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Transition Elements inspired Inorganic Pigments: The Importance of Coordination Geometry

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Crystalline inorganic oxides displaying bright colours attracted much attention from early days for application as genstones and pigments. Ruby $(Cr^{3+} \text{ doped } Al_2O_3)$ and Emerald $(Cr^{3+} \text{ doped } Be_3Al_2(SiO_3)_6)$ and Azurite $(Cu_3(CO_3)_2(OH)_2)$, Han blue $(BaCuSi_2O_6)$ and Turquoise (CuAl₆(PO₄)₄(OH)₈·4H₂O) for example found application as gemstones and pigments since ancient times.^[1] In addition to the naturally occurring gemstones and pigments, several man-made (synthetic) coloured solids were also developed to meet the demand.^[1] Y₂BaCuO₅, copper substituted apatites, Mn(III) substituted $YInO_3$ and $CaTaO_2N - LaTaON_2$ pervoskites are some of the more recent pigment materials for green, blue, red-yellow colours.^[2,3] A scientific inquiry into the origin of colours of inorganic solids is essential for a rational design and synthesis of coloured materials. While there are several causes for the colour of solids, the main factor that causes colour in an inorganic oxide containing transition metal ion is the electronic transitions within the partially filled d-states arising from the ligand field effects around the transition metal ion. Octahedral and tetrahedral are the most common geometries where the colour and optical absorption spectra of all the transition metal ions have been well-documented. Transition metal ions in less symmetric geometries such as distorted octahedral and five-fold coordinated (square pyramidal and trigonal bipyramidal) geometries produce colours different from those in regular octahedral and tetrahedral geometries in materials. The present talk would address some of these issues and our efforts towards identifying new chromophores employing transition metal chemistry.^[4-6]



 $LiZn_{0.85}Co_{0.15}BO_3 Ba_3(V_{0.75}Mn_{0.25}O_4)_2 Li_2MnO_3$

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