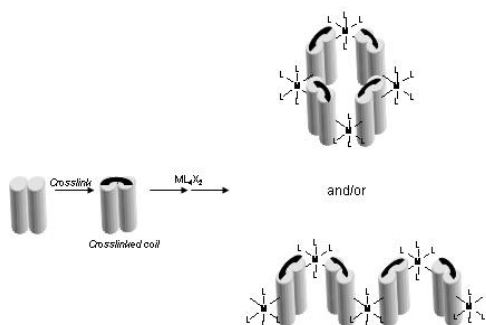


Metal-peptide Nanoassemblies

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Both non-covalent and disulfide crosslinked α -helical coiled-coils are used as bridging ligands to join together $[\text{Pt}(\text{en})\text{X}_2]$ coordination complexes in geometries dictated by the steric demands of the metal center, where en = ethylene diamine. The peptide used in this study were based on the IEALEGK heptad repeat which is known to form metal-substituted, two-stranded α -helical coiled-coils. However, in this work the non-natural amino acid 4-pyridyl alanine (Pal) was placed at the most solvent-exposed position of the second heptad repeat (PAL14). For some studies a cysteine residue was placed at position 19 which exists within the hydrophobic peptide-peptide interface of the coiled-coil (PAL14C19). These modifications were respectively made in order to incorporate a strong metal binding site into the peptide, and to engineer an inter-chain disulfide bond crosslink to stabilize the coiled-coil structure.



When $\text{Pt}(\text{en})(\text{NO}_3)_2$ was treated with PAL14, a metal-peptide “corner unit” was prepared in which the pyridine sites of two peptide chains were coordinated to the *cis* positions of the square-planar Pt center. The circular dichroism spectrum of a sample of purified Pt corner units shows that multiple corner units do indeed self-assemble through the formation of non-covalent α -helical coiled-coils. Results indicate that the non-covalent association of Pt-peptide corner units produces assemblies of multiple corner

units. The major product formed in this process corresponds to the assembly of perhaps 6 Pt-peptide corners. Related work involved the incubation of $\text{Pt}(\text{en})(\text{NO}_3)_2$ with the disulfide crosslinked PAL14C19 coiled-coil peptide. Here, SDS-PAGE and MALDI-MS shows evidence for the assembly of 1-5 metal-peptide units where lower molecular weight products was favored, in contrast to the behavior observed for the assembly of non-crosslinked PAL14 units.