MS29-O3 One-dimensional chains in PGM complexes- understanding metallophilic interactions

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Research in the field of supramolecular chemistry has delivered several novel compounds with exciting optical, magnetic and conductive properties in recent years. Of particular interest in our current work is the use of metallophilic interactions as part of the arsenal library in the construction of large network structures. Metallophilicity has been defined as the interaction between electron densities of large closed-shell or pseudo closed-shell metal centres with d^8 and d^{10} electron configurations with similar energies as hydrogen-bonding. Interactions of this kind facilitate the growth of infinite 1-D metallic chains between neighbouring metal centres along one direction of the crystal lattice. Materials containing such interactions often display tunable physical properties such as dichroism that can be directly influenced by changes to the interactions.

The current project was focused on an analogous series of complexes containing Rh(I) and Pt(II) metal centres with metallophilic interactions. Three classes of ligand systems were chosen for the study (Scheme 1 (**a**)) with accompanying illustration of the metallophilic interactions found in $[Rh(piv)(CO)_2]$ (piv= 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedionato) (**b**). Crystals of **1** with Rh(I) have been characterized by red-green dichroism with Rh···Rh distances of 3.264(3) Å whilst the Pt(II) analogue exhibits green-purple dichroism and Pt···Pt distances of 3.160(1) Å. In contrast Rh(I) complexes of **3** have much longer metallophilic interactions with Rh···Rh distances (3.641(1) Å) and red-yellow dichroism associated with the bulk material.

Several novel Rh(I) and Pt(II) complexes will be presented that display unique metallophilic interactions relating not only the importance of ligand choice in these systems but also the effect of different metals in the establishment of metallophilic interactions. In turn, the differences in chemical systems will be correlated to changes in the physical properties of the compounds thereby establishing a framework by which the design of future materials with desirable properties may be undertaken. Studies investigating the solid-state UV/Vis properties, charge transfer and excited state structures, fluorescence and mechanical effects such as pressure on the metallophilic interactions will also be highlighted.

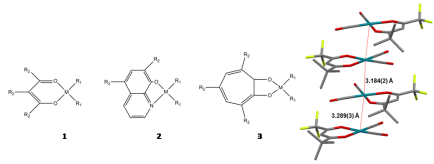

Figure 1. a) Selected Rh(I) and Pt(II) complexes (M = Rh, Pt; R = CO, $COHCH_3$; R' = substituents); b) metallophilic interactions in $[Rh(piv)(CO)_2]$ in an extended 1-D chain along the *a*-axis.

Keywords: Metallophilic interactions, 1-D chains, Platinum, Rhodium