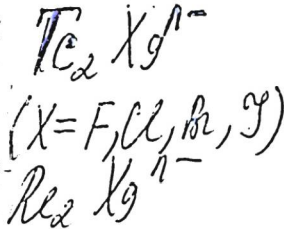


Tc-hal

135: 278307t Ligand Dependence of Metal-Metal Bonding in the d^3d^3 Dimers $M_2X_9^{n-}$ ($M^{III} = Cr, Mo, W$; $M^{IV} = Mn, Tc, Re$; $X = F, Cl, Br, I$). Stranger, Robert; Turner, Alison; Delfs, Christopher D. (Department of Chemistry The Faculties, The Australian National University, Canberra, 0200 Australia). *Inorg. Chem.* 2001, 40(17), 4093-4100 (Eng), American Chemical Society. The ligand dependence of metal-metal bonding in the d^3d^3 face-shared $M_2X_9^{n-}$ ($M^{III} = Cr, Mo, W$; $M^{IV} = Mn, Tc, Re$; $X = F, Cl, Br, I$) dimers has been investigated using d. functional theory. In general, significant differences in metal-metal bonding are obsd. between the fluoride and chloride complexes involving the same metal ion, whereas less dramatic changes occur between the bromide and iodide complexes and minimal differences between the chloride and bromide complexes. For $M = Mo, Tc$, and Re , change in the halide from F to I results in weaker metal-metal bonding corresponding to a shift from either the triple metal-metal bonded to single bonded case or from the latter to a nonbonded structure. A fragment anal. performed on $M_2X_9^{3-}$ ($M = Mo, W$) allowed detn. of the metal-metal and metal-bridge contributions to the total bonding energy in the dimer. As the halide changes from F to I , there is a systematic



Wong 10/5