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Electronic Structures of Tungsten-Chalcogen Multiple Bonds

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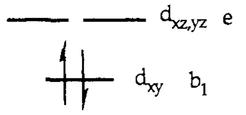
An intense interest in metal–ligand multiple bonding has arisen because complexes containing these functionalities are relevant in such diverse areas as nonlinear optics, catalysis, and biochemistry.[1-4] Recently, Parkin et al. have reported on a novel family of complexes of the general formula *trans*-$WE_2(PMe_3)_4$ (E = S, Se, Te) containing the trans-dielement functionality.[5,6] The crystal structure for E = Te[5] shows that steric constraints prohibit the phosphines from adopting a planar configuration, and the ligands are therefore ruffled, leading to D_{2d} symmetry for the complexes. An understanding of the electronic structures of these complexes is attractive because this is the first series of complexes wherein the multiply bonded ligand can be systematically varied through three different congeners of a single group of the periodic table.

Numerous studies have shown that the trans-dielement configuration leads to an axially compressed ligand field,[7] which for d^2 metal ions gives a frontier d-orbital energy diagram as follows (symmetry labels are for D_{2d}):



In the case of $ReO_2(py)_4^+$, the low-energy absorption arises from a $^1A_g \rightarrow {}^1E_g$ transition (in D_{4h} symmetry).[11] An analogous $^1A_1 \rightarrow {}^1E$ transition is also expected in the WE_2 complexes. Indeed, the low-energy feature in the electronic spectra of the WTe_2 complex is a weak ($\epsilon \sim 300$–400 M^{-1} cm^{-1}) ligand-field transition (Figure 1A) at 13 300 cm^{-1}. Related bands are present at 18 100 cm^{-1} in the WS_2 complex and as a shoulder at 16 100 cm^{-1} in the WSe_2 complex. As expected, the energy of this ligand-field transition increases in the order Te < Se < S, consistent with the expected degree of axial compression of the ligand field and hence the d_{xy}–$d_{xz,yz}$ splitting.[7-9] Interestingly, a second weak band is observed in each case at higher energy (WTe_2, 14 900 cm^{-1}; WSe_2, 19 000 cm^{-1}; WS_2, 21 000 cm^{-1}). This second band must also arise from a ligand-field transition, although comparable bands are not found in D_{4h} complexes such as $ReO_2(py)_4^+$.[11] We assign this feature to splitting of the ^1E state by Jahn–Teller distortion. Either b_1 or b_2 vibrational modes, such as the asymmetric WE_2 stretch, are Jahn–Teller active. These modes lift the degeneracy of the e level in D_{2d}, which splits into arbitrarily assigned b_1 and b_2 levels in C_{2v}:

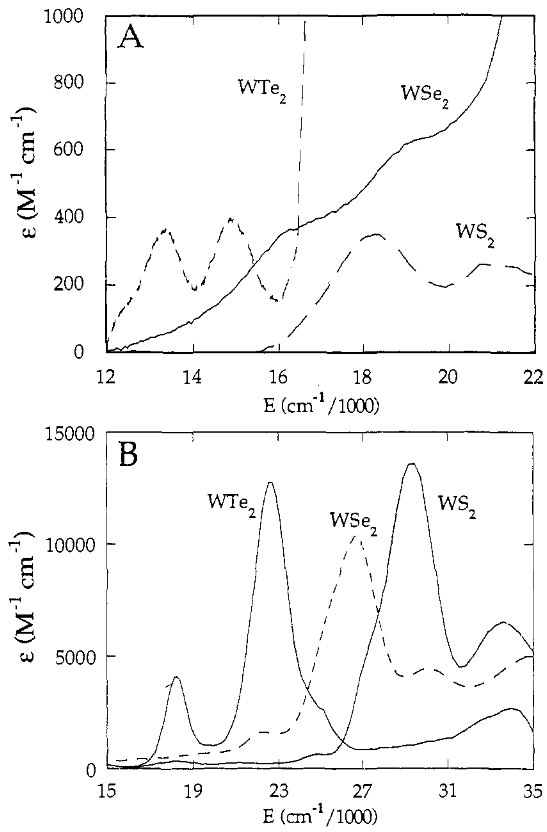
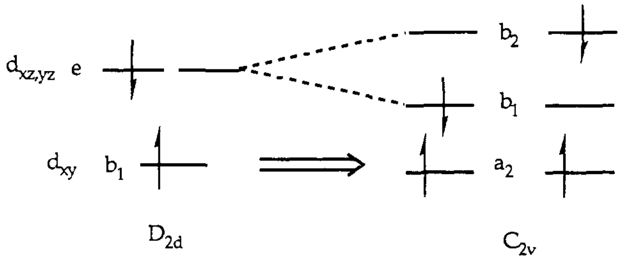


Figure 1. (A) Low-energy region of the electronic spectra of $WTe_2(PMe_3)_4$ (solid), $WSe_2(PMe_3)_4$ (dashed), and $WS_2(PMe_3)_4$ (solid) in benzene. (B) High-energy region of the same spectra. Metal complexes and solvents (Burdick and Jackson) were handled in a drybox, and optical spectra were acquired in inert-atmosphere cells using an OLIS-modified Cary 17.



A similar assignment has been made in the case of excited states of related $OsNX_4^-$ complexes, which can adopt C_{2v} symmetry via vibrations of the equatorial Cl^- ligands.[8]

In complexes where the multiply bonded ligand is a second-row element (as in M=O, M≡CH, or M≡N), LMCT transitions, which are formally π–π^* in the metal–ligand multiple bond, are not observed because the ligand $2p_{x,y}$ orbitals are too low in energy compared to the $d_{xz,yz}$ level.[7-11] However, in the WE_2 complexes reported here, we expect these transitions to occur at energies that are readily observable in the optical spectrum. Indeed, a strong ($\epsilon \sim 12\,000$ M^{-1} cm^{-1}) transition is observed for all three complexes (Figure 1B). This transition moves to higher energy in the order Te (22 600 cm^{-1}) < Se (26 700 cm^{-1}) < S (29 300 cm^{-1}). The changes in energy on moving to lighter

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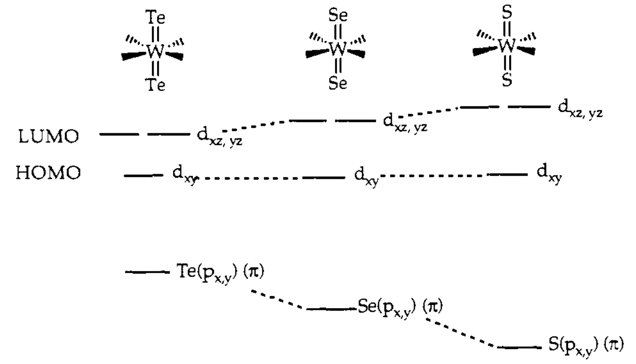
Scheme I



elements correspond to the changes in the known ionization potentials.[12] Thus, we can confidently assign this band to the $\pi-\pi^*$ transition $^1A_1 \rightarrow {}^1B_2$ (the only allowed component of the e → e transition), as shown in Scheme I. The valence-orbital ionization energy for oxygen is 4–5 eV lower than those for the heavier congeners,[12] and we can thereby estimate that the energy of the $\pi-\pi^*$ transition in $WO_2(PMe_3)_4$ would be >35 000 cm^{-1}. This accounts for the failure to observe a $\pi-\pi^*$ transition in related oxo complexes.[11]

In each complex, there is another band ~4400 cm^{-1} lower in energy than the $\pi-\pi^*$ band discussed above. The extinction coefficient of this band increases from 600 M^{-1} cm^{-1} in WS_2 up to 4000 M^{-1} cm^{-1} in WTe_2. This increase in intensity with the size of the chalcogen and the almost constant separation in energy of this band from the strong $\pi-\pi^*$ band argue for its assignment as the corresponding spin-forbidden transition, $^1A_1 \rightarrow {}^3B_2$. There is also a shoulder on the low-energy side of the band at 13 300 cm^{-1} in the WTe_2 spectrum that is likely the triplet component of the low-energy ligand-field transition.

The WE_2 complexes have provided the first opportunity to study the electronic structure of the doubly bonded trans-dielement moiety as a function of the position of the multiply bonded ligand in a single family of the periodic table. These studies show that the energy of the d_{xy}–$d_{xz,yz}$ ($n \rightarrow \pi^*$) transition increases in the order Te < Se < S. Since, in the absence of π bonding, the $d_{xz,yz}$ and d_{xy} levels would be degenerate, the extent of π bonding is reflected directly in the energies of the $n \rightarrow \pi^*$ transitions. Thus, the strength of the π bonds also increases in the order Te < Se < S. Further, we have demonstrated that the formally $\pi-\pi^*$ LMCT transitions, which are absent in the optical spectra of M=O complexes, are present when there is a double bond to a heavier element. Interestingly, the $\pi-\pi^*$ energy simply tracks the ionization potential of the multiply bonded element. Thus, the ligand-field bands offer more information on the nature of the metal–ligand multiple bonds than the $\pi-\pi^*$ bands, because the d–d transitions are apparently far more sensitive to the nature of the metal–ligand π bonding.

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