

## Synthesis of a family of Pt-Ag clusters: Ligands, solvents, unit cells and crystal quality

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The characteristic coordination indices of Pt<sup>II</sup> and Pt<sup>IV</sup> are combined with novel (OH) bridging systems to form a mixed-oxidation-state Pt cluster with a structurally unprecedented M<sub>4</sub>(OH)<sub>4</sub> core. The anion in (NBu<sub>4</sub>)<sub>2</sub>[Pt<sup>IV</sup>Pt<sup>II</sup><sub>3</sub>(C<sub>6</sub>Cl<sub>5</sub>)<sub>8</sub>(μ<sub>2</sub>-OH)<sub>2</sub>(μ<sub>3</sub>-OH)<sub>2</sub>] (1) has two (μ<sub>3</sub>-OH) and two (μ<sub>2</sub>-OH) units that bridge platinum atoms in different oxidation states. The geometry at the core of the cluster is described as a distorted half-hexagram. Compound (1) can host full-shell d<sup>10</sup> or s<sup>2</sup> Lewis-acid metals, which are held in place by Pt→M dative bonds. The syntheses of several solids, some of them with unbridged Pt→Ag bonds, without disrupting the fundamental core geometry of the anion (1), accredits the host potential of (1). Interesting relationships arise among ligands, solvents, unit cells and crystal quality. The role of weak C—Cl⋯Ag interactions in stabilizing these compounds is also described.