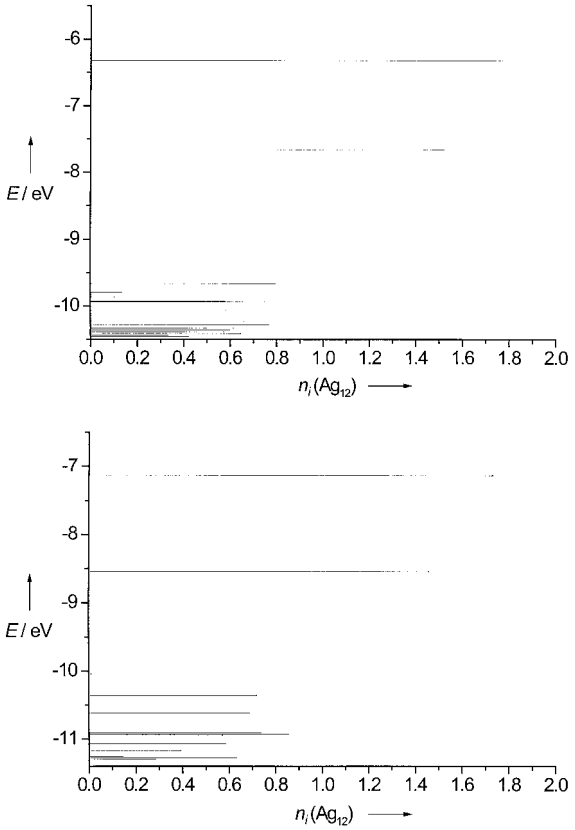

Figure 6. Orbital energy E and contribution of the cluster core to the Mulliken population, $n_i(Ag_{12})$, for the 20 highest lying molecular orbitals for model **A** (top) and model **B** (bottom). The data are based on the HF wave function in the DFT equilibrium geometry.

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Synthesis, Crystal Structure, and Binding Properties of the Mixed Valence Clusters $[Cu_{32}As_{30}(dppm)_8]$ and $[Cu_{26}Te_{12}(PEt_2Ph)_{12}]$**

Reinhart Ahlrichs, Jörn Besinger, Andreas Eichhöfer, Dieter Fenske,* and Axel Gbureck

Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday

A possible way to synthesize transition metal clusters bridged by main group elements is the reaction of a transition metal salt MX_n (M = metal, X = halide, acetate) with silylated derivatives of the heavier main Group 5 and 6 elements.[1] In this way, not only chalcogen bridged coinage-metal clusters were prepared, for example, $[Cu_{146}Se_{73}(PPh_3)_{30}]$[2] or $[Ag_{172}$-

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$Se_{40}(Se\mathit{n}Bu)_{92}(dppp)_4]$,[3] (dppp = bis(diphenylphosphanyl)-propane) but also phosphorus bridged clusters of copper and silver, such as $[Cu_{96}P_{30}\{P(SiMe_3)_2\}_6(PEt_3)_{18}]$ and $[Ag_{50}(PPh)_{20}Cl_7P(P\mathit{n}Pr_3)_{13}]$,[4, 5] could be obtained. Up to now, arsinidene bridged clusters of the coinage metals are known only for silver and gold, for example $[Ag_{14}(AsPh)_6Cl_2(PEt_3)_8]$ and $[Au_{10}(AsPh)_4(PhAsSiMe_3)_2(P\mathit{n}Pr_3)_6]$.[6] In contrast, polynuclear complexes of these metals with arsenic as a bridging ligand are unknown. Recently, by reactions of CuX (X = SCN, Cl, OAc) with tertiary phosphanes and $AsR(SiMe_3)_2$ (R = Ph, $SiMe_3$), we were successful in synthesizing the first arsinidene bridged copper cluster compounds, such as $[Cu_8(AsSiMe_3)_4(P\mathit{t}Bu_3)_4]$, $[Cu_{10}(AsPh)_4Cl_2(PMe_3)_8]$, $[Cu_{12}(AsPh)_6(PPh_3)_6]$, and $[Cu_{14}(AsPh)_6Cl_2(PEt_3)_8]$.[7] Herein we report the synthesis, single crystal X-ray analysis and the electronic structure of $[Cu_{32}As_{10}(dppm)_8]$ (**1**).

During the reaction of copper(I) chloride with the bidentate ligand bis(diphenylphosphanyl)methane (dppm) and $LiAs(SiMe_3)_2$ in dimethoxyethane (DME), a brilliant red solution is formed at $-20\,^{\circ}C$. With increasing temperature, the color of this solution becomes more intensive until at room temperature it turns black [Eq. (1)]. After reducing the volume of the solution, one obtains black needles of the arsenido bridged copper cluster $[Cu_{32}As_{10}(dppm)_8]$ (**1**) within a few days at rooms temperature.

$$CuCl + LiAs(SiMe_3)_2 \xrightarrow[(dppm)]{DME} [Cu_{32}As_{10}(dppm)_8] \quad \mathbf{1} \qquad (1)$$

Cluster **1** crystallizes in the monoclinic space group $P2_1/c$ with four formula units and twenty molecules of DME per unit cell.[8] The molecular structure of **1** is shown in Figure 1. The molecule itself displays no crystallographic symmetry. The most noticeable structural element of **1** is a nearly regular Cu_6 octahedron, which is formed by the atoms Cu27 to Cu32, and is situated in the cluster core. This central Cu_6 octahedron is enclosed by a complex network of 26 copper and ten arsenic atoms. At the surface, the cluster is completely protected by eight molecules of the bidentate phosphane ligand dppm.

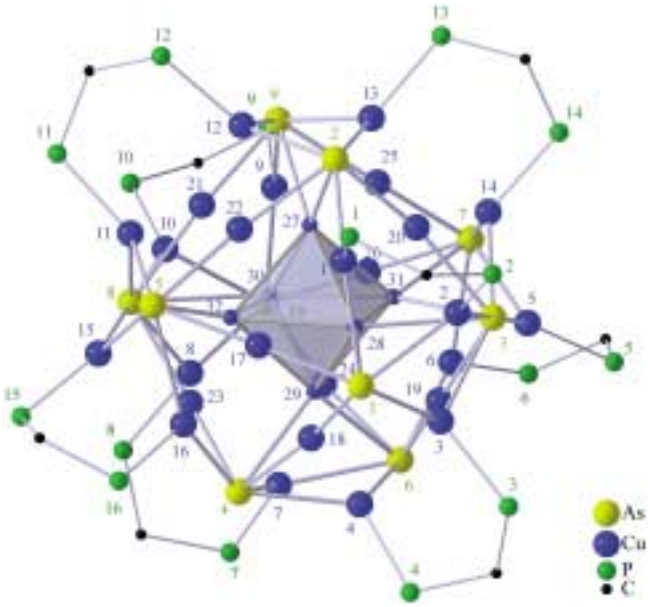

Figure 1. The molecular structure of **1** (phenyl groups are omitted for clarity). The Cu, As, and P atoms are indicated by blue, yellow, or green numbers respectively.

The shell-like structure of **1** can also be described in the following way: the core consists of a Cu_6 octahedron (first shell) surrounded by eight further copper atoms (Cu18 to Cu25) that are arranged like a distorted square antiprism (second shell). The edge lengths of the octahedron are 251.8(3) – 267.5(3) pm, those of the square antiprism vary from 347.4(3) to 489.5(3) pm. The shortest bond between two copper atoms of the first and the second shell is 239.9(3) pm which is considerably shorter than in copper metal (256 pm).[9] The residual 18 copper atoms form the third shell of **1** (Cu1 to Cu17, and Cu26), however, its structure can not be described in terms of a regular polyhedron. Cu1, Cu9, Cu11, and Cu14, and Cu3, Cu6, Cu8, and Cu16 lie roughly in the same plane as the faces of the square antiprism and bridge its edges. Cu4 and Cu7, and Cu12 and Cu13 are situated above or below the faces, respectively, and also bridge one edge each. The residual six copper atoms (Cu2, Cu5, Cu10, Cu15, Cu17, and Cu26) form a six-membered ring in boat conformation and occupy about six of the eight edges between the two basic planes of the square antiprism. The shortest bond between two copper atoms of the second and the third shell is 246.9(3) pm.

The arsenic atoms of **1** are embedded in the third shell of the cluster. Two pairs of arsenic atoms (As2 and As9, As6 and As4) are situated above and below the basic planes of the square antiprism of the second shell, bridging the remaining unoccupied edges (Cu20-Cu22, Cu21-Cu25, Cu18-Cu19, Cu23-Cu24). The remaining arsenic atoms (As1, As3, As5, As7, As8, As10) are arranged like a six-membered ring, in boat conformation, between the two square faces of the antiprism. All the arsenic atoms together form a distorted polyhedron similar to that of the boron atoms in the *closo*-borane $B_{10}H_{10}^{2-}$.[10] The Cu–As bond lengths, for the copper atoms of the second and third shell, vary from 234.8(1) to 265.3(3) pm. The copper atoms in **1** show three different coordination geometries. The centers Cu1 to Cu16 have a distorted trigonal planar geometry and are coordinated by two arsenic atoms and by a phosphorus atom from a dppm ligand. In contrast, the centers Cu17 to Cu26 are coordinated by two arsenic atoms in a nearly linear manner, and finally, the octahedrally arranged atoms, Cu27 to Cu32, interact only weakly with the arsenic atoms (260.6(1) - 292.8(2) pm).

In an alternative description, the outer cluster shell is constructed by six Cu_2As_2 four-membered rings, that are linked together by copper atoms (Cu17 to Cu26) that are linearly coordinated by two arsenic ligands. The phosphorus bound copper atoms Cu1 to Cu16 are localized within these Cu_2As_2 rings. Thereby, the centers of the Cu_2As_2 rings point towards the copper atoms of the central Cu_6 octahedron.

Assuming that the ten μ_5-As ligands in **1** have the formal charge of 3 – , then the Cu_{32} cluster has a total charge of 30 + . Thus, the cluster must be a mixed valence compound that consists of 30 Cu^{1+} and two Cu^0 centers. However, in light of the molecular structure this localized distribution of charges is not possible. It is noteworthy that even in **1** a tendency for the formation of nonstoichiometric compounds occurs, as also

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observed for β-Cu_3As, which possesses a substantial phase range.[11]

We found a similar situation in PR_3 stabilized copper chalcogenide clusters. Noteworthy is that in the Cu_2S and Cu_2Se clusters, examples being $[Cu_{28}S_{14}(PtBu_2Me)_{12}]$ and $[Cu_{72}Se_{36}(PPh_3)_{20}]$, a well-defined assignment of charges is possible.[12] In both cases, Cu^{1+} coexists with S^{2-} or Se^{2-} centers, respectively. In contrast, in the similar copper telluride clusters a definite tendency towards nonstoichiometric compositions is observed; for example compounds such as $[Cu_{44}Te_{23}(PPh_3)_{15}]$ and $[Cu_{16}Te_9(PPh_3)_8]$ contain copper atoms in the formal oxidation states 1+ and 2+.[13] In these cases, charge transfer bands of low intensity are observed in the 600–2000 nm range.

Compounds that contain copper atoms in the oxidation states 0 and 1+ side by side are rarer. In these compounds the charge transfer bands mentioned above are absent from the UV/Vis spectra. An example of this type of compound is the recently synthesized and characterized cluster $[Cu_{26}Te_{12}(PEt_2Ph)_{12}]$ (**2**), formally containing 24 Cu^{1+} and two Cu^0 centers.[13] A detailed description of the structure of **2** is given in ref [13]. As in **1**, a central Cu_6 octahedron (Figure 2)

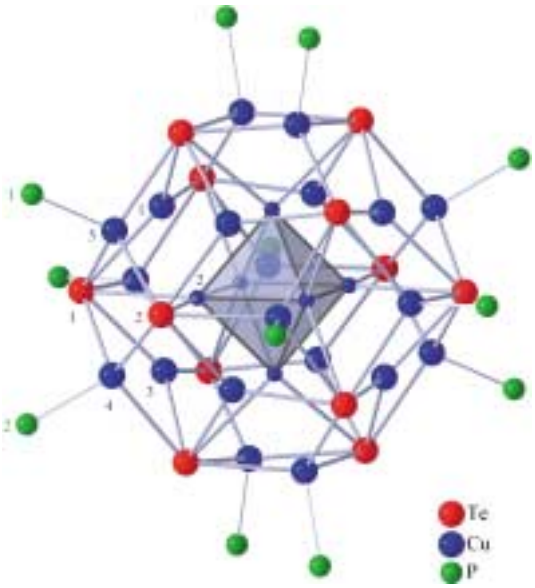

Figure 2. The molecular structure of **2** (organic groups are omitted for clarity. The Cu, Te, and P atoms are indicated by blue, red, or green numbers respectively.

exists, formed by Cu1 and Cu2 and their symmetry equivalents. In contrast to **1**, this octahedron is surrounded by a shell of 20 Cu and 12 Te^{2-} centers forming a distorted icosahedron (Te···Te 431.1–459.3(3) pm); 12 Cu atoms (Cu4, Cu5 and symmetry equivalent sites) occupy 12 Te_3 triangular faces. Binding to one further phosphorus atom (from the PEt_2Ph ligand) each, these copper atoms obtain a distorted tetrahedral coordination sphere (Cu–Te 266.1–271(1) pm; Cu–P 223.0–225.6(2) pm). The remaining eight Te_3 faces of the Te_{12} icosahedron are μ_3-bridged by Cu1 and Cu3 (and symmetry equivalent sites; Cu–Te 259.5–265.2(1) pm). These copper atoms lie below the Te_3 faces. The bond lengths within the aforementioned Cu_6 octahedron are relatively short (259.2–260.7(2) pm) so that the situation is similar to that in **1**. This also applies to the orientation of the Cu centers of the Cu_6 octahedron which are equally directed towards six four-membered Cu_2Te_2 rings at the cluster periphery.

Formally, one can assign the charge 4+ to the central octahedron in **1** and **2**. This corresponds to the situation in the cluster anion $[Ag_{12}(CF_3CO_2)_{14}]^{6-}$, recently prepared by us, where two Ag_6^{4+} clusters are connected to each other.[14] A similar situation was observed in Ag_3O, Ag_5SiO_4, and Ag_5GeO_4. In these compounds, d^{10}–d^{10} interactions between the silver centers were discussed.[15] However, Ab initio calculations show that in the case of the Ag_{12} cluster, the d^{10}–d^{10} interactions between the silver atoms are not important.[14]

To understand the electronic structures of the mixed valence compounds **1** and **2** Ab initio calculations for various model systems have been carried out.[16] The calculations also enable the geometrical structures of **1** and **2** to be checked. In the theoretical treatment the substituents of the phosphane ligands were, in each case, replaced by methyl groups to give the model compounds $[Cu_{32}As_{10}\{P(CH_3)_2CH_2P(CH_3)_2\}_8]$ (**1a**) from **1** and $[Cu_{26}Te_{12}\{P(CH_3)_3\}_{12}]$ (**2a**) from **2**. An even greater simplification, the use of H atoms instead of methyl groups, leads to the compounds $[Cu_{32}As_{10}(PH_2CH_2PH_2)_8]$ (**1b**) and $[Cu_{26}Te_{12}(PH_3)_{12}]$ (**2b**).

The calculated structural parameters of both the model compounds **1a** and **1b** agree very well with the experimental results from **1** (Table 1). The Cu–Cu bond lengths within the slightly compressed Cu_6 octahedron deviate by less than 4 pm from the experimental values. The calculated separations

Table 1. Selected interatomic distances for **1** and **1a**.

Separation[a]	**1** (experimental)	**1a** (DFT)
Cu(Oct)-Cu(Oct)	252.0–264.3	249.7–263.7
Cu(Oct)-Cu(Oct) (non bonding)	350.9, 370.4, 372.0	351.5, 370.1, 370.2
Cu(Oct)-Cu(Rem)	239.9–-263.4	244.0– 264.5
Cu-Cu (bridged by dppm)	256.1–259.1	251.5–252.1
Cu(P)-As	239.0–265.5	241.7–269.4
Cu(Rem)-As	233.6–247.5	238.8–255.5
Cu-P	221.3–230.5	225.6–231.8

[a] Cu(oct) = Cu atoms in the octahedron (cluster core); Cu(P) = Cu atoms bonded to P atoms; Cu(Rem) = remaining Cu atoms.

between the atoms of the octahedral core and the remaining Cu atoms also deviate only slightly from the experimental values. Only the calculated value of the surprisingly short Cu–Cu bond (239.9 pm) in **1** is too long (by 4.1 pm in **1a**). The influence of the smaller model ligand compared to dppm is seen in the separations between the Cu atoms bridged by this ligand. In **1a**, these distances are 4–7 pm shorter than in **1**; in **1b** they are calculated to be even shorter. In both experiment and theory the Cu–As bond lengths cover a broad range, from 238.8–296.5 in **1a** compared to 233.6–293.0 pm in **1**, but overall the range in theory and experiment agree very well. The results of the calculations for the model compounds **1a** and **1b** confirm the unusual structure of **1**.

The crystal structure of **2** exhibits an inversion center within the cluster and a C_3 axis running through two of the atoms of

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the octahedron. Without phosphane ligands the cluster has higher symmetry, namely T_h.[17] In **2a** and **2b**, the model ligands are adjusted according to this symmetry. This higher symmetry enabled us, for comparison, to carry out a complete geometrical optimization for **2b** at the Hatree–Fock (HF) level. In the following discussion, for a better comparison to the calculated values, the experimental separations were averaged to T_h symmetry. The density functional theory (DFT) equilibrium geometries of **2a** and **2b** reproduce very well the important structure parameters of **2**; for example, calculated Cu–Cu bond lengths within the cluster core deviate by less than 1% from the experimentally determined. Only the μ_3-bridging Cu atoms are moved slightly away from the Te centers towards the Cu atoms which are directly bound to the phosphane ligands. Thus the corresponding calculated Cu–Cu bonds are about 10 pm too short, while the calculated bonds of the μ_3-bridging Cu atoms to the Te atoms are about 10 pm too long. The remaining Cu–Te bond lengths of **2a** and **2b** again deviate by less than 1% from those of **2**. The structure calculated at the HF/SV(P) level of theory gives, in contrast to the DFT calculations, large deviations from the experimental values. The absence of the of electron correlation effects (in the HF/SV(P) treatment) elongates the bonds, especially the Cu–Cu bonds which are up to 45 pm longer than in **2**.

The aforementioned investigations on the cluster anion $[Ag_{12}(CF_3CO_2)_{14}]^{6-}$ showed energetic and spatial separation of the two highest occupied molecular orbitals, which are predominantly centered on two Ag_6 substructures and thus formally correspond to a model double Ag_6^{4+} cluster.[14] For **1** and **2**, analogous results would lead to Cu_6^{4+} fragments in the cluster core. To explain the electronic structure the orbital energies were investigated. The results of the DFT calculations were supplemented with the HF calculations in the DFT equilibrium geometry for the two more simplified clusters **1b** and **2b**.[16] Population analyses were performed, where the known basis-set dependence can be more or less avoided by combining only those atomic orbitals that are situated at the Cu atoms in the central octahedron. This yields a population n_i(Oct) that describes to which extent a MO is localized at the octahedron.[18] The independence from the chosen basis set was verified by a calculation with a modified SV(P) basis.[16]

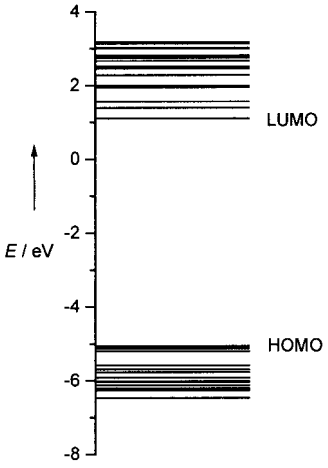

Figure 3. HF[SV(P)] orbital energies E for **1b**.

However, the results for the model clusters **1b** and **2b** differ from the silver cluster ion $[Ag_{12}(CF_3CO_2)_{14}]^{6-}$.[14] Neither DFT nor HF calculations exhibit a clear energetic separation of the frontier orbitals in **1b** and **2b** (Figure 3 and Figure 4 show the results of the HF calculations in the DFT equilibrium geometry). In both cases the HOMO is embedded in the almost bandlike structure of the remaining orbitals. Only the LUMO in **2b** is separated (by 2.1 eV) from the remaining unoccupied orbitals.

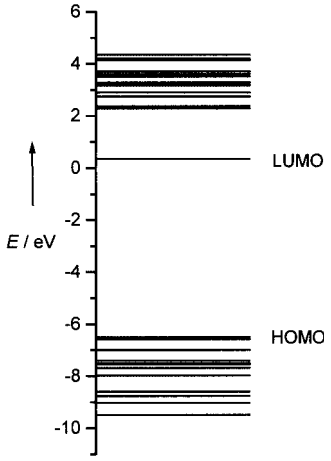

Figure 4. HF[SV(P)] orbital energies E for **2b**.

Furthermore, in contrast to $[Ag_{12}(CF_3CO_2)_{14}]^{6-}$, the frontier molecular orbitals in **1b** are located only to a small extent at the octahedron in the cluster core: for the HOMO in **1b**, $n_i(\text{Oct}) = 0.7$ (Figure 5); for the HOMO in **2b** $n_i(\text{Oct}) = 0.08$ (Figure 6). Orbitals with $n_i(\text{Oct}) > 1$ are found only for much lower lying energies: at 6.8 eV (**1b**) and 8.7 eV (**2b**) below the energy of the corresponding HOMO.

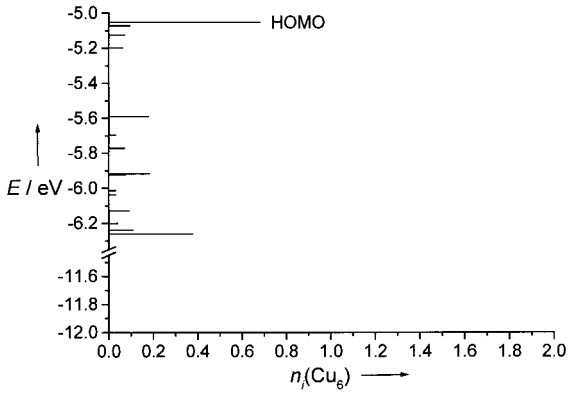

Figure 5. Contribution n_i(Oct) of the basis functions centered at the Cu_6 octahedron to the population of the MO ϕ_i for **1b**; E = HF[SV(P)] orbital energy.

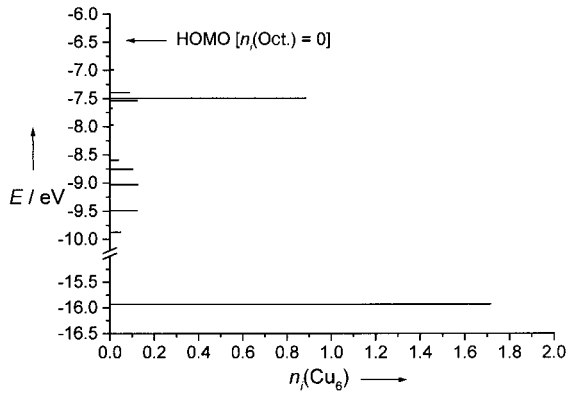

Figure 6. Contribution n_i(Oct) of the basis functions centered at the Cu_6 octahedron to the population of the MO ϕ_i for **2b**; E = HF[SV(P)] orbital energy.

These results—as well as the aforementioned tendency to form mixed valence compounds, which is in contrast to Cu_2S and Cu_2Se clusters—can be explained by the differences in ionization potentials (IP), electron affinities (EA), and

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electronegativities (EN), which are too small between Cu and As or Te for a discrete separation into Cu^{1+} and As^{3-}/ Te^{2-} ions; IP: 745.4(Cu), 946.5(As), 869.2(Te); EA: 118.5(Cu), 78.2(As), 190.2(Te); EN(Pauling): 1.9(Cu), 2.0(As), 2.1(Te). In other words, the formal charge assignment to give Cu^{1+} and As^{3-}/Te^{2-} centers produces an "additional" electron pair which is described by an MO that is embedded in the valence band formed by the arsenic 4p orbitals or the tellurium 5p orbitals, and the 4s orbitals of copper.

Experimental Section

$LiAs(SiMe_3)_2 \cdot 1.2\,THF$ (0.77 g, 2.4 mmol) was added to a suspension of CuCl (0.2 g, 2 mmol) and dppm (0.5 g, 1.3 mmol) in DME (50 mL) at $-20\,^{\circ}C$. A clear yellow solution was formed which as the temperature increased towards room temperature gradually turned a brilliant red, and was nearly black at room temperature. After reducing the volume of the solution by about half, black needlelike crystals of **1** were obtained in under two weeks (yield, based on CuCl, 0.12 g, 30 %). The C and H analyses of **1** fit the given formula.

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[8] X-ray structural analysis of **1**: STOE-IPDS ($Mo_{K\alpha}$ irradiation), data collection and refinement (SHELXS-86, SHELXL-93). Monoclinic, space group $P2_1/c$ (no. 14), $Z = 4$, cell (203 K): $a = 3088.0(6)$, $b = 2261.0(5)$, $c = 3303.0(7)$ pm, $\beta = 105.83(3)^{\circ}$, $V = 22187(8) \cdot 10^6$ pm^3, $\mu(Mo_{K\alpha}) = 46.43$ cm^{-1}; $2\Theta_{max} = 48^{\circ}$; 105 964 reflections, of which 33 395 are independent ($R_{int} = 0.1163$), 24 809 reflections with $I > 2\sigma(I)$, 2443 parameters; maximum / minimum electron density = 1.19 / -1.12 e$^- \cdot (10^6$ pm$)^{-3}$; $R_1 = 0.05$; $wR_2 = 0.131$. The positions of the H atoms were calculated, all other atoms were refined anisotropically except those of the DME molecules. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145570. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[17] If the symmetry threshold is lowered, S_6, a subgroup of T_h is found. Therefore, a geometry optimization in S_6 symmetry was performed in which the energy as well as in the calculated structure converged to the results of T_h symmetry.

[18] The combination of all basis functions would give for doubly occupied MOs $n_i = 2$; for the population n_i, however, only those basis functions are combined which are centered at the cluster core, that is, the Cu atoms of the octahedra in **1b** and **2b**. Thus, the closer the value of n_i is to 2, the more this orbital is localized at the cluster core.

A Blue Luminescent Starburst Molecule and Its Orange Luminescent Trinuclear Pd^{II} Complex: 1,3,5-tris(7-azaindol-1-yl)benzene (tabH) and $[Pd^{II}_3(tab)_2Cl_4]$**

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Luminescent organic and organometallic compounds have attracted much attention recently, mostly because of their potential applications in organic light-emitting devices (OLEDs).[1, 2] We have demonstrated previously that Al^{III} and B^{III} complexes of 7-azaindolyl (deprotonated 7-azaindole) are bright blue emitters[3] and capable of producing a bright blue light when in OLEDs.[4] Our recent efforts have focused on the modification of the 7-azaindolyl ligand to improve the stability and performance of compounds based on 7-azaindole. One of the modifications we carried out was to replace the proton on the indole nitrogen atom by an

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