Microsecond Photoluminescence and Photoreactivity of a Metal-Centered Excited State in a Hexacarbene–Co(III) Complex

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ABSTRACT: The photofunctionality of the cobalt–hexacarbene complex [Co(III)(PhB(MeIm)3)2]+ (PhB(MeIm)3 = tris(3-methylimidazolin-2-ylidene)(phenyl)borate) has been investigated by time-resolved optical spectroscopy. The complex displays a weak (Φ ∼ 10−4) but remarkably long-lived (τ ∼ 1 μs) orange photoluminescence at 690 nm in solution at room temperature following excitation with wavelengths shorter than 350 nm. The strongly red-shifted emission is assigned from the spectroscopic evidence and quantum chemical calculations as a rare case of luminescence from a metal-centered state in a 3d6 complex. Singlet oxygen quenching supports the assignment of the emitting state as a triplet metal-centered state and underlines its capability of driving excitation energy transfer processes.

Earth-abundant transition metal complexes have received increasing attention in recent years as photoactive components in prospective large-scale approaches for solar energy conversion and photocatalysis.1−3 Several first-row transition metals are interesting in this context, but unfortunately many 3d metal complexes suffer from short excited-state lifetimes compared to their 4d and 5d congeners.4,5 This is due to the presence of low-lying metal-centered (MC) states that facilitate fast, radiationless deactivation which limits their use in light-driven applications.6−9 Nevertheless, significant progress has recently been made to extend the excited-state lifetimes of 3d metal complexes, for example, by innovative ligand design to destabilize MC states by imposing a strong ligand field or by expanding investigations to a range of unconventional excited-state schemes beyond the common triplet metal-to-ligand charge transfer (3MLCT) state in d6 complexes.12,13 Though MC states are interesting for spin crossover (SCO) and light-induced excited-state spin trapping (LIETSST) applications,14−15 in contrast to charge transfer (CT) states they are typically too low in energy to be interesting for photochemical applications or to display visible emission.16 As a rare case among the d6 complexes, very weak emission was reported from the MC state in [Co(CN)6]3−,17,18 while such states have only rarely been possible to observe in Ru(II) and Fe(II) complexes.19,20 Recently, remarkable photoproperties for Co(III) complexes were reported by Hannan and Zysman-Coleman and co-workers.21 Excited states of mixed triplet ligand-to-metal charge transfer/ligand centered (3LMCT/LC) character showed up to 8.7 ns blue emission in solution at room temperature. The photophysical properties of these complexes were related to the strong σ-donor ligands they contain.21,22 Tris(carbene)borate-based scorpionate ligands incorporating a negatively charged boron atom in their backbone are very strong σ-donors, and among these the tris(3-methylimidazolin-2-ylidene)(phenyl)borate anion ([PhB(MeIm)3]) is one of the strongest.23,24 Hexacarbene complexes of Mn(IV) and Fe(III) featuring this ligand have been reported to exhibit extraordinary photophysical properties including photoluminescence.25,26 These findings spurred us to investigate the photophysics of [Co(III)(PhB(MeIm)3)2]+ (Figure 1) which was first reported in 2019 by Nishiura et al.27 Even though the complex showed no apparent absorption in the visible part of the spectrum, we nevertheless considered it interesting to obtain a new perspective on the excited-state properties of 3d6 complexes with strong σ-donor ligands.28,29

Figure 1. Crystal structure of [Co(PhB(MeIm)3)2]PF6. Ellipsoids drawn at 50% probability level. The counterion, solvent molecules, and hydrogen atoms omitted for clarity. Orange = Co; purple = B; blue = N; black = C.

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We synthesized [Co(PhB(MeIm)3)2]PF6 following our procedure for the analogous Fe compound (see the Supporting Information). The crystal structure of [Co(PhB(MeIm)3)2]PF6 is almost identical with the one reported by Nishiura et al. of the same complex featuring triflate as a counterion.27 Compared to [Fe(PhB(MeIm)3)2]PF6, the C−M−C cis angles in the Co complex are closer to 90° (87.7° to 88.7° vs 86.4° to 87.5°), and the M−C bond lengths are on average 0.061 Å shorter (1.935 Å vs 1.996 Å) in the Co complex, which should lead to a stronger ligand field splitting.26 The same trend for bond lengths has earlier been found in structurally similar Fe and Co complexes with the tris(methylimidazolin-2-ylidene)-hydroborate ligand.30

The absorption spectrum of [Co(PhB(MeIm)3)2]+ in acetonitrile is shown in Figure 2A. Very weak absorption features can be seen between 600 and 400 nm (ε<3 M−1 cm−1); a more detailed discussion in the Supporting Information), followed by a slightly stronger absorption band around 310 nm (ε310 nm = 400 M−1 cm−1). A significantly stronger band is peaking around 250 nm (ε250 nm = 18000 M−1 cm−1) and further rising toward shorter wavelengths (ε312 nm = 63800 M−1 cm−1). These absorption features are similar to those of [Co(CN)6]3− incorporating strongly σ-donating cyanide ligands, which suggests MC character for the weak features >300 nm and transitions with more CT character for the more intense bands at lower wavelengths.25 Upon excitation of the complex an orange-red emission peaking ∼690 nm is observed (Figure 2A, green spectrum). The excitation spectrum corresponding to this emission (Figure 2A, orange spectrum) qualitatively follows the absorption spectrum, indicating the coupling of absorptive and emissive states. For excitation at 266 nm, we estimate a lower limit for the quantum yield of 0.01% (see the Supporting Information). The absorption at the 250 nm band is 45 times higher than at the 310 nm band. The excitation spectrum, however, yields only a factor of 17±5 between those two bands, indicating that the quantum yield is about 2.5 times higher when exciting into the longer-wavelength absorption band.

Experiments were also performed to check for sensitivity of the emissive state toward oxygen quenching. A comparison of the emission from aerated and deaerated samples (Figure 2B) showed additional quenching (∼30%) of the excited Co complex in the presence of oxygen with the concomitant appearance of a new emission peak at ∼1275 nm (Figure 2C). Although limited in yield, this observation is indicative of the excited state of the Co complex undergoing intersystem crossing (ISC) to a triplet excited state capable of excitation energy transfer (EET) forming singlet oxygen, which would not be possible from a quintet state.32

Time-resolved photoluminescence (TRPL) in several solvents was measured at room temperature by using 266 and 310 nm excitation. All combinations of solvent and excitation wavelength yield a single-exponential decay (see the Supporting Information). Figure 3A shows the observed PL kinetics in MeCN and MeOH for 266 nm excitation, yielding remarkable emission lifetimes of 0.82 and 1.25 μs, respectively. The excited-state dynamics in MeCN was further investigated by using transient absorption (TA) optical spectroscopy (experimental details in the Supporting Information). Figure 3B shows the differential absorption spectrum recorded for excitation of the complex at 266 nm.
7 ns after excitation at 266 nm. A peak at 515 nm is formed on the picosecond time scale and does not change within the 10 ns accessible in this experiment. To explore the full decay process, single-wavelength nanosecond TA was measured. Probing the excited-state absorption (ESA) dynamics at 532 nm (Figure 3A) yields a very similar $\tau_{\text{ESA}} \sim 0.8 \mu$s lifetime as observed in TRPL. As both the emission and ESA signals have the same lifetime they can be associated with the population of the same state. The radiative lifetime of the emissive transition, its oscillator strength $f_i$ and molar absorption coefficient can furthermore be evaluated from the experimental lifetime and quantum yield as summarized in Table 1 (calculations in the Supporting Information).

Table 1. Summary of Key Photophysical Properties of $[\text{Co(PhB(MeIm)₃)₂}]^{3+}$ in MeCN$^{a}$

| $\lambda$ [nm] | $E$ [eV] | $\epsilon$ [M⁻¹ cm⁻¹] | $f$ | $\tau$ [μs] | $\Phi$ [%] |
|---------------|----------|-----------------|-----|------------|--------|
| abs 250       | 4.96     | 18000           | 1.7 $\times$ 10⁻¹ |          |        |
| 310           | 4.00     | 400             | 6.5 $\times$ 10⁻³ |          |        |
| ESA 515       | 2.41     | 600             | 0.80 |           |        |
| em 690        | 1.80     | 17              | 1 $\times$ 10⁻¹⁰ | 0.82 $>$ 0.01 |        |

$^a \lambda$ = wavelength of band, $E$ = energy of band, $\epsilon$ = molar absorption coefficient, $f$ = oscillator strength, $\tau$ = lifetime, $\Phi$ = quantum yield, abs = absorption, ESA = excited-state absorption, and em = emission.

of the $^3$MC state energy and a concomitant increase of the singlet ground-state ($^1$GS) energy. Thus, the observed vertical deexcitation energy from the relaxed $^1$MC state is only about 1.8 eV (690 nm), yet the calculated energy difference to the relaxed GS corresponds to more than 2.1 eV.

Key to achieving the experimentally observed, rare $^3$MC emission is that this state retains significantly higher energy than the $^1$GS also at its fully relaxed geometry. This is enabled by the very strong ligand field splitting (10 $D_q$ = 38600 cm⁻¹; more details in the Supporting Information) induced by the scornabate carbene ligands. At the same time these ligands form a tight and rather rigid coordination environment around the metal center. This could be beneficial to slow down nonradiative decay pathways as recently found for other transition metal complexes. In our photophysical model, the ESA feature at 515 nm could correspond either to MC transitions in analogy to the suggestions by Viaene et al. for $[\text{Co(CN)}₆]^{3-}$ or to CT transitions that are weakened due to the distorted geometry as suggested by Sun et al. The weak emission from the lowest excited state can be explained by the spin- and Laporte-forbidden nature of the transition to the $^1$GS, and its sensitivity to oxygen is indicative for triplet multiplicity. The photophysical properties of $[\text{Co(PhB-(MeIm)₃)₂}]^{3+}$ with UV absorption and orange/red emission most closely parallel similar behavior previously established for $[\text{Co(CN)}₆]^{3-}$ (at low temperatures) with the lowest energy excitation located at 396 nm and emission located at 714 nm. The excited-state lifetime of the $^1$T₁ state of $[\text{Co(CN)}₆]^{3-}$ was, however, found to be limited to <5 ns in aqueous solution at 22 °C. Furthermore, the excited-state lifetime of neither CT nor MC states in related Fe(II) complexes usually exceed a few
nanoseconds under ambient conditions.\textsuperscript{38} It is worth noting that the photophysical behavior of $[\text{Co}(\text{PhB(MeIm)}_3)_2]^+$ is fundamentally different from the blue-emitting Co complexes recently presented by Zysman-Colman, Hanan, and co-workers as well as from structurally related Fe carbene complexes.\textsuperscript{31,26,39} Instead of extending CT excited-state lifetimes as well as from structurally related Fe carbene complexes\textsuperscript{21,26,39} recently presented by Zysman-Colman, Hanan, and co-workers by destabilizing the MC states, here the $^3\text{MC}$ state itself is sufficiently high in energy above the $^3\text{GS}$ energy surface to become a long-lived emissive state. This atypical behavior for d$^6$ emitters more closely resembles the photophysics of transition metal complexes with MC states nested above the ground-state potential, such as some Cr(III) complexes, with long-lived emissive states.\textsuperscript{40}

In summary, $[\text{Co}(\text{PhB(MeIm)}_3)_2]^+$ shows microsecond emission from a $^3\text{MC}$ state which is unique for 3d$^6$ metal complexes. The capability of this complex to drive energy transfer reactions furthermore highlights the photofunctionality of this unconventional excited state. It will be important in further work to improve the light-harvesting capabilities through ligand design modifications while retaining the favorable $^3\text{MC}$ excited-state properties. Fortunately, carbene ligands can be tuned in regards to their $\sigma$- and $\pi$-properties, in contrast to earlier used CN$^-$ ligands. It will also be interesting to explore other avenues to utilize the long-lived excited MC state for a broader range of photochemical applications, for example, similar to the MC states that were recently suggested to play a key role in photoredox catalysis.\textsuperscript{41,42}

\section{ASSOCIATED CONTENT}

\subsection{Supporting Information}
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c12151.

Synthetic procedures and characterization of the complex by $^1\text{H}$ and $^13\text{C}$ NMR, HRMS, elemental analysis and XRD, description of other experimental methods and procedures as well as more detailed photophysical and quantum chemical considerations (PDF)

Crystallographic data of $[\text{Co}(\text{PhB(MeIm)}_3)_2]\text{PF}_6$ (CIF)

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\section{Notes}
The authors declare no competing financial interest.

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