

electron-transfer quenching of  $1^*$  to be competitive with radiative and nonradiative deactivation. This suggests that electron transfer from the d-s/XMCT excited state is unusually slow, perhaps because the enhanced Cu-Cu bonding in  $1^*$  lends a large inner sphere contribution to the total reorganization energy accompanying the electron transfer. In addition, electron transfer between  $1^*$  and Q leads to charge separation ( $1^+$  plus  $Q^-$ ) and adds a substantial outer sphere solvent reorganization energy as well. These properties are receiving more detailed attention in our laboratories.

### Spectroscopic Properties of $s^2$ Metal Clusters

The interactions between  $s^2$  ions in clusters should be similar to those for  $d^{10}$  ions. In the ground state the coupling of the metal centers should be weak and dependent on second-order mixing with unfilled higher energy orbitals. Consequently, the absorption spectra of clusters are analogous to those for mononuclear components. This is exemplified by the spectrum of  $Tl_4(OCH_3)_4$ , which shows an s-p absorption ( $\lambda_{max} = 227$  nm) close to that for  $Tl^+$  in methanol.<sup>73</sup> However, the empty p orbitals of the  $s^2$  clusters are metal-metal bonding in character while the HOMO is composed of the filled, antibonding, s orbitals; thus the s-p excited state of an  $s^2$  cluster should be significantly distorted from the ground state. In this context, it is notable that emission of the  $Tl_4(OCH_3)_4$  tetramer occurs at much longer wavelength ( $\lambda_{max}^{em} = 640$  nm) than that of the solvated  $Tl^+$  ion. Again, this large shift is attributed to excitation-induced distortions, presumably a contraction along the metal-metal bonds of the  $Tl(I)_4$  tetrahedron.

The compound  $Sn_6O_4(OCH_3)_4$  is another polynuclear  $s^2$  complex whose luminescence ( $\lambda_{max}^{em} = 565$  nm) was attributed to a cluster emission.<sup>74</sup> Again, the absorption spectrum seems to consist of the s-p band ( $\lambda_{max}^{abs} = 325$  nm) of the isolated mononuclear  $SnO_2(OCH_3)_2^{2-}$  components. HOMO to LUMO excitation should again

(73) Kunkely, H.; Vogler, A. *Inorg. Chim. Acta* 1991, 186, 155.

(74) Kunkely, H.; Vogler, A. *Chem. Phys. Lett.* 1991, 187, 609.

lead to enhanced intermetallic bonding, and the  $Sn(II)_6$  octahedron should undergo a contraction. This is apparently reflected in the considerable red shift of the emission bands.<sup>74</sup>

### Summary

A number of the  $d^{10}$  and  $s^2$  metal clusters are brightly luminescent, some with strongly medium dependent and temperature dependent spectral profiles. Such emissions are often from excited states assigned as having a mixed d-s/XMCT character, the key feature being enhanced electronic population in metal-metal bonding orbitals in these states as evidenced by the large Stokes shifts between excitation and emission maxima. The observation of such emission bands is strongly favored by relatively short metal-metal distances in the clusters. This behavior parallels that of the  $d^8$ - $d^8$  dimers held by bridging ligands in cofacial configurations for which excitation leads to substantially increased bonding between metal centers.<sup>47</sup> With  $\pi$ -unsaturated ligands L, emissions from XLCT excited states are often observed, and the luminescence thermochromism of such complexes is the result of different temperature and medium rigidity responses of these two types of excited states. The poor coupling between d-s/XMCT and XLCT states in clusters such as  $Cu_4I_4(py)_4$  can be attributed to high barrier heights for curve crossing owing to different distortion trajectories once the molecule is prepared in one of the respective excited states. Ongoing studies in these laboratories continue to survey different luminative  $d^{10}$  and  $s^2$  cluster systems and to apply an arsenal of synthetic, theoretical, photophysical, and photochemical tools to extend our quantitative understanding of the relevant excited states.

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## Additions and Corrections

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**Michael J.S. Dewar\* and Caoxian Jie:** Mechanisms of Pericyclic Reactions: The Role of Quantitative Theory in the Study of Reaction Mechanisms.

Page 537. As pointed out by Professor Borden, we wrongly attributed to him the ab initio HF/3-21G calculations of secondary deuterium kinetic isotope effects in the first two complete paragraphs on page 542. As the senior author, M.J.S.D. accepts full responsibility for this error and apologizes unreservedly.