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localizing environmental forces. The intensity of such a band as a function of the dimer (or subdimer) spin state and temperature has been evaluated by Cox,[18] and similar equations should apply to tetramers having one or more mixed-valence pairs. Either vibronic tunneling or thermal hopping is possible on the lower double-well surface with barrier height E_θ. Expressions for E_{op}, E_θ, and the transition intensity have been given by Girerd[19] for spin-coupled dimers; again similar expressions should be applicable for tetramers, utilizing the subdimer spin quantum number $\langle S_{34}\rangle$. (Note, however, that the transition moment expressions may be oversimplified, since they are based on Huckel type equations.)

A brief summary of some remaining issues is appropriate. The detailed understanding of the presence and properties of "spin-admixed" states (often found in synthetic clusters), while generally consistent with the energy level scheme indicated by the nonlinear model, requires a closer analysis of the way spin-orbit coupling (zero-field splitting) will mix states of different total spin. The presence of an unusual $S = {}^5/_2$ or ${}^7/_2$ state as the ground state in oxidized P clusters of nitrogenase is not explained by the present model; rather, the $S = {}^7/_2$ state found by the model behaves like the observed $S = {}^7/_2$ in Se Cp ferredoxin. The lowest lying $S = {}^5/_2$ state has similar predicted properties. If the oxidized P clusters are in fact $[Fe_4S_4]$ clusters in the +1 oxidation state, their unique Mossbauer hyperfine properties must be due to additional effects such as strong spin-orbit mixing of states or cluster-cluster interactions. It is possible that the cluster nuclearity and/or oxidation state are not those postulated above, and a completely new analysis would be required.

In our present modeling, we have not considered the possible effects of electron delocalization between different layers of the cluster, that is, between the mixed-valence pair and the other ferrous sites. We have found no strong indications that such mixing is present; the σ nature of the electron delocalization within the mixed-valence pair would argue against the importance of this delocalization. However, interlayer resonance effects may be significant in some cases, and this is still under investigation.

To treat the effects of spin-orbit coupling and/or interlayer resonance, one could start with the low-lying eigenstates from the nonlinear model and rediagonalize the appropriate perturbation matrix. This would provide a more concise approach than trying to diagonalize very large matrices de novo.

These two papers demonstrate the scope of a combined exchange-resonance coupling Hamiltonian. The theory has much greater explanatory power for the spin-state energies and (EPR, hyperfine) properties of iron-sulfur clusters than the standard Heisenberg coupling Hamiltonian, and several important physical ideas become apparent. These include the prominent role of electron delocalization (B term) and the countervailing effects produced by a major inequality in the Heisenberg parameters J_2 and J_1 (i.e. where α is small or negative). Both Heisenberg parameters are fairly small, and the $Fe^{2+}-Fe^{2+}$ parameter J_2 may be either antiferromagnetic or ferromagnetic (see P 1). Modest variations in the size of J_1 and J_2 produce a wide variety of spin ground states; the magnitude of B plays an important role by shifting the location in parameter space where spin-state crossings occur. External localizing forces are also very important and show that the protein or cluster environment exerts a very significant effect on the low-lying spin states, a conclusion already apparent from experimental studies.[2,3] Quantitative calculations play an important complementary role to the phenomenological models by determining reasonable ranges in parameter space where state energies and properties should be closely examined, as emphasized in P 1.

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Sharp-Line Electronic Spectroscopy and Metal-Ligand Geometry in the Pentaamminehydroxochromium(III) Complex

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The hydroxide ligand is a strong π-donor in metal complexes, and because the interaction is anisotropic, it can cause large perturbations of the t_{2g} subshell. This results in unexpectedly large splittings among the sharp-line transitions in $[Cr(NH_3)_5OH](ClO_4)_2$. The extent of these splittings depends on the orientation of the p orbital on the hydroxide oxygen, which in turn depends on the N-Cr-O-H dihedral angle. Ligand field calculations yielded an estimate of this angle of 20°, approximately midway between an eclipsed and a staggered conformation. The prominent 572 cm^{-1} accepting mode in the luminescence spectrum of $[Cr(NH_3)_5OH](ClO_4)_2$, previously identified with the Cr-O stretching mode, was assigned to the first overtone of the hydroxide internal rotation mode. This overtone is accidentally nearly coincident with a Cr-O-H bending mode in the IR spectrum, but these bands become well separated in spectra of the deuterated complex. The luminescent excited state could be construed as having predominantly $^2A_1$ (^2E_g) character (in C_{4v} and O_h notation).

Introduction

The splittings among the narrow electronic transitions arising within the t_{2g}^3 configuration of pentaammine complexes of chromium(III) have been controversial,[1-4] even following recently reported low-temperature measurements and sophisticated ligand field calculations.[5,6] The splitting of the two $^4A_{2g} \rightarrow {}^2E_g$ components in $[Cr(NH_3)_5X]^{2+}$ (X = Cl, Br, I) complexes is either very small (<20 cm^{-1})[3,5] or unusually large (170-320 cm^{-1}).[1,2,4,6] Very recent resonance line-narrowing experiments favor the latter

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interpretation, while the smaller splitting is attributed to inequivalent chromium sites.[7]

In 1977 Güdel published the sharp-line luminescence and excitation spectra of $[Cr(NH_3)_5OH](ClO_4)_2$ and concluded that the emitting state was a component of the octahedral $^2T_{1g}$ state.[3] The assignment of the excitation spectrum followed an energy level scheme in which two $^2T_{1g}$ components, split by 90 cm^{-1}, lay below the two components of the ^2E_g state by about 600 cm^{-1}. The doublet crossover was a reasonable outcome of the strong ligand field asymmetry, especially the π-asymmetry.[8] The third component of the $^2T_{1g}$ state was not assigned experimentally but was calculated to lie 1000–1500 cm^{-1} above the lowest two doublets.[3] Arguing from line widths in solution, Forster also concluded that $[Cr(NH_3)_5OH]^{2+}$ emitted from a component of the $^2T_{1g}$ state.[9,10] This behavior contrasts sharply with that of other pentaammine complexes, and the discrepancy would have to be attributed to the distinctive properties of hydroxide as a ligand.

These properties include relatively high σ and π donor strengths, attested to by reported angular overlap model (AOM) parameter values of $e_\sigma \cong 8500$ cm^{-1} and $e_\pi \cong 2000$ cm^{-1}, deduced from the splittings of the spin-allowed transitions in hydroxo complexes of Cr(III).[11] Another important aspect of hydroxide coordination is that the π-interaction should be anisotropic. As in carboxylate complexes, the M–O–H angle can be expected to be sufficiently close to 120° that of the two remaining electron pairs, one would be a lone pair (the third member of an sp^2 hybrid set) and the other would occupy a p orbital perpendicular to the plane defined by the M–O–H bond. This directional asymmetry can, in comparison to isotropically bonding ligands, cause a considerable alteration in the sharp-line splittings.

Furthermore, the actual effects on the sharp-line splittings will depend on the exact geometric relationship between the oxygen p orbital and the remainder of the metal complex. If the CrN_5O skeleton is assumed to have C_{4v} symmetry, then the unique hydroxide hydrogen positions range from an eclipsed orientation, in which the N–Cr–O–H dihedral angle (ψ) is 0°, to a staggered position, in which the dihedral angle is 45°. The perturbation of the metal d orbitals by the oxygen p electrons will vary with that angle.

We recently discussed the means by which an AOM formulation of the ligand field potential that uses exact ligand positions can be applied to the calculation of d–d transition energies, in particular those of sharp-line transitions, which are quite sensitive to the ligand geometry.[12]

Attempts to apply ligand field theory to the doublet splittings in pentaamminechromium(III) complexes have been largely unsuccessful.[1,2] The same is true for tetragonal complexes in general.[13] The problem is that ^2E_g splittings in such complexes are seldom calculated to be much larger than 50 cm^{-1} for any reasonable ligand field asymmetry, while the experimental values often appear to be much larger. Schmidtke et al. have argued that the fault lies in the assumption of spherically symmetric interelectronic repulsion (first term of eq 1). This point had been made by others,[1,13] but no workable strategy to adapt the interelectronic repulsion Hamiltonian to tetragonal complexes seemed to be possible. Ten independent matrix elements (i.e., adjustable parameters) appear in D_{4h} symmetry,[14] while approximations based on octahedral symmetry, sometimes going under the name differential orbital expansion,[15,16] have been shown to produce negligible effects on the doublet splittings.[17]

Schmidtke's contribution was to suggest that all the tetragonally adapted interelectronic repulsion matrix elements could be approximated with the use of one parameter, assuming that the largest effect was an increase in the effective occupation volume of metal π-symmetry electrons when engaged in bonding to ligands.[6] The increase in occupation volume leads to a reduction in repulsion forces from other electrons. In the context of $[Cr(NH_3)_5OH]^{2+}$, with the OH$^-$ on the z axis, this would mean that a d_{xy} electron, unperturbed by the NH_3 groups in the plane, would suffer greater repulsive forces than a d_{xz} electron, which is partially delocalized into an MO involving the hydroxide ion. We have adopted this approach in this paper and adapted it to the case of anisotropic π-bonding.

In this paper, we examine the suitability of this model to reproduce the sharp-line spectrum of $[Cr(NH_3)_5OH](ClO_4)_2$ as another representative of the pentaammine series, we analyze the consequences of anisotropic π-bonding by OH$^-$ on the sharp-line transitions, and we attempt to use the AOM model to predict the N–Cr–O–H dihedral angle in this complex.

Experimental Section

$[Cr(NH_3)_5OH](ClO_4)_2$ was prepared by the method of Linhard,[18] recrystallized twice from water, and air-dried. The compound was deuterated by repeatedly recrystallizing it from D_2O until the decrease in the relative intensities of the ν(N–H) and ν(O–H) lines in the IR spectrum indicated that 95% deuteration had occurred.

The apparatus for measuring luminescence and excitation spectra has been described previously.[5] The sharp-line excitation spectrum of microcrystalline $[Cr(NH_3)_5OH](ClO_4)_2$ at 13 K was measured by monitoring the luminescence from the no phonon band or the vibronic sideband at 763 nm, while the luminescence sideband at 745 nm was monitored for $[Cr(ND_3)_5OD](ClO_4)_2$. The excitation wavelength from the dye laser source was calibrated by using four neon optogalvanic resonance points.

Infrared spectra were measured with a Mattson Cygnus 25 FTIR spectrometer on samples dispersed in Nujol mulls on a polyethylene film (far-IR) or in KBr pellets (mid-IR). Room-temperature absorption spectra were recorded with a Hewlett-Packard Model 8451A diode array spectrophotometer.

Results and Discussion

Sharp-Line Electronic Transitions and the Cr–O–H Geometry. The AOM model previously described[12] was used to calculate transition energies for the five $^4A_{2g} \rightarrow \{^2E_g, {}^2T_{1g}\}$ components. The ligand field potential was developed from a molecular structure in which the six ligand atoms lie on the Cartesian axes while the angular position of the hydroxide hydrogen was varied. The ammine ligands were considered to interact with σ-symmetry only, expressed through the AOM parameter $e_{\sigma N}$, while hydroxide interacted with the metal ion with both σ- and π-symmetry, expressed through the parameters $e_{\sigma O}$ and $e_{\pi O}$. The π-interaction was confined to the direction perpendicular to the plane defined by the Cr–O–H bond, through the use of previously described techniques.[12] The Hamiltonian function used in the calculation was

$$\mathcal{H} = \sum_{i<j} \frac{e^2}{r_{i,j}} + V_{\mathrm{LF}} + \zeta\sum_i \mathbf{l}_i\cdot s_i + \alpha_{\mathrm{T}}\sum_i \mathbf{l}_i^2 + 2\alpha_{\mathrm{T}}\sum_{i<j} \mathbf{l}_i\cdot\mathbf{l}_j \quad (1)$$

the terms of which represent, respectively, the interelectronic repulsion, the ligand field potential, and the spin–orbit coupling, with the last two representing the Trees corretion.[19]

We have included Schmidthke's π-expansion parameter τ in the treatment of the interelectronic repulsion term.[6] The general two-electron matrix element can be written as the sum of two electrostatic terms, the second of which represents the interchange of one pair of electrons.

$$\langle ab|e^2/r_{12}|cd\rangle = V(a,b,c,d) - V(a,b,d,c) \quad (2)$$

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In Schmidtke's approximation the electrostatic terms are modified by a factor τ_L for each constituent metal wave function that overlaps with a ligand π orbital, ϕ_L. When only one type of ligand π orbital is involved, this may be written as

$$V(a,b,c,d) = \tau^n V^\circ(a,b,c,d) \qquad (3)$$

where n represents how many of the metal functions {a,b,c,d} overlap with a ligand π orbital, and V° is the spherically symmetric electrostatic term.

An anisotropically bonding ligand such as hydroxide ion causes additional difficulties. A ligand π orbital ϕ_L may overlap with more than one metal orbital, and the extent of the overlap varies with the angle of the ligand π orbital with respect to the metal orbitals, i.e., with respect to the axis system generated by the four ligands in the plane perpendicular to the M–L bond.

With a hydroxide ion on the z axis, π-expansion will take place only for d_{xz} and d_{yz} electrons. If the fully aligned interaction of the oxygen p orbital with a d_{yz} orbital results in a π-expansion parameter of τ, then we have assumed that the degree of π-expansion varies as the cosine of the angle (in the xy plane) between the oxygen p orbital and the metal d_{xz} or d_{yz} orbitals. Since the angle between the d_{yz} orbital and the ligand p orbital is already defined as ψ, we have

$$\tau_{xz} = 1 - (1 - \tau) \sin \psi$$
$$\tau_{yz} = 1 - (1 - \tau) \cos \psi \qquad (4)$$

Complete tables of (unmodified) electrostatic terms V°(a,b,c,d), expressed in Racah parameters B and C, have appeared in several places.[12,14] Each term must be modified as in eq 3:

$$V(a,b,c,d) = \tau_{xz}{}^n \tau_{yz}{}^m V^\circ(a,b,c,d) \qquad (5)$$

Here n and m are the number of occurrences of d_{xz} and d_{yz} among the set of wave functions {a,b,c,d}. If ref 12 is used as a source of the V°(a,b,c,d) expressions, it should be kept in mind that the Racah A terms were omitted from that table, but must be restored upon loss of spherical symmetry. For each term of the type V(a,b,a,b) an A must be added to the expressions in Table 2 of ref 12. Both τ and A become empirically adjustable parameters through this procedure, but we have chosen to keep them fixed during the spectral fitting.

The evaluation of the matrix elements for each of the terms in eq 1 over strong-field three-electron atomic wave functions has been discussed previously.[12] The secular determinant was set up over the complete 120 function basis set of antisymmetrized wave functions. Eigenvalues were assigned to the doublet or quartet manifold by analysis of the corresponding eigenvectors, as was described earlier.[5]

A particularly important point in the analysis of $[Cr(NH_3)_5OH]^{2+}$ presented here has to do with the effects of the angle ψ, which determines the extent of the π-interaction of the hydroxide with the d_{xz} and d_{yz} orbitals. In order to form an initial picture of the influence of the N–Cr–O–H dihedral angle on the eight sharp-line transitions in $[Cr(NH_3)_5OH](ClO_4)_2$, the transition energies were calculated by using ligand field parameters determined by Schmidtke from an analysis of the spin-allowed bands.[11] Figure 1 is a plot of the doublet transition energies as a function of ψ. The picture is qualitatively similar over a wide range of parameter values, including those generated in our subsequent spectral analysis.

Figure 1 shows a very large variation in the transition energies of two of the five $^4A_{2g} \rightarrow \{^2E_g, {}^2T_{1g}\}$ components with the hydroxide angular position (the C_{4v} descriptions of these states change considerably with ψ). This variation is unique only within a 45° range. The other three components do not vary as much with the dihedral angle, but all five components are sensitive to the ligand field asymmetry. As has been noted previously,[20] since the ligand field is two-dimensional (e_σ, e_π) the asymmetry can be expressed in several ways. The Cr(III) doublets in tetragonal complexes are relatively insensitive to $e_\sigma - e_\pi$ (or $3e_\sigma - 4e_\pi$), but are much more sensitive to the orthogonal ligand field component, $e_\sigma + e_\pi$.[20]

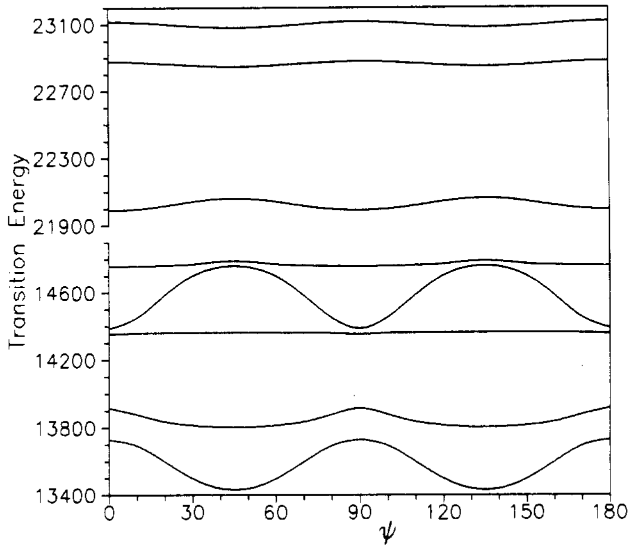

Figure 1. Calculated variation of sharp-line transition energies with the dihedral N–Cr–O–H angle ψ. Other parameters (in cm^{-1}): $e_{\sigma N}$ = 7180, $e_{\sigma O}$ = 6700, $e_{\pi O}$ = 2900, B = 540, C = 3200, α_T = 0, ζ = 270.

Table I. Vibronic Intervals in the 13 K Luminescence Spectra of $[Cr(NH_3)_5OH](ClO_4)_2$ and $[Cr(ND_3)_5OD](ClO_4)_2$[a]

peak no.[d]	$[Cr(NH_3)_5OH](ClO_4)_2$[b]			$[Cr(ND_3)_5OD](ClO_4)_2$[c]	
	$\bar{\nu}_0 - \bar{\nu}$	calcd[e]	IR	$\bar{\nu}_0 - \bar{\nu}$	calcd[e]
0	0 vs			0 vs	
1	66 m			62 w	
2	92 vw		91	89 vw	
3	122 vw		120	122 w	
4	159 vw				
5	178 vw			170 vw	
6	224 vw		224	202 w	
7	254 w		257		
8	285 m			259 s	
9	318 vw			310 m	
10	357 vw			333 vw	
11	366 vw			364 w	
12	397 vw				
13	435 vw		428	402 vw	
14			450	437 vw	
15	572 s		565	518 s	
16				565 vw	
1′	645 w	638			
				620 w	
3′	693 vw	684		634 vw	640
				705 vw	
6′	795 vw	796		721 vw	720
				762 vw	
9′				823 vw	828
	838 vw				
				842 vw	
15′	1124 vw	1144			
1″	1198 vw	1210			
	1565 vw				

[a] Data in cm^{-1}. [b] $\bar{\nu}_0$ = 13 680 cm^{-1}. [c] $\bar{\nu}_0$ = 13 688 cm^{-1}. [d] Primed numbers refer to combination bands with the 572-cm^{-1} (518 – D) accepting mode. [e] Calculated combination band frequencies.

Luminescence Spectra. The vibronic intervals from the sharp-line luminescence spectra of $[Cr(NH_3)_5OH](ClO_4)_2$ and $[Cr(ND_3)_5OD](ClO_4)_2$ are listed in Table I, and the spectrum of the deuterated complex is shown in Figure 2a. Both spectra consist of a region within 600 cm^{-1} of the 0–0 line, composed primarily of single quanta of metal–ligand vibrations, and a weaker series of combination bands beyond 600 cm^{-1}, together with a significant amount of unresolved vibronic intensity. There is a partial overlap in the 0–500-cm^{-1} region between vibronic intervals in the luminescence spectrum and IR frequencies, as indicated in Table I.

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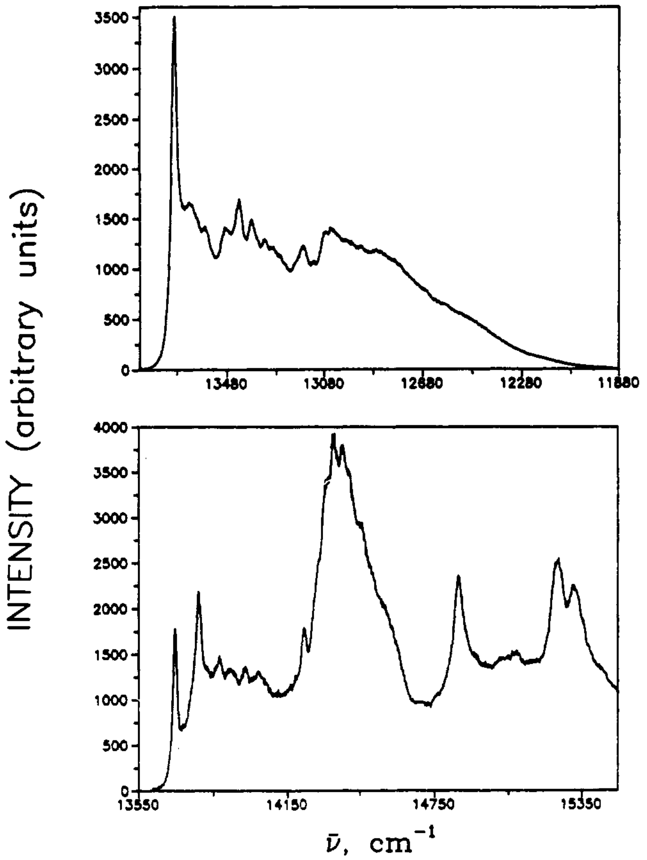

Figure 2. Luminescence (top, a) and excitation (bottom, b) spectra of $[Cr(ND_3)_5OD](ClO_4)_2$ at 13 K.

Güdel has assigned the combination band region primarily to a sequence involving a strongly anharmonic ν(Cr–O) stretching vibration (572 cm^{-1} in luminescence, 565 cm^{-1} in IR) as an accepting mode.[3] This assignment was a logical one in every respect. The Cr–O stretching mode would have A_1 symmetry in the C_{4v} point group, consistent with its role in forming progressions. Its appearance in the IR spectrum acts as confirmation, since only modes of A_1 or E symmetry are infrared active in C_{4v}. The ν(Cr–O) stretching mode has been found in the same region for complexes of other oxygen-containing ligands.[21]

The problem with this interpretation is immediately evident upon examination of the IR and luminescence spectra of the deuterated complex. In the luminescence spectrum, the strong 572-cm^{-1} band is shifted to 518 cm^{-1}, and this frequency again appears in combination bands above 600 cm^{-1}, for the most part with the same modes that are observed in combination bands in the spectrum of the undeuterated complex. However, no corresponding band is found in the IR spectrum. The 565-cm^{-1} IR band in the undeuterated complex appears, in fact, to be shifted to 459 cm^{-1}. There is one additional peculiarity: the strongest vibronic band in each spectrum, with the exception of the 572 (H) and 518 cm^{-1} (D) bands discussed above, is found at 285 (H) and 259 cm^{-1} (D). No IR band can be associated with either of these, and none of the combination bands in the luminescence spectra could be attributed to these as promoting modes.

It is interesting that the vibronic structure in related halopentaamminechromium(III) spectra differs in important respects.[5,6] Perhaps most noticeably, several δ(Cr–N–H) modes, with frequencies between 600 and 800 cm^{-1}, are prominent in the luminescence spectra of the halogen complexes, obscuring combination bands in the same region. Combination bands are seen above 800 cm^{-1} and are based on both ν(Cr–X) and ν(Cr–N) stretching vibrations as accepting modes, primarily the former.[5]

There is no evidence for the participation of the various δ-(Cr–N–H) vibrations in the resolved portion of the vibronic structure of the $[Cr(NH_3)_5OH](ClO_4)_2$ luminescence spectrum, which instead appears to be completely dominated by modes involving the Cr–OH group. This is actually not unreasonable. It is, in fact, the sizable perturbation of the electronic transition energies by the hydroxide orientation that is the subject of this paper. Similarly large transition dipole moments are a very likely consequence of motion involving changes in the orientation of that group. This would apply especially to the transitions depicted in Figure 1 that oscillate strongly in energy with the dihedral angle ψ, of which the lowest energy sharp-line transition is one.

Our assignments are based on the observation that the second strongest bands in the two luminescence spectra, mentioned above, lie at exactly half the frequencies of the strongest bands, upon which later progressions are formed. The 285 (H) and 259 cm^{-1} (D) bands we assign to a torsional motion, τ_{OH}, of the Cr–O–H group in the approximately 4-fold potential well provided by the rest of the molecule. This motion involves a rotation of the π-bonding p orbital on the oxygen atom with respect to the metal ion of exactly the type depicted in Figure 1.

The apparent agreement between the 565-cm^{-1} line in the IR spectrum of $[Cr(NH_3)_5OH](ClO_4)_2$ and the 572-cm^{-1} line in the luminescence spectrum we ascribe to a coincidence. The small difference between the two frequencies is significant. The $2\tau_{OH}$ overtone band is absent in the IR spectrum, while the 565-cm^{-1} line is either absent in the luminescence spectrum or is obscured by the 2 × 285 cm^{-1} overtone band. The 565-cm^{-1} IR line might be assigned to ν(Cr–O), which was Güdel's assignment,[3] in which case it would have approximate a_1 symmetry in C_{4v}, and might be forbidden in luminescence (see below). The shift to 459 cm^{-1} on deuteration seems too high, however. Another possibility is that it represents a δ(Cr–O–H) bending vibration, which would have e symmetry and would be allowed in IR and luminescence spectra, no matter which electronic transition were involved.

The symmetry species of a rotation about the *z* axis in the C_{4v} group is A_2, which may be assigned to τ_{OH}. This is inactive in IR spectra, and the lack of the corresponding band in the far-IR spectrum was one reason for the assignment. We also infer that it is vibronically inactive, or approximately so, in the luminescence spectra reported here. This follows from the assignment of the 572 (H) and 518 cm^{-1} (D) bands in the luminescence spectra to the first overtones. The greater intensity of the overtone implies that a selection rule exists against the fundamental, which, however, still appears in the spectrum due to the very large perturbation of the transition dipole moment by τ_{OH} together with an incomplete association of actual eigenfunctions with C_{4v} representations.

The anharmonicity in the 572 cm^{-1} (H) combining frequency observed by Güdel is consistent with its designation as an overtone of a torsional mode, which are known to be strongly anharmonic.[22] Torsional modes in some transition-metal complexes have been assigned frequencies near 200 cm^{-1}, either by direct observation[23] or through analysis of the temperature dependence of line broadening in IR spectra.[24]

Excitation Spectra. Vibronic intervals from the sharp-line excitation spectra of $[Cr(NH_3)_5OH](ClO_4)_2$ and $[Cr(ND_3)_5OD](ClO_4)_2$ are listed in Tables II and III, and the spectrum of the deuterated complex is shown in Figure 2b. The expected mirror image relationship between excitation and luminescence spectra is apparent in both cases in the region below 600 cm^{-1} from the lowest energy zero phonon band, but the correspondence is better for the undeuterated complex. The τ_{OH} torsional mode is seen only very weakly in the excitation spectrum of $[Cr(NH_3)_5OH](ClO_4)_2$, although the overtone band at 569 cm^{-1} is strong and scarcely shifted from the luminescence spectrum. In the $[Cr(ND_3)_5OD](ClO_4)_2$ spectrum, the fundamental is obscured, but the overtone band occurs unshifted from the luminescence spectrum.

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Table II. Peak Positions in the 13 K Sharp-Line Excitation Spectrum of $[Cr(NH_3)_5OH](ClO_4)_2$[a]

			vibronic freq	
$\bar{\nu} - 13689$	assignt[b]		excitation	lumin[c]
0 s	$R_1(^2A_1)$	ν_1	66	66
66 w	$R_1 + \nu_1$	ν_2	95	92
95 s	$R_1 + \nu_2$	ν_3	123	122
123 vw	$R_1 + \nu_3$	ν_4	176	178
176 w	$R_1 + \nu_4$	ν_5	219	224
219 m	$R_1 + \nu_5$	τ_{OH}	282	285
282 vw	$R_1 + \tau_{OH}$	ν_6	313	318
313 w	$R_1 + \nu_6$	ν_7	353	357
353 vw	$R_1 + \nu_7$	ν_8	403	397
403 w	$R_1 + \nu_8$			
569 s	$R_1 + 2\tau_{OH}$ (285)			
604 vw				
620 vw				
630 vs	T_1 (^2E)			
653 vw				
676 sh				
689 s	R_2 $(^2B_1)$			
817 w	$R_2 + \nu_3$ (128)			
897 w				
1112 s	T_2 $(^2A_2)$			
1147 vw	$R_1 + 4\tau_{OH}$ (287)			
1197 m	$T_1 + 2\tau_{OH}$ (284)			
1237 vw	$R_2 + 2\tau_{OH}$ (274)			
1362 m				
1433 vw				
1527 s	T_3 (^2E)			
1590 s	$T_3 + \nu_1$ (63)			
1665 vw	$T_2 + 2\tau_{OH}$ (277)			
1706 vw	$R_1 + 6\tau_{OH}$ (284)			
1823 w, br	$T_3 + \nu_6$ (296)			

[a] In cm^{-1}. [b] Values in parentheses represent the calculated (average) frequency of a single quantum of the vibrational mode listed. [c] Table I.

Table III. Peak Positions in the Sharp-Line Excitation Spectrum of $[Cr(ND_3)_5OD](ClO_4)_2$[a]

			vibronic freq	
$\bar{\nu} - 13698$	assignt[b]		excitation	lumin[c]
0 vs	R_1 $(^2A_1)$	ν_1	30	
30 vw	$R_1 + \nu_1$	ν_2		62
92 vs	$R_1 + \nu_3$	ν_3	92	89
123 vw	$R_1 + \nu_4$	ν_4	123	122
177 w	$R_1 + \nu_5$	ν_5	177	170
220 m	$R_1 + \nu_6$	ν_6	220	
280 m	$R_1 + \nu_7$	ν_7	280	
334 w	$R_1 + \nu_8$	ν_8	334	333
470 vw	$R_1 + \nu_9$	ν_9	470	
518 m	$R_1 + 2\tau_{OH}$ (259)	$2\tau_{OH}$	518	518
578 w	$R_1 + \nu_2 + 2\tau_{OH}$			
612 w	$R_1 + \nu_3 + 2\tau_{OH}$			
643 s	T_1 (^2E)			
682 s	R_2 $(^2B_1)$			
718 vw				
748 w	$R_2 + \nu_2$ (66)			
757 w				
794 vw	$R_1 + \nu_7 + 2\tau_{OH}$			
858 w	$R_2 + \nu_5$ (176)			
1068 vw				
1147 s	T_2 $(^2A_2)$			
1208 vw	$T_2 + \nu_2$ (61)			
1327 w	$T_2 + \nu_5$ (180)			
1349 w				
1362 w	$T_2 + \nu_6$ (215)			
1555 s	T_3 (^2E)			
1614 s	$T_3 + \nu_2$ (59)			
1751 vw				

[a] In cm^{-1}. [b] Values in parentheses represent the calculated (average) frequency of a single quantum of the vibrational mode listed. [c] Table I.

In assigning the five electronic origins in the excitation spectrum, we attempted to take some account of the vibronic structure expected with each origin. In a simplified C_{4v} analysis ignoring spin, the allowed vibrational coupling would be as follows:

$$\begin{aligned} &^4B_1 \rightarrow {}^2A_1(^2E_g) \quad b_1, e \\ &^4B_1 \rightarrow {}^2B_1(^2E_g) \quad a_1, e \\ &^4B_1 \rightarrow {}^2A_2(^2T_{1g}) \quad b_2, e \\ &^4B_1 \rightarrow {}^2E(^2T_{1g}) \quad a_1, a_2, b_1, b_2, e \end{aligned} \tag{6}$$

Vibrational modes of e symmetry can couple with all electronic transitions in this approximation, but otherwise the vibronic structure on the five origins would be expected to show considerable variation. Therefore, one possible stratagem for locating the electronic origins—looking for maximum coincidence in vibronic structure (frequencies and relative intensities)—should not be very effective for complexes with near-tetragonal symmetry.

Nevertheless, possible origins were subjected to examination for coincidences in vibronic structure and for plausible alternative assignments as vibronic lines, but a key point in the analysis was based on a comparison of corresponding lines in the deuterated and undeuterated complexes. The electronic origins were presumed to be relatively little shifted between the two compounds, and in fact the lowest energy zero phonon transition differs by just 9 cm^{-1} in the two excitation spectra. Any pair of corresponding lines, of course, could represent either an electronic origin or a vibronic interval based on a lower lying origin. The test that was applied to trial assignments was that corresponding vibronic intervals should not be greater in the spectrum of the deuterated complex than in that of the undeuterated. With only a few exceptions, deuteration should yield smaller vibrational frequencies if there is any change at all.

With these considerations the assignments listed in Tables II and III were arrived at. Each of the assigned origins in the excitation spectra is relatively intense. The ^2E_g (R_1, R_2) and $^2T_{1g}$ (T_1, T_2, T_3) designations are approximate and are discussed below. There is a greater than 1500 cm^{-1} spread between the lowest and highest energy transitions in the $^4A_{2g} \rightarrow \{^2E_g, {}^2T_{1g}\}$ group. We have not assigned the relatively strong line at 95 (H) and 92 cm^{-1} (D) above the lowest origin in the excitation spectra to an electronic origin, as did Güdel,[3] but have assigned it to a vibronic peak probably involving a lattice mode. For the undeuterated complex this mode appears at 92 cm^{-1} in the luminescence spectrum and 91 cm^{-1} (strong) in the IR spectrum.

A comparison of the assigned origins to Figure 1 reveals a large discrepancy in the separation of the second and third bands. This is largely a function of the ligand field asymmetry, and values for $e_{\sigma N}$, $e_{\sigma O}$, and $e_{\pi O}$ can easily be found that yield small separations in accord with the assignments of Tables II and III. The same considerations apply to the $^2T_{2g}$ splittings (see below).

More important from the viewpoint of the effect of geometry on the spectrum are the gaps between the first and second and between the fourth and fifth bands. Neither of the extreme orientations, staggered or eclipsed, matches the data, but a qualitative similarity does exist approximately midway between these two orientations. We had hoped to use the vibronic structure to effect at least a partial assignment of the electronic origins (eq 6), but there were an insufficient number of bands to do so. Furthermore, much of the observed vibronic structure (especially for the undeuterated complex) appears to derive from overtones of the τ_{OH} torsional mode, leaving little else for comparison.

Ligand Field Analysis. An optimization was performed based on the experimental sharp-line electronic peaks listed in Tables II and III, and the average energies of the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4T_{1g}$ transitions, for the latter of which two distinct bands are observed.[3,11] Güdel was also able to observe two closely spaced, sharp peaks in the $^4A_{2g} \rightarrow {}^2T_{2g}$ portion of the spectrum.[3] We have included these in the optimization, although one cannot tell whether the higher energy peak is a second origin or a vibronic satellite of the first.

The Hamiltonian function of eq 1 was used to calculate the eigenvalues as discussed above. The eight parameters varied during the optimization were the interelectronic repulsion parameters B, C, and α_T (the Trees correction parameter), the spin–orbit coupling parameter ζ, the AOM parameters $e_{\sigma O}$ and

Table IV. Experimental and Calculated Electronic Transition Energies for $[Cr(NH_3)_5OH](ClO_4)_2$ and $[Cr(ND_3)_5OD](ClO_4)_2$[a]

excited state	$[Cr(NH_3)_5OH](ClO_4)_2$		$[Cr(ND_3)_5OD](ClO_4)_2$	
	exptl	calcd[b]	exptl	calcd[c]
^2E_g, $^2T_{1g}$	13 689	13 683	13 698	13 693
	14 319	14 320	14 341	14 342
	14 378	14 376	14 380	14 393
	14 801	14 807	14 845	14 835
	15 216	15 186	15 253	15 211
$^2T_{2g}$	...	21 117	...	21 094
	21 871[d]	21 921	(21 871)[d]	21 916
	21 905[d]	21 968	(21 905)[d]	21 941
$^4T_{2g}$		18 455		18 414
	19 600[d]	19 762	(19 600)[d]	19 702
		20 600		20 540
$^4T_{1g}$	25 900[d]	25 587	(25 900)[d]	25 540
		27 401		27 338
	29 000[d]	28 650	(29 000)[d]	28 601

[a] Data in cm^{-1}. [b] Best-fit parameters: $e_{\sigma N} = 6587 \pm 25$, $e_{\sigma O} = 8392 \pm 46$, $e_{\pi O} = 2836 \pm 25$, $B = 815 \pm 10$, $C = 2586 \pm 33$, $\alpha_T = 130 \pm 10$, $\zeta = 39 \pm 113$ (all in cm^{-1}); $\psi = 20.3 \pm 0.4°$. [c] Best-fit parameters: $e_{\sigma N} = 6567 \pm 23$, $e_{\sigma O} = 8392 \pm 52$, $e_{\pi O} = 2836 \pm 28$, $B = 820 \pm 12$, $C = 2571 \pm 40$, $\alpha_T = 136 \pm 10$, $\zeta = 0 \pm 10^4$ (all in cm^{-1}); $\psi = 20.6 \pm 0.5°$. [d] Reference 3; quartet data applied to both complexes.

$e_{\pi O}$ for the hydroxide–chromium interaction and $e_{\sigma N}$ for the ammine–chromium interaction, and the dihedral angle ψ. Schmidtke's π-expansion parameter τ was fixed at 0.990, a value suggested by their analysis of $[Cr(NH_3)_5Cl]Cl_2$.[6] The Racah parameter A was fixed at 5000 cm^{-1}. Its value has little effect on the calculated peak positions. The function minimized was

$$f = 1000\sum D^2 + \sum Q^2 + 10T_a + T_b + 100S_Q + 1000S_D \quad (7)$$

where each term represent a difference between experimental and calculated transition energies or splittings: D, the five $\{^2E_g, {}^2T_{1g}\}$ energies; Q, the three $\{^4T_{2g}, {}^4T_{1g}\}$ energies; T_a, the lower-energy experimental $^2T_{2g}$ peak position; T_b, the high-energy $^2T_{2g}$ peak position; S_Q, the splitting of the $^4T_{1g}$ state; S_D, the splitting between the first two doublet peaks. The Powell parallel subspace procedure was used to find the global minimum.[25,26]

Table IV presents the results of the optimization. The fit is quite reasonable considering the level of approximation. The most significant approximation is probably that the bond angles are all 90°, since alteration of these angles could change the angle of interaction of the oxygen p orbital with the metal ion. The best-fit parameters are also listed in Table IV, with error margins calculated from the propagation of experimental errors[27] assumed to be 30 cm^{-1} for the quartets, 10 cm^{-1} for the lower $^2T_{2g}$ peak (30 cm^{-1} for the higher one), and 3 cm^{-1} for the $\{^2E_g, {}^2T_{1g}\}$ doublet positions.

In this analysis, hydroxide ion is found to be a strong π-donor ligand, as expected, and also a much stronger σ-donor than ammonia, a conclusion also reached in a study based primarily on the spin-allowed bands.[10] The value of $e_{\sigma N}$ in $[Cr(NH_3)_5OH](ClO_4)_2$ is markedly lower than in $[Cr(NH_3)_5Cl]Cl_2$ (6510 vs 7150), as determined in a similar study,[5] although some of the electronic assignments used in that study are probably wrong.[6,7] The value of zero for the spin–orbit coupling constant is not significant. The actual value is indeterminate. The influence of spin–orbit coupling on the transition energies and splittings in this complex is dwarfed by other factors. The negligible influence of spin–orbit coupling for this system also leads to the unrealistically large uncertainty from the error propagation calculation.

Because of the interest in the assignment of the lowest-energy doublet (the luminescent state) to tetragonal symmetry labels, we evaluated each of the ten eigenfunctions belonging to the lowest five doublet states by taking the dot products with pure D_4^* eigenfunctions belonging to the ^2E_g and $^2T_{1g}(O_h)$ components.[20]

Table V. D_4^* Parentage Coefficients for the Best-Fit Doublet Eigenfunctions of Table IV.

transition energy[a]	$^2E_g(O_h)$		$^2T_{1g}(O_h)$		
	$^2A_1$	$^2B_1$	$^2A_2$	$^2E'$	$^2E''$
13 683	0.718	0.003	0.162	0.000	0.000
14 320	0.001	0.015	0.000	0.431	0.439
14 376	0.002	0.949	0.001	0.007	0.008
14 807	0.204	0.000	0.764	0.000	0.000
15 186	0.000	0.000	0.000	0.498	0.487

[a] Calculated, from Table IV; in cm^{-1}. [b] See ref 14 for definitions of D_4^* wavefunctions.

Table VI. Experimental and Calculated Electronic Transition Energies for $[Cr(NH_3)_5OH](ClO_4)_2$ Using Güdel's Assignments[a]

excited state	transition energy		D_4^* label
	exptl[b]	calcd[c]	
^2E_g, $^2T_{1g}$	13 676	13 674	$^2A_2$ ($^2T_{1g}$)
	14 766	14 775	$^2E'$ ($^2T_{1g}$)
	14 261	14 233	$^2A_1 + {}^2B_1$ (^2E_g)
	14 322	14 342	$^2B_1 + {}^2A_1$ (^2E_g)
	...	15 074	$^2E''$ ($^2T_{1g}$)
$^2T_{2g}$	...	20 744	
	...	21 957	
	...	21 962	
$^4T_{2g}$		18 386	
	19 600	21 463	
		21 686	
$^4T_{1g}$	25 900	25 442	
		28 305	
	29 000	28 543	

[a] Data in cm^{-1}. [b] Reference 3. [c] Best-fit parameters: $e_{\sigma N} = 7155 \pm 28$, $e_{\sigma O} = 7501 \pm 39$, $e_{\pi O} = 3392 \pm 32$, $B = 785 \pm 17$, $C = 2501 \pm 49$, $\alpha_T = 178 \pm 9$, $\zeta = 4 \pm 93$ (all in cm^{-1}); $\psi = 5.2 \pm 0.2°$.

The results are shown in Table V for the best-fit parameters for $[Cr(NH_3)_5OH](ClO_4)_2$. Although there is significant mixing, the luminescent state is found to have predominantly $^2A_1$ (^2E_g) character, at odds with previous assignments.[3,9] There is some $^2A_2$ ($^2T_{1g}$) character as well, also unexpected. The labels implied by the coefficients in Table V were used in Tables II and III.

The analysis in terms of D_4^* or C_{4v} labels can be misleading in spite of the apparently unambiguous assignments following from Table V. The large anisotropic π-interaction between the hydroxide and the chromium yields an effective symmetry much lower than tetragonal, especially for values of the dihedral angle ψ far from the extremes, such as represented in Table V. When ψ is varied as in Figure 1, the extent to which the C_{4v} states are mixed in the resulting eigenfunctions changes, and the implied labels can change. To be noted from Table V is that the transition energies to the two states derived from the C_{4v} ^2E state ($^2E'$ and $^2E''$ in D_4^*) are separated by 900 cm^{-1}, a much larger splitting than would be expected in near-tetragonal symmetry.

The implied labels in Table V are the same as are obtained for the staggered orientation of the hydroxide at $\psi = 45°$. If ψ is decreased toward 0°, however, the symmetry label for the lowest state gradually changes to $^2A_2$ ($^2T_{1g}$), while the fourth doublet changes to $^2A_1$. These are the two states whose transition energies are predicted to oscillate strongly with the angle ψ.

The original intention of this work was to apply the ligand field apparatus described above to the assignments proposed by Güdel.[3] We later concluded that the vibronic analysis required a considerably different assignment. Nevertheless, the complex nature of vibronic spectra leaves an element of uncertainty to almost every electronic assignment of the Cr(III) doublets. We therefore went ahead with the ligand field optimization for Güdel's assignment of the $\{^2E_g, {}^2T_{1g}\}$ states, keeping the remainder of the spectral assignments the same. The results are shown in Table VI. The $\{^2E_g, {}^2T_{1g}\}$ doublets can be fit fairly well. The fifth doublet was not assigned by Güdel, but this calculation places it close to the position estimated by them. The least-squares error function in eq 7 is approximately 2.7 times higher for the Table VI assignments, even though the unassigned doublet was not included in

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the error calculation. We do not wish to claim that a better fit is necessarily proof for a particular electronic assignment, but we do note that a major reason for the larger error for Güdel's assignment was that the splitting of the $^4A_{2g} \rightarrow {}^4T_{2g}$ band was calculated to be too large. The optimized value of ψ in this case was 5.2°, predicting a nearly eclipsed orientation. The assignment of the doublet states to D_4^* eigenfunctions was similar to Güdel's,[3] in that the lowest two lines were derived from the $^2T_{1g}$ state. However, our analysis assigns the lowest state to $^2A_2$ ($^2T_{1g}$) rather than a ^2E ($^2T_{1g}$) component.

Conclusions. The ligand field asymmetry caused by the strong anisotropic π-interaction with hydroxide ion in $[Cr(NH_3)_5OH](ClO_4)_2$ causes the five sharp-line components of the $^4A_{2g} \rightarrow \{^2E_g, {}^2T_{1g}\}$ transitions to split to such an extent that the association with the octahedral parents is practically unrecognizable, certainly not from the distribution of energy levels and only with caution from an eigenfunction analysis.

Forster has attempted to identify Cr(III) complexes whose lowest, luminescent excited state is derived from the octahedral $^2T_{1g}$ state by an unusually broad phosphorescence in solution.[9,10] A theoretical basis for this is an orbital analysis in the C_{4v} point group, showing that the tetragonal ^2E state derived from O_h $^2T_{1g}$ is the only one of the group $\{^4A_{2g}, {}^2E_g, {}^2T_{1g}\}$ to have a different configuration than the ground state.[7] The present analysis for $[Cr(NH_3)_5OH](ClO_4)_2$ shows no tetragonal ^2E character for the luminescent state, although it is one of the complexes found to exhibit a broad phosphorescence.[8] This does not necessarily contradict Forster's conclusions, since the effective electronic symmetry is not really tetragonal. An orbital population analysis of the type used by Ceulemans[28] yields a configuration of $(xy)^{0.98}(xz)^{0.76}(yz)^{1.23}$ for the lowest doublet state ($^2A_1$). The difference between that and the nearly pure $(xy)(xz)(yz)$ of the ground state could be a source of the broadening. However, it is also possible that hydroxo complexes will exhibit luminescence broadening due simply to the large perturbations in the transition energy, as seen in Figure 1, caused by the zero-point torsional motion of the hydroxide, as long as the luminescent state is one showing oscillatory behavior.

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Synthesis, Absorption Spectra, and Photochemical Behavior of Mono- and Dinuclear Ruthenium(II) Complexes

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Syntheses, characterization, absorption spectra (including their solvent dependence), and photochemical behavior of some novel mono- and dinuclear ruthenium(II) complexes containing 2,3-dpp and 2,5-dpp as bridging ligands (dpp = bis(2-pyridyl)pyrazine) are reported. The complexes are $[Ru(2,n\text{-dpp})(\eta^6\text{-}C_6H_6)Cl]PF_6$ (**1**, $n = 3$; **2**, $n = 5$), $[(\mu\text{-}2,n\text{-dpp})[Ru(\eta^6\text{-}C_6H_6)Cl]_2](PF_6)_2$ (**3**, $n = 3$; **4**, $n = 5$), and $[Cl(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}2,n\text{-dpp})Ru(CO)_2Cl_2]PF_6$ (**5**, $n = 3$; **6**, $n = 5$). For comparison purposes, the same properties of some closely related mono- and dinuclear ruthenium(II) complexes are also reported. The absorption spectra of all the complexes show intense ligand-centered (LC) bands in the UV region and broad, moderately intense, metal-to-ligand charge-transfer (MLCT) bands in the visible region. In the heteroligated dinuclear complexes two different MLCT transitions are expected, but only one absorption maximum is present in the spectra because the metal fragments exhibit similar chromophoric properties. The energy position of the MLCT band is practically unaffected by solvent polarity in the complexes that do not contain carbonyl ligands, whereas for the other complexes a small red shift is observed in low-polarity solvents. The two heteroligated complexes are strongly photosensitive in fluid solution, with release of a CO ligand. Quantum yields for the reactant disappearance are 0.2 and 0.01 for 2,3-dpp and 2,5-dpp complexes, respectively. The differences in the quantum yields are attributed to intramolecular energy transfer from the reactive $Ru(CO)_2Cl_2$ to the unreactive $Ru(\eta^6\text{-}C_6H_6)Cl$ moiety, which competes with the photoreaction in the 2,5-dpp complex.

Introduction

Photophysical and photochemical properties of N-heterocyclic ruthenium(II) complexes have been the object of extensive investigations in the last 15 years because of their outstanding interest for theoretical purposes and potential applications. In particular, Ru(II)-polypyridine complexes have been used as reactants and/or mediators in light-induced and light-generating electron-transfer processes.[2-4] In recent years there has been a further growth of interest in these complexes[5-13] because they can be used as building blocks to design (i) more complex systems capable of performing useful light-induced functions ("photochemical molecular devices"[14]) and (ii) multielectron-transfer catalysts.[11-16]

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