Low Temperature Luminescence Properties of Mono- and Dinuclear Tetraamine Complexes of Rhodium(III) and Iridium(III)

MARK E. FRINK,[a] PETER C. FORD[a] and L. H. SKIBSTED[b]

[a] Department of Chemistry and Quantum Institute, University of California, Santa Barbara, California 93106, USA and [b] Chemistry Department, Royal Veterinary and Agricultural University, Thorvaldsensvej 40, DK-1871 Copenhagen V, Denmark

Solid state, 77K, photoluminescence spectra and emission lifetimes for several mono- and dinuclear "tetraamine" rhodium(III) complexes are reported ("tetraamine"=A_4=$(NH_3)_4$, $(en)_2$ or $(tn)_2$; en=ethylenediamine, tn=1,3-propanediamine). For the dihalo complexes $[Rh(tn)_2X_2]ClO_4$; (X=Cl or Br), the *trans* complexes showed smaller Stokes shifts of emission maxima from lowest energy absorption maxima (both assigned as ligand field transitions) as well as longer excited state lifetimes than do the analogous *cis* complexes. The difference in lifetimes is interpreted in terms of possible nonradiative deactivation mechanisms and media effects on these pathways. The photophysical properties of these complexes closely mimic those of the $[Rh(NH_3)_4X_2]X$ analogs, an indication that the ligand field strengths of $(NH_3)_4$ and $(tn)_2$ are comparable. The photophysical properties of several *cis* and *trans* aquo(hydroxo)"tetraamine" rhodium(III) complexes as well as the dinuclear "diols" $[A_4Rh(\mu\text{-}OH)_2RhA_4](ClO_4)_4$ [A_4= $(NH_3)_4$ or $(en)_2$] and $[(en)_2Ir(\mu\text{-}OH)_2Ir(en)_2]$-$(ClO_4)_4$ are also described.

Earlier investigations have shown that electronic excitation of haloamine complexes of rhodium(III) and iridium(III) leads to weak emissions from the lowest energy ligand field (LF) excited states.[1-4] Such emissions usually are quite weak, and reliable luminescence spectra often can only be recorded at low temperatures. At 77 K such spectra generally are broad gaussian-shaped bands, and the emission lifetimes are in the microsecond range. The same complexes are photoactive toward ligand substitution reactions in ambient temperature, fluid solutions, and the excited state(s) considered responsible for the photoreaction chemistry have been concluded to be the same low energy "triplet" LF states from which emission originates.[5] Thus, the low temperature emission properties provide information relevant to the photochemical properties (*e.g.*, the energies of the lowest energy LF states as functions of ligand identity and stereochemistry) as well as being of intrinsic interest in terms of photophysical phenomena. In this context, we report the 77 K emission spectra and lifetimes of several related mononuclear and dinuclear rhodium(III) complexes and compare these properties to an analogous iridium(III) dinuclear complex.

EXPERIMENTAL

Materials. $[Rh(NH_3)_4(\mu\text{-}OH)_2Rh(NH_3)_4]$ $(ClO_4)_4,2H_2O$,[6] the ethylenediamine compounds *trans*-$[Rh(en)_2(H_2O)(OH)](ClO_4)_2$,[7] *cis*-$[Rh(en)_2(H_2O)(OH)]S_2O_6$,[6] $[Rh(en)_2(\mu\text{-}OH)_2$-$Rh(en)_2](ClO_4)_4$,[6] and $[Ir(en)_2(\mu\text{-}OH)_2Ir(en)_2]$-$(ClO_4)_4$,[8] and the 1,3-propanediamine complex salts *trans*- and *cis*-$[Rh(tn)_2(H_2O)(OH)](ClO_4)_2$,[9] and *trans*- and *cis*-$[Rh(tn)_2X_2]ClO_4 \cdot xH_2O$ (X= Cl or Br)[10] were all synthesized and purified by published methods.

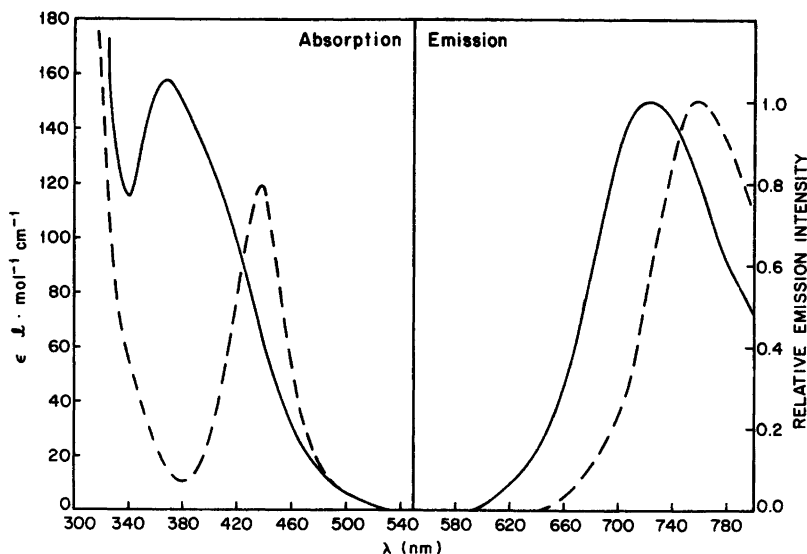Luminescence experiments were carried out on samples prepared as KBr pellets as previously

described. The complexes as the microcrystalline salts were mixed with powdered KBr (1–4 % sample/KBr) and these samples were pressed into pellets under vacuum with a Carver Laboratory Press. The KBr (Mallinckrodt) used was "Infrared Grade" and was oven dried before use. For spectral measurements, each pellet was held between two quartz plates in a stainless steel holder and immersed in liquid nitrogen.

Instrumentation. Luminescence lifetimes and emission spectra were obtained using a DCR-1A Nd/YAG laser as the excitation source with the detection system and analysis methods previously described.[12] Excitation wavelengths of 355 and 266 nm were used and emission spectra were corrected for photomultiplier response.

RESULTS AND DISCUSSION

The emission spectrum of each of the complexes studied showed a broad structureless band, gaussian in shape (see Fig. 1). The energies of the peak maximum (ν_{max}) and width at half height ($\nu_{½}$) for the emission bands from each complex studied are summarized in Tables 1 and 2. Also listed are ν_{o-o} values, which are estimates of the 0−0 transition energy for these complexes as calculated according to the equation:[3]

$$\nu_{o-o} = \nu_{max} + 1.29\nu_{½} \qquad (1)$$

Lifetime measurements showed that the emissions decayed according to simple exponential behavior with the exception of the two *trans*-aquohydroxo complexes *trans*-[Rh(tn)₂(H₂O)(OH)](ClO₄)₂ and *trans*-[Rh(en)₂(H₂O)(OH)](ClO₄)₂. The emission lifetimes of the complexes showing normal exponential behavior were calculated by linear-regression after a logarithmic transformation of the emission intensity at the emission maximum as illustrated in Fig. 2.[12]

Table 1 compares the photophysical properties of the 1,3-propanediamine complexes Rh(tn)₂X₂⁺ to those of the analogous tetraammines.[13] Under these conditions (77 K, solid salts) the emission properties for the two series are quite similar, *i.e.*, the lifetimes of the analogous (tn)₂ and (NH₃)₄ complexes are nearly identical, while the ν_{max} (and ν_{o-o}) values for the tetraammines are consistently larger by a small amount. These observations suggest the comparable ligand field strengths of (tn)₂ and (NH₃)₄.

Table 1. Emission lifetime and emission and absorption spectra for bis(1,3-propanediamine)- and tetraamminerhodium(III) complexes.

Complex	Bis(1,3-propanediamine)[a] Emission[c]				Absorption[d]	Tetraammine[b] Emission[c]				Absorption[d]
	τ μs	ν_{max} μm⁻¹	$\Delta\nu_{½}$ μm⁻¹	ν_{o-o} μm⁻¹	ν_{max} μm⁻¹	τ μs	ν_{max} μm⁻¹	$\Delta\nu_{½}$ μm⁻¹	ν_{o-o} μm⁻¹	ν_{max} μm⁻¹
trans-[RhA₄Cl₂]⁺	7.3	1.34	0.24	1.65	2.39	6.9	1.37	0.31	1.77	2.42
cis-[RhA₄Cl₂]⁺	2.0	1.35	0.27	1.70	2.83	2.3	1.42	0.29	1.79	2.78
trans-[RhA₄Br₂]⁺	8.1	1.32	0.17	1.54	2.27	8.2	1.36	0.26	1.70	2.29
cis-[RhA₄Br₂]⁺	2.4	1.38	0.26	1.71	2.72	2.2	1.41	0.31	1.81	2.65

[a] A₄=(tn)₂, perchlorate salts. Absorption data from Ref. 10. [b] A₄=(NH₃)₄, halide salts. Emission data from Ref. 13, absorption data from Refs. 17 and 18. [c] 1–4 % in KBr pellets at 77 K. Experimental precision on emission lifetimes 10 % or better. [d] Lowest energy ligand field band. Dilute aqueous solution at room temperature.

Fig. 1. Absorption spectra of the lower energy ligand field band plus the normalized emission spectra of *cis*-[Rh(tn)$_2$Br$_2$]ClO$_4$ (solid line) and *trans*-[Rh(tn)$_2$Br$_2$]ClO$_4$ (dashed line). Absorption spectra in 298K aqueous solution, emission spectra in 77 K KBr pellets.

For both series, it is seen that lifetimes are relatively insensitive to whether X=Cl or Br, but the *trans* complexes consistently have longer lifetimes by a factor of 3−4 than do the respective *cis* complexes. {An analogous difference between *cis* (0.21 ns) and *trans* (0.94 ns) geometries has been found for the lifetimes of the iridium(III) complexes *cis*- and *trans*- [Ir(en)$_2$Cl$_2$]Cl · H$_2$O}.[14] The difference between the stereoisomers may lie in the greater symmetry of the *trans* complexes with a D_{4h} coordination environment and a ^3E lowest energy LF state as compared to the C_{2v} symmetry and $^3B_1$ lowest energy LF state of the *cis* complexes.

Given that, for these complexes in the low temperature rigid media, emission is weak and

Table 2. Emission lifetime and emission and absorption spectra for Hydroxoaquatetraamine- and Dinuclear Hydroxobridged Tetraamine Rhodium(III) and Iridium(III).

Complex	Emission[a]				Absorption[b]
	τ μs	v_{max} μm^{-1}	$\Delta v_{1/2}$ μm^{-1}	v_{0-0} μm^{-1}	v_{max} μm^{-1}
trans-[Rh(en)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$	2−5[c]	1.46	0.28	1.82	2.91
cis-[Rh(en)$_2$(H$_2$O)(OH)]S$_2$O$_6$	3.2	1.43	0.32	1.85	3.10
trans-[Rh(tn)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$	4−6[c]	1.46	0.29	1.82	2.87
cis-[Rh(tn)$_2$(H$_2$O)(OH)](ClO$_4$)$_2$	2.5	1.40	0.26	1.74	3.08
cis-[Rh(NH$_3$)$_4$(H$_2$O)(OH)]$^{2+d}$	5.0	1.44	0.30	1.82	3.04
[(NH$_3$)$_4$Rh(OH)$_2$Rh(NH$_3$)$_4$](ClO$_4$)$_4$,2H$_2$O	0.42	1.41	0.31	1.81	2.98
Δ,Λ-[(en)$_2$Rh(OH)$_2$Rh(en)$_2$](ClO$_4$)$_4$	0.67	1.36	0.32	1.76	3.02
Δ,Λ-[(en)$_2$Ir(OH)$_2$Ir(en)$_2$](ClO$_4$)$_4$	0.038	1.30	0.36	1.77	3.69

[a] 1−4 % in KBr pellets at 77 K. Experimental precision on emission lifetimes 15 % or better except where otherwise noted. [b] Lowest energy ligand field band. 1 M NaClO$_4$ aqueous solution at room temperature from Refs. 6−9. [c] Non-exponential decay. The limits correspond to the limiting slopes in a logarithmic plot; *cf.* Fig. 2. [d] In 4:1 CH$_3$OH/H$_2$O glass at 77 K, Ref. 12.
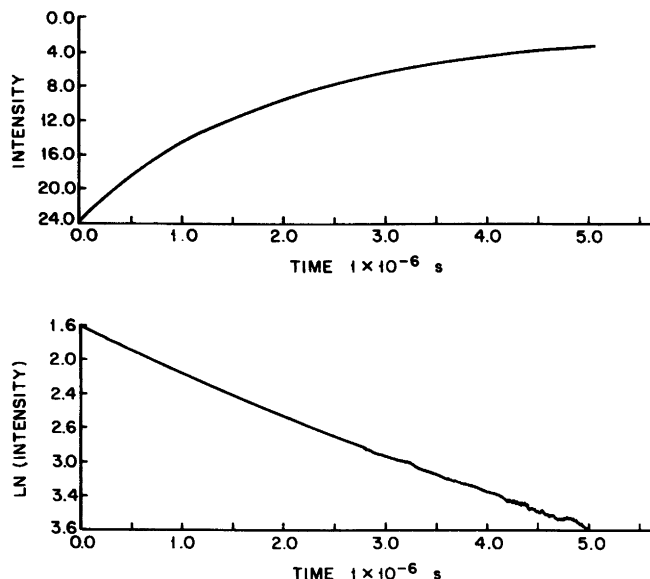
Fig. 2. Upper: Emission decay curve for cis-[Rh(tn)$_2$Br$_2$]ClO$_4$ plotted as the emission intensity (monitored at 720 nm) vs. time. Lower: The same data plotted as the ln (intensity) vs. time giving a slope of 4.43 · 10^5 s^{-1} (τ=2.26 μs) with a linear correlation of 0.9989. The data plotted is a signal averaged (by computer) for 64 excitation pulses at λ_{ex}=355 nm. Sample in KBr pellet at 77 K.

photoreactions are indetectably small, the predominant mechanisms for depletion of the excited state are nonradiative deactivations. Thus for the present systems the lifetime can be approximated as $\tau=(k_n)^{-1}$, where k_n is the rate constant for nonradiative deactivation. Changes in the coordination sphere leading to perturbations of the lifetime thus are largely the result of perturbations in the nonradiative mechanisms. The relative insensitivity of the RhA$_4$X$_2$$^+$ lifetimes to whether X=Cl or Br suggests that the differences in the ligand field strengths or spin orbit coupling constants of these two halides are minor compared to other parameters (such as the metal ion spin-orbit coupling constants or excited state symmetries) dominating the deactivation mechanisms.

Thus, k_n for the Ir(III) complexes is much larger than for similar Rh(III) ions, a fact consistent with the much larger spin-orbit coupling constant of the heavier metal. The same argument (greater spin orbit coupling) may be applied to explain the short lifetimes of the dinuclear "diol" ions. However, the failure to find emission sufficient to measure lifetimes of mononuclear cis-dihydroxo complexes prevents

direct comparison to single metal analogs.

Nonradiative decay mechanisms for such complexes have been discussed in terms of weak coupling and strong coupling limits, the former predicted to behave according to the energy gap law.[15,16] For such cases where $d-d$ emission lifetimes appear to be dominated by weak coupling mechanisms, plots of ln(k_n) vs. ν_{max} have been shown to be linear with negative slopes as predicted by the energy gap law. In the present case, such a plot for the cis complexes does appear to be linear with a negative but very small slope. In contrast, the trans complexes show, if anything, an opposite correlation, k_n values decreasing somewhat with a decreasing energy gap. Thus, it appears that the dominant mechanisms for deactivation at these low temperatures may differ for the cis and trans ions. Notably, for the dihalo ions, room temperature photochemical experiments in solution all show the cis ions to be dramatically more photoactive than the trans analogs, suggesting that one factor influencing the low temperature 77 K emission lifetimes is a strong coupling mechanism contributing more to deactivation for the cis than for the trans ions.[19]

Another major difference between the cis and

trans complexes may be in their interactions with the medium. The partial molar volumes of the *cis* and *trans* isomers of $Rh(NH_3)_4Cl_2^+$ and $Rh(NH_3)_4Br_2^+$ have been measured in aqueous solution, and in each case the *cis* isomer has the smaller $\bar{V}$ value by more than 16 cm^3/mol.[20] This observation suggests that the *cis* complexes are more strongly solvated owing to the less symmetrical distribution of charge within the complex. A consequence of this may be a more efficient coupling to the proton modes of the medium and hence more efficient noradiative deactivation. Notably, the emission lifetimes of the *cis* tetraamine complexes have been shown to be much more dependent on the nature of the medium, even at the same temperature (77 K), than the corresponding *trans* complexes.[21]

Comparisons of the spectral features for *cis*- and *trans*-dihalo pairs (Table 1) also show that the *cis* complexes of both series consistently have the slightly higher energy emission maxima (and ν_{0-0} values). However, the energy differences between the emission maxima of analogous *cis*- and *trans*- complexes are much smaller than found for the absorption maxima (Fig. 1) where the ν_{max} values for the lowest energy LF absorption band are an average 0.4 μm^{-1} larger for the *cis* configuration. These differences suggest that the *cis* complexes in the thermally equilibrated excited state (triplet LF state) may be more distorted from their ground state configurations than are the *trans* analogs. Again this observation is consistent with the greater reactivities of the *cis* complexes toward photosubstitution and the proposed strongly coupled contribution to nonradiative deactivation.

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