Inorganic Chemistry

Communication

pubs.acs.org/IC

Ligand Control of Donor−Acceptor Excited-State Lifetimes

Jing Yang,[†] Dominic K. Kersi,[†] Logan J. Giles,[†] Benjamin W. Stein,[†] Changjian Feng,[‡]
Christopher R. Tichnell,[§] David A. Shultz,*[,§] and Martin L. Kirk*[,†]

[†]Department of Chemistry and Chemical Biology, The University of New Mexico, MSC03 2060, 1 University of New Mexico, Albuquerque, New Mexico 87131-0001, United States

[§]Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204, United States

[‡]School of Pharmacy, The University of New Mexico, MSC03 2060, 1 University of New Mexico, Albuquerque, New Mexico 87131-0001, United States

Supporting Information

ABSTRACT: Transient absorption and emission spectroscopic studies on a series of diimineplatinum(II) dichalcogenolenes, LPtL′, reveal charge-separated dichalcogenolene → diimine charge-transfer (LL′CT) excited-state lifetimes that display a remarkable and nonperiodic dependence on the heteroatoms of the dichalcogenolene ligand. Namely, there is no linear relationship between the observed lifetimes and the principle quantum number of the E donors. The results are explained in terms of heteroatom-dependent singlet−triplet (S−T) energy gaps and anisotropic covalency contributions to the M−E (E = O, S, Se) bonding scheme that control rates of intersystem crossing. For the dioxolene complex, **1-O,O′**, $E(T_2) > E(S_1)$ and rapid nonradiative decay occurs from S_1 to S_0. However, $E(T_2) \le E(S_1)$ for the heavy-atom congeners, and this provides a mechanism for rapid intersystem crossing. Subsequent internal conversion to T_1 in **3-S,S** produces a long-lived, emissive triplet. The two LPtL′ complexes with mixed chalcogen donors and **5-Se,Se** show lifetimes intermediate between those of **1-O,O′** and **3-S,S**.

Square-planar compounds of the (dithiolene)Pt(diimine) series have generated considerable interest because of their rich photophysical properties and their remarkable photoluminescent behavior.[1−8] These d^8 platinum(II) compounds possess a flexible electronic structure that results in a low-energy ligand-to-ligand charge-transfer (LL′CT) or mixed-metal ligand-to-ligand charge-transfer (MMLL′CT) transition that absorbs strongly in the visible-to-near-infrared (NIR) region of the spectrum and possesses considerable dithiolene → diimine charge-transfer character. The LL′CT transition in this class of compounds has been of particular interest to us in furthering our understanding of biradical charge-separated states because the LL′CT excited state results in a large degree of charge separation along the long (z) axis of the molecule (Figure 1) to formally create an excited (dithiolene$^{\bullet+}$)Pt(diimine$^{\bullet-}$) LL′CT state with open-shell donor−acceptor biradical character. Long-lived luminescence is observed following visible photoexcitation of the LL′CT band for (bdt)Pt(di-*tert*-Bu-bpy), **3-S,S**, and other (dithiolene)Pt(diimine) complexes.[2] This emissive behavior is absent for the corresponding catecholate complex, **1-O,O′**, which fully relaxes to the ground state within 630 ps.[9]

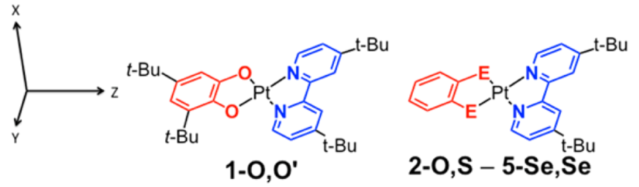

Figure 1. Structures of LPtL′ complexes **1-O,O′**, **2-O,S**, **3-S,S**, **4-S,Se**, and **5-Se,Se**, where E,E = O,S, S,S, S,Se, and Se,Se. The donor ligand is depicted in red and the acceptor fragment in blue.

The ground-state electronic absorption spectra for **1-O,O′**, **2-O,S**, **3-S,S**, **4-S,Se**, and **5-Se,Se** are all characterized by the presence of a broad LL′CT band with nearly equivalent absorption maxima that occur in a narrow energy range between 16950 cm^{-1} for **1-O,O′** and 18350 cm^{-1} for **3-S,S** (Table 1; for spectra, see the Supporting Information). The spectral similarities derive from the fact that they all possess similar $a_2^2b_1^2b_1^0$ ground-state configurations (in effective C_{2v} symmetry), where the filled a_2^2 and b_1^2 donor orbitals are dominantly composed of − and + combinations of out-of-plane E_{p_x} orbitals, respectively. The b_1 lowest unoccupied molecular orbital (LUMO) is primarily localized on the bipyridine acceptor. The electronic structure similarity among these compounds is further exemplified by the similar nature of their transient absorption (TA) difference spectra (Figure 2, inset). The TA difference spectra show a ground-state bleach of the LL′CT band (545−564 nm), and the decay of the TA spectra is associated with a ground-state recovery time constant, τ_{TA} (Table 1).

A Jablonski diagram describing the relevant photophysical processes for **1-O,O′−5-Se,Se** is presented in Figure 3. The diagram is composed of the S_0 ground state, the S_1 ($a_2^2b_1^1b_1^1$; $^1A_1$) and S_2 ($a_2^1b_1^2b_1^1$; $^1B_2$) excited states, and their corresponding triplet T_1 ($^3A_1$) and T_2 ($^3B_2$) states. In the two-state limit (i.e., two-level approximation), the rate constant for intersystem crossing (ISC) to the triplet manifold is governed by spin−orbit coupling (SOC) according to[10]

$$k_{ISC} \propto \langle S_n|\mathbf{L}_x|T_n\rangle^2/\Delta E_{ST}^2 \qquad (1)$$

Received: January 28, 2014
Published: April 28, 2014

dx.doi.org/10.1021/ic500217y | *Inorg. Chem.* 2014, 53, 4791−4793

Table 1. Photophysical Properties of LL′Pt Complexes[a]

	1-O,O′	2-O,S	3-S,S	4-S,Se	5-Se,Se
E_{abs} (~S_1−S_0) (cm^{-1})	16880 (592 nm)	17750 (564 nm)	18350 (545 nm)	18050 (554 nm)	18000 (555 nm)
E_{PL} (cm^{-1})		13500 (740 nm)	14250 (702 nm)	14300 (700 nm)	14250 (702 nm)
Stokes (cm^{-1})		4217	4104	3765	3773
τ_{PL}(ns)[a]		46 ± 10	608 ± 10	540 ± 10	154 ± 10
τ_{TA} (ns)[a]	~0.6[b]	23 ± 10	621 ± 10	511 ± 10	166 ± 10

[a] PL = photoluminescence; TA = transient absorption. [b] Reference 9.

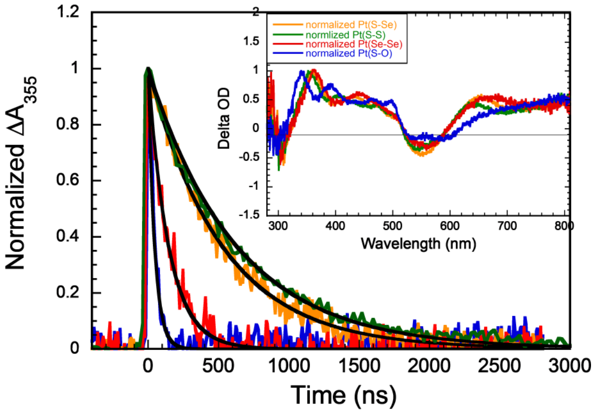

Figure 2. (A) Kinetic traces for **2-O,S** (blue), **3-S,S** (green), **4-S,Se** (orange), and **5-Se,Se** (red) in degassed CH_2Cl_2 at 298 K, obtained by monitoring compound-specific transient absorbances between 340 and 363 nm (excitation at the LL′CT absorption maximum). Inset (B): TA difference spectra recorded immediately following a 5 ns gate delay (pump: 5 mJ/pulse at the LL′CT absorption maximum).

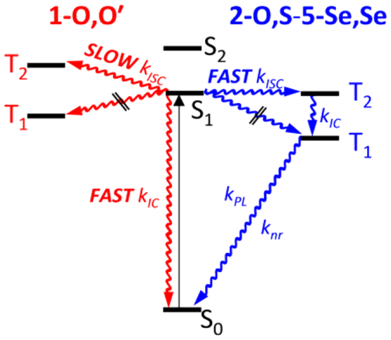

Figure 3. Jablonski diagram for the observed photoprocesses in nonemissive **1-O,O′** (left) and emissive complexes (right). Spin−orbit-promoted ISC from S_1 to T_1 is symmetry-forbidden, while spin−orbit-promoted ISC from S_1 to T_2 is symmetry-allowed. See the text.

Because $\langle S_1|\mathbf{L}_i|T_1\rangle = \langle A_1|\mathbf{L}_i|A_1\rangle = 0$ ($\mathbf{L}_i$ are the orbital angular momentum operators, which transform as a_2, b_1, and b_2 in C_{2v} symmetry), the $S_1 \rightarrow T_1$ process is symmetry-forbidden and k_{ISC} is expected to be small. The same holds true for $T_1 \rightarrow S_0$ ISC, leading to ground-state recovery from the triplet manifold. In contrast, ISC between S_1 and T_2 *is* symmetry-allowed because $\langle A_1|\mathbf{L}_x|B_2\rangle \neq 0$, and the ISC rate will be maximal when S_1 and T_2 are close in energy (eq 1).

Across the entire **1-O,O′−5-Se,Se** series, the observed rates of ground-state recovery vary by nearly 3 orders of magnitude. The fast ground-state recovery rate for **1-O,O′** (630 ps) occurs by $S_1 \rightarrow S_0$ back-electron transfer (i.e., internal conversion, IC). Because the $S_1 \rightarrow T_1$ ISC is symmetry-forbidden, it does not compete with $S_1 \rightarrow S_0$ IC to recover the ground state. Although ISC between S_1 and T_2 is allowed, our spectroscopic calculations indicate that the T_2 state of **1-O,O′** is ~1500 cm^{-1} *above* S_1.[10−12] In marked contrast to **1-O,O′**, the heavy-atom congeners are all emissive, suggesting that their T_2 states lie *below* S_1. This supports the idea that fast ISC occurs via a SOC-allowed $S_1 \rightarrow T_2$ pathway followed by rapid IC to T_1. The $S_1 \rightarrow T_2$ ISC is primarily mediated by the degree of Pt d-orbital character admixed into the a_2 HOMO−1, b_1 highest occupied molecular orbotal (HOMO), and the b_1 LUMO because $\langle Pt(xz)|\mathbf{L}_x|Pt(xy)\rangle \neq 0$.

For **2-O,S**, **3-S,S**, **4-S,Se**, and **5-Se,Se**, three processes are potentially responsible for the observed differences in the T_1 lifetimes (differences in the $T_1 \rightarrow S_0$ lifetimes may also be influenced by vibrationally-activated nonradiative decay via Pt−E stretching modes; relaxation dominated by these modes should decrease with increased mass of the E donor, but this is not borne out by experiment): (1) the relative T_1−S_0 energy gaps, (2) the orbital allowedness of $T_1 \rightarrow S_0$ ISC, and (3) ligand SOC. First, although an energy gap law argument might be used to explain why **2-O,S** possesses the shortest T_1 lifetime, this does not explain the observed T_1 lifetimes for **3-S,S−5-Se,Se** (Table 1) because the T_1 energies (E_{PL}) determined from luminescence measurements are essentially equivalent. Second, ISC between T_1 and S_0 is disfavored in **3-S,S** and **5-Se,Se** because the group theoretical arguments mentioned above result in $\langle A_1|\mathbf{L}_i|A_1\rangle = 0$. However, bonding calculations indicate a large anisotropic covalency in low-symmetry **2-O,S** that manifests itself in a rotation of the Pt(dπ) orbital component of the HOMO toward the Pt−S bond, effectively mixing some Pt(*xy*) character into the HOMO to give $\langle \Psi_{T_1}|\mathbf{L}_x|\Psi_{S_0}\rangle \propto \langle Pt(xy)|\mathbf{L}_x|Pt(xz)\rangle \neq 0$ and an enhanced nonradiative ground-state recovery rate. This orbital rotation is markedly less apparent in **4-S,Se** because of the similar Pt−S and Pt−Se covalencies (i.e., effective C_{2v} symmetry), and this is reflected in the similar τ values for **3-S,S** and **4-S,Se**. Finally, ligand SOC represents a potentially important mechanism for modulating T_1 lifetimes across the **3-S,S−5-Se,Se** series. Although direct SOC-induced ISC between T_1 and S_0 is orbitally forbidden in C_{2v} symmetry, mechanisms for overcoming this forbiddeness derive from spin-vibronic and vibronic SOC, which couple states of different spin multiplicity.[13−15] Only out-of-plane a_2 and b_1 vibrations are effective in mixing the out-of-plane E_{p_x} orbitals with the in-plane E_{p_y} and E_{p_z} orbitals. This results in linear combination of atomic orbital (LCAO)-expanded matrix elements of the type $\langle E_{p_x}|\mathbf{L}_z|E'_{p_y}\rangle$ and $\langle E_{p_x}|\mathbf{L}_y|E'_{p_z}\rangle$ being nonzero and a ligand SOC contribution to $T_1 \rightarrow S_0$ ISC. Because the SOC constant for selenium is ~4.5 times that of sulfur ($\zeta_{Se} = 1659$ cm^{-1}; $\zeta_S = 365$ cm^{-1}; $\zeta_O = 154$ cm^{-1}),[16] one would expect shorter T_1 lifetimes as a function of selenium ligation, and this is observed experimentally across the **3-S,S−5-Se,Se** series.

Understanding the electronic structure contributions to k_{ISC}, k_r, and k_{nr} provides keen insight into the continued development of these and related compounds as key components of dyes for solar cells and for photonics. For **1-O,O′**, the T_2 state lies above

S_1 and $S_1 \rightarrow T_1$ ISC does not compete with rapid IC to recover the ground state. In marked contrast to **1-O,O′**, the close energy match between S_1 and T_2 for the heavy-atom congeners of the series provides a mechanism for enhanced $S_1 \rightarrow T_2$ ISC. Coupled with energy gap law effects, anisotropic covalency, and ligand SOC, these factors modulate excited-state lifetimes by at least 3 orders of magnitude. Exquisite ligand control of these processes suggests that heteroatom effects can be utilized to further modify excited-state lifetimes in a controlled manner. Efforts along these lines are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterization, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: shultz@ncsu.edu.
*E-mail: mkirk@unm.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.L.K. acknowledges the NSF (Grants CHE-0616190 and IIA-1301346) for financial support. D.A.S. acknowledges financial support from the NSF (Grant CHE-1213269).

■ REFERENCES

(1) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949.

(2) Cummings, S. D.; Eisenberg, R. *Prog. Inorg. Chem.* **2004**, *52*, 315.

(3) Hissler, M.; McGarrah, J. E.; Connick, W. B.; Geiger, D. K.; Cummings, S. D.; Eisenberg, R. *Coord. Chem. Rev.* **2000**, *208*, 115.

(4) Paw, W.; Cummings, S. D.; Mansour, M. A.; Connick, W. B.; Geiger, D. K.; Eisenberg, R. *Coord. Chem. Rev.* **1998**, *171*, 125.

(5) Zuleta, J. A.; Bevilacqua, J. M.; Proserpio, D. M.; Harvey, P. D.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 2396.

(6) Zuleta, J. A.; Chesta, C. A.; Eisenberg, R. *J. Am. Chem. Soc.* **1989**, *111*, 8916.

(7) Zuleta, J. A.; Burberry, M. S.; Eisenberg, R. *Coord. Chem. Rev.* **1990**, *97*, 47.

(8) Adams, C. J.; Fey, N.; Parfitt, M.; Pope, S. J. A.; Weinstein, J. A. *Dalton Trans.* **2007**, 4446.

(9) Best, J.; Sazanovich, I. V.; Adams, H.; Bennett, R. D.; Davies, E. S.; Meijer, A.; Towrie, M.; Tikhomirov, S. A.; Bouganov, O. V.; Ward, M. D.; Weinstein, J. A. *Inorg. Chem.* **2010**, *49*, 10041.

(10) Turro, N. J.; Ramamurthy, V.; Scaiano, J. *Modern Molecular Photochemistry of Organic Molecules*; University Science Books: Mill Valley, CA, 2010.

(11) No ligand-field states are likely to be found between T_2 and S_0. We base this upon the fact that the first (triplet) excited state of (en)$PtCl_2$ (en = ethylenediamine) is at 23700 cm^{-1} (ref 12), and the ligand field of **1-O,O′− 5-Se,Se** is likely larger than that provided by the combination of en and Cl^- ligands. In addition, a Jablonski diagram similar to that in Figure 3 is observed for aromatic hydrocarbons (e.g., the anthracene T_2 state is only 1000 cm^{-1} below S_1), and k_{ST} is controlled by either $S_1 \rightarrow T_2$ or $S_1 \rightarrow T_1$ ISC mechanisms depending on substituent(s) (ref 10). In the present case, S_1−T_2 energy matching and fast ISC is achieved by sulfur and/or selenium heteroatoms on the donor fragment.

(12) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; 2nd ed.; Elsevier: New York, 1984.

(13) Henry, B. R.; Siebrand, W. *J. Chem. Phys.* **1971**, *54*, 1072.

(14) Tatchen, J.; Gilka, N.; Marian, C. M. *Phys. Chem. Chem. Phys.* **2007**, *9*, 5209.

(15) Kimachi, S.; Satomi, R.; Miki, H.; Maeda, K.; Azumi, T.; Onishi, M. *J. Phys. Chem. A* **1997**, *101*, 345.

(16) *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, FL, 2006; p 617.