

**Title:** Investigations into the Nature of Bonding in Oxychlorides of Group 5 (V, Nb, Ta) Elements: Sigma-Hole Interactions or Charge Transfer?

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**Abstract:** The  $\text{VOCl}_3$  crystal structure is a network of chains of weakly interacting  $\text{VOCl}_3$  monomers, with 3.4Å long V--O contacts. One row below lies Niobium, and the  $\text{NbOCl}_3$  crystal structure is made up of similar chains of  $\text{NbOCl}_3$ , however with much shorter Nb--O intermonomer contacts of 2.5Å. The shorter intermonomer contacts of the latter correlate with the extent of a positive electrostatic potential center that is induced by the interatomic oxygen atom. The polarization induces a *sigma hole* on the Nb atom in the same place as the  $\sigma^*$  orbital, and there is a possible competition between sigma-hole interactions and charge-transfer. We have investigated the nature of these Nb--O interactions at the B3LYP level with cc-PVTZ basis sets. We have further probed the gas phase structures of  $\text{MOCl}_3$  (M=V, Nb, Ta) dimers and tetramers to determine their structural preferences and nature of bonding. A future point of interest is how these properties correlate to the solid state  $\text{MOCl}_3$  structures, and whether or not they offer insights on a theoretical basis for crystals.