The cluster $\text{Ag}_{44}\text{SePh}_{30}$, originally prepared from silver selenolate, upon oxidative decomposition by $\text{H}_2\text{O}_2$ gives the same cluster back, in an apparently reversible synthesis. Such an unusual phenomenon was not seen for the corresponding thiolate analogues. From several characterization studies such as mass spectrometry, Raman spectroscopy, etc., it has been confirmed that the degraded and as-synthesized selenolates are the same in nature, which leads to the reversible process. The possibility of making clusters from the degraded material makes cluster synthesis economical. This observation makes one to consider cluster synthesis to be a reversible chemical process, at least for selenolates.

Synthesis and characterisation of noble metal quantum clusters is becoming one of the most fascinating topics of materials research due to their unique size-dependent properties. Ultra small size and enhanced optical properties make them widely applicable in a variety of applications such as surface enhanced Raman scattering (SERS), catalysis, sensing, sensing, and many others. Numerous examples include, $\text{Ag}_{44}(\text{SR})_{30}$, $\text{Ag}_{44}(4\text{-FTP})_{30}$, and $\text{Ag}_{44}(3\text{-FTP})_{30}$, where $\text{SR}$, 4-FTP and 3-FTP correspond to the thiolate functional groups. In most of the cases, the clusters have been examined without any ligands. In other corresponding clusters also but interestingly, except for selenolated $\text{Ag}_{44}$, no other systems (including thiolated $\text{Ag}_{44}$, which is chemically most similar) show this property. The clusters examined include, $\text{Ag}_{44}(\text{SPh})_{30}$, $\text{Ag}_{44}(4\text{-FTP})_{30}$ and $\text{Ag}_{44}(3\text{-FTP})_{30}$ where SPh, 4-FTP and 3-FTP correspond to the thiolate forms of thiophenol, 4-flurothiophenol and 3-flurothiophenol, respectively. A larger silver cluster, $\text{Ag}_{152}(\text{PET})_{60}$ was also studied. To explore this phenomenon in more detail, we have oxidised the cluster using peroxide to form selenolates and then the reversibility was checked using borohydride reduction. Several other characterisation studies were done to understand the reversibility.

A two phase solution state route as described in our previous report has been used to synthesize the cluster. Initially, silver trifluoroacetate ($0.0714 \text{ mmol}$) was dissolved in 7.2 mL acetonitrile and stirred for 5 min. Benzene selenol ($0.0471 \text{ mmol}$) was added to that solution and was left to stir for another 15 min (resulting in solution A). In another conical flask, 28.6 mL acetonitrile solution of $\text{NaBH}_4$ ($0.286 \text{ mmol}$) was kept for stirring for 30 min (solution B). Then, solution B was added to solution A and the reaction mixture was left to stir for 3 h at room temperature. A wine red colored cluster was formed after 3 h and it was stored in a refrigerator at $\sim 4 \text{ °C}$.

Crystal structures of mixed ligand protected $\text{Ag}_{14}$, $\text{Ag}_{16}$ and $\text{Ag}_{12}$ clusters have been solved. Recently, the crystal structure of the very first complete thiolate protected $\text{Ag}_{44}$ cluster has been reported by Bigioni and Zheng groups. The $\text{Ag}_{44}(\text{SR})_{30}$ cluster forms a Keplerate solid of concentric icosahedral and dodecahedral atom shells to form a hollow cage which is further protected by six $\text{Ag}_{3}(\text{SR})_{3}$ units in an octahedral geometry. A similar structure has been proposed for the selenolate analogue of the $\text{Ag}_{44}$ cluster which shows an identical optical spectrum with a shift, as expected from the difference in ligands. In most of the cases, the clusters have been examined in terms of their stability. As silver clusters are easily oxidisable under aerobic conditions, they degrade rapidly to form thiolates or selenolates and studies on intact clusters are limited.

In this work, we report the reversible formation of the $\text{Ag}_{44}$ cluster from selenolates. The reversibility has been checked for other corresponding clusters also but interestingly, except for selenolated $\text{Ag}_{44}$, no other systems (including thiolated $\text{Ag}_{44}$, which is chemically most similar) show this property. The clusters examined include, $\text{Ag}_{44}(\text{SPh})_{30}$, $\text{Ag}_{44}(4\text{-FTP})_{30}$ and $\text{Ag}_{44}(3\text{-FTP})_{30}$ where SPh, 4-FTP and 3-FTP correspond to the thiolate forms of thiophenol, 4-flurothiophenol and 3-flurothiophenol, respectively. A larger silver cluster, $\text{Ag}_{152}(\text{PET})_{60}$ was also studied. To explore this phenomenon in more detail, we have oxidised the cluster using peroxide to form selenolates and then the reversibility was checked using borohydride reduction. Several other characterisation studies were done to understand the reversibility.

A two phase solution state route as described in our previous report has been used to synthesize the cluster. Initially, silver trifluoroacetate ($0.0714 \text{ mmol}$) was dissolved in 7.2 mL acetonitrile and stirred for 5 min. Benzene selenol ($0.0471 \text{ mmol}$) was added to that solution and was left to stir for another 15 min (resulting in solution A). In another conical flask, 28.6 mL acetonitrile solution of $\text{NaBH}_4$ ($0.286 \text{ mmol}$) was kept for stirring for 30 min (solution B). Then, solution B was added to solution A and the reaction mixture was left to stir for 3 h at room temperature. A wine red colored cluster was formed after 3 h and it was stored in a refrigerator at $\sim 4 \text{ °C}$.
Similar methodologies have been followed for thiol protected clusters also. More details are given in the ESI.

The Ag$_{44}$(SePh)$_{30}$ cluster$^{41}$ shows five intense bands at 1.41 (879), 1.82 (681), 2.16 (574), 2.40 (516) and 2.82 (440) eV (nm) along with three broad bands centered around 1.27 (970), 1.95 (635) and 3.14 (395) eV (nm) in its absorption spectrum. The cluster kept under aerobic conditions will lose its optical identity gradually and a yellow precipitate appears. Reversible cluster formation was observed first from the degraded cluster. Upon addition of adequate amount of borohydride and constant stirring, we observed that the degraded selenolate, formed from the cluster (selenolate$^1$) can be reformed to the Ag$_{44}$ cluster in 15 minutes. However, degradation under aerobic conditions typically takes 5–7 days and time dependent observation was difficult. So, an external oxidizing agent, hydrogen peroxide, was added to a controlled amount so that we can monitor oxidation in real time. Photographs at different stages of the reaction are given in Fig. 1A. The cluster is wine red in color but upon addition of H$_2$O$_2$, the color changes to yellowish-brown and finally to yellow which confirms the formation of silver selenolate. The reaction was monitored through absorption spectroscopy where the distinct features of the Ag$_{44}$(SePh)$_{30}$ cluster are lost and subsequently a new peak around 450 nm along with a hump at 430 nm started appearing, due to selenolate. As time progresses, the baseline of the spectrum started increasing because of the low solubility of selenolate in acetonitrile. During the reduction of this selenolate$^1$ with NaBH$_4$, the color changes in the reverse order and finally the solution becomes clear and attains wine red color which confirms the formation of the Ag$_{44}$ cluster. The corresponding UV/Vis spectra are given in Fig. 1C where the spectra also change in the reverse order. The sharp selenolate peak disappears and all the features of Ag$_{44}$ started appearing with time. The reaction time is controlled by the concentration of the cluster, the amount of H$_2$O$_2$ and NaBH$_4$. Constant stirring is also important for this case. For more clarity, these reversible cycles are shown by selecting the intensity of the 516 nm peak for five consecutive cycles (Fig. S1, ESI$^\dagger$).

Similar experiments have been tried for Ag$_{44}$(SPh)$_{30}$ which is the thiol analogue of Ag$_{44}$(SePh)$_{30}$. For this cluster, upon addition of H$_2$O$_2$ (all concentrations were kept constant) thiolates were formed, as expected. The UV/Vis spectra (Fig. S2A, ESI) clearly show a sharp peak near 350 nm corresponding to thiolates and the features of the Ag$_{44}$(SPh)$_{30}$ cluster have been lost completely. Reduction of this degraded thiolate (thiolate$^1$) has resulted in a broad hump near 400 nm and the cluster feature did not develop suggesting that the system was not reversible. We have studied Ag$_{44}$(4-FTP)$_{30}$ (Fig. S2B, ESI$^\dagger$) and Ag$_{44}$(3-FTP)$_{30}$ (Fig. S2C, ESI$^\dagger$) also but they both do not show the reversible formation. The ‘Ag$_{44}$(4-FTP)$_{30}$ derived thiolate’ form nanoparticles by reduction. The plasmonic feature can be seen in the optical spectrum (Fig. S2B, ESI$^\dagger$) while a hump at 480 nm can be observed in the case of ‘Ag$_{44}$(3-FTP)$_{30}$ derived thiolate’ under the same conditions. Degradation to thiolate is not reversible in the larger cluster, Ag$_{152}$(PET)$_{60}$ (Fig. S3, ESI). In the cluster literature, the only case of reversibility was observed by Anand et al.$^{45}$ who reported that the reversible transformation of human serum albumin protected Ag$_9$ to the Ag$_{14}$ cluster. Note that the cluster core changes during this transformation. Therefore, the reversibility seen in the case of Ag$_{44}$(SePh)$_{30}$ is unprecedented. As Au clusters are chemically different in most of their properties,$^{46}$ a similar study was not attempted on them.

To find the reason for this unique transformation, a detailed characterization of selenolate$^1$ was performed.
Initially, matrix assisted laser desorption ionization mass spectrometry (MALDI MS) was performed for the cluster as well as for selenolate 1 (Fig. 2). Ag₄₄(SePh)₃₀ shows a peak centered around m/z 9500 using DCTB as the matrix and as expected, selenolate 1 does not show any feature. Electrospray ionization mass spectrometry (ESI MS) shows 3, 4 features (Fig. 2a) of Ag₄₄(SePh)₃₀ which confirm the purity of the cluster. As selenolates have very less solubility, a methanol-acetonitrile mixture was used for the ESI measurement. Some selenolate species such as Ag₃(SePh)₂, Ag₂(SePh)₂ and Ag(SePh)₂ have been observed in the negative ion mode. For confirmation, ESI-MS was also taken for the reversibly formed Ag₄₄ cluster which shows the same feature as depicted in Fig. 2A.

We thought that comparison of selenolate 1 with the as-synthesized selenolate (selenolate 2) and similar thiolate samples (synthesis procedures are given in ESI†) might be useful to understand this phenomenon. UV/Vis spectroscopy for both the cases have been compared (Fig. S4, ESI†) but drastic differences are seen for thiolates (Fig. S4A, ESI†). As-synthesized thiolate (thiolate 2) shows a sharp peak at 237 nm and a broad hump at 277 nm whereas thiolate 1 shows four broad humps at 240, 280, 360 and 420 nm, respectively. Selenolate 1 shows a peak at 464 nm along with a hump at 430 nm and similar two peaks at 430 and 450 nm were observed for selenolate 2. So, selenolates 1 and 2 might be the same as it appears in absorption spectroscopy. To understand it better, laser desorption ionization mass spectrometric (LDI MS) analysis was attempted for the thiolates and selenolates (Fig. 3). It is important to mention here that LDI MS has been used as these thiolates and selenolates have very less solubility, so it was difficult to perform electrospray ionization (ESI) or matrix assisted laser desorption ionization (MALDI) mass analysis. Here also similar trends have been observed in absorption spectroscopy. Systematic Ag₂S losses have been observed for both the thiolates (Fig. 3A) but the loss start from higher mass (m/z 4500) for thiolate 2 while it started from m/z 1800 for thiolate 1, that too with much lower intensity (an expanded view of a peak at m/z 1375 is shown in the inset of Fig. 3A). Interestingly, in the lower mass, intensity gradually increases for thiolate 2 and some shifts have also been observed. The data suggest that thiolates 1 and 2 are different in nature. Selenolates show similar features and systematic Ag₄Se losses have been seen (Fig. 3B) from almost the same mass region and the isotope pattern is also similar (inset of Fig. 3B). The reason for the complicated fine structure of selenolates compared to thiolates is because of the isotopes of Se. Selenium has six isotopes namely, ⁷⁴Se (0.89%), ⁷⁶Se (9.37%), ⁷⁷Se (7.63%), ⁷⁸Se (23.77%), ⁸⁰Se (49.61%), and ⁸²Se (8.73%), which contribute significantly to the fine mass spectral features compared to sulfur which has only one predominant isotope, namely ³²S (95%). Raman spectroscopy was used to confirm that selenolates are the same but thiolates are different in nature (Fig. S5, ESI†). Although detailed peak assignments have not been done, many are assigned based on the literature.⁴⁷ From a comparative study, we can see that Raman features for selenolates 1 and 2 (Fig. S5A, ESI†) are the same but differences are there for thiolates (Fig. S5B, ESI†). From a SEM/EDAX analysis, the ratio of Ag : Se for the degraded selenolate species is found to be 1 : 0.68 (3 : 2.04) which is very close to the atomic ratios present in the cluster (Fig. S7, ESI†). Non-stoichiometry in thiolates was found earlier⁴⁸−⁵¹ and a similar case is expected for selenolates also. Parikh et al. have shown the existence of silver rich thiolates...
using elemental analysis.\textsuperscript{52} Li et al.\textsuperscript{48,49} and Sun et al.\textsuperscript{50} have shown the crystal structures of metal rich thiols. McLachlan and Ibers have shown sulphur and selenium rich silver thiolates.\textsuperscript{53} So it is not difficult to rationalize the existence of non-stoichiometric thiolates or selenolates in our experiments. In detail such thiolates may be structures with sulphide cores with thiolate shells, although the authors refer to them as thiolates.

From all these data it is confirmed that degraded and as-synthesized selenolates are the same in nature but they are different in the case of thiolates. For the thiol case, irreversibility has been observed because of the different nature of the thiolates and may be upon reduction, thiolates have many possibilities to make diverse clusters or bigger nanoparticles.

In summary, we have synthesized selenolate and thiolate analogues of Ag$_{44}$ clusters using similar synthetic methodologies. Unusual reversible formation of the Ag$_{44}$ cluster from selenolate was observed. This phenomenon has not been seen for the corresponding thiolates. Several characterization techniques have been used to understand the reversibility. It has been found that degraded selenolates and as-synthesized selenolates are the same in nature but they are different in the case of thiolates, which is responsible for this unusual property. This opens up a new possibility of making clusters from the degraded materials, which may be economical for precious metals like gold and silver. The most important aspect of this finding appears to be that cluster synthesis is proven to be reversible, at least in the limited case of selenolates. This suggests that clusters may be treated just as molecules in their chemistry.

We thank the Department of Science and Technology, Government of India for constantly supporting our research program on nanomaterials. I. C. thanks IITM for research fellowships.

Notes and references


Published on 06/10/2014. Downloaded by Indian Institute of Technology Chennai on 06/11/2014 11:13:28.