Inorg. Chem. **1993,** *32,* 5629-5632

Luminescence of Rhenium(I) Complexes with Highly Sterically Hindered α-Diimine Ligands

Arden P. Zipp,[*,†] LouAnn Sacksteder,[‡] Julie Streich,[‡] Andrew Cook,[†] J. N. Demas,[*,‡] and B. A. DeGraff[*,§]

Chemistry Departments, State University of New York,
Cortland, New York 13045, University of Virginia,
Charlottesville, Virginia 22901, and James Madison
University, Harrisonburg, Virginia 22807

Received October 28, 1992

Introduction

Luminesence-based probes and sensors are of great interest because of their high sensitivity and potential specificity. Fiber-optic-based luminescence sensors are presently used to measure O_2, pH, pCO_2, temperature, and immunoassay results.[1-4] Luminescence probes based on α-diimine complexes of platinum group metals, in particular, show great promise. The ligands and metal can be systematically varied to change spectroscopic and chemical properties.[5-8] The use of α-diimines that are sterically hindered in the position adjacent to the ring nitrogens (2,9 in 1,10-phenanthroline, phen) results in Os(II) and Ru(II) complexes with very low or nonexistent room-temperature luminescence yields. This has discouraged[9] work on other sterically hindered d^6 systems.

Luminescence of complexes is critically dependent on the proper excited-state ordering and spacing,[5-7] and the primary cause for the poor luminescence of hindered RuL_2L' complexes (L and L' are bidentate) is probably that steric crowding forces ligands into unfavorable geometries for good ordering of ligand-localized (LL), metal-localized (d–d), and metal-to-ligand charge-transfer (MLCT) states.[5-7] However, for MLX_4 complexes with small X groups, the X's may not sterically interfere with 2,9-substituents in phen's. We have successfully synthesized several new $ReL(CO)_3py^+$ (py = pyridine, L = substituted phen) complexes with methyl or phenyl groups in the critical 2,9-positions and find that the complexes form easily, exhibit excellent luminescent properties, and show promise as sensors.

Phenyl substituents in nonsterically crowded positions on α-diimine ligands enhance luminescent properties, increase MLCT extinction coefficients, and red-shift MLCT absorptions.[11] Thus, we hoped to enhance the visible absorption of Re(I) complexes, which otherwise have favorable properties for sensors.

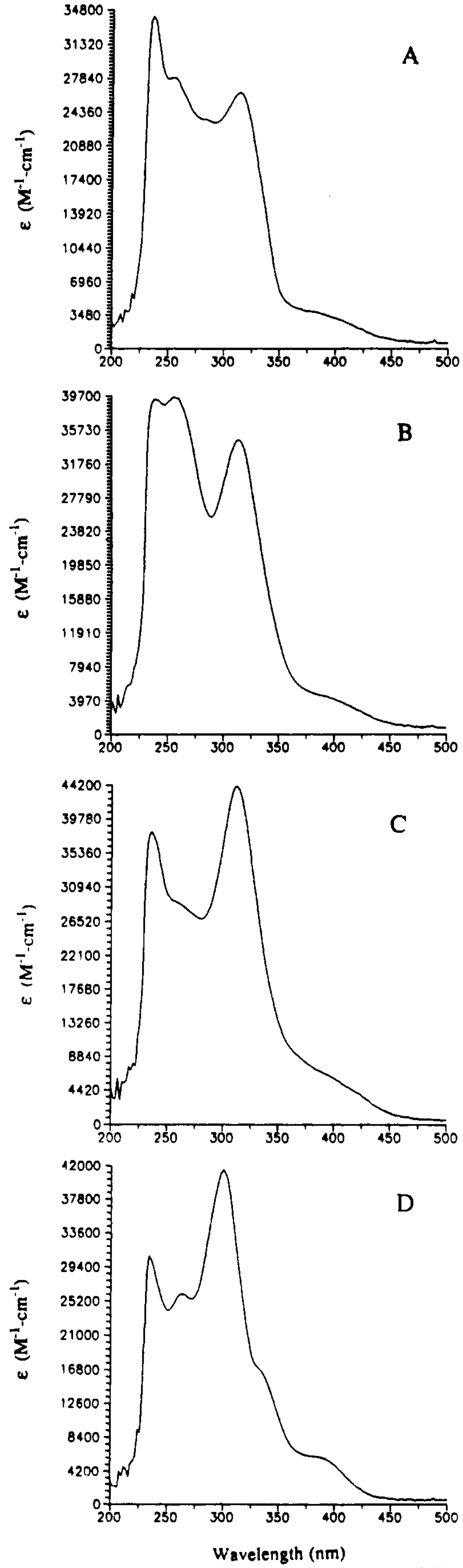

Figure 1. Room-temperature absorption spectra of $LRe(CO)_3(py)^+$ in CH_2Cl_2: (A) L = 2,9-Ph_2phen; (B) L = 2,5,9-Ph_3phen; (C) 2,4,7,9-Ph_4phen; (D) 2,9-Me_2-4,7-Ph_2phen.

---

[*] Authors to whom correspondence should be addressed.
[†] State University of New York.
[‡] University of Virginia.
[§] James Madison University.

(1) Lieberman, R. A.; Wlodarczyk, M. T., Ed. *Chemical, Biochemical, and Environmental Sensors*; The International Society for Optical Engineering: Bellingham, WA, 1988; Vol. 1172.
(2) Diamandis, E. P.; Christopoulos, T. K. *Anal. Chem.* **1990,** *62,* 1149A.
(3) Wolfbeis, O. S. In *Molecular Luminescence Spectroscopy Methods and Applications: Part 2*; Schulman, S. G., Ed.; John Wiley and Sons: New York, 1988; p 283.
(4) Angel, S. M. *Spectroscopy* **1989,** *2* (4), 37.
(5) *J. Chem. Educ.* **1983.** *60* (10), Oct, entire issue.
(6) Juris, A.; Balzani, V.; Barigellitti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988,** *84,* 85.
(7) Demas, J. N.; DeGraff, B. A. *Anal. Chem.* **1991,** *63,* 829A.
(8) Sacksteder, LouAnn; Demas, J. N.; DeGraff, B. A. *J. Am. Chem. Soc.*, in press.
(9) (a) Klassen, D. M.; Hudson, C. W.; Shaddix, E. L. *Inorg. Chem.* **1975,** *14,* 2733. (b) Klassen, D. M. *Inorg. Chem.* **1976,** *15,* 3166.
(10) (a) Gamache, R. E., Jr.; Rader, R. A. *J. Am. Chem. Soc.* **1985,** *107,* 1141. (b) Bell, S. E. J.; McGarvey, J. J. *Chem. Phys. Lett.* **1986,** *124,* 336. (c) Palmer, C. E. A.; McMillin, D. R. *Inorg. Chem.* **1987,** *26,* 3837.
(11) Lin, C.-T.; Böttcher, W.; Chou, M.; Creutz, C.; Sutton, N. *J. Am. Chem. Soc.* **1976,** *98,* 6536.

0020-1669/93/1332-5629$04.00/0

Table I. Luminescence Properties of $ReL(CO)_3py^+$ Complexes

no.	L	τ_0(298 K) (μs)	$10^{-8}k_q$ (M^{-1} s^{-1})	Φ	$10^{-5}k_r$ (s^{-1})	$10^{-5}k_{nr}$ (s^{-1})	τ_{intr} (μs)	τ(77 K)^a (μs)
1	2,9-Ph_2phen	3.01	3.4	0.304	1.01	2.31	9.90	12.51 89% 10.62 11% 27.81
2	2,5,9-Ph_3phen	4.69	4.1	0.317	0.68	1.45	14.8	63.33 66% 11.79 22% 59.53 12% 353.8
3	2,4,7,9-Ph_4phen	6.22	3.3	0.354	0.57	1.04	17.6	17.09 76% 12.75 24% 30.83
4	2,9-Me_2-4,7-Ph_2phen	13.86	3.8	0.320	0.23	0.49	43.3	21.84 72% 16.21 28% 36.30

[a] Multiexponential. Weighted average.

Experimental Section

Materials. The 2,9-diphenyl phen's were prepared by literature methods[12] and purified by chromatography on silica gel (benzene–hexane). The remaining phen's were obtained from G. Frederick Smith Chemical Co. or Sigma Chemical Co. The complexes were synthesized as described earlier.[13]

Optical Measurements. Absorption and steady-state and lifetime luminescence measurements including quantum yield (Φ) determinations are described elsewhere.[13,14] All 298 K decays were single exponentials. The 77 K decays were fit with two or three exponentials.[15] Ground-state heterogeneity was tested using the excitation spectra ratio method.[16]

Results and Discussion

Figure 1 shows 298 K absorption spectra of the complexes. All complexes showed MLCT transitions in the 360–450-nm region and LL transitions at higher energies. Phenyl-substituted ligands gave more intense absorptions and extended them to lower energies than unsubstituted or methyl-substituted phen's. The effect was greatest for the 2,4,7,9-Ph_4phen complex followed by the 2,9-Me_2-4,7-Ph_2phen.

Radiative (k_r) and nonradiative (k_{nr}) decay rate constants for the emissions were obtained from Φ and observed lifetime, τ_{obs}:

$$\tau_{obs} = (k_r + k_{nr})^{-1} \tag{1}$$

$$\Phi = k_r \tau_{obs} \tag{2}$$

Equation 2 assumes a unity intersystem crossing yield.[17] The intrinsic lifetime, τ_{intr}, is the τ that would be measured in the absence of nonradiative decay:

$$\tau_{intr} = 1/k_r \tag{3}$$

All 298 K emissions are characteristic MLCT emissions (broad, structureless; τ_{intr}'s = 10–40 μs). The emission maxima at 298 K are as follows: **1**, 564 nm; **2**, 564 nm; **3**, 582 nm; **4**, 555 nm. Thus, we assign all 298 K emissions to predominantly MLCT transitions.[18]

Table I summarizes the data. Despite a 5-fold variation in k_r with L, the k_{nr}'s vary similarly to yield a nearly invariant Φ. Thus, L varies the rate constants similarly. For the 77 K decays, which are fit to double (**1**, **3**, **4**) or triple exponentials (**2**), we report a preexponential factor weighted mean lifetime, τ_M

$$\tau_M = \sum \alpha_i \tau_i / \sum \alpha_i \tag{4}$$

as well as each τ's preexponential contribution (α).

Figure 2 shows 77 K emissions. **1** is clearly an MLCT emission. The distinct structure in **2** suggests a significant component of π–π^* phosphorescence, and **3** and **4** show a dominant MLCT emission with a slight asymmetry in the region where an LL phosphorescence would appear. Thus, we assign the 77 K emissions of **1**, **3**, and **4** to predominantly MLCT emissions with perhaps a small LL component in **3** and **4**. The emission of **2** is principally a π–π^* phosphorescence with probably some admixture of MLCT emission. The τ's support these assignments. Roughly 30% of the total decay of **2** has a τ of 60 μs or longer with 10% of the emission having a τ of 350 μs. This is more characteristic of a π–π^* phosphorescence, which has become more allowed via heavy metal atom enhanced spin–orbit interactions and/or state mixing with nearby allowed MLCT states. The remaining τ's are consistent with a dominant MLCT emission.

A phenyl at the 5-position is much more effective at decreasing the MLCT/π–π^* splitting since only the 2,5,9-triphenyl derivative gives a 77 K π–π^* phosphorescence. Similar results were observed for Re(I)/5-Phphen complexes.[13] All complexes were photochemically stable (room lights for several days); the spectra and lifetime were invariant.

The O_2 quenching constants, k_q's, were similar to those for other non-phenyl-containing $ReL(CO)_3X$ complexes. Since the phenyls exert no steric shielding for O_2 quenching, the excited state can be treated as distributed over the entire L including the phenyls. Similar behavior is observed with phenyl-substituted Ru(II) complexes.[19]

Temperature variations in luminescence properties are due to the different sensitivities of MLCT and LL π–π^* state energies to solvent properties and the rates of molecular–solvent relaxation at different temperatures relative to τ. Because of their polar nature, the MLCT state energies depend strongly on solvent organization while the less polar π–π^* state energies are virtually insensitive to solvent properties. At 298 K, the complex and the environment can relax to the thermally equilibrated excited (*thexi*) state, in a time short relative to τ, which significantly lowers the MLCT state energy. However, in a rigid 77 K glass, solvent viscosity prevents thermal equilibration in a time comparable to τ.

The diagrams of Figure 3 explain the emission changes with temperature and ligand. At 298 K all emissions are MLCT in character, and the lowest excited state is MLCT. At 77 K all the emissions are blue-shifted, but **2** shows significant change in

---

(12) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P. *Tetrahedron Lett.* **1982**, *23*, 5291.

(13) Sacksteder, LouAnn; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *19*, 4335.

(14) Leasure, R. M.; Sackstede, LouAnn; Nesselrodt, D. N.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1991**, *30*, 3722.

(15) (a) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431. (b) Daniels, R. W. *An Introduction to Numerical Methods and Optimization Techniques*; North Holland, Inc.: New York, 1978. (c) Demas, J. N.; Demas, S. E. *Interfacing and Scientific Computing on Personal Computers*; Allyn & Bacon: New York, 1990.

(16) Sacksteder, L.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1989**, *28*, 1787.

(17) (a) Demas, J. N.; Taylor, D. G. *Inorg. Chem.* **1979**, *18*, 3177. (b) Taylor, D. G.; Demas, J. N. *J. Chem. Phys.* **1979**, *71*, 1032.

(18) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998.

(19) Demas, J. N.; Harris, E. W.; McBride, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 3547.

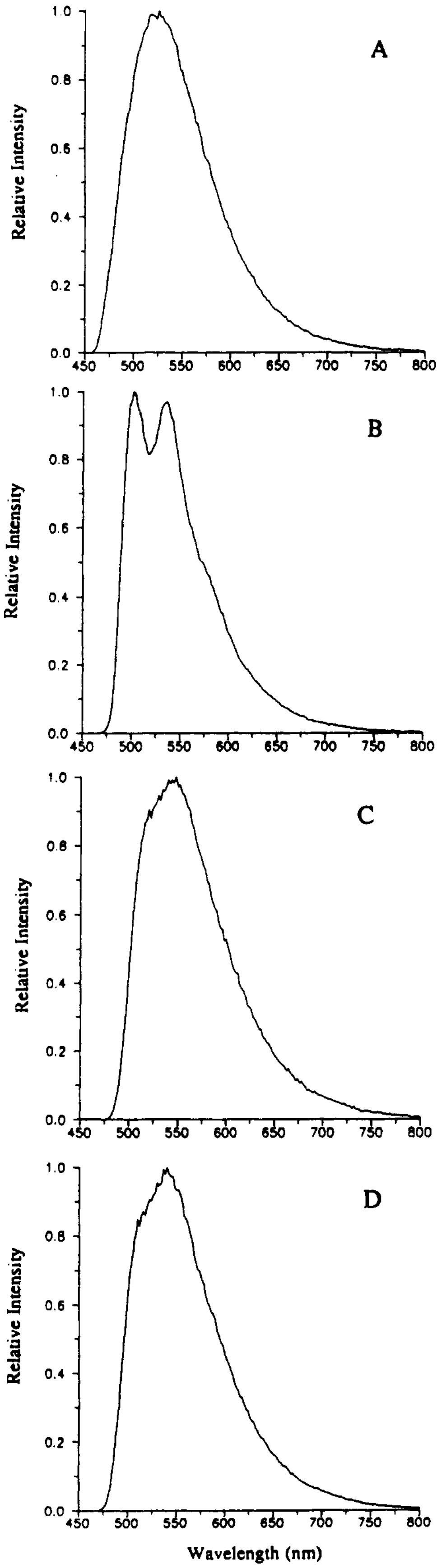

Figure 2. Low-temperature (77 K) emission spectra in 4:1 MeOH–H_2O (λ_{ex} = 390 nm): (A) L = 2,9-Ph_2phen; (B) L = 2,5,9-Ph_3phen; (C) L = 2,4,7,9-Ph_4phen; (D) L = 2,9-Me_2-4,7-Ph_2phen.

structure consistent with the $^3\pi$–π^* state being the lowest one. The 298 and 77 K emissions of **1**, **3**, and **4** belong to the model of Figure 3A; all emissions are clearly MLCT.

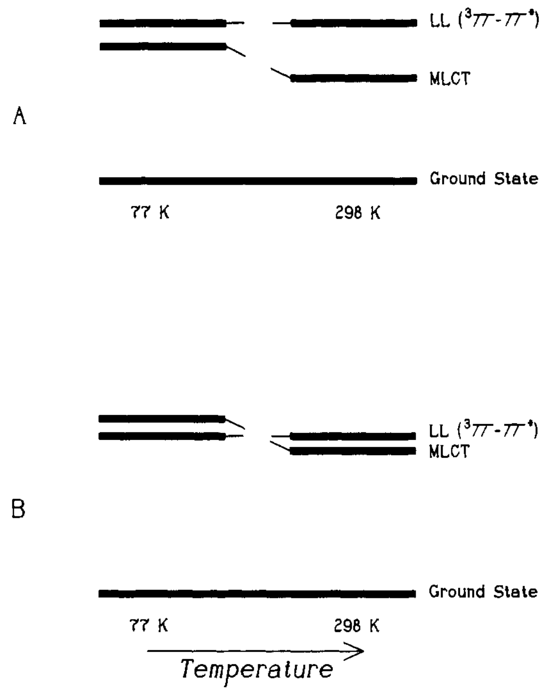

Figure 3. State diagrams as a function of temperature and ligands: (A) for complexes **1**, **3**, and **4**; (B) For complex **2**.

While the MLCT state energies increase for all complexes at 77 K, the inversion of the LL and MLCT states for **2** appears to be due to a smaller LL–MLCT state gap. The increase in MLCT state energy on cooling inverts the states in **2** but not in the other complexes.

It is possible to estimate the magnitude of the energy difference between the thexi and unequilibrated MLCT states. To do this, we choose **1**, which has the purest MLCT emission at 77 and 298 K. The 0–0 state energy is taken as the energy at which the emission intensity falls to 10% of its peak intensity on the high-energy side. This yields an energy difference of about 1.2×10^3 cm^{-1} due to solvent reorganization energies of the MLCT state. Assuming this figure is similar in the remaining complexes, then the ^{3}LL state must be within about 1×10^3 cm^{-1} of the thexi state for **2** for the emission to become a ^{3}LL phosphorescence at 77 K. The suggestion of some ^{3}LL phosphorescence in **3** and **4** at 77 K suggests the ligand state is not too far removed in these cases either.

The multiexponential 77 K τ's probably arise from environmental site heterogeneity with molecules in different sites exhibiting different τ's. For example, in rigid glasses, **1**–**4** can probably exist in different environments and the phenyl groups can exist in different rotameric states. These states could have different energies from variations in delocalization or polarity interactions. Since MLCT emissions are sensitive to these effects, a range of τ's could exist and give complex kinetics. Site effects have been observed for Pt(II)[20] and Re(I) systems.[14] However, the excitation spectra do not show ground-state heterogeneity. Apparently, the emissions all have a common orbital parentage.

The number of τ's in the decay fits is not necessarily the number of sites. Complex decay distributions are well represented by a sum of two or three exponentials,[21] and it is most likely that the complex decay curves reflect a τ distribution rather than a few discrete τ's.

The ease of forming complexes, their stability, and the normalcy of their emission properties compared to those of analogous

---

(20) Sacksteder, LouAnn; Baralt, E.; DeGraff, B. A.; Lukehart, C. M.; Demas, J. N. *Inorg. Chem.* **1991**, *30*, 2468.

(21) Demas, J. N.; DeGraff, B. A. *Optical Based Methods of Analysis*; SPIE: Billingham, WA, 1992; Vol. 1681, p 2.

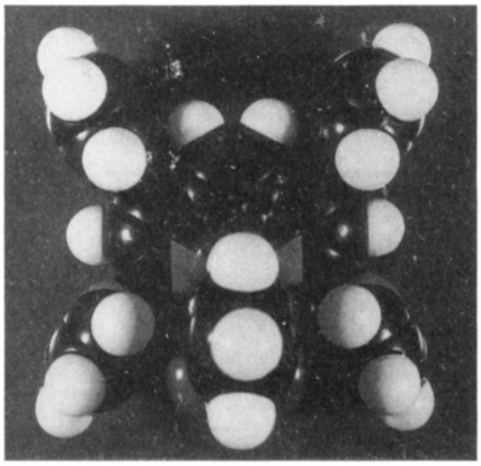

Figure 4. Molecular model of **1** showing the absence of steric crowding between the phenyls and the CO's.

complexes with nonsterically hindered ligands experimentally verifies that 2,9 steric crowding in phen's is not a serious issue either with phenyls that can rotate or with the smaller methyl substituents (see Figure 4). Thus, unlike the case of sterically hindered $Ru(L_2L')^{2+}$ complexes, inductive effects or variations in the ligand HOMO and LUMO dictate emission changes.

There are several significant features. (1) High Φ's coupled with relatively long τ's can exist with L's that are heavily phenyl-substituted and have potentially strong steric crowding. (2) Φ's and τ's are enhanced over those of their unsubstituted phen analogues. (3) The MLCT absorption bands noticeably red-shift, and their intensities are roughly doubled. (4) All complexes have appreciable absorptions beyond 400 nm with **3** and **4** being the best. (5) All are excited by the readily available 442-nm He–Cd laser line, but still not as strongly as desired. Nevertheless, they are an improvement. The parent $(phen)Re(CO_3)py^+$ has a τ of only 1.5 μs in deoxygenated CH_2Cl_2 and negligible 442-nm absorption.[13]

3 and **4** are especially attractive O_2 sensors. The τ's are quite long, and $I_{nitrogen}/I_{oxygen}$ for **4** in CH_2Cl_2 is about 60, which promises excellent sensitivity.

Thus, phenyl substituents can be used to tune excited-state properties in useful ways and in the 4-, 7-, and 5-positions should make attractive intercalative DNA binders. Additionally, the use of sterically hindered ligands should be reconsidered in systems such as Ru(II) and Os(II).

Acknowledgment. We gratefully acknowledge support by the National Science Foundation (Grants 88-17809 and 91-18034), Hewlett Packard for the gift of the 8450A spectrophotometer, and Mr. Henry Wilson for his kind assistance. Support from the Faculty Research Program at SUNY Cortland is gratefully acknowledged by A.P.Z., J.S., and A.C. Paul Pharr wrote the control program for our Tektronix 2221 oscillscope.