Clusters on Clusters: *closo*-Dodecaborate as a Ligand for Au_{55} Clusters

Günter Schmid,*[a] Raphaël Pugin,[a] Wolfgang Meyer-Zaika,[a] and Ulrich Simon[a]

Dedicated to Professor Gerhard Fritz on the occasion of his 80th birthday

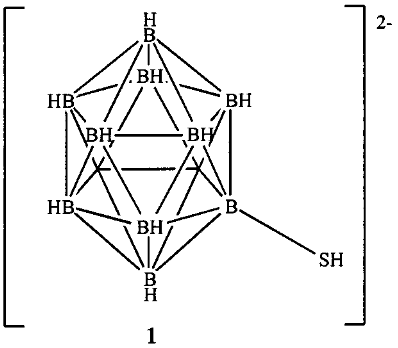
Keywords: Gold clusters / *closo*-Dodecaborate / Conductivity / Charging energy

The exchange of PPh_3 in $Au_{55}(PPh_3)_{12}Cl_6$ by $Na_2[B_{12}H_{11}SH]$ using a phase-transfer reaction from CH_2Cl_2 to water needs 6 weeks for reaction, but finally results in the quantitative formation of $Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ (**2**). Cluster **2**, which is of considerable stability in aqueous solution, has been characterized by ^{1}H-NMR, ^{11}B-NMR, and IR spectroscopy as well as by transmission electron microscopy (TEM). The Na^+ cations can be exchanged by $(octyl)_4N^+$ making the resulting cluster **4** soluble in polar organic solvents. The electrical properties of **2** and **4** are compared with those of $Au_{55}[Ph_2PC_6H_4SO_3N(octyl)_4]_{12}Cl_6$ (**3**), the ammonium derivative of the sodium salt. Cluster **3** shows the expected increase of activation energy in the temperature range of 130–250 K owing to the increase of cluster spacing compared with the sodium derivative. However, clusters **2** and **4**, show electromigration in the electric field, caused by the huge amount of ionic charges in the ligand shell.

Introduction

Over the past decade, the effect of particle size on the electronic properties of ligand-protected metal clusters and colloids has been discussed as one of their most exciting physical properties.[1−6] Since the two-shell cluster $Au_{55}(PPh_3)_{12}Cl_6$[7] has a metal core diameter of 1.4 nm, which is of the order of characteristic length scales such as the de Broglie wavelength, the mean free path or the phase relaxation length, this cluster can be considered as a zero-dimensional quantum dot containing just a few metallic electrons.[4−6,8] Moreover, physical investigations such as impedance[4−6] or charge-transport measurements,[9] as well as scanning tunnelling spectroscopy,[10,11] have clearly indicated the existence of size effects for this cluster, where the protective ligand shell acts as a well-defined insulating barrier around the clusters. A protective ligand shell is an essential condition for control of the growth of the metal particles to prevent them from coalescence or Ostwald ripening. It is of fundamental interest to modify the nature and the thickness of this ligand shell in order to study its influence on the electronic properties. Understanding of this will allow the control of a specific size−property relationship of these solid-state nanomaterials enabling building blocks to be tailored for nanoelectronic devices.[4−6]

In the present work we report the use of disodium mercaptoundecahydro-*closo*-dodecaborate $Na_2[B_{12}H_{11}SH]$ (**1**) (BSH, see Figure 1) as a protective ligand to stabilize Au_{55} clusters for two main reasons: to elaborate new highly stable Au_{55} clusters with Au−S bonds by the use of different bulky ligands, and to follow our prospective work concerning the correlation between cluster spacing and charging energy determined by electronic intercluster tunnelling processes.



1

Figure 1. Formal structure of the BSH ligand

A secondary aspect concerns the use of BSH in Boron Neutron Capture Therapy (BNCT).[12] This therapy is a binary treatment modality that can selectively irradiate tumour tissues. BNCT uses drugs containing the ^{10}B isotope that are capable of preferentially accumulating in the tumour which is then irradiated with low-energy neutrons. The interactions of the ^{10}B nucleus with a thermal neutron (neutron capture) causes it to split releasing a lithium nucleus and an alpha particle, so damaging the tumour cells. $Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ (**2**), described in the following, is highly soluble in water and contains 144 boron atoms per molecule, perhaps enabling a drastic increase of the boron concentration in tumour tissues.

Results and Discussion

In a previous work[13] we described the exchange of the PPh_3 ligands in $Au_{55}(PPh_3)_{12}Cl_6$ by $Ph_2PC_6H_4SO_3Na$ in a phase-transfer reaction to give the water-soluble gold cluster $Au_{55}(Ph_2PC_6H_4SO_3Na)_{12}Cl_6$. More recently, owing to the lability of the triphenylphosphane coordinated to the surface gold atoms and to the well-known affinity of thiol

---

[a] Institut für Anorganische Chemie, Universität Essen
Universitätsstraße 5−7, D-45117 Essen, Germany
E-mail: guenter.schmid@uni-essen.de

1434−1948/99/1111−2051 $ 17.50+.50/0

$$\begin{array}{ccccccc} Au_{55}(PPh_3)_{12}Cl_6 & + & 12\ (B_{12}H_{11}SH)Na_2 & \xrightarrow[\text{r.t., 6 weeks}]{} & Au_{55}[(B_{12}H_{11}SH)_{12}Cl_6 & + & PPh_3 \\ & & \mathbf{1} & & \mathbf{2} & & \\ CH_2Cl_2 & & \text{water} & & \text{water} & & CH_2Cl_2 \end{array} \qquad (1)$$

functions to gold atoms, we reported the synthesis of a new Au_{55} cluster protected by a thiol-functionalized oligosilsesquioxane (T_8−OSS−SH) ligand, causing excellent solubility in nonpolar hydrocarbons, such as pentane.[14]

Combining these two methods, we have now succeeded in synthesizing a novel *closo*-borate stabilized Au_{55} cluster by a phase-transfer reaction.

The phase-transfer reaction, which in the past has allowed us to substitute PPh_3 by $Ph_2PC_6H_4SO_3Na$, took two days,[13] whereas only two hours were necessary for the synthesis of the thiol-functionalized oligosilsesquioxane gold cluster in organic solvents.[14] Two reasons may be responsible for the extraordinary long reaction time to prepare **2**. First, in contrast to T_8−OSS−SH where a propyl chain separates the thiol function from the bulky oligosilsesquioxane cage, the thiol group in **2** is directly coordinated to the *closo*-borane cluster, so that all bulky protective ligands are very close to the metal core. Second, electrostatic interactions should play a decisive role. Since each *closo*-borate ligand is doubly charged, the observed rapid exchange of half of the PPh_3 molecules by six $[BSH]^{2-}$ anions generates a twelve-fold negatively charged, water-soluble gold cluster. Repulsive electrostatic forces make it progressively more difficult to add additional $[BSH]^{2-}$ ligands. This last point is supported by the ^{1}H-NMR signals and by elementary analyses after different reaction times. Actually, both show that the first six PPh_3 ligands were substituted after a couple of days, one week more being necessary for the next three ones and a further five weeks more for the three last ones. Nevertheless, the expected $Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ cluster with a total of twenty four negative charges is formed in almost quantitative yield.

After the reaction time of six weeks the $^{13}C\{^1H\}$-NMR, as well as the $^{31}P\{^1H\}$-NMR, spectra of the product do not give any signal and so indicate the absence of PPh_3. This is supported by the ^{1}H-NMR spectrum, where signals for aromatic protons cannot be detected. Elementary analyses indicate only traces of carbon. On the other hand, the presence of BSH is clearly indicated by a broad multiplet in the ^{1}H-NMR spectrum between $\delta = 0.2$ and 2.8 and by the $^{11}B\{^1H\}$-NMR spectrum showing a broad signal between $\delta = -20$ and -11 and a singlet at $\delta = -7.8$. Compared with the spectrum of free BSH the multiplicity is lost due to the coordination to a large metal cluster. The broad ^{11}B-NMR signal can be attributed to the three initial doublets of the free BSH (see Experimental Section). The singlet at $\delta = -7.8$ is caused by the B atom directly bound to the thiol function. In contrast to the corresponding singlet for free BSH ($\delta = -9.6$), it is low-field shifted owing to the coordination of the thiol group to gold. Infrared investigations resulted in bands at $\tilde{\nu} = 2500.6$ (ν B−H), 1061.7 (ν asym. B−S), 973.2 and 947.9 (δ asym. B−S), 836.5 and 723 cm^{-1} (ν B−B). The signals of $Au_{55}(PPh_3)_{12}Cl_6$ at 1584.9 and 1478.7 (ν C=C arom.), 1434.7 and 1097.9 (ν P−Ph), 1328.5, 1026.4, and 690.3 cm^{-1} (δ C−H) could not be observed.

Practical advantages of the new cluster **2** are the solubility and the improved stability. It is soluble in numerous polar solvents like acetone, ethanol, acetonitrile, or methanol, but also in water which allows us to expect possible clinical applications. Transmission electron microscopy (TEM) investigations showed exclusively 1.4 nm particles (Figure 2). Figure 3 shows a model of the relevant cluster part $[Au_{55}(B_{12}H_{11}SH)_{12}]^{24-}$.

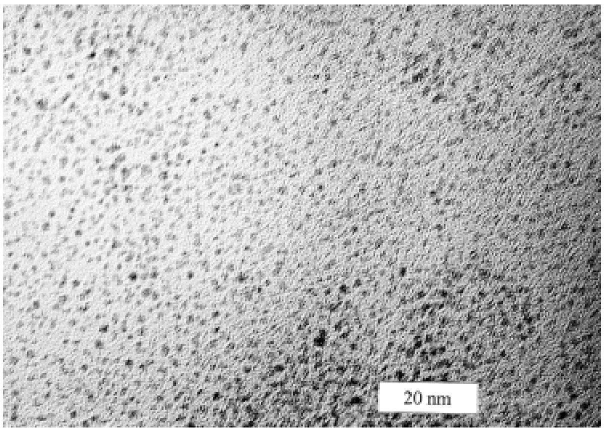


Figure 2. TEM image of $Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ clusters indicating the monodispersity

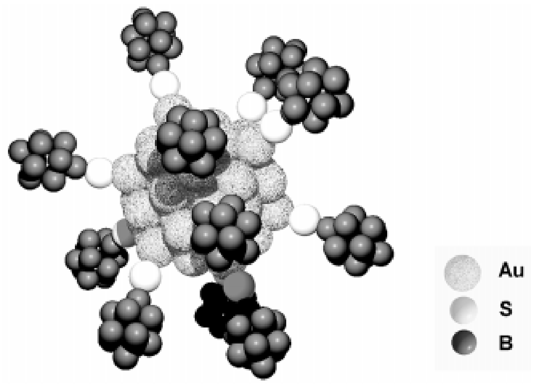


Figure 3. Computer model of the cluster part $[Au_{55}(B_{12}H_{11}SH)_{12}]^{24-}$; the H atoms are omitted

No aggregation was observed in cluster solutions over several months. Compared to the very labile $Au_{55}(PPh_3)_{12}Cl_6$, which aggregates in solution after a couple of hours, this most remarkable change allows reliable investigations not only in the solid state, but also in solutions. Thus, by UV measurements the characteristic plasmon resonance between 500−600 nm of colloids could be excluded.

The unusual stability of **2** compared with $Au_{55}(PPh_3)_{12}Cl_6$ is explained by the greater affinity of thiol func-

$$\underset{\text{water}}{Au_{55}(Ph_2PC_6H_4SO_3Na)_{12}Cl_6} + \underset{CH_2Cl_2}{12\ BrN(octyl)_4} \rightarrow \underset{CH_2Cl_2}{\underset{\mathbf{3}}{Au_{55}[Ph_2PC_6H_4SO_3N(octyl)_4]_{12}Cl_6}} + \underset{\text{water}}{12\ NaBr} \qquad (2)$$

$$\underset{\text{water}}{Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6} + \underset{CH_2Cl_2}{24\ BrN(octyl)_4} \rightarrow \underset{CH_2Cl_2}{\underset{\mathbf{4}}{Au_{55}[(B_{12}H_{11}SH)\{N(octyl)_4\}_2]_{12}Cl_6}} + \underset{\text{water}}{24\ NaBr} \qquad (3)$$

tions to bind surface gold atoms compared with phosphanes and in particular it is the repulsive electrostatic forces between the 24-fold negatively charged clusters. This is probably the main reason why coalescence between clusters is efficiently suppressed since approaches of two clusters are prevented. Similar explanations allowed us in previous works to compare the stability of $Au_{55}(PPh_3)_{12}Cl_6$ to those of the water soluble $Au_{55}(Ph_2PC_6H_4SO_3Na)_{12}Cl_6$.[13] Actually, although $Au_{55}(PPh_3)_{12}Cl_6$ degrades after two hours if dissolved, the water-soluble cluster stays stable in solution without significant aggregation over weeks. Comparison with cluster **2** suggests that this is probably due to the combination of strong and bulky ligands and of repulsive Coulomb forces.

To investigate the chemical properties and to see if the size of the ligand shell could still be increased, we tried to exchange Na^+ by the bulkier tetraoctylammonium cation. For comparison, this was first realized with the water-soluble cluster $Au_{55}(Ph_2PC_6H_4SO_3Na)_{12}Cl_6$.

This phase-transfer reaction was completed after 3 h and cluster **3** was isolated in almost quantitative yield as a dark-brown solid. The integration of the aryl and alkyl ^1H-NMR signals gave a 1:1 ratio of $Ph_2PC_6H_4SO_3^-$ and $[(octyl)_4N]^+$. Moreover, the elementary analyses agreed well with the expected values. Based on these promising results the corresponding phase-transfer reaction was attempted with $Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ (**2**). The reaction worked as well as that in Equation 2. Cluster **4** was obtained in good yield and was characterized by ^1H NMR and TEM. This cation-exchange reaction did not induce any aggregation of the particles and the size distribution of **4** was found by TEM to be as good as that of **2**.

The availability of these new compounds raised the question of how the charge-transport properties are affected by the modified ligand shell as compared to $Au_{55}(PPh_3)_{12}Cl_6$. As described earlier,[4–6,15] single-electron charging effects occur in three-dimensional dense packings of ligand-stabilized metal clusters. The charging energy, involving a thermally activated tunnelling process through the insulating ligand shell, corresponds to the activation energy E_A of the conductivity of the cluster arrangements and therefore depends on the cluster size, as well as on the cluster spacing. While the size is determined by the number of the metal atoms forming the cluster, i.e. 55 in the materials discussed here, the cluster spacing corresponds to the thickness of the ligand shell. Therefore, by modifying the thickness of the ligand shell, a correlation between cluster spacing and charging energy could be established. Actually, a charging energy of 0.15 eV was observed for $Au_{55}(PPh_3)_{12}Cl_6$, having a 0.35 nm thick ligand shell, i.e. a cluster spacing of 0.7 nm. This value increases linearly with the spatial separation of the metallic cores up to 0.26 eV for the previously described $Au_{55}(T_8{-}OSS{-}SH)_{12}Cl_6$, which corresponds to a cluster spacing of 2.8 nm.[16]

This shows that the charging energy in three-dimensional cluster arrangements can be tailored chemically by varying the cluster spacing due to incorporation of bulky ligands or by introduction of spacer molecules. In this context the electrical properties of the clusters **2**, **3**, and **4** are of considerable interest. In contrast to the materials we have examined before, it was not possible to obtain mechanically stable pellets with dense cluster packing. Therefore the clusters were dissolved and then deposited on interdigital microelectrodes (see Experimental Section). Whilst an optically homogeneous layer of **2** with an average thickness of 50−100 μm was formed, **3** and **4** remained as highly viscous films on the microelectrode structure. The temperature dependence of the conductivity was determined in a temperature range of 130−293 K.

According to earlier measurements a temperature dependence $\sigma(T) \sim (T_0/T)^\gamma$ was expected (Mott′s conductivity law). At low temperature $\gamma = 1/d + 1$, where d is the dimensionality of the system, reflecting a variable-range hopping process. Going to higher temperatures up to room temperature, the charge transport is dominated by nearest neighbour hops of single electrons instead of hops of variable range, thus being simply activated with $\gamma = 1$ (Arrhenius behaviour). Here the activation energy E_A ($= k_BT_0$) is the energy to transfer one electron from an initially neutral cluster to a next neighbouring neutral cluster via the insulating ligand shell.[15][17] Thus, E_A represents the charging energy, or chemically speaking, the disproportionation energy, which is size and distance dependent.

All samples show significant conductivity at room temperature and thermally activated behaviour. No evaluable results could, however, be obtained from samples **2** and **4** due to pronounced conductance fluctuations during the measurements. This, at a first glance, might be attributed to the huge amount of ionic charges provided by the 12 two-fold negatively charged borate ligands on each cluster. This may lead to electromigration of the clusters in the electric field during the measurements, leading to a fluctuating degree of disorder in the samples. A detailed analysis of this problem will be subject of our future works.

In contrast, the measurements on cluster **3**, which has just 12 instead of 24 charges on its ligand shell, showed a reliable temperature dependence. However, neither a $\sigma(T) \approx 1/T$ nor a $\sigma(T) \approx 1/T^{1/4}$ behaviour could be observed over the whole temperature range. As displayed in Figure 4, it seems to be possible to divide the temperature range tentatively into a high-temperature and a low-temperature part; in the low-temperature part, which ranges from 130 K up to approx. 250 K an E_A of 0.16 eV could be deduced, while the high-temperature part above displays an E_A of 0.95 eV.

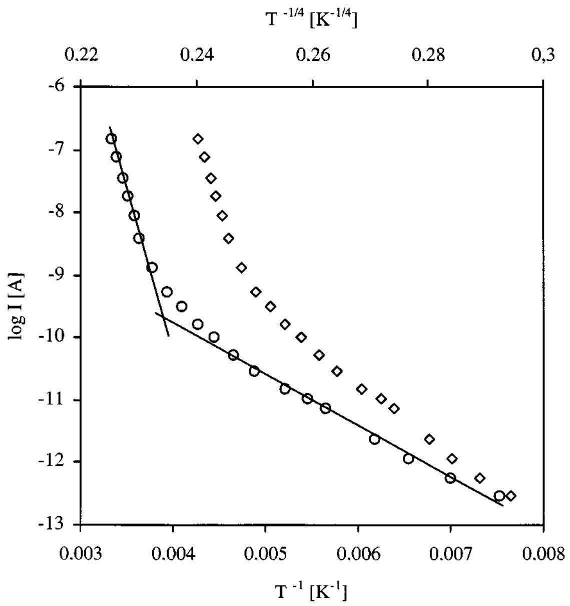


Figure 4. Temperature-dependent current I at a constant voltage $U = 5$ V of **3** according to the Arrhenius relation (circles) and according to Mott's conductivity law (rhombs); below 250 K $E_A = 0.16$ eV and above $E_A = 0.95$ eV

Although it is difficult to determine the exact size of the highly flexible ammonium octyl chains, a cluster spacing of 2.90 ± 0.01 nm might be derived from geometrical considerations if the alkyl chains are stretched. With respect to the previously described linear dependence of the E_A of the cluster spacing, an E_A of 0.24 ± 0.02 eV is expected, which is significantly higher than the 0.16 eV determined here. Thus it seems evident that the alkyl chains are folded and lie close to the central nitrogen atom to give an effective cluster spacing, which is comparable to that in the sodium derivative, even though Na^+ is considerably smaller than $N(octyl)_4{}^+$. It may also be that the ammonium ions interact strongly with the phenyl rings by hydrophobic−hydrophobic interactions, whereas the Na^+ ion in **2** occupies a position at the periphery of the ligand shell. The rapid increase of E_A above 250 K might originate from an electromigration process during the measurements resulting in disorder, with an increased cluster to cluster and an increased cluster to electrode spacing. Structural deviations from ideal arrangements induce huge effects in the electrical response, especially in the nanometre size range.[18,19,20] Keeping in mind that cluster **3** is a highly viscous liquid instead of a solid, like the Na^+ analogue, it seems to be consistent that this kind of field-induced disorder appears in the octyl ammonium form **3** and not in the Na^+ form.

Conclusions

The series of known Au_{55} clusters bearing 12 $B_{12}H_{11}SH^{2-}$ ions as ligands has been extended by the synthesis of a very special example: the cluster $Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ (**2**) and its tetraoctylammonium derivative consisting of a 24-fold negatively charged anion with 144 B atoms per molecule. This high concentration of B atoms and the very good solubility in water, accompanied by a remarkable stability, makes this cluster a promising candidate for boron neutron capture therapy. The synthesis succeeds via the exchange of PPh_3 in $Au_{55}(PPh_3)_{12}Cl_6$ by the borate, based on a phase-transfer reaction from dichloromethane to water. The bulkiness of the thiols and especially its two-fold negative charge result in a six-week reaction time. Nevertheless, the reaction is quantitative. ^{1}H- and ^{11}B-NMR spectra, elementary analyses, and transmission electron microscopy have been used to prove the composition and size of the clusters. The sodium cations can be exchanged by tetraoctylammonium making the cluster **4** oily, but also soluble in polar solvents like acetone or alcohols.

In addition to the novel clusters **2** and **4** we synthesized the cluster $Au_{55}[Ph_2PC_6H_4SO_3N(octyl)_4]_{12}Cl_6$ (**3**) to enable a comparison of its electrical properties with those of **2** and **4**. Cluster **3** consists of a twelve-fold negatively charged anion, whereas **2** and **4** have the extreme charge of −24.

The electrical properties of the new compounds **2** and **4** are significantly different from the properties of the clusters investigated previously. While cluster **3** shows an activation energy in the temperature range of 130−250 K which is comparable to the corresponding Na^+ form, above that temperature the microstructure of the samples seems to be affected by the electric field due to electromigration. The latter is also assumed to be the reason for the extraordinary behaviour of **2** and **4**. Although this is just a tentative explanation for the properties observed, it may hint to a principle limit of modifiability of the ligand shell with respect to the possible application in nanoelectronic devices, since the huge amount of ionic charges in the ligand shell seems to induce structural instabilities in the samples under test

Experimental Section

General: $(B_{12}H_{11}SH)Na_2$ (BSH) was commercially available from BORON BIOLOGICALS. As it is highly hygroscopic all reactions were performed using standard Schlenk techniques. Before use it was characterized by NMR spectroscopy: ^{1}H NMR (D_2O): δ = 0.25−1.92 (br. m, 12 H, BH and SH). $^{11}B\{^1H\}$ NMR (D_2O): δ = −19.55 (d, 1 B, −BH), ^1J(BH) = 125.2 Hz, −16.00 (d, 5 B, −BH), ^1J(BH) = 134.8 Hz, −14.00 (d, 5 B, −BH), ^1J(BH) = 135.0 Hz, −9.6 (s, 1 B, B−SH). − The solvents were dried and purified by standard procedures. − NMR spectra were recorded with a Bruker DPX working at 300 MHz for ^{1}H, 75.5 MHz for $^{13}C\{^1H\}$, 121.5 MHz for $^{31}P\{^1H\}$ and 96.3 MHz for $^{11}B\{^1H\}$. − Infrared spectra were recorded on a BIO-RAD FTS-175 spectrometer. − TEM images were obtained using a Philips CM 200 FEG microscope working with 200 kV accelerating voltage and to confirm the absence of colloidal particles, electronic spectra of cluster solutions were measured on a Varian Cary-1 UV/Vis spectrometer. − Elementary analyses were carried out by the Analytical Laboratory of the Fachbereich Chemie of the University of Essen. − For electrical measurements the samples were deposited from solvent on gold interdigital microelectrodes (structural width = 10 μm) on a quartz substrate.[21,22] After drying the samples in vacuum they were kept under argon during the measurements. Current measurements were performed in a voltage range of ± 5 V using a Keithley 6517 electrometer with an integrated voltage source in a low-temperature measuring cell.

$Au_{55}(PPh_3)_{12}Cl_6$ and $Au_{55}(Ph_2PC_6H_4SO_3Na)_{12}Cl_6$ were synthesized according to described procedures.[7][13]

$Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ (2): To a solution of 16.7 mg (76.09 μmol) of $[(B_{12}H_{11}SH)Na_2]$ (**1**), dissolved in 125 mL of distilled water and placed in a 250-mL flask, a solution of 80 mg (5.64 μmol) of $Au_{55}(PPh_3)_{12}Cl_6$, dissolved in 60 mL of CH_2Cl_2, was added under vigorous stirring. After 4−6 days the water phase showed a dark brown colour. After a total reaction time of 6 weeks, the emulsion was placed in a separating funnel to separate the water phase carefully from the colourless organic phase and to wash it 4 times with 30 mL of CH_2Cl_2 to remove PPh_3. The solvent was removed under vacuum at room temperature. The brown product was then dissolved in 25 mL of distilled water and filtered through an ANOTOPE® filter (Merck, 20 nm porous diameter) and was precipitated by CH_2Cl_2 and separated. The filtration pad was washed with copious amounts of CH_2Cl_2 and the fine microcrystalline black powder dried overnight under vacuum. Yield: 52 mg (68%). − IR (KBr): $\tilde{\nu}$ = 2500.6 cm^{-1}, vs (ν B−H), 1061.7, m (ν asym B−S), 973.2, w and 947.9, w (δ asym B−S), 836.5, m and 723, w (ν B−B). − ^1H NMR (D_2O): δ = 0.20−2.80 (br. m, 12 H, BH and SH). $^{11}B\{^1H\}$ NMR (D_2O) (10 mm ∅ NMR tube): δ = −20 to −11 (br. m., 11B, *o*-, *m*-, *p*- BH), −7.8 (s, 1 B, B−SH). − ^{31}P- and ^{13}C-NMR signals could not be observed. $Au_{55}B_{144}Cl_6H_{144}Na_{24}S_{12}$ (13683.26 g mol^{-1}): calcd. C 0.00, H 1.05, S 2.81, Na 4.10, Au 79.17; found C 1.30, H 1.26, S 2.72, Na 5.16, Au 77.01.

$Au_{55}[Ph_2PC_6H_4SO_3N(octyl)_4]_{12}Cl_6$ (3): To a solution of 50.0 mg (3.24 μmol) of $Au_{55}(Ph_2PC_6H_4SO_3Na)_{12}Cl_6$, dissolved in 50 mL of distilled water and placed in a 200-mL flask, a solution of 21.5 mg (39.32 μmol) of $[(octyl)_4N]Br$, dissolved in 50 mL of CH_2Cl_2, was added under vigorous stirring. After 3 h the water phase was colourless whereas the organic phase was dark brown. The emulsion was placed in a separating funnel, the organic phase was carefully separated from the colourless water phase and washed 4 times with 30 mL of distilled H_2O to remove NaBr. The solvent was removed at room temperature under vacuum. The brown product was then dissolved in 20 mL of CH_2Cl_2 and filtered through an ANOTOPE® filter (Merck, 20 nm porous diameter). The solvent was evaporated under vacuum and the gold cluster **3** was precipitated by pentane and separated. The filtration pad was washed with copious amounts of pentane, the black microcrystalline powder was dried overnight under vacuum. Yield: 57 mg (85%). This cluster is slightly soluble in benzene and soluble in polar solvents like CH_2Cl_2, $CHCl_3$, acetone, or acetonitrile. − IR (KBr): $\tilde{\nu}$ = 3000−2850 cm^{-1}, s (ν C−H), 1584.7, m and 1478.5, m (ν C=C arom), 1434.8, s and 1097.9, s (ν P−Ph), 1370.0, m (δ C−H), 1328.5, w 1026.6, w and 690.4, vs (δ C−H). − ^1H NMR ($CDCl_3$): δ = 0.85 (t, 12 H, $N[(CH_2)_7\mathit{CH_3}]_4$), 1.26−1.62 (br, 48 H, $N[CH_2(\mathit{CH_2})_6CH_3]_4$), 3.27 (br, 8 H, $N[\mathit{CH_2}(CH_2)_6CH_3]_4$), 7.30−8.30 (m, 14 H, $\mathit{Ph_2}P\mathit{C_6H_4}SO_3$). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 35.90 (s, $Ph_2\mathit{P}C_6H_4SO_3$). − $C_{600}H_{984}Au_{55}Cl_6N_{12}O_{36}P_{12}S_{12}$ (20737.3 gmol^{-1}): calcd. C 34.75, H 4.75, N 0.8, S 1.84, Na 0.00, Au 52.24; found C 34.40, H 4.78, N 0.9, S 1.44, Na 0.19, Au 50.32.

$Au_{55}[(B_{12}H_{11}SH)(N(octyl)_4)_2]_{12}Cl_6$ (4): To a solution of 40.0 mg (2.92 μmol) of $Au_{55}[(B_{12}H_{11}SH)Na_2]_{12}Cl_6$ (**2**) dissolved in 40 mL of distilled water and placed in a 200-mL flask, a solution of 40 mg (70.16 μmol) of $[(octyl)_4N]Br$, dissolved in 40 mL of CH_2Cl_2, was added under vigorous stirring. After 3 h reaction, the water phase was colourless, the organic phase presented a dark brown colour. Then, the emulsion was placed in a separating funnel, the organic phase was carefully separated from the colourless water phase and washed 4 times with 30 mL of distilled H_2O in order to remove NaBr. The solvent was removed at room temperature under vacuum. The brown product was dissolved in 20 mL of CH_2Cl_2 and filtered through an ANOTOPE® filter (Merck, 20 nm porous diameter). After removing the solvent under vacuum, **4** was precipitated by pentane but could not be isolated as a powder. A dark-brown oil was obtained which was washed several times with a few mL of pentane and dried overnight under vacuum. This cluster was slightly soluble in benzene and soluble in polar solvents like CH_2Cl_2, $CHCl_3$, acetone, or acetonitrile. − IR (KBr): $\tilde{\nu}$ = 3000−2850 cm^{-1}, s (ν C−H), 2500.0, vs (ν B−H), 1375.0, m (δ C−H), 1060.5, m (ν asym B−S), 972.1, w and 946.5, w (δ asym B−S), 836.0, m and 723, w (ν B−B). ^1H NMR ($CDCl_3$): δ = 0.10−2.25 (br, 132 H, BH and SH, $N[(CH_2)_7\mathit{CH_3}]_4$, $N[CH_2(\mathit{CH_2})_6CH_3]_4$), 3.30 (br, 16 H, $N[\mathit{CH_2}(CH_2)_6CH_3]_4$). Due to its viscous nature elemental analyses could no be performed.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 452) and the Fonds der Chemischen Industrie is gratefully acknowledged.

---

[1] G. Schmid (Ed.), *Clusters and Colloids − From Theory to Applications*, VCH, Weinheim, **1994**.

[2] L. J. de Jongh (Ed.) in *Physics and Chemistry of Metal Cluster Compounds*, Kluwer Academic Publ., Dordrecht, **1994**.

[3] Y. Volokitin, J. Sinzig, L. J. de Jongh, G. Schmid, I. I. Moiseev, *Nature* **1996**, *384*, 621.

[4] G. Schön, U. Simon, *Colloid Polym. Sci.* **1995**, *273*, 101.

[5] G. Schön, U. Simon, *Colloid Polym. Sci.* **1995**, *273*, 202.

[6] U. Simon, *Adv. Mater.* **1998**, *10*, 1487.

[7] G. Schmid, R. Boese, R. Pfeil, F. Bandermann, S. Meyer, G. H. M. Calis, J. W. A. van der Velden, *Chem. Ber.* **1981**, *114*, 3634.

[8] U. Simon, G. Schmid, G. Schön, *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 250.

[9] R. P. Andres, Th. Bein, M. Dorogi, S. Feng, J. I. Henderson, C. P. Kubiak, W. Mahoney, R. G. Osifchin, R. Reifenberger, *Science*, **1996**, *272*.

[10] R. Houbertz, T. Feigenspan, F. Mielke, U. Memmert, U. Hartmann, U. Simon, G. Schön, G. Schmid, *Europhys. Lett.* **1994**, *28, 9*, 641.

[11] L. F. Chi, M. Hartig, T. Drechsler, Th. Schaak, C. Seidel, H. Fuchs, G. Schmid, *Appl. Phys. Lett. A* **1998**, *66*, 187.

[12] A. H. Soloway, W. Tjarks, B. A. Barnum, F.-G. Rong, R. F. Barth, I. M Codogni, J. G. Wilson, *Chem. Rev.* **1998**, *98*, 1515.

[13] G. Schmid, N. Klein, L. Korste, U. Kreibig, D. Schönauer, *Polyhedron* **1988**, *7*, 605.

[14] G. Schmid, R. Pugin, J.-O. Malm, J.-O. Bovin, *Eur. J. Inorg. Chem.* **1998**, *6*, 813.

[15] M. P. J. van Staveren, H. B. Brom, L. J. de Jongh, *Physics Reports* **1991**, *208*, 1.

[16] G. Schmid, *J. Chem. Soc., Dalton Trans.* **1998**, 1077.

[17] U. Simon, R. Flesch, H. Wiggers, G. Schön, G. Schmid, *J. Mater. Chem.* **1998**, *8*, 517.

[18] V. Gasparian, U. Simon, *Physica B* **1997**, *249*, 289.

[19] U. Simon, V. Gasparian, *Phys. Stat. Sol. B* **1998**, *205*, 223.

[20] R. Pelster, U. Simon, *Colloid Polym. Sci.* **1999**, *277*, 2.

[21] C. Plog, W. Maunz, P. Kurzweil, E. Obermeier and C. Scheibe, *Sensors and Actuators, B* **1995**, *24*, 584.

[22] U. Simon, U. Flesch, W. Maunz, R. Müller, C. Plog, *Microporous Mesoporous Mater.* **1998**, *21*, 111.

Received May 31, 1999
[I99199]