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Mass spectrometric study on the neutral nanocluster $[Cd_{32}Se_{14}(SePh)_{36}L_4]$ (L = THF, $OPPh_3$) upon charged ligand exchange

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Abstract

Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) has been applied to the neutral 1.4 nm sized cluster $[Cd_{32}Se_{14}(SePh)_{36}(L)_4]$ upon targeted exchange of the neutral ligands L by various anionic ligands in solution. Use of $SePh^-$ as a 'charging ligand' leads to virtually monodisperse ion beams constituted of the intact cluster as tetra- and tri-anions. An electrostatic model is employed which is consistent with the proposed charge distribution of four excess charges being localized at the corner sites of the tetrahedron. The experimental results suggest a general applicability of charged ligand exchange to obtain monodisperse cluster ion beams.

1. Introduction

An ongoing issue in semiconductor nanostructures is related with examining the size evolution of the electronic, optical and electrical properties [1–5]. Recent advances in new synthetic routes have made it possible to yield monodisperse, semiconducting molecular clusters with well-defined chemical formulas and structures [6–9]. Molecular clusters such as $[Cd_{32}E_{14}(E'R)_{36}(L)_4]$ (E = Se, S; E′ = Se, S; L = neutral ligand) [10–12] with a size nearing 2 nm in diameter are composed of tens of atoms and can be viewed as the molecular limit of the bulk semiconductor [13–15], since the bonding in such clusters, as in larger semiconductor nanocrystals, resembles that of the bulk semiconductor.

Any potential application in nanotechnology will require a level of understanding presently not yet available for most nanoobjects [16]. Soft ionization techniques are called for to extend condensed-phase studies to the gas phase allowing isolated nanoparticles to be investigated in the absence of particle–particle interaction or other 'matrix' effects. Beyond this analytical aspect, new developments in mass spectrometry (intensive ion sources, ion guiding/trapping, size selection, detection) can be expected to play a major role in preparative scale mass spectrometry, e.g., in deposition experiments. In this context, electrospray mass spectrometry (ESI-MS) of inorganic semiconducting nanoparticles and clusters is a fairly new and rapidly developing field [17–19]. In a pioneering study Bowmaker and co-workers [20] probed small ionic CdS clusters by electrospray MS including evidence for the parent ion $[Cd_{10}S_4(SPh)_{10}]^{4-}$. Later they showed that in mixed ionic solutions of $(Me_4N)_4[Cd_{10}S_4(SPh)_{10}]$ and $(Me_4N)_4[Cd_{10}Se_4(SPh)_{10}]$ as well as mixtures of $(Me_4N)_4[M_{10}S_4(SPh)_{10}]$ (M = Cd and Zn) ligand exchange and even metal exchange takes place on a time scale of hours at room temperature [21]. Intermolecular

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ligand exchange has been also observed in mass spectrometric probes of $[Cd_8Se(SePh)_{12}Cl_4]^{2-}$ cluster ions [22]. Recently, Strouse and co-workers [23] applied ESI-MS techniques to probe the $[Cd_{32}S_{14}(SPh)_{36}(DMF)_4]$ cluster. Heavy fragmentation in the source was observed, their results indicate a favored cleavage (upon collision-induced dissociation) along a specific crystallographic plane of the CdS core.

In this work, we set out to investigate the possibility of charging the neutral clusters $[Cd_{32}Se_{14}(SePh)_{36}L_4]$ (L = THF, $OPPh_3$) by negative-ion ligand exchange/attachment in a well defined way in order to make them accessible for electrospray mass spectrometry.

2. Experimental methods

Single crystals of the two different clusters $[Cd_{32}Se_{14}(SePh)_{36}(THF)_4]$ (Ph = C_6H_5, THF = C_4H_8O) (**1**) and $[Cd_{32}Se_{14}(SePh)_{36}(OPPh_3)_4]$ (**2**) were synthesized according to recently published procedures and their structures determined via single-crystal X-ray diffraction [24]. As depicted in Fig. 1 both compounds exhibit the same tetrahedral cluster core structure $[Cd_{32}Se_{14}(SePh)_{36}L_4]$ with the ligands L occupying the apex positions. The CdSe cluster framework is built up of 13 fused adamantane cages with four barrelene cages at each of the corners. Adamantane cages are the building blocks of the cubic zincblende structure of cadmium selenide while barrelene cages constitute the hexagonal wurtzite type. Thus, the cluster core resembles a tetrahedral piece of the sphalerite structure type of bulk cadmium selenide, where each edge of the tetrahedron measures 1.47 nm (taken between cadmium atoms at the apex positions).

As anionic species we employed commercially available halogenide ions (as quaternary ammonium salts) as well as the sodium salt of $SePh^-$. The following sample solutions were freshly prepared under nitrogen atmosphere prior to the electrospray mass spectrometric probes. Solution I contains **1** in dry tetrahydrofuran (THF) at a concentration of about 1.5×10^{-3} mmol/l, to which a fourfold stoichiometric excess of NaSePh was added (also as a solution in THF). Solutions II and III comprise **2** (at concentrations of 1.1×10^{-3} and 9.6×10^{-4} mmol, respectively) in dry 1,2-dichloroethane together with the fourfold equivalent of the quaternary ammonium salts N^nPent_4Cl ($^nPent = C_5H_{11}$) and N^nBu_4Br ($^nBu = C_4H_9$), respectively.

Mass spectra were taken on a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Bruker Daltonics, APEX II) equipped with a 7T superconducting magnet and a cylindrical Infinity cell. The electrospray ion source which was recently modified by a home-built ion funnel for improved sensitivity [25]. The solutions were sprayed at typical flow rates of about 200 μl/h and nebulized using dry nitrogen. The desolvation capillary (stainless steel, 0.5 mm i.d.) was heated to 80 °C. After accumulation in a linear hexapole ion trap

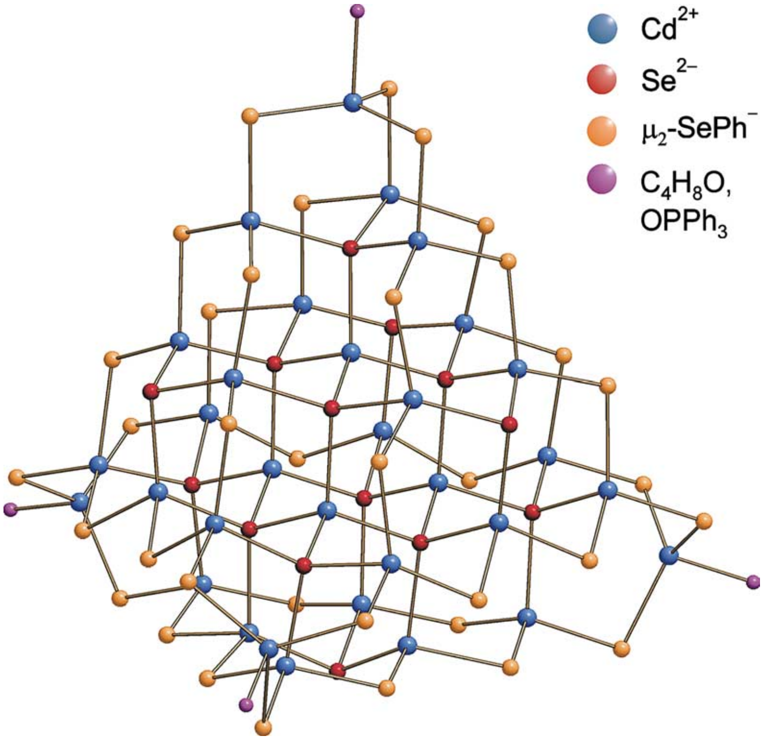

Fig. 1. The $Cd_{32}Se_{50}O_4$ cluster core as a section of the tetrahedral molecular structures of $[Cd_{32}Se_{14}(SePh)_{36}(OC_4H_8)_4]$ (**1**) and $[Cd_{32}Se_{14}(SePh)_{36}(OPPh_3)_4]$ (**2**) as obtained from X-ray diffraction.