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Construction of Miniature Organo-Rhodium Boxes

Many types of molecular cages exist in which ions, atoms or molecules can be trapped. These cages are usually held in suspension and are typically constructed from bifunctional ligands, with square planar or tetrahedral metal centres at the vertices. Until now there have been no cubic shaped organometallic cages. However, if octahedral transition metal building blocks could be constructed, then the assembly of cubic-shaped structures should be possible.

Now, researchers from the University of Illinois have succeeded in constructing a molecular box from a cubic array of cyano-linked rhodium and cobalt octahedra (K. K. Klausmeyer, T. B. Rauchfuss and S. R. Wilson, *Angew. Chem. Int. Ed.*, 1998, **37**, (12), 1694–1696).

Tricyanometalates $Et_4N[Cp^*Rh(CN)_3]$ and $K[CpCo(CN)_3]$ (where $Cp^* = C_5Me_5$, $Cp = C_5H_5$) were used to prepare a series of molecular "squares", by reaction with $[Cp^*RhCl_2]_2$ or $[(cymene)RuCl_2]_2$ (cymene = 4-isopropyltoluene). To assemble the box from the "squares" the chloride ligands were removed by $AgPF_6$. The "molecular boxes" of most interest have the structure $[(C_5R_5)_8M_8(\mu\text{-}CN)_{12}]$ (M = Rh or Co) and are a subunit of hexacyanometalates, of which Prussian blue is one example.

The most interesting box has alternate rhodium and cobalt atoms at the vertices, linked by CN groups. Each metal atom can adopt its preferred octahedral position. The box has edges 5.1 Å long with a volume of ~ 132 Å^3, giving enough space inside to encapsulate a caesium atom. The box is also soluble so it could therefore be used for trapping molecules in solution.