.4	
	$\mathrm{Ru(CN)_6}^{4-}$	3.0×10^8	−0.78	~+0.9	electron transfer
	$\mathrm{Os(CN)_6}^{4-}$	5.0×10^8	−1.12	~+2.9	electron transfer
$[\mathrm{Eu}\subset 2.2.1]^{3+}$[e] (0.22 ms[g])	$\mathrm{Cr(CN)_6}^{3-}$	2.0×10^6[h]	>0	−0.60	energy transfer
	$\mathrm{Fe(CN)_6}^{4-}$	5.0×10^8[i]	−1.47	~0.0	electron transfer
	$\mathrm{Co(CN)_6}^{3-}$	$<4.0 \times 10^5$	>0	~+0.4	
	$\mathrm{Ru(CN)_6}^{4-}$	2.0×10^8[i]	−0.96	~+0.9	electron transfer
	$\mathrm{Os(CN)_6}^{4-}$	6.0×10^8[i]	−1.32	~+2.9	electron transfer
$[\mathrm{Eu}\subset 2.2.1]^{3+}-2\mathrm{F}^-$[e] (1.00 ms[j])	$\mathrm{Cr(CN)_6}^{3-}$	2.0×10^5	>0	−0.60	energy transfer
	$\mathrm{Fe(CN)_6}^{4-}$	3.0×10^7	−1.17	~0.0	electron transfer
	$\mathrm{Co(CN)_6}^{3-}$	$<1.0 \times 10^5$	>0	~+0.4	
	$\mathrm{Ru(CN)_6}^{4-}$	2.0×10^5	−0.66	~+0.9	electron transfer
	$\mathrm{Os(CN)_6}^{4-}$	5.0×10^6	−1.02	~+2.9	electron transfer
$\mathrm{Tb_{aq}}^{3+}$[e] (0.40 ms[f])	$\mathrm{Cr(CN)_6}^{3-}$	1.0×10^8	≫0	−1.0	energy transfer
	$\mathrm{Fe(CN)_6}^{4-}$	6.0×10^8	~+1.6	~−0.4	energy transfer
	$\mathrm{Co(CN)_6}^{3-}$	4.0×10^6	≫0	~0.0	energy transfer
	$\mathrm{Ru(CN)_6}^{4-}$	5.0×10^5	~+2.1	~+0.5	energy transfer
	$\mathrm{Os(CN)_6}^{4-}$	$<5.0 \times 10^5$	~+1.8	~+2.5	
$[\mathrm{Tb}\subset 2.2.1]^{3+}$[e] (1.30 ms[k])	$\mathrm{Cr(CN)_6}^{3-}$	2.0×10^6[h]	≫0	−1.00	energy transfer
	$\mathrm{Fe(CN)_6}^{4-}$	7.0×10^5	~+1.4	~−0.4	energy transfer
	$\mathrm{Co(CN)_6}^{3-}$	4.0×10^5	≫0	~0.0	energy transfer
	$\mathrm{Ru(CN)_6}^{3-}$	$<1.0 \times 10^4$	~+1.9	~+0.5	
	$\mathrm{Os(CN)_6}^{4-}$	*l*	~+1.6	~+2.5	
$[\mathrm{Tb}\subset 2.2.1]^{3+}-2\mathrm{F}^-$[e] (3.10 ms[j])	$\mathrm{Cr(CN)_6}^{3-}$	2.0×10^5	≫0	−1.00	energy transfer
	$\mathrm{Fe(CN)_6}^{4-}$	4.0×10^4	~+1.7	~−0.4	energy transfer
	$\mathrm{Co(CN)_6}^{3-}$	6.0×10^3	≫0	~0.0	energy transfer
	$\mathrm{Ru(CN)_6}^{4-}$	$<5.0 \times 10^3$	~+2.2	~+0.5	
	$\mathrm{Os(CN)_6}^{4-}$	$<1.0 \times 10^3$	~+1.9	~+2.5	

[a] Estimated experimental error ±20%, unless otherwise noted. [b] Obtained from the potentials of the redox couples and from the work terms.[40] The excited-state potentials were calculated from the zero–zero spectroscopic energies reported in footnote *c* and from the ground-state reduction potentials. The values (vs NHE) used for these latter quantities are −0.38 V ($\mathrm{Eu_{aq}}^{3+}$),[41] −0.21 V ($[\mathrm{Eu}\subset 2.2.1]^{3+}$),[26] −0.51 V ($[\mathrm{Eu}\subset 2.2.1]^{3+}-2\mathrm{F}^-$),[26] ~−3.7 V ($\mathrm{Tb_{aq}}^{3+}$),[39] ~−3.5 V ($[\mathrm{Tb}\subset 2.2.1]^{3+}$), and ~−3.8 V ($[\mathrm{Tb}\subset 2.2.1]^{3+}-2\mathrm{F}^-$). The two last values have been estimated assuming the same shift for the reduction potentials with respect to the aquo ion as those observed for the analogous Eu^{3+} species. For the quenchers the following reduction potentials (vs NHE) were used: +0.43 V ($\mathrm{Fe(CN)_6}^{3-/4-}$), +0.64 V ($\mathrm{Os(CN)_6}^{3-/4-}$), +0.94 V ($\mathrm{Ru(CN)_6}^{3-/4-}$).[49] The oxidized forms of $\mathrm{Co(CN)_6}^{3-}$ and $\mathrm{Cr(CN)_6}^{3-}$ are not known. A lower limiting value of +1.6 V (vs Pt electrode in DMF) has been reported for oxidation of $\mathrm{Cr(CN)_6}^{3-}$.[50] The lowest energy CT absorption bands of $\mathrm{Co(CN)_6}^{3-}$ (50 600 cm^{-1}) and $\mathrm{Cr(CN)_6}^{3-}$ (38 600 cm^{-1}) have been recently assigned to ligand-to-metal charge-transfer transitions.[51-53] The reduction potentials for the $\mathrm{Co(CN)_6}^{2-/3-}$ and $\mathrm{Cr(CN)_6}^{2-/3-}$ couples are therefore estimated to be >+2 V. [c] Obtained from the difference between the zero–zero spectroscopic energies of the lowest excited states of donor and acceptor.[11] The following reported values were used: $E^{00}(\mathrm{Eu}^{3+}) = 2.14$ eV,[39] $E^{00}(\mathrm{Tb}^{3+}) = 2.54$ eV,[39] $E^{00}(\mathrm{Cr(CN)_6}^{3-}) = 1.54$ eV,[45] $E^{00}(\mathrm{Co(CN)_6}^{3-}) \sim 2.5$ eV.[46] For $\mathrm{Fe(CN)_6}^{4-}$, $\mathrm{Ru(CN)_6}^{4-}$, and $\mathrm{Os(CN)_6}^{4-}$ the E^{00} values of ~2.2, ~3.1, and ~5.1 eV, respectively, were estimated from the lowest absorption features[47] by assuming the same excited-state distortion as for $\mathrm{Co(CN)_6}^{3-}$.[46] [d] Assuming an outer-sphere mechanism. [e] The following values have been obtained for the number of coordinated water molecules (estimated error ±0.5):[38] $\mathrm{Eu_{aq}}^{3+}$, 9.0, and $\mathrm{Tb_{aq}}^{3+}$, 9.0 (Horrocks, W. DeW.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334); $[\mathrm{Eu}\subset 2.2.1]^{3+}$, 3.3, and $[\mathrm{Tb}\subset 2.2.1]^{3+}$, 2.0;[16] $[\mathrm{Eu}\subset 2.2.1]^{3+}-2\mathrm{F}^-$, 0.4, and $[\mathrm{Tb}\subset 2.2.1]^{3+}-2\mathrm{F}^-$, 0.3.[17] [f] Reference 37. [g] Reference 14. [h] Estimated experimental error ±50%; solubility factors prevented us from obtaining a more accurate value. [i] These values are in reasonable agreement with those obtained from luminescence intensity measurements.[27] [j] Reference 17. [k] Reference 16. [l] A progressive increase in the lifetime up to 1.39 ms for $[\mathrm{Os(CN)_6}^{4-}] = 3.7 \times 10^{-3}$ M was observed (see text).

Table II. Bimolecular Rate Constants (k_q, $M^{-1}\ s^{-1}$) for Electron- and Energy-Transfer Quenching

	Energy Transfer		
	$^*\mathrm{Eu_{aq}}^{3+}$	$^*[\mathrm{Eu}\subset 2.2.1]^{3+}$	$^*[\mathrm{Eu}\subset 2.2.1]^{3+}-2\mathrm{F}^-$
$\mathrm{Cr(CN)_6}^{3-}$	1.0×10^8	2.0×10^6	2.0×10^5
	$^*\mathrm{Tb_{aq}}^{3+}$	$^*[\mathrm{Tb}\subset 2.2.1]^{3+}$	$^*[\mathrm{Tb}\subset 2.2.1]^{3+}-2\mathrm{F}^-$
$\mathrm{Cr(CN)_6}^{3-}$	1.0×10^8	2.0×10^6	2.0×10^5
$\mathrm{Fe(CN)_6}^{4-}$	6.0×10^8	7.0×10^5	4.0×10^4
$\mathrm{Co(CN)_6}^{3-}$	4.0×10^6	4.0×10^5	6.0×10^3
$\mathrm{Ru(CN)_6}^{4-}$	5.0×10^5	$<1.0 \times 10^4$	$<5.0 \times 10^3$
$\mathrm{Os(CN)_6}^{4-}$	$<5.0 \times 10^5$	*a*	$<1.0 \times 10^3$
	Electron Transfer		
	$^*\mathrm{Eu_{aq}}^{3+}$	$^*[\mathrm{Eu}\subset 2.2.1]^{3+}$	$^*[\mathrm{Eu}\subset 2.2.1]^{3+}-2\mathrm{F}^-$
$\mathrm{Fe(CN)_6}^{4-}$	6.0×10^8	5.0×10^8	3.0×10^7
$\mathrm{Ru(CN)_6}^{4-}$	3.0×10^8	2.0×10^8	2.0×10^5
$\mathrm{Os(CN)_6}^{4-}$	5.0×10^8	6.0×10^8	5.0×10^6

[a] No quenching; see footnote *l* in Table I.

and $[\mathrm{Ln}\subset 2.2.1]^{3+}-2\mathrm{F}^-$ are well-defined species, Ln^{3+} ions in aqueous solution are known to give rise to different species depending on the experimental conditions. Under our conditions (1 M ionic strength, KCl), according to Choppin and Ketels[31] and Khopkar and Narayanankutty,[32] there are ~44% $\mathrm{Ln_{aq}}^{3+}\cdot\mathrm{Cl}^-$ outer-sphere species, whereas, according to Breen and Horrocks,[33] ~10% of the corresponding inner-sphere species would be present. Since the rate of interchange[33-35] of these species is much faster than the deactivation rate constant of the excited state of the lanthanide ion, in the quenching processes they may be dealt with as a unique species that will be indicated by $\mathrm{Ln_{aq}}^{3+}$.

Properties of the Excited Eu^{3+} and Tb^{3+} Species. The properties of the electronically excited states of Eu^{3+} and Tb^{3+} species are well-known.[36] Luminescence originates from the f–f intraconfigurational $^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_J$ and $^5\mathrm{D}_4 \rightarrow {}^7\mathrm{F}_J$ transitions, respectively. The f–f transitions have predominantly electric dipole character and are therefore forbidden by the Laporte rule. Because of this

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prohibition, the radiative lifetimes of the luminescent states are particularly long (millisecond range). The measured decay times for the complexes in H_2O solution at room temperature (Table I) are shorter than the radiative lifetimes because of efficient vibronic coupling with the high-frequency O–H vibrations[37,38] and, for the Eu^{3+} species, also because of nonradiative deactivations via CT levels.[36] Nevertheless, the luminescent excited state is sufficiently long-lived to participate in encounters with other species. The zero–zero energies of the $^5D_0$ and $^5D_4$ excited states of the Eu^{3+} and Tb^{3+} species are 2.14 and 2.54 eV,[39] respectively, and are only slightly affected by the coordination sphere.[23,38] The excited-state reduction potentials are calculated[40] from the zero–zero spectroscopic energies and from the ground-state reduction potentials. These latter quantities have the values –0.38,[41] –0.21,[26] and –0.51 V[26] for Eu_{aq}^{3+}, $[Eu\subset 2.2.1]^{3+}$, and $[Eu\subset 2.2.1]^{3+}$–$2F^-$, respectively, yielding the values +1.76, +1.93, and +1.63 V for the corresponding excited-state potentials. For the Tb^{3+} species the ground-state reduction potentials are estimated to be quite large and negative (–3.7 V vs NHE electrode for the aquo ion[39]), making the excited states extremely poor oxidants. Finally, the ground-state oxidation potentials of both Eu^{3+} and Tb^{3+} species are extremely large and positive (>+3.3 V vs NHE electrode for the aquo ions[39]), so that their excited states are not expected to be able to play the role of reductants.

Quenching Mechanisms. It is well-known[4,25,42] that the most efficient quenching processes of electronically excited states of coordination compounds are electron and energy transfer. Energy transfer may take place via an exchange or Coulombic mechanism.[43] Using the formalism of the Förster theory,[44] for our systems containing a Eu^{3+} species and $Cr(CN)_6^{3-}$ we have obtained for the critical distance a value of <3 Å, which is much lower than the outer-sphere encounter distance (~8 Å for $Eu_{aq}^{3+}\cdots Cr(CN)_6^{3-}$ and ~10 Å for $[Eu\subset 2.2.1]^{3+}\cdots Cr(CN)_6^{3-}$) where the exchange mechanism is expected to become effective. Moreover, if the Coulombic mechanism were the only quenching mechanism operative at the encounter distance, the constants for quenching the three Eu^{3+} or Tb^{3+} species by the same quencher should be nearly equal, contrary to what is observed (Tables I and II). Therefore, it seems reasonable to conclude that in our systems the mechanism mainly responsible for energy-transfer quenching is the exchange mechanism, the rate constants of which are difficult to calculate.[43] The occurrence of energy transfer via an exchange mechanism from lanthanide ions to organic molecules with excitation of the triplet level was previously reported and discussed by Ermolaev et al.[25]

For our systems, quenching by exchange energy transfer and by electron transfer via an outer-sphere mechanism may be written as follows (Ln = Eu or Tb species; M = Cr(III), Fe(II), Co(III), Ru(II), or Os(II); *z* = 4 or 3):

energy transfer

$$*Ln^{3+} + M(CN)_6^{z-} \rightarrow Ln^{3+} + *M(CN)_6^{z-} \qquad (4)$$

reductive electron transfer

$$*Ln^{3+} + M(CN)_6^{z-} \rightarrow Ln^{2+} + M(CN)_6^{(z-1)-} \qquad (5)$$

oxidative electron transfer

$$*Ln^{3+} + M(CN)_6^{z-} \rightarrow Ln^{4+} + M(CN)_6^{(z+1)-} \qquad (6)$$

The occurrence of and the competition among these processes are governed by thermodynamic and kinetic factors.

For the energy-transfer process, the relevant thermodynamic parameters are the 0–0 excited-state energies, E^{00}, of the donor and acceptor excited states.[4,11] As we have seen above, E^{00} is 2.14 eV for the Eu^{3+} species and 2.54 eV for the Tb^{3+} species. For $Cr(CN)_6^{3-}$ and $Co(CN)_6^{3-}$, the E^{00} values are resonably well-known (1.54[45] and ~2.5 eV,[46] respectively), whereas, for $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$, values of ~2.2, ~3.1, and ~5.1 eV can be roughly estimated from the lowest energy absorption features,[47] assuming that the excited-state distortion is the same as in $Co(CN)_6^{3-}$.[46] It follows that for the excited Eu^{3+} species energy transfer is exergonic only with the $Cr(CN)_6^{3-}$ quencher, whereas for the excited Tb^{3+} species energy transfer is exergonic with $Cr(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and $Co(CN)_6^{3-}$. It should also be noted that for $Cr(CN)_6^{3-}$ the upper $^2T_1$ excited state (E^{00} = 1.62 eV[48]) can also come into play.

For the redox quenching processes the relevant thermodynamic parameters are the redox potentials of the excited and ground states involved. The data concerning the Eu^{3+} and Tb^{3+} excited species have been reported above. The reduction potentials of the $Fe(CN)_6^{3-/4-}$ (+0.43 V), $Ru(CN)_6^{3-/4-}$ (+0.94 V), and $Os(CN)_6^{3-/4-}$ (+0.64 V) couples are known.[49] As far as $Co(CN)_6^{3-}$ and $Cr(CN)_6^{3-}$ are concerned, their oxidized forms are not known. A lower limiting value of +1.6 V (vs Pt electrode in DMF) has been reported for the oxidation of $Cr(CN)_6^{3-}$.[50] The lowest energy CT absorption bands of the Co(III) (50 600 cm^{-1}) and Cr(III) (38 600 cm^{-1}) hexacyanide complexes are attributed not to metal-to-ligand charge-transfer transitions but to ligand-to-metal charge-transfer transitions.[51-53] Therefore, it seems safe to estimate the reduction potentials of the $Co(CN)_6^{2-/3-}$ and $Cr(CN)_6^{2-/3-}$ couples to be >+2 V. It follows that reductive electron transfer is (i) exergonic for each excited Eu^{3+} species with $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$, (ii) most likely endergonic for quenching of the Eu^{3+} species by $Cr(CN)_6^{3-}$ and $Co(CN)_6^{3-}$, and (iii) extremely endergonic for all systems involving Tb^{3+} species. Finally, since both Eu^{3+} and Tb^{3+} are extremely difficult to oxidize (see above) and the cyanide complexes difficult to reduce, oxidative electron-transfer quenching (eq 3) can safely be ruled out in all cases on thermodynamic grounds.

The nuclear reorganizational parameters are expected to be negligible for energy transfer from the lanthanide species to $Cr(CN)_6^{3-}$ (weak coupling limit)[12] but not so small for energy transfer to the other cyanide complexes (because of their excited-state distortion)[11,12] and for the electron-transfer processes (because of the outer-sphere contribution).[3] The last two processes should thus be treated within the strong coupling limit category.[12]

The thermodynamic data for the energy transfer ($\Delta G_{en}°$) and reductive electron-transfer ($\Delta G_{el}°$) quenching processes are collected in Table I. When these data are examined on the assumption of an outer-sphere mechanism, the nature of the quenching process can be straightforwardly assigned in all cases, even without a quantitative evaluation of the nuclear reorganizational parameters.

Kinetic Scheme. Since the species involved in the quenching processes studied in this paper are ions of opposite charge and may give rise to outer-sphere and inner-sphere precursor complexes (see below), the appropriate kinetic scheme is that shown in Figure 2.[54] In this scheme, k_d and k_{-d} are the diffusion and dissociation rate constants, k_e is either an energy-transfer or electron-transfer rate constant, k_b is the rate constant for deactivation (either via back-electron transfer to the ground state or via deactivation of the electronically excited acceptor), k_c and k_{-c} are the rate constants for formation or dissociation of an inner-sphere precursor

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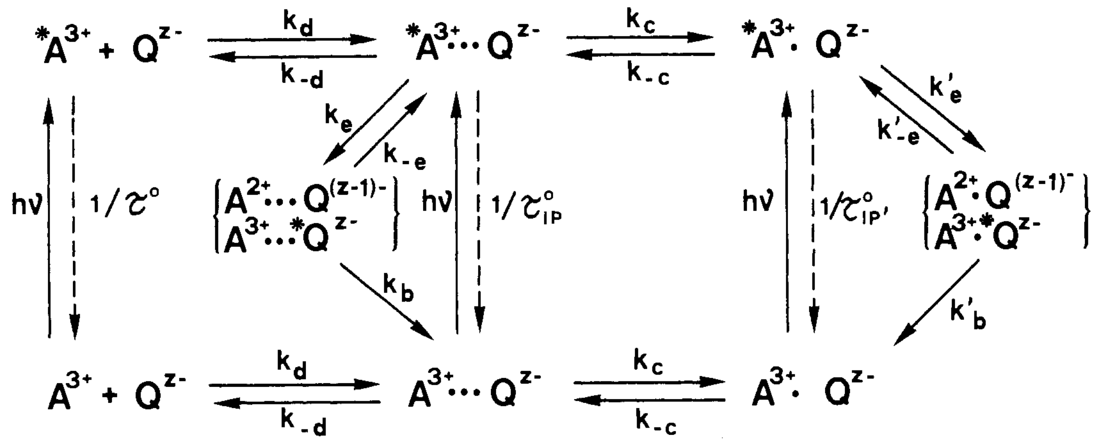

Figure 2. General kinetic scheme for the energy- or electron-transfer quenching of Ln^{3+} species by cyanide complexes. A^{3+} = europium or terbium species (Figure 1), Q^{z-} = cyanide complexes. $\mathrm{A}^{3+}\cdots\mathrm{Q}^{z-}$ and $\mathrm{A}^{3+}\cdot\mathrm{Q}^{z-}$ represent outer- and inner-sphere encounter complexes, respectively. For more details, see text.

complex, k'_e and k'_b are the inner-sphere analogues of k_e and k_b, $\tau°$ is the emission lifetime of the free excited state, and $\tau_{IP}°$ and $\tau_{IP'}°$ are the emission lifetimes due to radiative and nonradiative (excepting electron or energy transfer deactivations of the excited state in outer- and inner-sphere ion pairs. While $\tau_{IP}°$ is expected to be equal to $\tau°$,[55] $\tau_{IP'}°$ may be different because the lifetime of the excited Eu^{3+} and Tb^{3+} species is affected by the number of coordinated water molecules and some water molecules can be replaced by the reaction partner in the inner-sphere ion pair.

Formation of ion pairs in the ground state is a necessary condition for static quenching,[42] and for some of our systems clear evidence for ion-pair formation has been obtained.[27] Under the experimental conditions used for the quenching experiments in solution, static quenching can be ruled out because the fraction of Eu^{3+} or Tb^{3+} species associated in ion pairs is negligible. Furthermore, the rate constants obtained for the dynamic quenching process (Table I) are always much smaller than the diffusion constant (estimated to be $k_d \sim 7 \times 10^9$ M^{-1} s^{-1} [3]), indicating that dissociation of the encounters is much faster than energy or electron transfer.

Trends in the Values of the Quenching Constants. The experimental quenching constants have been ordered in Table II in an attempt to highlight the following observed trends:

(1) For energy-transfer quenching, the rate constants decrease strongly in the series $\mathrm{Ln_{aq}}^{3+} > [\mathrm{Ln}\subset 2.2.1]^{3+} > [\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$.

(2) The data concerning $\mathrm{Cr(CN)_6}^{3-}$ show that the rate of energy transfer is insensitive to the nature of the lanthanide ion (but strongly sensitive to its coordination sphere; see above).

(3) For $\mathrm{Tb_{aq}}^{3+}$ the rate of energy-transfer quenching is smaller for $\mathrm{Cr(CN)_6}^{3-}$ than for $\mathrm{Fe(CN)_6}^{4-}$ whereas for $[\mathrm{Tb}\subset 2.2.1]^{3+}$ and $[\mathrm{Tb}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$ the reverse is true.

(4) For electron-transfer quenching, the rate constants are almost the same for $\mathrm{Ln_{aq}}^{3+}$ and $[\mathrm{Ln}\subset 2.2.1]^{3+}$ but much smaller for $[\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$.

(5) For definitely exergonic processes, the energy- and electron-transfer rate constants are comparable in the case of $\mathrm{Ln_{aq}}^{3+}$, but quenching by energy transfer is much slower in the case of $[\mathrm{Ln}\subset 2.2.1]^{3+}$ and $[\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$.

(6) Finally, it should be noted that even in cases of moderate or large exergonicity the quenching process is not diffusion controlled.

Structure of the Precursor Complex. The observed trends cannot be explained on the basis of a generalized outer-sphere mechanism. As mentioned in the Introduction, different structures for the precursor complexes can be expected for the quenching processes involving the $\mathrm{Ln_{aq}}^{3+}$, $[\mathrm{Ln}\subset 2.2.1]^{3+}$, and $[\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$ species. The water molecules that surround the aquo ions can be replaced by the cyanide complex anions to yield an intimate ion pair. Because of the lack of directionality of the lanthanide coordination sphere, such an intimate ion pair may involve, rather than a CN bridge, association of Ln^{3+} to three CN ligands of one face of the octahedral cyanide complex (Figure 3). This replacement of coordinated water molecules is expected to cause (in the absence of quenching effects) an increase in the excited-state lifetime[38] because the C–N vibrations have a frequency much lower than the O–H vibrations. An increase in the lifetime of excited Tb^{3+} ions when the solvent is replaced by triphenylene was already observed by Breuninger and Weller.[24] Unfortunately, solubility factors prevented us from studying this effect for $\mathrm{Ln_{aq}}^{3+}$ in solution, but it could be observed in the solid state: as mentioned above, the luminescence lifetime of the solid species obtained from $\mathrm{Eu_{aq}}^{3+}$ and $\mathrm{Co(CN)_6}^{3-}$ is considerably longer than the luminescence lifetime of $\mathrm{EuCl_3{\cdot}6H_2O}$.

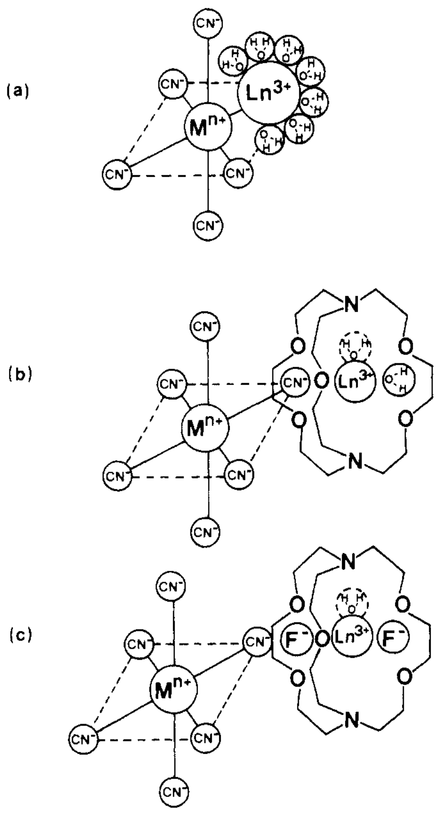

Figure 3. Model structures of the precursor complexes for the quenching processes of $\mathrm{Ln_{aq}}^{3+}$, $[\mathrm{Ln}\subset 2.2.1]^{3+}$, and $[\mathrm{Ln}\subset 2.2.1]^{3+}\text{–}2\mathrm{F}^-$ species by cyanide complexes: (a) intimate ion pair; (b) CN-bridged ion pair; (c) outer-sphere ion pair.

In the $[\mathrm{Ln}\subset 2.2.1]^{3+}$ species, some water molecules are still coordinated to the central metal through the cryptand holes.[14,16] One can expect that one of these water molecules will be replaced

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by a CN group of the cyanide complexes, thereby giving rise to a CN-bridged ion pair (Figure 3). The slight enhancement of the $[\mathrm{Tb}\subset 2.2.1]^{3+}$ lifetime on addition of $\mathrm{Os(CN)_6}^{4-}$ supports this hypothesis, which was previously advanced on the basis of the spectroscopic properties of the $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$\mathrm{M(CN)_6}^{4-}$ ion pairs (M = Fe, Ru, Os).[27,28]

For the $[\mathrm{Ln}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-$ species, neither intimate nor CN-bridged ion pairs are plausible in view of the smaller positive charge of the species and of the presence of F^- ions in the cryptand holes.[17] This picture is confirmed by the behavior of the IPCT band in the $[\mathrm{Eu}\subset 2.2.1]^{3+}/\mathrm{Fe(CN)_6}^{4-}$ system on addition of F^- anions. The presence of this band for F^- concentrations, corresponding to the formation of the $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$\mathrm{F}^-$ species,[17,26] indicates that a charge-transfer process from the iron hexacyanide to the europium species still takes place, presumably in a CN-bridged ion pair as for the $[\mathrm{Eu}\subset 2.2.1]^{3+}/\mathrm{M(CN)_6}^{4-}$ (M = Fe, Ru, Os) systems.[27,28] The decrease in intensity and the blue shift may be due to the smaller positive charge on the Eu species. This disappearance of the IPCT band when only the $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-$ species is present[17,26] indicates that in this case no CN-bridged ion pair is formed. Thus, only formation of outer-sphere ion pairs (Figure 3) is conceivable in the $[\mathrm{Ln}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-/\mathrm{M(CN)_6}^{z-}$ systems.

The trends shown by the quenching constants (Table II) can be at least in part rationalized on the basis of the three different types of precursor complexes discussed above (Figure 3):

(i) The quenching constants can never be diffusion controlled (point 6 above) because energy- or electron-transfer processes in the outer-sphere precursor complex are intrinsically nonadiabatic owing to the poor overlap of the f lanthanide orbitals with the orbitals of the reaction partner.[56] Inner-sphere processes possible for the $\mathrm{Ln_{aq}}^{3+}$ and $[\mathrm{Ln}\subset 2.2.1]^{3+}$ species (Figure 3) may be intrinsically adiabatic, but they cannot be faster than the rate of formation of the bridged or intimate ion pairs.[57]

(ii) The strong decrease of the rate constants for energy-transfer quenching in the series $\mathrm{Ln_{aq}}^{3+} > [\mathrm{Ln}\subset 2.2.1]^{3+} > [\mathrm{Ln}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-$ (point 1 above) can be accounted for on the basis of the involvement of intimate, CN-bridged, and outer-sphere precursor complexes, respectively, with the electronic factor decreasing along the series and controlling the rate of the process.

(iii) The increase in the energy-transfer rate in going from the $\mathrm{Tb_{aq}}^{3+}/\mathrm{Cr(CN)_6}^{3-}$ to the $\mathrm{Tb_{aq}}^{3+}/\mathrm{Fe(CN)_6}^{4-}$ system (point 3) can be accounted for by the fact that the rate of formation of the intimate ion pair is likely to increase with the increasing negative charge of the quencher. The opposite trend shown by the data concerning the $[\mathrm{Tb}\subset 2.2.1]^{3+}$ and $[\mathrm{Tb}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-$ systems with the same quenchers is indicative of formation of looser precursor complexes where the less solvated quencher ($\mathrm{Cr(CN)_6}^{3-}$) may better approach the lanthanide species.

(iv) The rate of electron-transfer quenching of $\mathrm{Eu_{aq}}^{3+}$ and $[\mathrm{Eu}\subset 2.2.1]^{3+}$ in the intimate and bridged ion pairs could be almost adiabatic and controlled by water displacement, whereas electron-transfer quenching of $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-$ is controlled by electronic factors in an outer-sphere complex (point 4).

(v) The observation reported under point 5 seems to suggest that the rate constant of energy-transfer processes is more sensitive to orbital overlap (and thus to center-to-center distance between the two species) than is that of electron transfer.

(vi) The insensitivity of the energy-transfer rate constants to the nature of the central lanthanide ion (point 2) suggests that metal–metal orbital coupling via nephelauxetic effects[58] or charge-transfer perturbations[12] has comparable (presumably very small) influence for the two lanthanide ions.

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Registry No. Eu^{3+}, 22541-18-0; Tb^{3+}, 22541-20-4; $[\mathrm{Tb}\subset 2.2.1]^{3+}$, 71238-22-7; $[\mathrm{Eu}\subset 2.2.1]^{3+}$, 65013-29-8; $[\mathrm{Tb}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-$, 110353-51-0; $[\mathrm{Eu}\subset 2.2.1]^{3+}$–$2\mathrm{F}^-$, 110316-49-9; $\mathrm{Cr(CN)_6}^{3-}$, 14875-14-0; $\mathrm{Fe(CN)_6}^{4-}$, 13408-63-4; $\mathrm{Co(CN)_6}^{3-}$, 14897-04-2; $\mathrm{Ru(CN)_6}^{4-}$, 21029-33-4; $\mathrm{Os(CN)_6}^{4-}$, 19356-45-7.

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Tetramethyldiplatinum(III) (Pt–Pt) Complexes with 2-Hydroxypyridinato Bridging Ligands. 2. Reversals of Ligand Orientations[1]

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The compounds $[\mathrm{Pt_2(CH_3)_4(hp)_2(py)_2}]$ and $[\mathrm{Pt_2(CH_3)_4(fhp)_2(py)_2}]$, where hp represents the 2-hydroxypyridinate anion ($\mathrm{C_5H_4NO^-}$) and fhp represents the 2-hydroxy-6-fluoropyridinate anion ($\mathrm{C_6H_3FNO^-}$), can be converted to the corresponding monopyridine adducts by chromatography on silica gel. The surprising aspect of these conversions is that the arrangement of the hp and fhp ligands changes to head-to-head (HH) from head-to-tail (HT) and that, upon treatment with excess pyridine, the HH monopyridinates are reconverted to the HT bis(pyridine) adducts. The structures of $[\mathrm{Pt_2(CH_3)_4(hp)_2(py)}]$ (**1**) and $[\mathrm{Pt_2(CH_3)_4(fhp)_2(py)}]$ (**2**) were established by X-ray crystallography. Also reported here is the preparation of $[\mathrm{Pt_2(CH_3)_4(bhp)_2(py)}]$ (**3**), where bhp = the 2-hydroxy-6-bromopyridinate anion. This has the expected HH structure. Crystallographic data are as follows. For **1**: $P\bar{1}$, $a = 9.637$ (2) Å, $b = 12.246$ (3) Å, $c = 8.573$ (3) Å, $\alpha = 85.71$ (3)°, $\beta = 91.98$ (3)°, $\gamma = 92.35$ (2)°, $Z = 2$ ($R = 0.030$; $R_w = 0.043$). For **2**: $P2_1/n$, $a = 9.458$ (3) Å, $b = 15.851$ (6) Å, $c = 14.156$ (4) Å, $\beta = 102.82$ (2)°, $Z = 4$ ($R = 0.030$; $R_w = 0.044$). For **3**: $P\bar{1}$, $a = 9.493$ (2) Å, $b = 13.198$ (4) Å, $c = 9.046$ (2) Å, $\alpha = 91.55$ (4)°, $\beta = 97.73$ (3)°, $\gamma = 92.33$ (4)°, $Z = 2$ ($R = 0.045$; $R_w = 0.057$).

Introduction

During the past two decades there has been a dramatic increase in the number of papers concerning the chemistry of platinum complexes where the platinum atoms are formally in the +3 oxidation state.[2,3] The majority of these complexes are binuclear and have either two or four bidentate ligands bridging the two d^7 metal centers. The coordination spheres are generally completed by the binding of two anionic or neutral donor ligands to the

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