

Studies of transuranic organometallic complexes provide particularly valuable insight into covalent contributions to the metal-ligand bonding, in which the subtle differences between the transuranium actinide ions and their lighter lanthanide counterparts are of fundamental importance for effective remediation of nuclear waste. Unlike the organometallic chemistry of uranium, which has focused strongly on U(III) and has seen some spectacular advances, that of the transuranics is significantly technically more challenging and has remained dormant. In the case of neptunium, it is limited mainly to Np(IV). Here we report the synthesis of three new Np(III) organometallic compounds, and the characterization of their molecular and electronic structures. These studies suggest that Np(III) complexes could act as single molecule magnets, and that the lower oxidation state of Np(II) is chemically accessible. Significant d- and f-electron contributions to key Np(III) orbitals are observed, in comparison with lanthanide analogues, showing that fundamental neptunium organometallic chemistry can provide new insight into the behaviour of f-elements.