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$[\{Ag(tBuNH_2)_2\}_4][\{Ag(tBuNH_2)(tBuN{=}CHCH_3)\}_2][Ag_{12}(CF_3CO_2)_{14}]$: A Compound with an Ag_{12}^{8+} Cluster Core**

Peter Reiß, Florian Weigend, Reinhart Ahlrichs, and Dieter Fenske*

Dedicated to Professor Herbert W. Roesky
on the occasion of his 65th birthday

The tendency of silver to form subvalent compounds has been observed in the structures of, for example, Ag_3O,[1] Ag_5GeO_4,[2] Ag_5SiO_4,[3] and $Ag_6Ge_{10}P_{12}$.[4] These compounds contain octahedral Ag_6^{4+} cluster units in which two electrons of a 6-center 2-electron (6c2e) bond occupy the lowest bonding molecular orbital (a_{1g}). Furthermore, the influence of $d^{10}-d^{10}$ interactions is invoked to explain the existence of these silver clusters.[2, 3, 5]

The reaction of silver trifluoroacetate with LiNH*t*Bu leads to the formation of **1**, a molecular compound which contains two similar Ag_6^{4+} units connected to give an Ag_{12}^{8+} cluster.

$$[\{Ag(tBuNH_2)_2\}_4]^{4+}[\{Ag(tBuNH_2)(tBuN{=}CHCH_3)\}_2]^{2+}[Ag_{12}(CF_3CO_2)_{14}]^{6-} \quad \mathbf{1}$$

Herein, in addition to the X-ray structure analysis of **1**[6] we present quantum chemical calculations to elucidate the electronic structure in the metal cluster.

Complex **1** features a central Ag_{12} cluster clamped by μ_2 bridging trifluoroacetate ligands. This core is surrounded by six silver diamine units (Figure 1). In four of them, the silver atoms (Ag(13) to Ag(16)) are linearly coordinated by two $tBuNH_2$ ligands which are formed by the protonation of the $(tBuNH)^-$ units. Additionally, two $[Ag(tBuNH_2)(tBuN{=}CHCH_3)]^+$ ions (Ag(17) and Ag(18)) are present, the structure for Ag(17) is presented in Figure 2. A *tert*-butylamine ligand and a *tert*-butylacetateimine ligand both bind to a silver atom in this fragment. The atom N(10) has a trigonal planar coordination sphere and the N–C bond length (N(10)-C(63) = 123(3) pm) is significantly shorter than a N–C single bond.

The existence of $[Ag(tBuNH_2)(tBuN{=}CHCH_3)]^+$ ions could be demonstrated conclusively by electrospray ionization mass spectroscopy, however, the reaction pathway that yields these unexpected units is not yet clear. The C_2H_4 group bound to N(10) is probably generated by the cleavage of the solvent diethyl ether. In this case the resulting ethanal would react with dissolved amido or amine ligands to form imine groups which then coordinate to an Ag^+ ion or to a $[Ag(tBuNH_2)]^+$ unit.

The Ag–N bond lengths in the six complex ligands (average 214 pm) are in agreement with the values reported for

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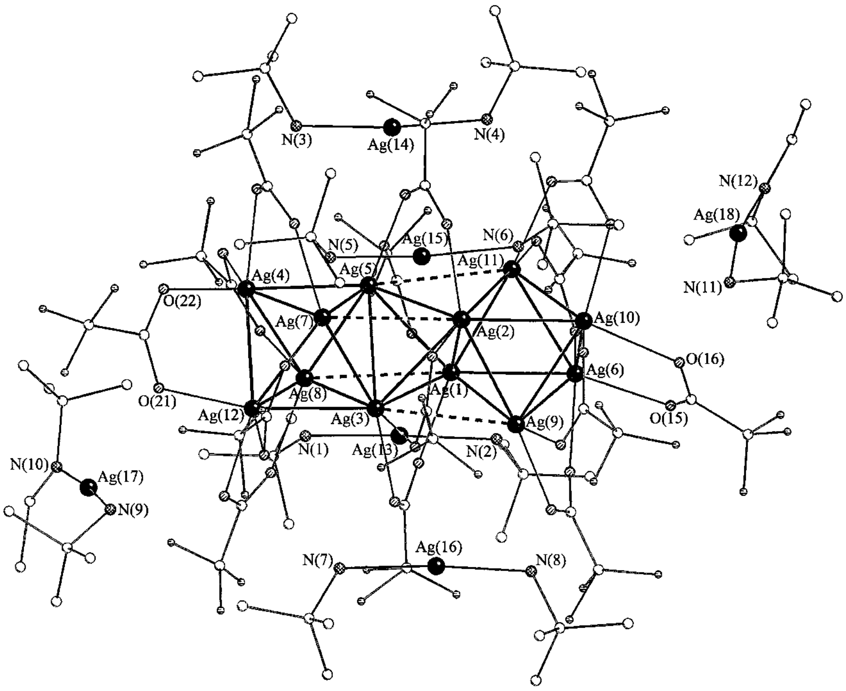

Figure 1. Molecular structure of **1** (hydrogen atoms are omitted for clarity).

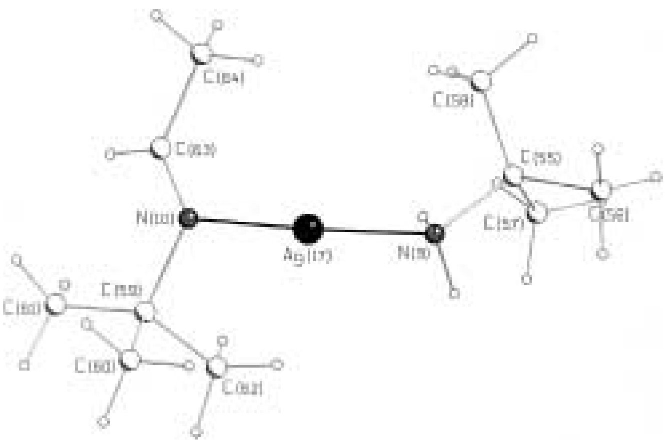

Figure 2. Structure of the $[Ag(tBuNH_2)(tBuN{=}CHCH_3)]^+$ ions in **1**.

linear silver diamine and silver diimine cations.[7] The $[Ag(tBuNH_2)_2]^+$ ligands as well as the $[Ag(tBuNH_2)(tBuN{=}CHCH_3)]^+$ groups are connected to the cluster core by N–H···O and C–H···F hydrogen bonds.

If the charge of the outer complex ligands (6+) and the charge of the fourteen trifluoroacetate ligands (14−) is taken into account, a net charge of 8+ results for the Ag_{12} cluster unit. This polyhedral framework with 20 triangular faces and a total length of 760 pm can be described as two octahedrons rotated by 90° away from one another, both octahedrons share one edge with a central tetrahedron. These two shared edges are the longest Ag–Ag bonds within the polyhedron; all the other metal–metal bonds are significantly shorter than those found in silver metal (289 pm).

These short metal–metal bond cannot be caused solely by the constraining effect of the chelate ligands since in each octahedral unit six of twelve edges are not bridged by ligands (Figure 3). In fact, the shortest Ag–Ag bonds (average 275.9(3) pm) are observed for these nonbridged edges which indicates the existence of additional attractive interactions. This interaction could be described by a 12c4e bond for the metal framework, giving an average formal oxidation number of 2/3 for the silver atoms.

The topology of the Ag_6^{4+} units in the silver suboxides[1–3] agrees well with that of **1** even when the oxygen coordination sphere is considered (this is naturally not true for the edges Ag(1)-Ag(2) and Ag(3)-Ag(5), which belong to the central tetrahedron). The centers Ag(6), Ag(10), Ag(4), and Ag(12) have a trigonal pyramidal coordination environment while the other silver atoms show a bent coordination. Both these coordination modes are found in the silver suboxide species however the O-Ag-O angles do not deviate from 90° as much as those found in **1**. The trifluoroacetate ligands bound to Ag(4)/Ag(12) or Ag(6)/Ag(10), show an average out-of-plane angle of 8.0(7)° with respect to the surface of the octahedron. Therefore, the almost ideal D_{2d} symmetry of the Ag_{12} cluster core is perturbed and thus the cluster anion as a whole is chiral with approximate D_2 symmetry.

The Ag_{12} framework in **1** shows a remarkable similarity to the In_{12} framework in $[In_{12}(tBu_3Si)_8]$[8] and the Al_{12} framework in $[Al_{12}\{N(SiMe_3)_2\}_8]^-$.[9] All three metal polyhedrons can be regarded as small fragments of a cubic closed packed array of metal atoms. Further examples of subvalent coinage-metal clusters include the compound $[Ag_{13}Fe_8(CO)_{32}]^{4-}$[10]

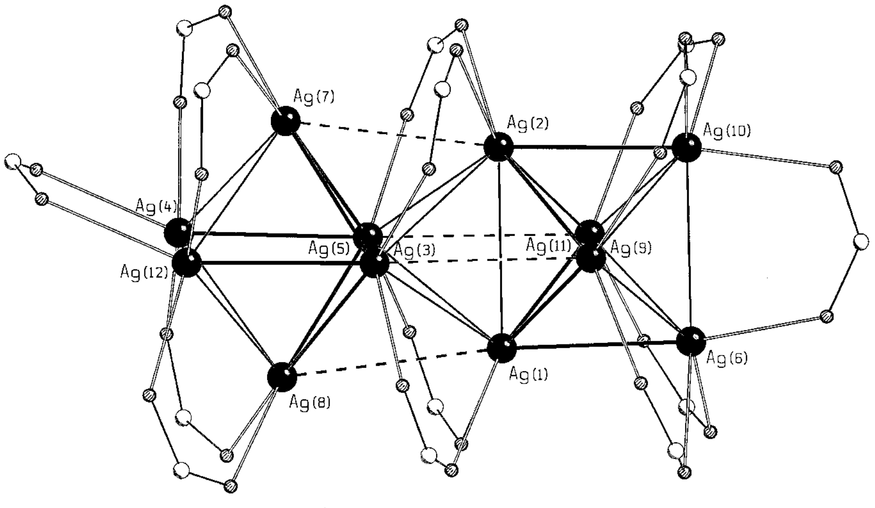

Figure 3. Representation of the Ag_{12}^{8+} cluster in **1** with bridging ligands (CF_3 groups are omitted for clarity).

and also the dimetallic Ag/Au clusters synthesized by Teo et al.[11]

To check the structure geometry and to investigate the electronic structure Ab initio calculations were carried out for two model compounds. To identify the physical effects relevant for the structure the results of several different Ab initio treatments were compared. All the calculations were performed with the TURBOMOLE program package.[12] For the density functional theory (DFT) calculations[13] the Becke–Perdew (BP) functional was used,[14, 15] for all the elements (auxiliary) basis sets of the SV(P) type[16] were chosen; the inner 28 electrons of the silver atoms were represented by effective core potentials (ECPs) which include a treatment of scalar relativistic effects.[17] The Coulomb part was calculated within the RI (resolution of the identity) approximation.[16c] The MP2 calculations were carried out using the RI-MP2 method.[18] For these and the HF calculations the following basis sets (and corresponding auxiliary basis sets) were used:[16] TZVPP basis for Ag centers, TZVP basis (triple zeta valence with one polarization function) for N and O centers, SV(P) basis (split valence plus polarization) for C and H centers. The 1s(C,N,O) and the 4s(Ag) orbitals were neglected in all MP2 calculations ("frozen core" approximation).

We considered two model compounds; **A** derived from **1** by the substitution of the CF_3 groups by H atoms and the *t*Bu groups by Me groups; the smaller model compound **B** differs

$[\{Ag(MeNH_2)_2\}_4][\{Ag(MeNH_2)(MeN{=}CHCH_3)\}_2][Ag_{12}(HCO_2)_{14}]$ **A**

$[\{Ag(NH_3)_2\}_4][Ag_{12}(HCO_2)_{12}]$ **B**

from **A** in that the $[Ag(MeNH_2)(MeN{=}CHCH_3)]^+$ units are missing, and the Ag atoms Ag(6) and Ag(10) as well as Ag(4) and Ag(12) are no longer bridged by chelate ligands. In this way charge neutrality is preserved and D_{2d} symmetry is obtained.

The model **B** was calculated at the levels DFT, HF, and MP2, **A** only with the efficient DFT method.[16c] The relevant parameters for the optimized geometric structures are collected in Table 1. The parameters for DFT(**A**), DFT(**B**), and MP2(**B**) agree well with the experimental values and thus justify the choice of methods and the model system **B**; the deviations are usually smaller than 15 pm. An exception is the Ag(4)–Ag(12) edge of the octahedron which is bridged in **A**, but not in **B**; the calculated bond length is 35 pm too long for DFT(**B**).

The comparison of MP2(**B**) and HF(**B**) allows an investigation of the physical effects that are relevant for the geometric structure. Compared to MP2, the HF structure shows a pronounced increase in the length of the bridged Ag–Ag bonds in the tetrahedron and in the octahedron ($d_{HF} - d_{MP2} \approx +65$ pm) as well as for the nonbridged edges of the octahedron (+20 to +50 pm). The edge Ag(4)–Ag(12), which is nonbridged in **B**, is opened completely. Clearly these bonds are "soft" as small deviations in the potential hypersurface lead to large changes in the bond lengths.

These investigations show that the geometric structure of the cluster core is determined mainly by electron-correlation effects (the HF method neglects the dynamic electronic correlation which MP2 accounts for by means of perturbation theory). To investigate whether particular electrons are in any way responsible for the correlation effects we calculated correlation energies regarding only an, energetically well separated, subset of orbitals. The density of states, $D(\varepsilon)$, which results from the HF wave function[19] in the DFT geometry is shown in Figure 4; its shape implies a partition of the MOs, also shown in Figure 4. Furthermore, the contributions to the Mulliken electron gross population are listed (separately for each atom type) which arise from the particular groups of MOs.

Table 1. Selected bond lengths [pm] for the calculated structures and for the experimental structure.

	B			A	1
Ag–Ag[a]	DFT	MP2	HF	DFT	Experimental
1	320	305	309	306–307	297–305
2	285	275	296	278–281	273–279
3	279	275	330	284–289	275–278
4	278	275	338	278–283	277–282
5	281	271	338	286–295	282–287
6	320	295	546	293–296	284–285
Ag–O	230–234	225–227	224–242	231–246	229–241
Ag–N	216–217	211	234–239	215–218	208–216

[a] The Ag–Ag bonds are numbered as follows: 1) Common edge of octahedron and tetrahedron (1–2 and 3–5,). 2) Octahedral edge, non-bridged (1–9, 1–11, 2–9, 2–11, 3–7, 3–8, 5–7, 5–8). 3) Octahedral edge, non-bridged (1–6, 2–10, 3–12, 4–5). 4) Octahedral edge, bridged (4–7, 4–8, 12–7, 12–8, 6–9, 6–11, 10–9, 10–11). 5) Tetrahedral edge, bridged (1–3, 1–5, 2–3, 2–5). 6) Octahedral edge, bridged in **A**, non-bridged in **B** (4–12 and 6–10).

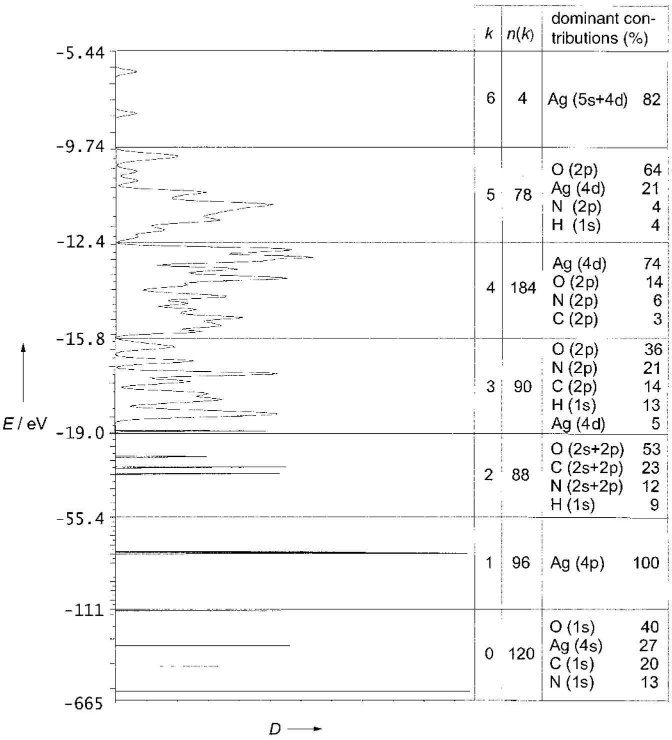

Figure 4. Density of states *D* (in arbitrary units) resulting from the HF wave function in the DFT equilibrium geometry for model **B** and partitioning of the different energy states into groups *k*. At the right hand side Mulliken electron gross populations *n*(*k*) are listed separately for each atom type and shell. The HF orbital energies are superimposed as Gauss functions of width 0.2 eV to aid comprehension and to reflect the situation to the solid state.

Next an interpolation (characterized by a parameter I) was performed between the DFT equilibrium geometry ($I=0$) and the HF geometry ($I=1$). For several values of I the following energies were calculated:

- $E_0 = E_{HF}$
- $E_1 = E_{HF} + E_{MP2}$ (partitions 1–6, "full" MP2 energy)
- $E_2 = E_{HF} + E_{MP2}$ (partition 4, mainly 4*d*-electrons of the Ag-atoms, "4d(Ag)")
- $E_3 = E_{HF} + E_{MP2}$, (partitions 1–3, 5, 6)
- $E_4 = E_{DFT}$

The differences from the corresponding value for $I=0$ (DFT geometry) for all the calculated energies are shown in Figure 5. As expected, the DFT and the "full" MP2 energy (partition 1–6) increase from the DFT equilibrium geometry to the HF equilibrium geometry, whereas the HF energy decreases. Remarkably, both E_3 (E_{HF}+correlation contributions mainly from 4d(Ag)) and E_4 (E_{HF}+correlation contributions of all electrons except for 4d(Ag)) display a shape very similar to that of the HF energy. The cluster geometry is therefore predominantly determined by the effects of electron correlation between the 4d(Ag) electrons and the other electrons and not by correlation effects between the 4d(Ag) electrons alone, that is, not by $d^{10}-d^{10}$ interactions between the silver atoms.

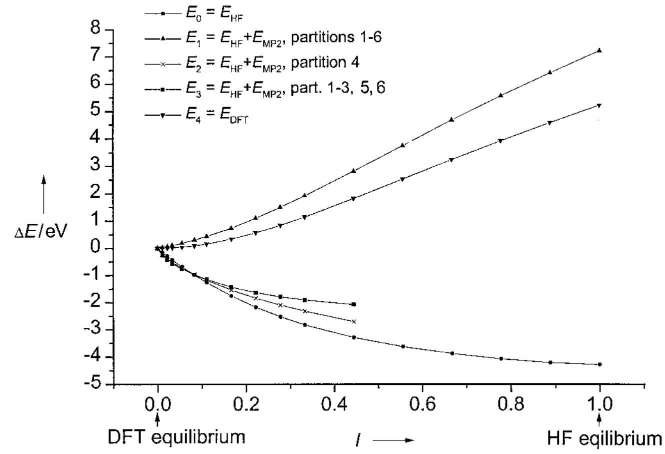

Figure 5. Dependency of calculated total energies on the geometric structure (interpolation parameter *I*, see text). Changes Δ compared to the corresponding energy in the DFT structure are plotted for DFT, HF, and (HF + MP2). In the MP2 calculations, electrons from different groups of orbitals are correlated. E_1 accounts for correlation of all (relevant) electrons, E_2 mainly contains correlation contributions of the 4d(Ag) electrons, E_3 contains contributions of all the other electrons.

For a more detailed investigation a series of MP2 calculations at $I=0.11$ was carried out, where only the electrons from partition 4 (4d(Ag)) and those of one or more other partitions were considered (Table 2). It is evident that mainly electrons from orbitals with an energy similar to that of the 4d(Ag) electrons are relevant for correlation effects; but only when all the valence electrons are included (as in the "full" MP2 calculation and the DFT calculation), does one get a higher energy for $I=0.11$ than for $I=0$. Thus the cluster core geometry is determined by correlation of the 4d(Ag) electrons with the majority of the valence electrons of the other atoms.

Further insight in the electronic structure is obtained by investigating the energetic and spatial orientation of the frontier orbitals of the HF wave function in the DFT equilibrium structure for **A** and **B**. The orbital energy and the contribution of the Ag_{12} cluster core to the Mullikan gross population, $n_i(Ag_{12})$, for the 20 highest occupied MOs $|i\rangle$ are shown in Figure 6. The two highest occupied MOs are energetically well separated from the others and mainly localized in the Ag_{12} cluster core: $n_i(Ag_{12}) = 1.5$ and 1.7 (for a complete localization on the cluster core $n_i(Ag_{12}) = 2$). The MOs below these ($n_i(Ag_{12}) = 0-0.9$) are either more delocalized ($n_i(Ag_{12}) \cong 1$) or localized somewhat outside the cluster core ($n_i(Ag_{12}) \cong 0$).

Experimental Section

All experimental steps were carried out in a dry nitrogen atmosphere using standard Schlenk techniques and avoiding exposure to light. LiNH*t*Bu (0.13 g 1.72 mmol) was added to a stirred suspension of $AgCF_3CO_2$ (0.38 g, 1.72 mmol) in absolute diethyl ether (25 mL), reaction time 5 min. The resulting dark solution was kept at 0 °C for 5 days and then filtered to remove a brown precipitate. Storing the resulting yellow solution at −40 °C for 4 weeks afforded clumps of yellow crystals of **1** in 35 % yield. The C, H, and N analyses of **1** correspond to the formula specified.

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Table 2. Energy differences ΔE_i of a structure that is interpolated between DFT and HF equilibrium geometry (interpolation parameter $I=0.11$, see text) and of the DFT equilibrium structure ($I=0$) for HF and DFT energy as well as for different MP2 energies in which electrons from different energy partitions were considered (see Figure 4).

i	Correlated energy partitions *k*							Number of correlated electrons	$\Delta E_i = E_i(I=0.11) - E_i(I=0)$ [eV]
	0	1	2	3	4	5	6		
0	HF							0	−1.2662
1	–	×	×	×	×	×	×	540	+0.4325
2	–	–	–	–	×	–	–	184	−1.1793
3	–	×	×	×	–	×	×	356	−1.1501
4	–	×	–	–	×	–	–	280	−1.1643
5	–	–	×	–	×	–	–	272	−0.9099
6	–	–	–	×	×	–	–	274	−0.5173
7	–	–	–	–	×	×	–	262	−0.7887
8	–	–	–	–	×	–	×	188	−1.1165
9	–	–	–	–	×	×	×	266	−0.6738
10	–	–	–	×	×	×	–	352	−0.1591
11	–	–	–	×	×	×	×	356	+0.0009
12	–	–	×	×	×	×	×	444	+0.2658
13	DFT							(660)	+0.1548

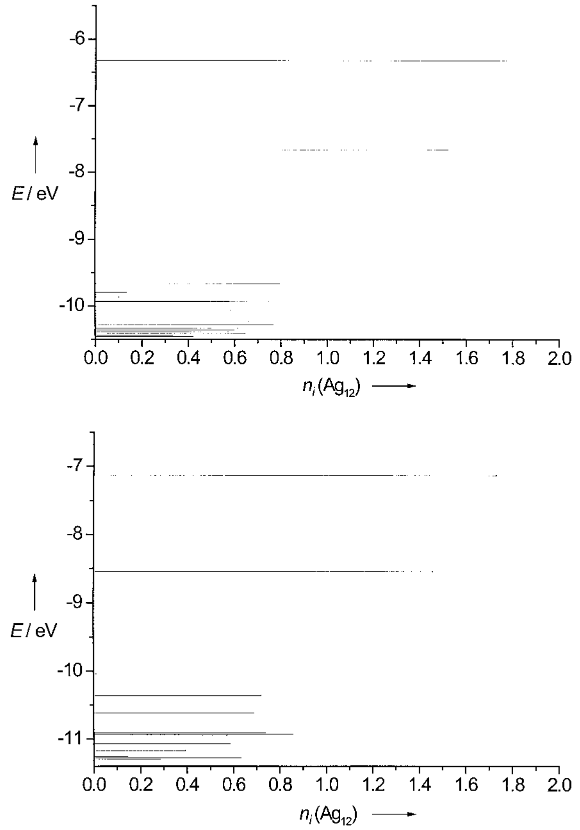

Figure 6. Orbital energy E and contribution of the cluster core to the Mulliken population, $n_i(Ag_{12})$, for the 20 highest lying molecular orbitals for model **A** (top) and model **B** (bottom). The data are based on the HF wave function in the DFT equilibrium geometry.

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[6] X-ray structure analysis of **1**: STOE-IPDS ($Mo_{K\alpha}$-radiation), data collection and refinement (SHELXS-86, SHELXL-93). Monoclinic, space group $P2_1$ (No. 4), $Z = 2$, unit cell dimensions (190 K): $a = 1539.5(4)$, $b = 3180.0(6)$, $c = 1553.7(4)$ pm, $\beta = 105.23(2)°$, $V = 7339(3) \times 10^6$ pm^3; μ($Mo_{K\alpha}$) = 24.55 cm^{-1}; $2\Theta_{max} = 50.2°$; 26208 reflections, 20871 independent reflections ($R_{int} = 0.104$), 14349 reflections with $I > 2\sigma(I)$, 1637 parameters; largest differential peak and hole = 1.46/ – 1.13 e($\times 10^6$ pm)$^{-3}$; absolute structure parameter = – 0.03(5); $R_1 = 0.061$; $wR_2 = 0.157$. Coordinates of the hydrogen atoms were calculated for idealised positions, all other atomic coordinates (except for these of the disordered fluorine atoms) were refined using anisotropic displacement parameters. 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-144150. 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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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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