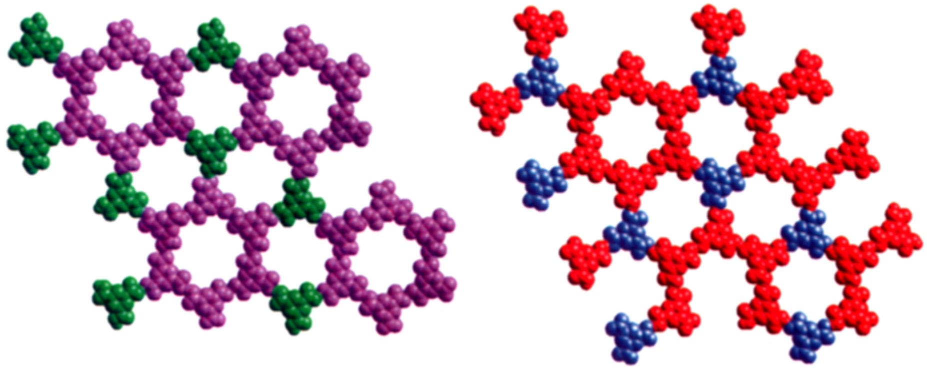

Fig. 2. The two independent honeycomb grids in **2**. Left: Grid consists of H_3TMA molecules (green) and $HTMA^{2-}$ ions (magenta) in the ratio 1:3; right: Grid consists of TMA^{3-} ions (blue) and H_2TMA^- ions (red) in the ratio 1:3. The grids are sustained by $O-H\cdots O^-$ bis(carboxylate) hydrogen bonding. Cations, omitted for the sake of clarity, fill the void space of the cavities and cross link parallel honeycomb grids.

Keywords: crystal engineering · hydrogen bonds · solid-state structures · trimesic acid

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[15] Trimesic acid was treated with *N,N*-dicyclohexylamine in a molar ratio of 1:3 in MeOH to give **1**. Hexagonal crystals of **1** were obtained from a 1:1 mixture of 1-butanol and MeOH. Crystals lose solvent and crystallinity at 45 C and sublime above 240 C. Crystal structure data for **1**: $[NH_2(cyclo\text{-}C_6H_{11})_2]_3[C_6H_3(CO_2)_3]\cdot x\,MeOH$, hexagonal, $P6_3$, $a = 17.6903(3)$, $b = 17.6767(6)$, $V = 4790.7(2)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.121$ Mg m^{-3}. 2495 reflections of 3952 with $I_{net} > 3F$ were measured at 173 K on a Siemens SMART CCD area detector using the 2θ scan mode. Three MeOH molecules are hydrogen-bonded to the grid outside the cavity and there appear to be several disordered MeOH molecules within the honeycomb. The latter could not be readily resolved. Final *R* factors of $R_f = 0.057$ and $R_w = 0.055$ were obtained.
Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-76. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: teched@chemcrys.cam.ac.uk).

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[17] Crystals of **2** were formed serendipitously from attempted cocrystallization of 4,4'-bipyridine and trimesic acid in dimethyl formamide (DMF). Compound **2** crystallized over a period of two months at room temperature, presumably by decomposition of DMF, m.p. > 300 C. Crystal structure data for **2**: $[NH_2(CH_3)_2]_{12}[C_6H_3(CO_2H)_3]\,[C_6H_3(CO_2H)_2(CO_2)]_3[C_6H_3(CO_2H)\,(CO_2)_2]_3\text{-}[C_6H_3(CO_2)_3]$, trigonal, $R\bar{3}$, $a = 33.412(5)$, $b = 17.465(3)$, $V = 16885(4)$ Å^3, $Z = 18$, $\rho_{calcd} = 1.311$ Mg m^{-3}. 2766 reflections of 4889 with $I_{net} > 3F$ were measured at 290 K on an Enraf-Nonius CAD4 diffractometer using the ω scan mode, final *R* factors of $R_f = 0.053$ and $R_w = 0.049$ were obtained [15].

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Synthesis and Structure of the Nanoclusters $[Hg_{32}Se_{14}(SePh)_{36}]$, $[Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$, $[P(Et)_2(Ph)C_4H_8OSiMe_3]_5[Cd_{18}I_{17}(PSiMe_3)_{12}]$, and $[N(Et)_3C_4H_8OSiMe_3]_5[Cd_{18}I_{17}(PSiMe_3)_{12}]$**

Silke Behrens, Marco Bettenhausen, Anne C. Deveson, Andreas Eichhöfer, Dieter Fenske,* Almut Lohde, and Ulrike Woggon

Nanoclusters and colloids from the semiconducting II–V and II–VI compounds are particularly interesting with respect to their optical and electronic properties in comparison to those of the solid bulk materials.[1] The influence of the size of the molecules and particles in the nanometer scale plays an important role in determining the band-gap ("size quantization effect"). An exact interpretation of the measured effects is made more difficult by a size distribution of the particles, which is usually found to be the case for colloids. The synthesis and structural characterization of cluster molecules with a defined size and structure provide an interesting approach to this class of compounds.[2]

In the case of the cadmium chalcogenide clusters, the largest structurally characterized clusters reported to date are **1a**[3] and **1b**.[4] We have already isolated and structurally characterized

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[*] Prof. Dr. D. Fenske, Dipl.-Chem. S. Behrens, Dipl.-Chem. M. Bettenhausen, Dr. A. C. Deveson, Dr. A. Eichhöfer
Institut für Anorganische Chemie der Universität
Engesserstrasse, Gebäude-Nr. 30.45, D-76128 Karlsruhe (Germany)
Fax: Int. code +(721)661921
e-mail: eich@achibm6.chemie.uni-karlsruhe.de

A. Lohde, Dr. U. Woggon
Institut für Angewandte Physik der Universität Karlsruhe (Germany)

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a large number of copper chalcogenide clusters,[5] amongst which is one of the largest known characterized clusters $[Cu_{146}Se_{76}(PPh_3)_{30}]$.[6] Herein we describe the first synthesis and structural characterization of mercury and cadmium selenide clusters as well as cadmium phosphide clusters **2**–**5** [Eqs. (a)–(e)].

$[Cd_{32}S_{14}(SPh)_{36}]\cdot 4DMF$ **1a**

$[Cd_{32}S_{14}(SCH_2CH(OH)CH_3)_{36}]\cdot 4H_2O$ **1b**

The reaction of $[Fe(CO)_4(HgCl)_2]$ with $PhSeSiMe_3$ in toluene [Eq. (a)] gave a red solution from which a mixture of yellow crystals of $[Hg(SePh)_2]$ and red crystals of **2a** were formed after a few days. Figures 1 and 2 show the molecular structure of the $Hg_{32}Se_{50}$ cluster of **2a**. The compound crystallizes in the cubic space group *P*23, and the cluster molecules possess *T* symmetry.

$$[Fe(CO)_4(HgCl)_2] \xrightarrow[\text{toluene}]{PhSeSiMe_3} [Hg_{32}Se_{14}(SePh)_{36}]_{cub} + [Hg(SePh)_2] \qquad (a)$$

2a

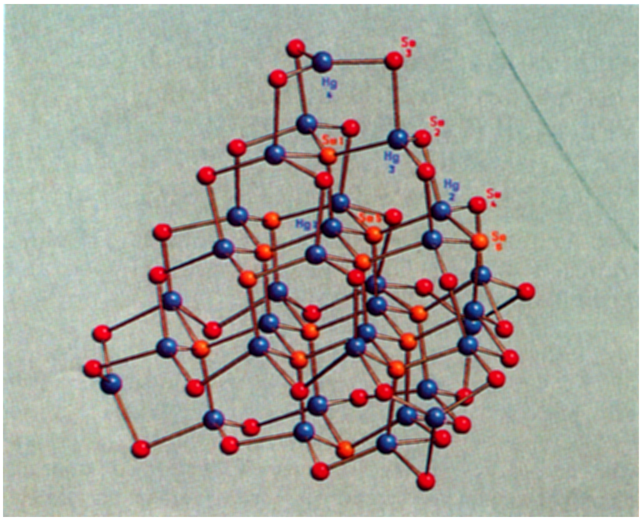

Fig. 1. Molecular structure of the $Hg_{32}Se_{50}$ cluster of **2a**. Hg: blue; Se^{2-}: orange; Se from $SePh^-$: red. Selected bond lengths [pm] and angles [°] (deviations ±0.3 pm and ±0.1°): Hg(1,2,3)–Se: 257.5–269.9, Hg4–Se3: 256.7; Se-Hg(1,2,3)-Se 91.0–130.1 (distorted tetrahedral coordination by Se); sum of the angles at Hg4 (trigonal planar coordination by Se): 360.0°

The core of the cluster, which comprises 13 HgSe adamantane cages, is a section of the sphalerite structure, which is also found in HgSe.[7] The corners of the cluster are made up of barrelanoid HgSe cages that are characteristic of the wurzite structure of HgSe. The Hg atoms Hg1–Hg3 have distorted tetrahedral environments, coordinated by the Se atoms of SePh (red) and Se ligands (orange) (Se-Hg-Se: 91.0(1)–130.1(1)°). The four Hg atoms Hg4 at the corners of the tetrahedral cluster have almost trigonal-planar coordination from the three Se atoms of the SePh ligands (Se-Hg-Se: 120.0(1)°). This is very remarkable because these Hg atoms are not sterically shielded by the phenyl groups (Fig. 2). The diameter of **2a** is thus about 2400 pm. The Hg–Se bond lengths lie between 256.7 and 269.9(3) pm, which correspond to those distances in HgSe (262 pm).[8] The structure of **2a** resembles that of the reported cadmium sulfide clusters[3, 4] and also that of the cadmium selenide cluster **3** (see below). However in these structures the cadmium atoms at the corners of the cluster have tetrahedral environments through additional coordination of solvent molecules or phosphane ligands.

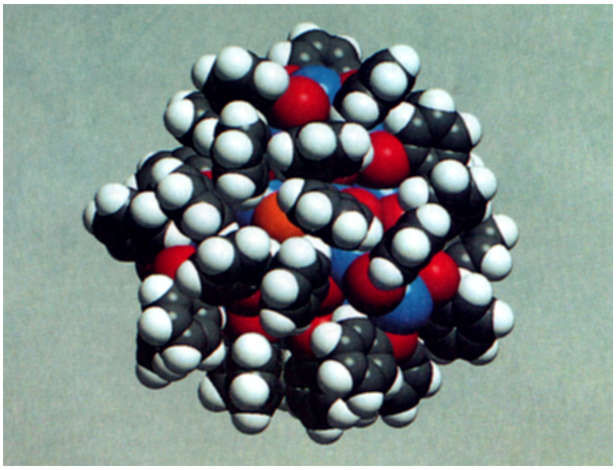

Fig. 2. Space-filling model of **2a**. Hg: blue; Se^{2-}: orange; Se from $SePh^-$: red; C: grey; H: white.

The reaction of $HgCl_2$ with $PhSeSiMe_3$ in toluene [Eq. (b)], and subsequent layering of the red reaction solution with heptane, resulted in the formation of red needlelike crystals of **2b**,

$$HgCl_2 \xrightarrow[\text{toluene/heptane}]{PhSeSiMe_3} [Hg_{32}Se_{14}(SePh)_{36}]_{trig} + [Hg(SePh)_2] \qquad (b)$$

2b

which have the same empirical formula as **2a**, but crystallize in the trigonal space group $P3_2$. The two modifications differ only in the packing of the cluster molecule in the crystal (Fig. 3). The arrangement of the cluster molecules in **2a** is such that channels with a diameter of about 700 pm are formed.

The red color of the crystals shows that the electronic structure of the cluster differs from that of the black semimetal HgSe in the macroscopic state (ΔE_g = — -0.06 eV at 300 K).[9] To obtain a more accurate analysis of the optical and electronic properties of compounds **2a** and **2b**, the absorption and luminescence spectra were measured. The absorption spectrum of **2b**, recorded in the solid state on a glass slide layered with indium tin oxide at 10 K, shows two maxima at 539 nm (2.3 eV) and 496 nm (2.5 eV) (Fig. 4). The luminescence spectrum of this sample (dotted line in Fig. 4), measured with an excitation wavelength of 436 nm at 10 K, shows a maximum at 670 nm (1.85 eV). The red solution of **2b** in THF shows weak maxima at 549 nm (2.26 eV) and 504 nm (2.46 eV) in the absorption spectrum at room temperature. In comparison to the absorption maxima of the Cd_{32} clusters,[3, 4] those for **2b** show a strong shift to larger wavelengths.

Treatment of $[CdCl_2(PPh_3)_2]$ with $PhSeSiMe_3$ in acetone afforded colorless crystals of **3** [Eq. (c)]. In analogy to the struc-

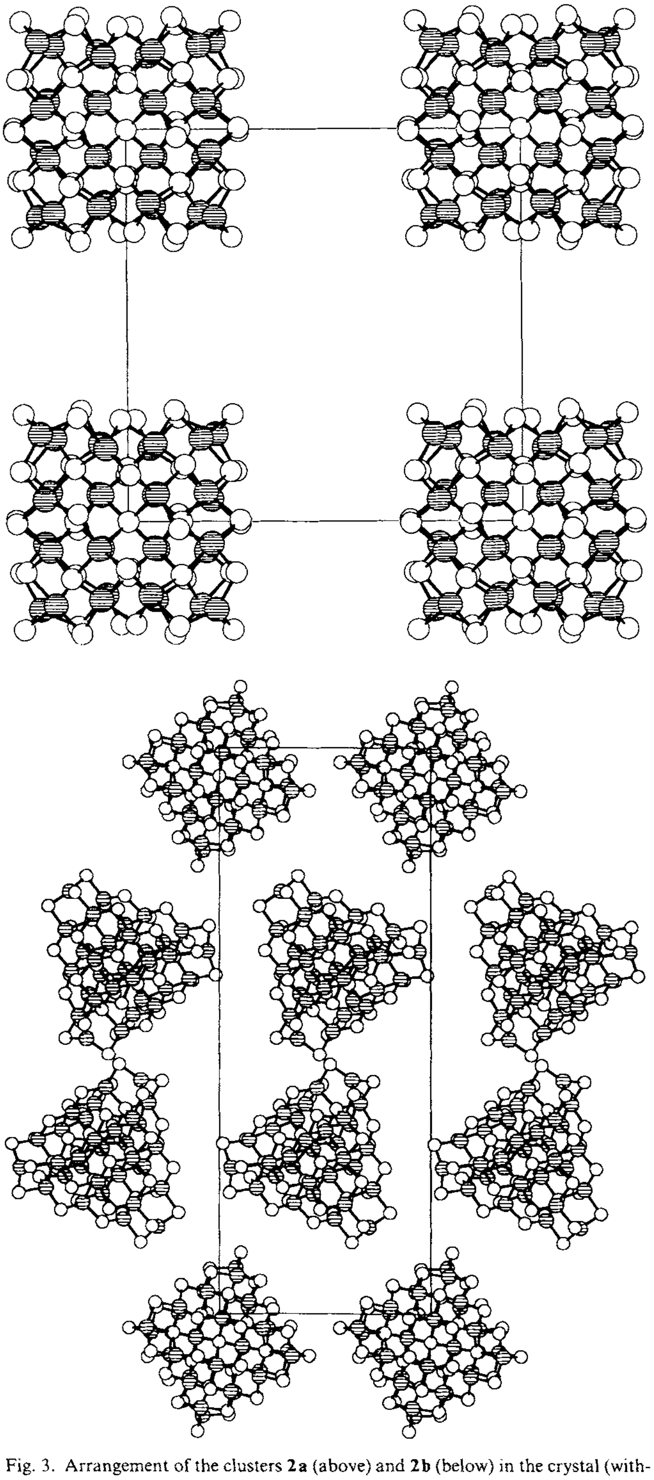

Fig. 3. Arrangement of the clusters **2a** (above) and **2b** (below) in the crystal (without C and H atoms). Hg: ▨; Se: ○.

tures of **2a** and **2b**, the skeleton of the $Cd_{32}Se_{50}$ cluster is built up from two characteristic structural units; the center of the cluster is of the sphalerite type and the corners of the cluster are formed by wurzite-analogous cages. The Cd atoms have distorted tetrahedral environments, coordinated by Se atoms from the SePh and Se ligands and by the P atoms of the PPh_3 ligands (Se-Cd-Se: 89.0–126.9(1)°, Se-Cd-P: 96.1–109.5(2)°). The Cd–Se bond lengths lie between 255.9 and 267.9(3) pm. This is comparable to the bulk material CdSe (zinc blende structure) in which the Cd–Se bond length is 262 pm.[10]

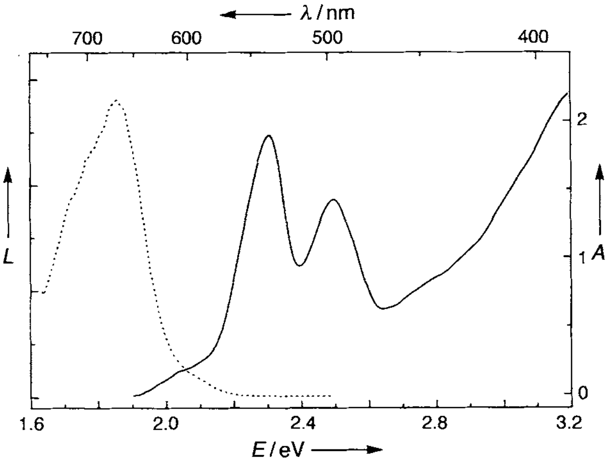

Fig. 4. Absorption (full line) and luminescence spectra (dotted line) of **2b** in the solid state on an indium tin oxide layered glass holder at 10 K. A = absorption. L = luminescence.

The reaction of CdI_2 with PEt_2Ph and $P(SiMe_3)_3$ in THF [Eq. (d)] led to the formation of a pale yellow solution, which

$$CdI_2 + 2\,PEt_2Ph + P(SiMe_3)_3 \xrightarrow[-\,ISiMe_3]{THF/RT} [PEt_2(Ph)C_4H_8OSiMe_3]_5[Cd_{18}I_{17}(PSiMe_3)_{12}] \tag{d}$$

4

when layered with hexane produced a yellow oil (of unknown composition) and colorless, strongly refracting crystals of **4**. The analogous cluster anion also crystallized from the reaction of CdI_2 with NEt_3 and $P(SiMe_3)_3$ in THF as the compound **5** [Eq. (e)]. In both structures the cations were particularly difficult to refine in the difference Fourier analysis such that for each structure only three of the cations could be localized. The two missing cations are highly disordered. The formation of the cations can be ascribed to the cleavage of THF molecules by reactive $SiMe_3$ groups, which then can attack the tertiary phosphane or amine, leading to the formation of C–P or C–N bonds, respectively.

$$CdI_2 + NEt_3 + P(SiMe_3)_3 \xrightarrow[-\,ISiMe_3]{THF/RT} [NEt_3C_4H_8OSiMe_3]_5[Cd_{18}I_{17}(PSiMe_3)_{12}] \tag{e}$$

5

Complex **4** crystallizes in the chiral space group $P2_12_12_1$, **5** in $P\bar{1}$. The structure of the cluster anion of **4** and **5** is shown in Figure 5 (the data for **4** are discussed). The 18 Cd atoms are μ_3-bridged by the P atoms of the 12 $PSiMe_3$ groups and the eight I atoms I10–I17, in such a way that a spherical cluster is formed. The terminal I atoms I1–I9 are coordinated to the Cd atoms Cd1–Cd9. Apart from Cd12, Cd16, and Cd17, which are coordinated by I and P atoms in a distorted trigonal planar environment, all other Cd atoms have near tetrahedral coordination. The Cd–I distances lie between 300.7 and 329.1(2) pm for the bridging I atoms and between 271.0 and 284.9(8) pm for the terminal I atoms. The Cd–P bond lengths range between 244.8 and 255.5(5) pm.

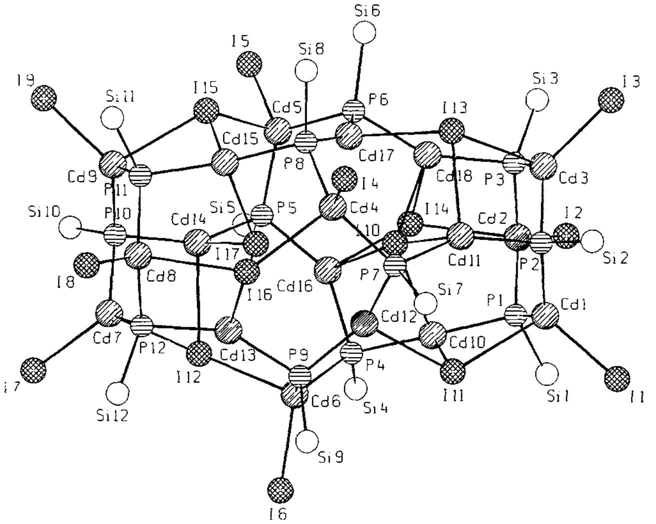

Fig. 5. Molecular structure of the cluster anion of **4** and **5**.

The cluster anions of **4** and **5** do not show any resemblance to any known bulk material structure of cadmium phosphides[11] or cadmium iodophosphides.[12] However, one might expect that the presence of the halogen atoms and the reactive $PSiMe_3$ groups could well lead to further reaction and that aggregation of the clusters to form the above-mentioned cadmium iodophosphides might be possible. Cadmium halogenophosphides are semiconductors in their macroscopic states. Sections of the solid-state structure in the form of ligand-stabilized cluster molecules would be very interesting with regard to investigations of larger quantum effects, as observed for the Q-Cd_3P_2 particles.[11]

Experimental Procedure

Preparation of compounds **2**–**5** (all steps were performed under a nitrogen atmosphere and absolute solvents were used).

2a: $PhSeSiMe_3$ (0.38 mL, 1.50 mmol) was added to a suspension of $[Fe(CO)_4(HgCl)_2]$ (0.48 g, 0.75 mmol) in toluene (25 mL). From the resulting clear red solution a yellow precipitate quickly formed. After a few days red cubes of **2a** crystallized.

2b: $PhSeSiMe_3$ (0.37 mL, 1.48 mmol) was added dropwise to a suspension of $HgCl_2$ (0.2 g, 0.74 mmol) in toluene (25 mL). The resulting clear red solution was layered with heptane and within a few hours the solution lightened in color and yellow crystals of $Hg(SePh)_2$ and red needlelike crystals of **2b** were formed.

3: $PhSeSiMe_3$ (0.46 mL, 1.86 mmol) was added to a suspension of $CdCl_2(PPh_3)_2$ (0.33 g, 0.47 mmol) in acetone (25 mL). This produced a clear, pale yellow solution, from which colorless rhomboids of **3** crystallized.

4 and **5**: A solution of CdI_2 (0.36 g 0.98 mmol) in THF (50 mL) was treated with PEt_2Ph (0.32 g, 1.96 mmol) (for **4**) or NEt_3 (0.1 g, 0.99 mmol) (for **5**). $P(SiMe_3)_3$ (0.5 g, 1.99 mmol) was added to the clear solutions. Layering the pale yellow reaction mixtures with hexane resulted in the formation of colorless crystals of **4** and **5** after three days.

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[7] Crystal structure analysis data: STOE IPDS diffractometer, Siemens rotating anode, $Mo_{K\alpha}$, 180 K (**2a**, **2b**) and 200 K (**3**–**5**). **2a**: $a = 2224.5(3)$ pm, $V = 11008(2) \times 10^6$ pm^3; space group $P23$ (No. 195), $Z = 1$, $\mu(Mo_{K\alpha}) = 15.3$ mm^{-1}, $2\theta_{max} = 45°$; 29085 reflections of which 4816 were independent, 4035 observed with $I > 2\sigma(I)$, 94 parameters (Hg, Se anisotropically, and C isotropically refined; the phenyl rings, some of which were highly disordered, were refined as rigid groups with idealized geometry, some of them with a common U(eq) value for the whole ring), $R = 0.054$, max. residual electron density 1.89 e Å^{-3}. There are probably solvent molecules also in the unit cell, but these cannot be refined due to high disorder. **2b**: $a = 2275.3(3)$, $c = 5302.0(11)$ pm, $V = 23772(7) \times 10^6$ pm^3; space group $P3_2$ (No. 145), $Z = 3$, $\mu(Mo_{K\alpha}) = 21.2$ mm^{-1}, $2\theta_{max} = 45°$; 50168 reflections of which 33565 were independent, 21430 observed with $I > 2\sigma(I)$, 1106 parameters (Hg, Se anisotropically, and C isotropically refined; the phenyl rings, some of which were highly disordered, were refined as rigid groups, some of them with a common U(eq) value for the whole ring), $R = 0.113$, max. residual electron density 2.24 e Å^{-3}. There are probably solvent molecules also in the unit cell, but these cannot be refined due to high disorder. **3**: $a = 2534.05(76)$, $b = 6813.53(94)$, $c = 2540.53(36)$ pm, $\beta = 113.519(20)°$, $V = 40220(14) \times 10^6$ pm^3; space group $P2_1/n$ (No. 14), $Z = 4$, $\mu(Mo_{K\alpha}) = 6.229$ mm^{-1}, $2\theta_{max} = 42°$, 134694 reflections of which 40678 were independent, 27073 observed with $I > 2\sigma(I)$, parameters 1333 (Cd, Se, P anisotropically, and C isotropically refined, the phenyl rings, some of which were highly disordered, were refined as rigid groups. One of the μ_2Se atoms has a very high temperature factor and it is not possible to locate the attached phenyl ring. It is possible that this could be a Cl^- ion), $R = 0.0868$, max. residual electron density 1.65 e Å^{-3}. It was not possible to find all the C atoms of the phenyl rings in the Fourier difference map. **4**: $a = 2422.2(5)$, $b = 3132.1(6)$, $c = 3673.7(7)$ pm, $V = 27871(10) \times 10^6$ pm^3; space group $P2_12_12_1$ (No. 19), $Z = 4$, $|E^2 - 1| = 0.748$, $\mu(Mo_{K\alpha}) = 3.43$ mm^{-1}, $2\theta_{max} = 45°$; 85711 reflections of which 36240 were independent, 31559 observed with $I > 2\sigma(I)$, 1113 parameters (Cd, I, P, Si in the cluster anion were refined anisotropically), $R = 0.061$, max. residual electron density 2.02 e Å^{-3}, the Flack parameter has a value of 0.38(3), which is an indication of an inversion twin. However this parameter cannot be taken as conclusive as not all of the atoms could be found in the Fourier difference map. **5**: $a = 2041.3(6)$, $b = 2341.7(8)$, $c = 2830.4(9)$ pm, $\alpha = 91.08(3)$, $\beta = 96.58(3)$, $\gamma = 113.43(2)°$, $V = 12301.45(5) \times 10^6$ pm^3; space group $P\bar{1}$ (No.2), $Z = 2$, $\mu(Mo_{K\alpha}) = 3.84$ mm^{-1}, $2\theta_{max} = 45°$; 37934 reflections of which 26189 were independent, 16340 observed with $I > 2\sigma(I)$, 1019 parameters (Cd, I, P, Si in the cluster anion were refined anisotropically), $R = 0.083$, max. residual electron density 2.18 e Å^{-3}. Due to high disorder it was not possible to find all the atoms in the Fourier difference map. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-405068 (**2a**), CSD-405069 (**2b**), CSD-405470 (**3**), CSD-405070 (**4**), and CSD-405071 (**5**).

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