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Similar luminescent behavior in an established rhenacarborane complex, [3,3-$(CO)_2$-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$] and a new complex anion, [3,3,3-$(CO)_3$-8-I-*closo*-3,1,2-$ReC_2B_9H_{10}$]$^-$

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Abstract

The compounds [3,3-$(CO)_2$-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$] and [NEt_4][3,3,3-$(CO)_3$-8-I-*closo*-3,1,2-$ReC_2B_9H_{10}$] have been shown to be emissive in MeTHF at 77 K, with λ_{max} in the blue region of the visible spectrum. Emission from [3,3,3-$(CO)_3$-8-I-*closo*-3,1,2-$ReC_2B_9H_{10}$]$^-$, which has been structurally characterized, is phosphorescent with a single exponential decay lifetime, $\tau = 1.65$ ms. The complex [3,3-$(CO)_2$-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$] also emits in the solid state at 298 K and has been shown by diffuse-reflectance UV–vis measurement to have a band gap of 2.66 eV.

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In recent years Re(I) polypyridyl complexes have received much attention with regard to their luminescent characteristics for sensing and electronic communication applications [1]. To date there have been no reports of any kind of emissive behavior from Re(I) complexes, where the rhenium atom is an integral vertex in a metallacarborane cage system. The prototypical complex for such behavior is Cs[3,3,3-$(CO)_3$-*closo*-3,1,2-$ReC_2B_9H_{11}$] (**1**) [2]. However, flourometry measurements on this complex, even in 2-methyltetrahydrofuran (MeTHF) at 77 K, have afforded no observable emission of visible light. The synthesis and spectroscopic characterization of the complex [3,3-$(CO)_2$-3-NO-*closo*-3,1,2-$ReC_2B_9H_{11}$] **(2a)** has been more recently reported

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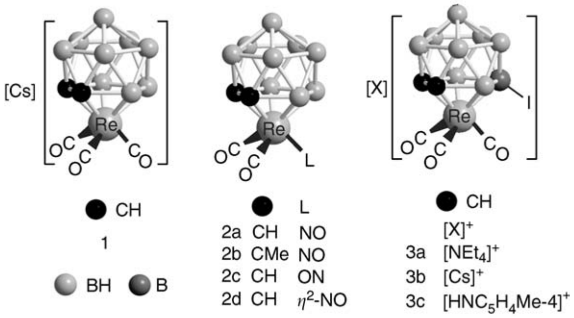
[3]. While some critical photophysical data for solutions of the complexes **2** have been disclosed, notably the IR-photoanalysis by Bitterwolf et al. of the nitrosyl ligand dynamics in low-temperature matrix-isolated complex **2b** [4], we reveal herein one of the first reports of visible light emission from a d-block metallacarborane, where the chromophore comprises an endopolyhedral polyhedral skeletal electron (PSE)-contributing metal vertex. We also report herein a related new complex anion, $[3,3,3\text{-}(CO)_3\text{-}8\text{-}I\text{-}closo\text{-}3,1,2\text{-}ReC_2B_9H_{10}]^-$ (**3**), which is emissive in MeTHF at 77 K. Hawthorne et al. have recently reported, albeit weak, stereogenerated luminescence from a nickelacarborane sandwich complex $[3,3',1,1',2,2'\text{-}commo\text{-}Ni(C_2B_9H_{11})_2]$ and its derivatives with cage carbon substituents [5]. Also described by Laguna et al. is the luminescence from *nido*-carborane-diphosphine anions, and its modification by the attachment of exopolyhedral three-coordinate gold-phosphine fragments [6].



The UV–vis absorption spectra of solutions of **2a** have been previously reported [$\lambda_{max}(\varepsilon) =$ 355(500), 420 nm ($200\,M^{-1}\,cm^{-1}$)] [4], although we note an additional, intense absorption at 250 nm ($7700\,M^{-1}\,cm^{-1}$) [7]. Since the lower intensity absorptions have been attributed to nitrosyl reorientations to give species **2c** and **2d** [4], the higher energy excitation is assigned to a $Re^{I} \rightarrow NO^{+}$ MLCT transition, as described in the cyclopentadienide analog $[Re(NO)(CO)_2(\eta^5\text{-}C_5H_5)][PF_6]$ [8]. The photoluminescence excitation and emission spectra of **2a** measured in MeTHF at 77 K are shown in Fig. 1 [9]. Excitation takes place in the UV region ($\lambda_{ex} = 285$ nm, trace A) with corresponding emission of blue light

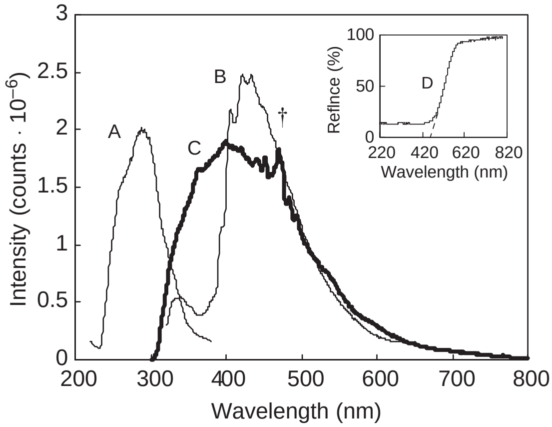


Fig. 1. Photoluminescence spectra of complex **2a**: trace A (excitation, $\lambda_{em} = 435$ nm), trace B (emission, $\lambda_{ex} = 285$ nm), 50 μM solution measured in MeTHF glass at 77 K, trace C (emission, $\lambda_{ex} = 250$ nm), trace D (diffuse-reflectance UV–vis spectrum), solid microcrystalline sample at 298 K.

($\lambda_{em} = 435$ nm, trace B), resulting in a Stokes shift of ca. $12\,100\,cm^{-1}$. Vibrational fine structure was observed in the emission spectrum ($\Delta\nu \approx 800\,cm^{-1}$), too low to be associated with a stretching vibration. However, analysis of the DFT-computed highest occupied molecular orbital (HOMO) (Fig. 2), whose emission vibrational fine-structure will be most closely related to, reveals primarily Re d_{z^2} character, with some significant contribution from the cage. Of note is the involvement of β-B–H σ bonding in the cage face. Relaxation to such a ground state orbital, might well promote vibrational activity in one of the many deformation modes associated with the cage, known to take place in this energy regime of the vibrational spectrum [10], especially one that heavily involves this β-B–H bond. Luminescence is undetectable in any solvent at room temperature, but solid microcrystalline **2a** is strongly and broadly emissive at 298 K [$\lambda_{ex} < 300$ nm, $\lambda_{em} \approx$ 400 nm (trace C)]. This emission increases in intensity markedly as λ_{ex} is decreased to the instrumental limit of 200 nm. This behavior may be attributed in part to the simple band structure observed in the diffuse-reflectance UV–vis measurement (trace D, inset) on a solid microcrystalline sample, which revealed an unstructured band profile with a band gap energy, $E_g = 2.66$ eV,