

ABSTRACT

Irradiations of the transition metal-to-transition metal charge transfer (MMCT) absorption bands of a series of cyanide-bridged chromium(III)–ruthenium(II) complexes at 77 K leads to near-infrared emission spectra of the corresponding chromium(II)–ruthenium(III) electron transfer excited states. The lifetimes of most of the MMCT excited states increase more than 10-fold when their amine ligands are perdeuterated. These unique emissions have weak, low frequency vibronic sidebands that correspond to the small excited-state distortions in metal–ligand bonds that are characteristic of transition metal electron transfer involving only the non-bonding metal centered d-orbitals suggesting that the excited-state Cr(II) center has a triplet spin configuration. However, most of the electronically excited complexes probably have overall doublet spin multiplicity and exhibit an excitation energy dependent dual emission with the near in energy Cr(III)-centered and MMCT doublet excited states forming an unusual mixed valence pair.