

dium/benzophenone and CaH_2 , respectively, and stored under argon in Schlenk vessels. All reactions were conducted under argon by using Schlenk techniques.²⁴

Low-temperature infrared spectra were recorded on a Nicolet 20SXB FT-IR spectrometer with a Specac Model P/N 21.000 variable-temperature cell equipped with inner and outer CaF_2 windows. Solutions for analysis were transferred to the precooled IR cell via cannulation from an external Schlenk vessel maintained at -78°C . The transfer cannula was wrapped in dry ice to prevent undue warming. Dry ice/acetone was used as coolant, and the reported cell temperature, taken to be accurate to $\pm 1^\circ\text{C}$, was determined with a copper-constantan thermocouple. The ^{13}C NMR spectrum was recorded at 75 MHz on a Varian 300-VXR spectrometer.

Since the acid and ester carbonyl stretching bands exhibit partial overlap, the infrared band shapes of these CO bands were calculated by using a numerical procedure in order to determine the ratio of their areas. Absorbances were digitized from 1650 to 1550 cm^{-1} at 1- cm^{-1} intervals and entered into files on the university VAX 11/85 computer. Following baseline correction, the spectra were fit by a model consisting of Lorentzian band shapes, each characterized by a peak frequency (ν), maximum intensity (I), and half-width [fwhh] (Δ). Since the instrument resolution (2 cm^{-1}) is far less than the observed bandwidths ($\sim 20 \text{ cm}^{-1}$), it was unnecessary to convolute the model spectrum with a resolution (slit) function. The parameters were varied to minimize the squared deviation between the experimental and calculated intensities by using a nonlinear regression procedure.²⁵ A representative experimental and calculated spectrum of [1] and [2] at -70°C is shown in Figure 1B. Given that the area of a Lorentzian peak is proportional to the product of the bandwidth and the maximum intensity, the area ratio of the different anions is calculated easily as $A_2/A_1 = (I_2\Delta_2)/(I_1\Delta_1)$.

Reaction of $\text{Fe}(\text{CO})_5$ with $[\text{Et}_4\text{N}][\text{OH}]$. To 5.0×10^{-3} mL of $\text{Fe}(\text{CO})_5$ (0.038 mmol) in 10 mL of THF at -78°C was added 2.9×10^{-2} mL of a 1.3 M methanolic $[\text{Et}_4\text{N}][\text{OH}]$ solution. The reaction leading to [1] $[\text{Et}_4\text{N}]$ and [2] $[\text{Et}_4\text{N}]$ was instantaneous based on low-temperature IR analysis. IR (-70°C , THF) ν_{CO} : 2022 (m), 1922 (m), 1908 (vs), 1897 (s), 1621 (vw, ester), 1604 (w, acid) cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR [-78°C , THF/ C_6D_6 3:1 (v/v)]: δ 213.8 (1 C, COOH), 220.2 (4 C, broad, terminal carbonyls). Note: the resonances associated with [2] $[\text{Et}_4\text{N}]$ were not observed due to their low concentration relative to [1] $[\text{Et}_4\text{N}]$.

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Crossover from Metal-Centered to Ligand-Centered Emission in Rhodium(III) Polypyridine Complexes: $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+}$, $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$, $\text{Rh}(\text{phen})_2(\text{CN})_2^+$

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With respect to the enormous amount of work performed in recent years on the photophysics of ruthenium(II) polypyridine compounds,¹ relatively little attention has been devoted to analogous complexes of rhodium(III).²⁻¹¹

Among Rh(III) polypyridine complexes, the best studied case is that of the tris(1,10-phenanthroline)rhodium(III) ion, $\text{Rh}(\text{phen})_3^{3+}$, which exhibits in 77 K matrices an intense ($\Phi \approx 1$)³ structured ligand-centered (LC) phosphorescent emission.²⁻⁵ An interesting observation (first made by Bolletta et al.⁶ and later confirmed in other laboratories^{7,8}) is that the exceedingly weak emission detectable in room-temperature solutions of this complex consists mainly of a broad band assignable to a metal-centered (MC) d-d transition. This was explained on the basis of fast equilibration at room temperature between the lowest LC triplet state and a thermally accessible upper MC state.⁶⁻⁸ This experimental result was subsequently questioned by Watts,⁹ who attributed the broad-band emission observed by the other groups to impurities.

In order to contribute to the understanding of the photophysical behavior of Rh(III) polypyridine complexes, we have now studied some mixed-ligand complexes of the type *cis*- $\text{Rh}(\text{phen})_2\text{XY}^{n+}$ ($\text{X} = \text{Y} = \text{CN}$, $n = 1$; $\text{X} = \text{Y} = \text{NH}_3$, $n = 3$; $\text{X} = \text{NH}_3$, $\text{Y} = \text{Cl}$, $n = 2$). The approach is that of using the X and Y ligands (hereafter called ancillary ligands) to change the energy of the MC states in a predictable way without substantially affecting that of the LC state and to look for qualitative effects of the change in the LC-MC energy difference on the emission properties of these complexes.

Experimental Section

Materials. Rhodium(III) chloride hydrate, 1,10-phenanthroline, hydrazine hydrate, and ethylene glycol were commercial products (Fluka) of reagent grade. Tetrastilled water was used throughout.

Syntheses. The starting material for the synthesis of the complexes, $[\text{Rh}(\text{phen})_2\text{Cl}_2]\text{Cl}$, was prepared according to literature procedures.¹²

$[\text{Rh}(\text{phen})_2(\text{CN})_2]\text{Cl}$. This complex was prepared and purified with the procedure described by Gillard.¹² Anal. Calcd for $[\text{Rh}(\text{phen})_2(\text{CN})_2]\text{Cl} \cdot 2\text{H}_2\text{O}$: C, 53.21; H, 3.44; N, 14.32. Found: C, 52.38; H, 3.41; N, 13.83.

$[\text{Rh}(\text{phen})_2\text{Cl}(\text{NH}_3)](\text{PF}_6)_2$ and $[\text{Rh}(\text{phen})_2(\text{NH}_3)_2](\text{PF}_6)_3$. These two complexes were synthesized by the Gillard method¹² with appropriate modifications, particularly concerning purification procedures.

$[\text{Rh}(\text{phen})_2\text{Cl}(\text{NH}_3)](\text{PF}_6)_2$. To an aqueous solution (10 mL) containing 0.15 g of $[\text{Rh}(\text{phen})_2\text{Cl}_2]\text{Cl}$ was added 0.5 mL of NH_3 (25%). The reaction mixture was boiled for 30 min. An excess of NaClO_4 (0.2 g) was added to the cooled solution, which was concentrated until crystallization. The product was redissolved in water and purified by ion-exchange chromatography with cationic CM-Sephadex C-25 resin. Some unreacted $\text{Rh}(\text{phen})_2\text{Cl}_2^+$ was first eluted with 0.05 M NaHCO_3 ; then the desired product was collected with 0.2 M NaHCO_3 as eluant. The eluted solution was concentrated, and precipitated NaHCO_3 was eliminated by filtration. Then the product was precipitated by addition of NH_4PF_6 to the solution. Finally, the resulting pale yellow product was recrystallized from water; 70% yield. Anal. Calcd for $[\text{Rh}(\text{phen})_2\text{Cl}(\text{NH}_3)](\text{PF}_6)_2$: C, 35.78; H, 2.38; N, 8.69. Found: C, 34.70; H, 2.27; N, 8.51.

$[\text{Rh}(\text{phen})_2(\text{NH}_3)_2](\text{PF}_6)_3$. To an aqueous solution (10 mL) containing 0.15 g of $[\text{Rh}(\text{phen})_2\text{Cl}_2]\text{Cl}$ were added a large excess (2 mL) of NH_3 (25%) and a catalytic amount of hydrazine hydrate (0.001 g). The reaction mixture was boiled for 5 min. To the cooled solution was added 0.2 g of NaClO_4 , and the resulting solution was allowed to stand at 5°C for a few days. The resulting brown precipitate was removed by filtration and dissolved in water, and the solution was loaded onto a cationic CM-Sephadex C-25 column. Uncharged impurities were first eluted with water; then elution was continued with successive aliquots of 0.05 and 0.2 M NaHCO_3 solutions to remove $\text{Rh}(\text{phen})_2\text{Cl}_2^+$ and $\text{Rh}(\text{phen})_2\text{Cl}(\text{NH}_3)^{2+}$, respectively. Finally, the desired colorless product was eluted with 0.5 M NaHCO_3 , precipitated with NH_4PF_6 , and recrystallized from water; 50% yield. Anal. Calcd for $[\text{Rh}(\text{phen})_2(\text{NH}_3)_2](\text{PF}_6)_3$: C, 30.92; H, 2.38; N, 9.01. Found: C, 29.91; H, 2.21; N, 8.70.

The values of the elemental analyses for C, N, and H are all somewhat low but are in the correct ratio, suggesting the presence of some ($\leq 4\%$) NaCl or NaPF_6 in the analyzed samples. The spectra (λ_{max} and ϵ_{max})

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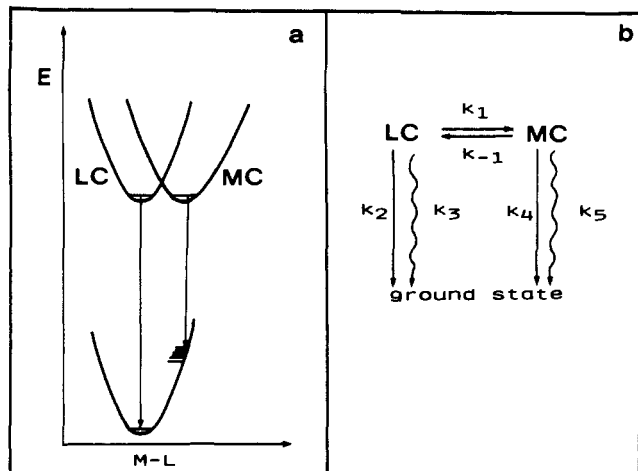


Figure 1. (a) Potential energy curves for a Rh(III) polypyridine complex (relative energy ordering of LC and MC states depending on the complex). (b) Kinetic scheme where interconversion of the excited states (k_1 , k_{-1}) and radiative (k_2 , k_4) and radiationless (k_3 , k_5) deactivation processes are considered.

of all the complexes agreed with those given by Gillard.¹²

Apparatus. The emission spectra (Perkin-Elmer MPF 44E spectrofluorometer equipped with a R928 Hamamatsu tube) were taken by exciting at 350 nm and were corrected for instrumental response by using an NBS standard lamp. Emission lifetimes and ESA spectra were measured by using a laser-flash photolysis apparatus (Applied Photophysics detection system coupled with a frequency-doubled J&K System 2000 ruby laser, pulse half-width 20 ns).

Results and Discussion

The photophysical behavior of Rh(III) polypyridine complexes can be discussed in terms of two relevant low-energy excited states: (i) the lowest state centered on the polypyridine ligands (LC triplet) and (ii) the lowest state centered on the metal (MC triplet). Potential energy curves of these two states as a function of metal-ligand stretching are sketched in Figure 1a to emphasize the distorted nature of the MC state vs the undistorted character of the LC state. A kinetic scheme taking into consideration the interconversion and deactivation processes of these two states is given in Figure 1b.

The emission spectra obtained at 77 K in 50% water/ethylene glycol matrices are plotted on a normalized arbitrary intensity scale in Figure 2, showing a sharp structured band shape for $\text{Rh}(\text{phen})_2(\text{CN})_2^+$ and $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ and a broad structureless band shape in the case of $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+}$. The lifetimes of these emissions at 77 K are as follows: $\text{Rh}(\text{phen})_2(\text{CN})_2^+$, 70 ms; $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$, 30 ms; $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+}$, 70 μs . The energies, band profiles, and lifetimes of these emissions, when compared with those of previously studied cases,^{2-5,13,14} dictate the following assignments: LC for $\text{Rh}(\text{phen})_2(\text{CN})_2^+$ and $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$; MC for $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+}$. In this series of complexes, the energy of the LC state is practically independent of the nature of the ancillary ligands, as shown by the almost coincident emission spectra of $\text{Rh}(\text{phen})_2(\text{CN})_2^+$ and $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ (Figure 2). That of the MC state, on the other hand, depends on the ligand field strength of the ancillary ligands, increasing in the order $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+} < \text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+} < \text{Rh}(\text{phen})_2(\text{CN})_2^+$. Evidently, the zero-zero energy of the LC state is intermediate between those of the MC states of $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+}$ and $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$.

For $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+}$, increasing the temperature from 77 K toward room temperature caused a gradual decrease in the intensity and lifetime of the emission, with no substantial change in band shape. At room temperature the complex was practically nonluminescent. This behavior is typical of MC phosphorescence of Rh(III) complexes^{2,13-16} and is probably associated with ac-

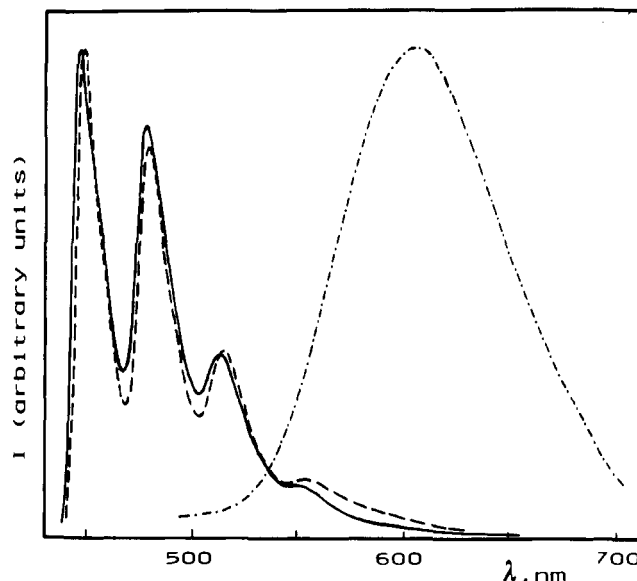


Figure 2. Low-temperature (77 K) emission spectra in 50% water/ethylene glycol glasses of $\text{Rh}(\text{phen})_2(\text{CN})_2^+$ (—), $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ (---), and $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}^{2+}$ (-·-·).

tivated crossing of the MC state with ground-state surfaces, i.e., with the temperature dependence of k_5 . Taking the zero-zero energy of the MC state from the onset¹⁷ of the broad emission band and that of the LC state from the first maximum of the structured bands in Figure 2, the energy gap between the minima of MC and LC states is estimated to be $0.34 \mu\text{m}^{-1}$. This would suggest that thermal population of the upper LC state via the k_{-1} process at higher temperatures is very inefficient in this complex.

For $\text{Rh}(\text{phen})_2(\text{CN})_2^+$, increasing the temperature from 77 K toward room temperature caused a gradual decrease in the intensity and lifetime of the emission, with no substantial change in band shape. At room temperature, a very weak emission was detected as a distinct structured band superimposed on the scattered light of the spectrofluorometer. By the use of pulsed laser excitation to time-resolve emission from scattered light, a reasonably clean emission spectrum (Figure 3a) could be obtained for this complex. Despite some broadening of the structure, this emission is still clearly LC in character. The emission decayed as a single exponential with a lifetime of 1.2 μs in aqueous solution at 298 K. Laser-flash photolysis experiments revealed the presence of an intense transient absorption signal that decayed with the same kinetics and lifetime as the emission and can thus be assigned to excited-state absorption (ESA). The ESA spectrum (Figure 3b) is coincident with that previously obtained for $\text{Rh}(\text{phen})_3^{3+}$ and confirms the LC assignment. Evidently, in this complex the MC state is sufficiently higher in energy with respect to the LC state that even at room temperature its fractional population is exceedingly small ($<10^{-4}$) and no MC emission occurs. This is also likely the reason for the long lifetime of the $\text{Rh}(\text{phen})_2(\text{CN})_2^+$ excited state in room-temperature solutions.

For $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$, increasing the temperature from 77 K to room temperature also caused a gradual decrease in intensity and lifetime, but in this case the decrease was accompanied by a substantial change in band shape. This is shown in Figure 4a, where the spectra at two different temperatures are normalized to the same intensity of the highest energy maximum. The temperature range in which this phenomenon can be analyzed is relatively narrow (approximately 170–200 K), as at lower temperatures the band shape is practically coincident with the 77 K one while at higher temperatures the analysis becomes difficult because of the weakness of the emission compared with the level of diffuse light. Over this useful temperature range, the emission

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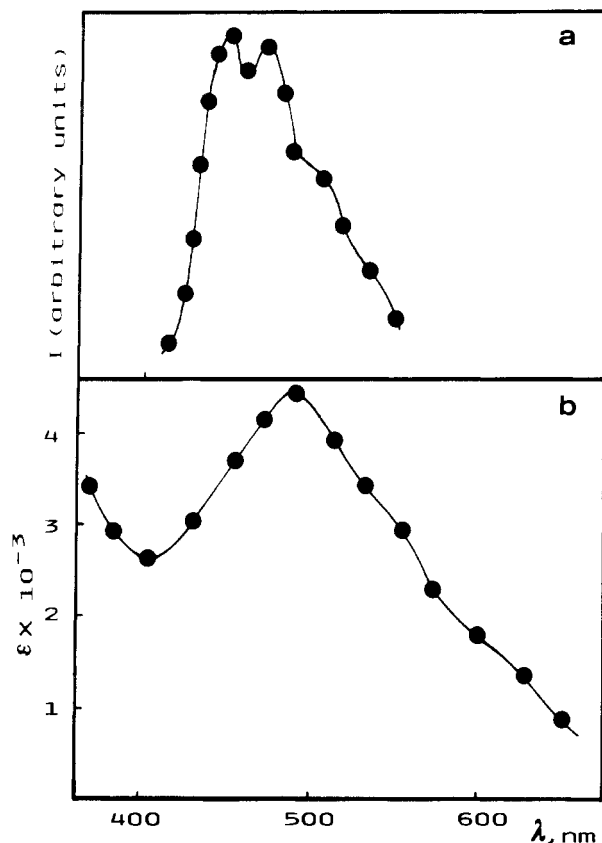


Figure 3. (a) Emission spectrum (see text) and (b) ESA spectrum of $\text{Rh}(\text{phen})_2(\text{CN})_2^+$ at room temperature in aqueous solution.

spectra can be analyzed as the superposition of a structured band with a 77 K like profile and a broad structureless band (Figure 4b). The relative importance of the structureless component increases with increasing temperature. The ratio between the areas (wavenumber scale) of the structureless and structured components gives an appreciably linear Arrhenius-type plot. Within the large error limits due to the narrow temperature range, the apparent activation energy and the preexponential factor are $0.11 \pm 0.02 \mu\text{m}^{-1}$ and $\sim 10^3$, respectively. In the 150–200 K temperature range, the lifetimes of the structureless and structured component, while decreasing with increasing temperature, are always coincident. At room temperature, the complex is practically nonemitting.

The behavior of $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ in the 170–200 K temperature range clearly indicates the presence of *both* LC and MC emissions, with a MC/LC intensity ratio that increases with temperature. The identical lifetimes obtained for the two emissions probably indicate that the two states are in thermal equilibrium, i.e., $k_1 > (k_2 + k_3)$ and $k_{-1} > (k_4 + k_5)$.¹⁸ In this hypothesis, the experimental "activation energy" ($0.11 \pm 0.02 \mu\text{m}^{-1}$) of the MC/LC intensity ratio corresponds to the energy difference between the LC and MC states, and the preexponential factor ($\sim 10^3$) to the ratio of the radiative rate constants of the two states, k_4/k_2 , neglecting entropy terms.¹⁸ It is indeed known^{13,19} that radiative rate constants for MC emissions are 2–3 orders of magnitude larger than those of LC phosphorescence of Rh(III) complexes. This explains why the MC emission can be observed even when, as in this case, the equilibrium fractional concentration

(18) There is another limiting case in which the kinetic scheme of Figure 1b predicts identical lifetimes for the two emissions even in the absence of equilibrium ($(k_4 + k_5) > k_{-1}$): that in which the decay of MC is much faster than the MC \rightarrow LC conversion ($(k_4 + k_5) > k_1$). In this case, the experimental "activation energy" of the intensity ratio would correspond to the difference between the activation energies of the k_1 and k_3 processes, and the preexponential factor would be equal to $(k_4/k_2)R$ where R is the ratio of the preexponential factors of k_1 and k_3 .

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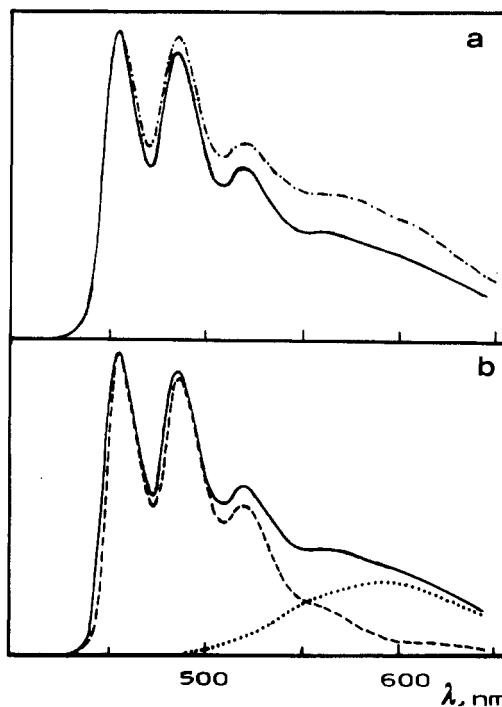


Figure 4. (a) Emission spectra of $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ at 177 K (—) and 186 K (---). (b) Analysis of the spectrum at 177 K as superposition of LC (···) and MC (---) component bands.

of this state is very small. It is expected that the fractional population of the MC state will further increase in going toward room temperature, although its observation is then hampered by the overall decrease in lifetime and intensity. The conclusion is that in $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ the MC excited state is sufficiently close in energy to the lowest LC state to be thermally accessible and give rise to observable dual emission. From this point of view, the behavior of $\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ resembles that of $\text{Rh}(\text{phen})_3^{3+}$, for which thermal population of the MC state and dual emission were previously observed.^{6–8}

This work shows that, in complexes containing the $\text{Rh}(\text{phen})_2^{3+}$ chromophoric unit, it is possible to tune the MC–LC energy gap by a suitable choice of the ancillary ligands so as to go from MC emitters ($\text{Rh}(\text{phen})_2\text{Cl}_2^+$ and $\text{Rh}(\text{phen})_2(\text{NH}_3)\text{Cl}_2^+$) to LC emitters ($\text{Rh}(\text{phen})_2(\text{CN})_2^+$) through complexes that, in an appropriate temperature range, exhibit dual LC and MC emission ($\text{Rh}(\text{phen})_2(\text{NH}_3)_2^{3+}$ and $\text{Rh}(\text{phen})_3^{3+}$).

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Crystal Structure of $\text{SF}_5\text{CHCF}_2\text{OSO}_2$

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Introduction

The preparation, reactions, and structure of β -fluorosulfones are of considerable interest to chemists. Previously, we reported

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