**Metal Clusters**

**PS07.03.01 CRYSTAL STRUCTURE OF 6,9-BIS(4-STILBAZOLE)-NIDO-DECABORANE(12), 6,9-(PhC,H2)_2-PyB10H12**

A single-crystal X-ray study has been performed for the title decaborane(14) derivative. The sample used was prepared by the well known type of displacement reaction of \( \text{SMe}_2 \cdot \text{B}_{10} \text{H}_{12} \) with 4-stilbazole and was recrystallized from hot dimethylformamide.

The most interesting feature of the compound is that four crystallographically independent asymmetrical molecules exist in the unit cell due to different arrangements of both the two cycle aromatic pyridine and phenol fragments and those in respect to the three-dimensional aromatic \( \text{B}_{10} \text{H}_{12} \) nido-cluster.

The nitrogen atoms of pyridine are linked to the 6,9-boron atoms on the open face of the \( \text{B}_{10} \text{H}_{12} \) basket at the mean distance of 1.60 Å. The following mean bond lengths are B-B 1.80, C-N 1.35, C-C 1.40 and 1.38 Å for Py and Ph, respectively.

Crystal data: dark red color, triclinic P1, \( a=11.285(1), b=13.061(2), c=21.176(2) \) Å, \( \alpha=85.37(1), \beta=102.26(1), \gamma=115.58(1) \), \( V=2750.7(7) \) Å³, \( Z=4, D_m=1.65 \) g·cm⁻³, CAD-4, λ MoKα.

As a solid, this compound exhibits a photosensitivity (λ(★) = 653 nm) with the quantum yield approximating that of rhodamine 6G.

**PS07.02.14 CRYSTAL STRUCTURE AND EPR DATA OF A DINUCLER Cu(II) COMPLEX, \([\text{Cu(N3)}(\text{NCO})\text{dietfem}]^+\)**

J. Zukerman-Schpector,1 O.E. Piro,2 E.E. Castellano,3 C.A. De Simone,4 D.M. Martino5 and C.A. Steren5

The [Cu(N3)(NCO)’dietfem] molecules are arranged as centrosymmetric dimers in which two azide ligands bridge neighboring copper ions in an asymmetric head-on fashion. The Cu(I) ion is coordinated to five nitrogen atoms which form a distorted tetragonal pyramid. At the pyramid base are the two N atoms of a diEttem molecule \[\text{d}[\text{Cu(N3)}=2.00(1), 2.12(1) \) Å, an azide end atom \[\text{d}[\text{Cu-N}]=1.90(1) \) Å and a NCO group \[\text{d}[\text{Cu-N}]=1.95(1) \) Å. At the pyramid apex is the other, inversion related to the first one, azide atom in the dimer \[\text{d}[\text{Cu-N}]=2.38(1) \) Å.

The Cu-N contact links the monomers within a dimer providing an electronic path to transmit the superexchange coupling between the Cu(I) unpaired electrons. Neighboring dimers are coupled by weak N-H-O contacts. Single crystal EPR data at X-band show that the pair of resonances expected for neighboring, magnetically nonequivalent dimers, collapse into a single line, a signature of dimers superexchange coupling. The observed crystal gyromagnetic tensor is used to disclose the electronic and magnetic structure around Cu(II) ions. The compound crystallizes in the space P211, with \( a=8.336(1), b=17.40(5)(3), c=8.376(1) \) Å, \( \beta=109.73(2)^\circ \) and \( \gamma=90^\circ \).

**PS07.03.02 INCOMPLETE CUBANES \( \text{M}_2\text{X}_6\text{S}_6\text{P}_4\text{O}_{14}\text{N}_8\text{H}_8\text{O} \)**

J. Huang,5 D. Li,5 W. M. Lee6 and K.B. Shin7

The \( \text{[Cu(N3)(NCO)diEttem]}^2 \) crystal structure is well known type of displacement reaction of \( \text{SMe}_2 \cdot \text{B}_{10} \text{H}_{12} \) with \( \text{B}_{10} \text{H}_{12} \) cluster. In both compounds there is a free formate ion. In 1 two of the cation sites are disordered and are occupied by either potassium or ammonium ions. 2 is either disordered or has a lower symmetry than C2/m, but refinement in lower symmetry space groups did not give a lower R-value.

Cluster compounds of the type \( \text{M}_2\text{X}_6\text{S}_6\text{P}_4\text{O}_{14}\text{N}_8\text{H}_8\text{O} \) (\( \text{M}=\text{Mo}, \text{W} \)) are being studied as catalysts for homogeneous hydrosulphurization e.g. \( \text{CuH}_2 \text{S}+2\text{H}_2\text{S}+\text{CuH}_2\text{S} \)

The structures of two such compounds have been studied: 1 \( (\text{NH}_4)_{1-x} \cdot \text{K}_x \cdot \text{[Mo}_3\text{O}_4(\text{CHO})_6(\text{H}_2\text{O})_2\text{CHO})_2\text{H}_2\text{O} \) (\( x=0.80 \)) and 2 \( \text{K}_5(\text{W}_3\text{S}_4(\text{CHO})_6(\text{H}_2\text{O})_2\text{CHO})_2\text{H}_2\text{O} \). The cell dimensions of \( x=11.01(1), b=13.31(2), c=10.99(1) \) Å, \( a=106.817(7), b=91.651(9), = 88.4009(6), Z=2 \) (R(F) = 0.026 for \( N_m = 3972 \) and \( N_i = 451.2 \) is monoclinic, space group C2/m with \( a=19.09(6), b=14.34(7), c=13.627(5) \) Å and \( b=1.189(3) \), \( Z=4 \), (R(F) = 0.049 for \( N_m = 2656 \) and \( N_i = 226 \).

The most interesting feature of the compound is that four crystallographically independent asymmetrical molecules exist in the unit cell due to different arrangements of both the two cycle aromatic pyridine and phenol fragments and those in respect to the three-dimensional aromatic \( \text{B}_{10} \text{H}_{12} \) nido-cluster.

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