07-Crystallography of Organometallic and Coordination Compounds

The synthesis and structure of [(Bu₂CpMe)(C≡CPh)] in which four copper atoms are added to the [(Bu₂CpMe)]

The title compound was obtained by reaction of (µ-H₂)₄VS with CuCl in a solution of dimethylformamide (DMF) containing Na₂SPh, Na₂S₂K₃ and MeCN. The reaction mixture was stirred for 20 hours and then filtered. After standing for several days at room temperature black crystals were collected and used for X-ray diffraction.

Crystal data were collected on an Enraf-Nonius CAD4 diffractometer. The space group is P1 with a = 10.391(2), b = 12.393(2), c = 12.586(5) Å, α = 78.67(2), β = 82.49(2), γ = 81.59(2). ν = 1563.2 Å³ and Z = 1. 4538 reflections with 1<θ<14° were used for the structure determination and gave a final R of 0.039 and R1 of 0.042.

The structure is shown in Figure 1. The unit cell contains only one molecule, a [V₂(C≡CPh)]⁻[(Cu(dcst))3⁻] cation and three [Et₃NF]⁺ cations. The anion is formed of a central V₂ tetrahedron surrounded by a tetragon of four copper atoms. The V₂ core has retained the ideal geometry of free tetrahedron with S-V-S angles and V-S bond lengths ranging from 108.2(1) to 110.9(1)° and 2.173(1) to 2.370(3) Å respectively. Each copper atom is bound across an edge of the V₂ tetrahedron with a μ₃ coordination to each sulfur atom. The Cu–S bond lengths are quite similar. The V₂Cu₃ aggregate approximates D₃d symmetry which is also observed for Nd₂Cu₄ and V₂Cu₃ cores.

The V–Cu near distance of 2.61(1) Å implies intermetallic contacts between heterometallic atoms. Four copper atoms have two types of geometries. One is trigonal with an SPh group coordinated; the other is a distorted tetrahedron with a chelating PhPh₂ group. The Cu–S bond lengths (2.166(1)–2.182(1) Å) are the same as those in [Ph₂Cu₂SPh₂]⁻ (2.18(1) Å), however Cu–S bond lengths are equivalent to those in [Ph₂Cu₃(SPh)]⁻. These may be attributed to transfer of charge from Cu to V, similar to dislocation from Cu to In₃[H₂(In₃)₃] for Cu-In₃ cluster complexes.

Further studies on spectroscopic characterisation and electrochemistry for this compound are in progress.

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Figure 1. Structure of [V₂(C≡CPh)]⁻[(Cu(dcst))3⁻]

PS-07.03.19 (M₃(µ₂-CO)(P₅(CH₃)₅PPh₃))²⁺ CLUSTERS OF PALLADIUM AND PLATINUM AND THEIR REACTIONS WITH MOLECULES AND IONS. TRACKING DOWN AN ELUSIVE ANION. Kenneth W. Mair,†, Liubica Manojlovic-Muir and James Fullard, Chemistry Department, The University, Glasgow G12 8QQ, Scotland.

The chemical processes which occur during the addition of a small molecule or ion to triangular cluster complexes [M₃(µ₂-CO)(µ-dppm)]²⁺ (M = Ni, Pd or Pt; dppm = P₃(CH₃)₅PPh₃, respectively) mimic related reactions at metal surfaces; they can therefore be used to model the behaviour of such surfaces during heterogeneous catalysis. We have previously described complexes arising from the addition of thiocyanate, cyanide, alkyne, alkynes, phosphines and phosphines, and tributylstannane(II) to triangular dppm clusters of the platinum group metals (Puddephatt, R.J., Manojlovic-Muir, L.J., Mair, K.W., Polymedon, 1990, 9, 2367; Manojlovic-Muir, L.J., Mair, K.W., Mirza, H.A., Puddephatt, R.J., Organometallics, 1992, 11, 3340).

We now report the isolation of an iodide, Re(CO)₃ and AuPPh₃ to the [M₃(µ₂-CO)(µ-dppm)]²⁺ framework. The gold-phosphine complex [P₅(CH₃)₅AuPPh₃](µ-dppm)]PF₆ crystals in the cubic space group Pm3m with a = 40.69 Å. The cation geometry has been clearly established from data collected at room temperature and reduced to R = 0.057 however, there is little evidence for the presence, let alone position, of the counterion. The results of a refinement based on new data collected at 120 K will be presented.