

**MS33-P3** New polynuclear Re-M cyanide complexes (M = Cu, Ag)Monika K. Krawczyk<sup>1</sup>, Rahman Bikas<sup>1</sup>, Marta S. Krawczyk<sup>2</sup>

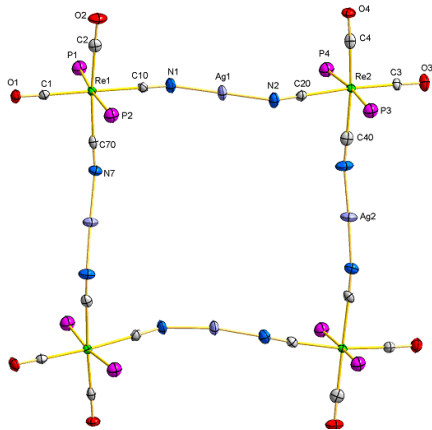
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New class of mixed-metal square-shaped polynuclear clusters based on rhenium(I) phosphine complexes have been obtained. The heteronuclear complexes are comprising of the core that consists of Re and Cu or Ag atoms bridged by cyanide ligands resulting in the formation of cyclic structure with approximate square geometry. In studied complexes Re atoms are located in vertices of the square, while Cu or Ag atoms along with coordinated CN<sup>-</sup> ligands form their sides.

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**Figure 1.** Structure of square-shaped  $[\text{Re}_4(\mu\text{-CN})_4\text{Ag}_4(\mu\text{-NC})(\text{CO})_2\text{P}_4]$  unit in studied complex. The aromatic rings attached to phosphorus atoms in  $\text{PPh}_3$  groups are omitted for clarity.

**Keywords:** rhenium complexes, cyanide complexes, heteronuclear clusters

**MS33-P4** Disappearing Superstructure in Crystals of Pentaphosphaferrocene-Based SupramoleculesEugenia V. Peresyapkina<sup>1,2</sup>, Alexander V. Virovets<sup>1,2</sup>, Manfred Scheer<sup>1</sup>

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Since 2002, we have been systematically investigating an inorganic analogue of ferrocene, pentaphosphaferrocene,  $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$  ( $\text{Cp}^{\text{R}} = \eta^5\text{-C}_5\text{R}_5$ ,  $\text{R} = \text{Me}$  ( $\text{Cp}^{\text{Me}}$ ),  $\text{CH}_2\text{Ph}$  ( $\text{Cp}^{\text{Bn}}$ ),  $\text{PhC}_4\text{H}_9$  ( $\text{Cp}^{\text{BIG}}$ )). It showed an unprecedented ability to assemble in giant supramolecules [1-7] when reacted to  $\text{Cu}(\text{I})$  halides ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). These supramolecules reach 2.1–4.6 nm in size and can be isolated in astonishingly high yields. Their molecular structure is usually based on inorganic hollow cage, in which the  $\text{cyclo-P}_5$  ring of the  $[\text{Cp}^{\text{R}}\text{Fe}(\eta^5\text{-P}_5)]$  ligand is coordinated to single or various aggregated  $\text{CuX}$  units. The single-layered cages often follow fullerene topology involving single  $\text{CuX}$  units [1-4]. The multi-layered cages [1-2, 6] are constructed of  $\text{Cu}_n\text{X}_m$  polynuclear fragments.

The X-ray structural analysis of these compounds faces many difficulties as low diffraction power, disorder in  $\text{Cu}_n\text{X}_m$  halide core, disorder of guest molecules and  $\text{Cp}^{\text{R}}$  ligands. The disorder can be interpreted as formation of solid solutions of co-crystallizing supramolecules with different, but similar structure. In some cases, we observed superstructural effects pointing to partial ordering. The aging of the crystals in the mother liquor unexpectedly leads the superstructure to disappear. For example, the diffraction pattern of freshly prepared  $(\text{CH}_2\text{Cl}_2)_{3,4} \cdot [(\text{Cp}^{\text{Bn}}\text{FeP}_5)_5]_{12} \cdot (\text{CuI})_{54} \cdot (\text{MeCN})_{1,46}$  demonstrates superstructural ordering accompanied with doubling of the triclinic unit cell (see figure 1, blue). In the supercell two crystallographically unique supramolecules are related by pseudo body-centering translation. While aging, the diffraction pattern shows as superstructural reflections gradually fade. The resulting subcell (figure 1, red) contains only one unique supramolecule [1]. Other examples will also be discussed.

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