Cluster Compounds

Synthesis and Structure of $[Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}(thf)_4][InCl_4(thf)]_2$—A Combined Approach of Theory and Experiment**

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Dedicated to Professor Martin Jansen on the occasion of his 60th birthday

The synthesis, structure, and physical properties of nanosized metal and semiconductor cluster molecules is of topical interest.[1] For the synthesis of metal chalcogenide cluster compounds, we have used the reaction of metal salts MX (M = Cu, Ag, Au; X = Cl, $OOCCH_3$) with bis- or monosilylated main-group element derivates $E(SiMe_3)_2$ or $RESiMe_3$ (E = S, Se, Te; R = organic group) in the presence of tertiary phosphanes PR_3.[2] The driving force of this reaction is the formation of $XSiMe_3$. In this way, a large number of cluster compounds have been synthesized and structurally characterized, for example, $[Cu_{146}Se_{72}(PPh_3)_{30}]$,[3] $[Ag_{172}Se_{40}(Se\mathit{n}Bu)_{92}dppp]$ (dppp = bis(diphenylphosphanyl)propane),[4] $[Ag_{188}S_{94}(PR_3)_{30}]$ (R = *n*Pr, *n*Bu)[5] and $[Ag_{262}S_{100}(S\mathit{t}Bu)_{62}(dppb)_6]$ (dppb = bis(diphenylphosphanyl)butane).[6] Calculations reveal that the PR_3-stabilized cluster complexes are metastable intermediates on the way to forming the corresponding binary phases.[7] Ternary compounds, however, offer a broader spectrum of tunable properties and are viable candidates for technical use, for example, $CuInSe_2$ is one of the most promising materials for thin-film technology in solar cells,[8] and conversion efficiencies of up to 18.8% have been achieved with $Cu(In,Ga)Se_2$ under laboratory conditions;[9] $AgInS_2$, $AgIn_5S_8$, and $AgGaS_2$ are of interest as materials for non-linear optical devices.[10] This prompted us to investigate the synthesis of ternary cluster compounds composed of elements of Group 11, 13, and 16. Similar to the synthetic approach for binary clusters outlined above, the reaction of mixtures of the metal halides with $E(SiMe_3)_2$ (E = Se, S) yielded cluster compounds such as $[Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]$,[11] $[Cu_{20}Ga_{10}Cl_4Se_{23}(PEt_2Ph)_{12}]$[12] and $[M_6M'_8Cl_4E_{13}(PPh_3)_6]$, (M = Cu, Ag; M′ = Ga, In; E = S, Se).[11,13] Interestingly, the stoichiometric composition and structure of the cluster molecules differ from the corresponding bulk material. We report herein the synthesis, structural characterization, and theoretical investigation of $[Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}(thf)_4][InCl_4(thf)]_2$ (**1**).

Compound **1** has been prepared by treating a suspension of silver benzoate, dppm and $InCl_3$ with $S(SiMe_3)_2$ in tetrahydrofuran at −50 °C. The reaction mixture was stirred at room temperature giving an orange solution. After several days, yellow crystals of **1** formed [Eq. (1)]

$$1.26\,PhCO_2Ag + 0.5\,dppm + InCl_3 + 1.8\,S(SiMe_3)_2 \xrightarrow{THF} [Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}(thf)_4][InCl_4(thf)]_2\ \mathbf{1} \quad (1)$$

The molecular structure of **1** has been determined by single-crystal X-ray structural analysis.[14] The assignment of the atom positions solely on the basis of the X-ray analysis is virtually impossible due to similar scattering factors of the atom pairs silver/indium and sulfur/chlorine. However, the final structure description was independently obtained by chemical intuition and quantum chemical calculations, and the chemical composition was confirmed by Fourier transfer mass spectrometry (FTMS) as detailed below.

The ionic compound **1** crystallizes in the space group $P\bar{1}$, with the cluster cation $[Ag_{26}In_{18}Cl_6(dppm)_{10}(thf)_4]^{2+}$ residing on a crystallographic inversion center (Figure 1a). The two anions $[InCl_4(thf)]^-$ are formed by trigonalbipyramidally coordinated indium atoms (In–Cl: 235.0(4)–241.9(4) pm; Cl-In-Cl: 96.41(12)–119.80(15)°; In–O: 245.7 pm). The indium atoms in the cation display mostly a distorted tetrahedral coordination environment: In4–In9 and symmetry equivalent atoms are coordinated by four sulfur atoms (S-In-S: 97.92(8)° to 116.88(7)°), while the remaining six indium atoms (In1–In3 and symmetry equivalent atoms) are each surrounded by three sulfur and one chlorine ligand (S-In-S: 103.63(8)° to 123.48(8)°; Cl-In-S: 93.94(11)° to 113.5(10)°) with In–S bond lengths ranging from 240.6(3) (In3-S17′) to 252.4(2) pm (In7-S2). Additional weak coordination of In3 and In3′ by a THF molecule (In-O: 272.5 pm) causes a distortion of the tetrahedral symmetry leading to a distorted trigonalbipyramidal coordination.

The 26 silver atoms display a larger variety of coordination geometries: distorted linear, trigonal, and tetrahedral. Eight of the silver atoms exhibit distorted tetrahedral coordination by either four sulfur atoms (Ag12, Ag12′, Ag13, Ag13′) or one phosphorus and three sulfur atoms (Ag9, Ag9′, Ag10, Ag10′). Twelve of the silver atoms have distorted trigonal environments (Ag1-Ag3, Ag6-Ag8 and symmetry equivalent atoms), which are bonded to two sulfur atoms and one phosphorus atom of the bidentate phosphane ligand (dppm). For these atoms, the values of the angular sum

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[**] This work was supported by the Deutsche Forschungsgemeinschaft (Research Center for Functional Nanostructures) and the Fond der Chemischen Industrie. dppm = bis(diphenylphosphanyl)methane.

 DOI: 10.1002/ange.200460052

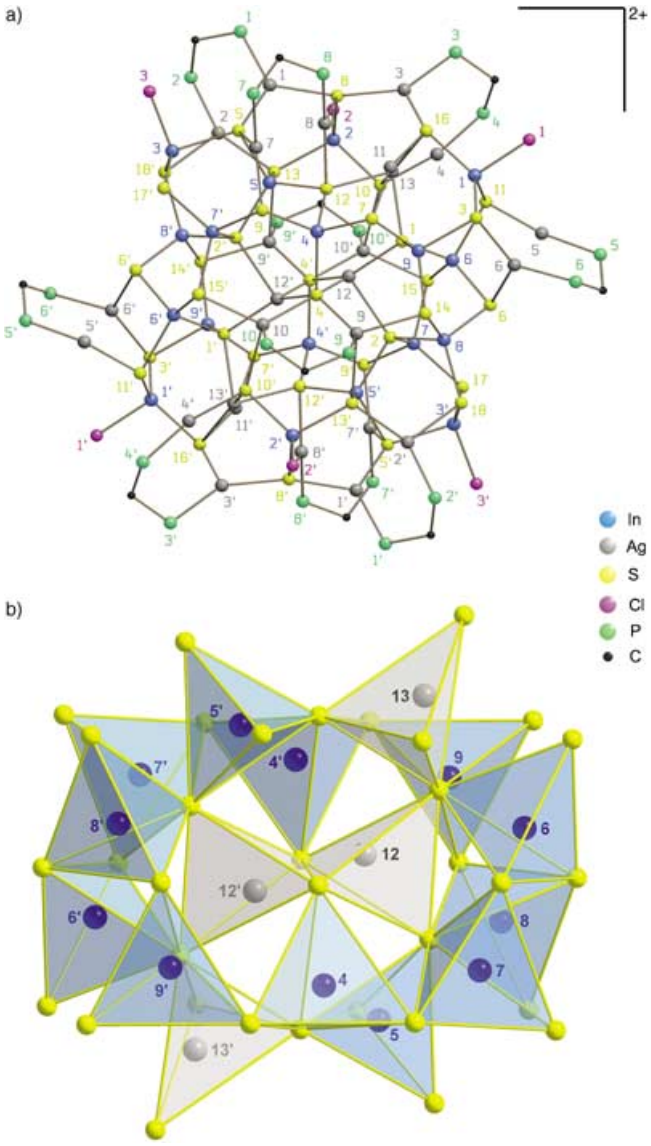

Figure 1. a) Molecular structure of the cluster cation $[Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}(thf)_4]^{2+}$ in **1** (phenyl rings of the phosphane (dppm) and coordinating THF molecules are omitted for clarity). Atoms are labeled with numbers only. b) Inner section of **1**, which displays similar indium and silver positions that are tetrahedrally coordinated by four sulfur atoms, nonbonding S–S separations range from 345.5 pm (S1-S2) to 479.2 pm (S10-S16).

range from 358.35° for Ag3 to 359.92° for Ag6. The remaining six silver atoms have a distorted linear coordination of either two sulfur atoms (Ag11, Ag11′) or one sulfur atom and one phosphorus atom (Ag4, Ag4′, Ag5, Ag5′) with angles: S-Ag-S 159.24(8)° and P-Ag-S 170.45(8), whereas Ag5 und Ag5′ are also weakly coordinated by a THF molecule (Ag–O: 261.8 pm). In contrast to the In–S bond lengths, the Ag–S separations cover a broader range from 238.3(2) (Ag4–S10) to 281.7(2) (Ag12–S4). The shortest separation of silver atoms in **1** is found to be 282.3 pm (Ag12-Ag12′), which is comparable with metal–metal distances in other silver sulfide complexes and clusters considered to be nonbonding.[5,6,15] Common values were also found for the Ag–P bond lengths, which range from 237.5(3) pm to 250.0(3) pm.

If we assume a maximum M–S distance of 281.7(2) pm for M = Ag and 256.5(2) pm for M = In, we find four different bridging modes for the S^{2-} ligands. S17 binds as μ_2-ligand and S4 is coordinated to five metal atoms. The atoms S1, S3, S6, S7, S9, S11, S14, S15, and S18 act as μ_3-bridging ligands, whereas S2, S5, S8, S10, S12, S13, and S16 are μ_4-bridging ligands.

Although the $\{Ag_4In_{12}S_{34}\}$ cluster core of **1** (Figure 1b) consists of corner-sharing tetrahedra of sulfur atoms with a central metal atom, their arrangement does not result in an ordered and layered structure, as in the related bulk material. $AgInS_2$ crystallizes at normal pressure and room temperature in the chalcopyrite structure, which is closely related to the cubic zincblende structure.[16] The sulfur atoms form a cubic network with ABC layering and the metal atoms occupy $^1/_2$ of the tetrahedral holes with the silver and indium atoms perfectly distributed over these sites.

A mass-spectrometric analysis was performed to determine charge state and stoichiometry of the two ions constituting **1**. We employed a modified electrospray/ionization source interfaced to a high-resolution Fourier transform ion cyclotron resonance (FTICR) mass spectrometer.[17] The source had been modified by introducing an ion funnel to improve ion sensitivity while keeping collisional fragmentation of ions to a minimum.

Figure 2 displays a mass spectrum of an electrosprayed yellow solution of **1** in 1,2-dichloroethane. The positive-ion mass spectrum is dominated by a single peak centered at $m/z = 5040.7$. Mass differences between silver and indium as well as between sulfur and chlorine are substantial and allow an unequivocal assignment of this peak to the doubly charged ion of $[Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}]^{2+}$. The THF solvent molecules present in the single crystal of **1** are lost upon redissolving/

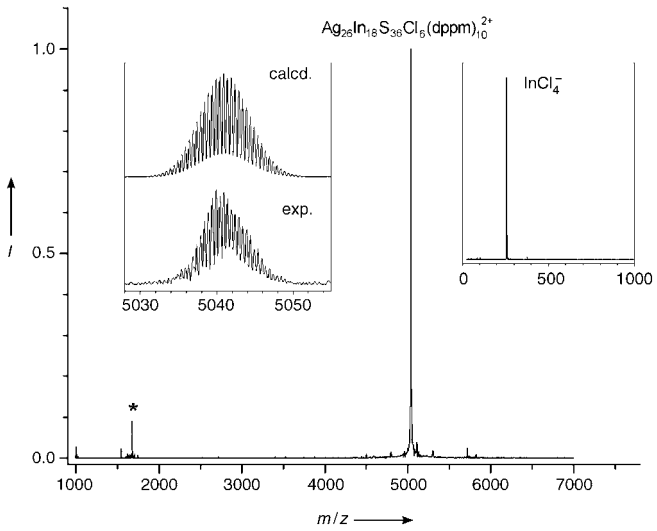

Figure 2. Electrospray mass spectra of **1** in $C_2H_4Cl_2$. Left inset: Comparison between experimentally observed high-resolution parent-cation peak around $m/z = 5040.7$ and isotopomer simulation. Right inset: Corresponding negative-ion mass spectrum. (Peak marked with an asterisk is due to an electronic artefact)

spraying, which indicates the very weak interaction of THF with the stable cluster ion. The highly resolved parent-ion peak is compared to the calculated isotope distribution in the left inset of Figure 2. Note that the charge state of the parent-ion peak is evidenced by the isotopomer splitting of 0.5 mass units. As a second inset in Figure 2 a negative-ion mass spectrum is shown that depicts a single peak at $m/z = 256.8$ that can be attributed to $InCl_4^-$. Again the isotopomer splitting is in excellent agreement with the simulated one (not shown).

Assignment of atoms: The XRD yields the location of atoms in space but it is almost impossible to assign atoms to crystallographic sites for two reasons: the silver and indium atoms have virtually identical X-ray structure factors and bond lengths for Ag–S and In–S are also very similar, around 250 pm.[18] Therefore molecular electronic-structure calculations have been performed to tackle this problem at the density functional theory (DFT) level.[19] The calculations were carried out for the model compound in which the phenyl groups were replaced by hydrogen atoms, thus leading to $[Ag_{26}In_{18}S_{36}Cl_6(H_2PCH_2PH_2)_{10}]^{2+}$ **2**, with 176 atoms. Since it is impossible to consider all possible distributions of silver and indium atoms on the sites in question, we made the following assumptions in the interpretation of the XRD and in the calculations, which have been tested in preliminary treatments:

1) terminal M–X is identified as In–Cl, since this guarantees local charge neutrality;[20]
2) the bidentate dppm binds to silver atoms;
3) the central metal pair must be silver atoms: Ag12,Ag12′ (replacement by indium atoms yields a computed interatomic distance of 385 pm instead of 283 pm);
4) the position Ag11 must be occupied by silver atoms as it is coordinated by only two sulfur atoms with short bond lengths.[21]

We are thus left with only six additional alternatives besides the one shown in Figure 1 a (in C_i symmetry): Ag13 can be swapped with In4 to In9 (Figure 1 b). All seven cases have been structurally optimized with the relatively small SV(P)[22] basis. The energies obtained are compared in Table 1. Next we checked results by the larger TZVP and TZVPP[22] bases, including structure optimization, which confirmed the energetic ordering for the most stable isomers.

Table 1: Computed relative DFT energies (kJ mol^{-1}) of isomers of **2**, with basis sets SV(P) and TZVPP.[a]

In	SV(P)	TZVPP
	0	0
6	45	15
5	94	95
9	177	
8	197	
4	257	
7	271	

[a] The column In indicates the indium center to be interchanged with Ag13 according to Figure 1 a.

The atom assignment given in Figure 1 a corresponds to the structure which is calculated to be the most stable one.

A comparison of calculated and experimental bond lengths is shown in Figure 3. Figure 3 a,b,c demonstrate a good convergence towards experiment on basis set expansion. TZVP and TZVPP differ mainly in the set of f functions for all atoms except hydrogen. The improvement obtained from TZVP to TZVPP is somewhat unexpected but can be rationalized as follows. Some atoms, especially sulfur and silver, have a "nonisotropic" surrounding of counterions leading to appreciable electric fields and an ensuing polarization of electron distributions, which require f functions for a proper description. All directly bonded In–S and In–Cl are calculated (TZVPP) with errors of less than 6 pm. Ag–S and Ag–P distances up to 270 pm show larger variations in experiment, which indicates less uniform bonding characteristics. This is in line with larger deviations between calculated and measured distances. There is only a single Ag–S distance with a deviation larger than 12 pm, which is at the cluster surface (Ag10–S10, deviation of 21 pm). Ag–X distances in the range from 270 to 360 pm include X = Ag, In, and S; the corresponding atoms are never directly bonded. Errors go up to 43 pm (Ag9–Ag10) for silver atoms connected by dppm. This deficiency is partly due to the replacement of phenyl groups with a hydrogen atom.[23]

The good agreement shown in Figure 3 c is exceptional as in neutral compounds Ag–P is typically calculated to be too large, by about 10–15 pm, mainly because DFT does not properly describe dispersion interactions that tend to shorten bond lengths. However, **2** is a dication and the positive charge of the cluster core enhances Ag–P bonding, thus decreasing the deficiency of DFT. Figure 3 d shows the errors in interatomic distances for the second best structure in energy, which is only 15 kJ mol^{-1} higher (TZVPP). In this case, In6 has been interchanged with Ag13 according to Figure 1 a. This causes a large rearrangement of the neighborhood of In6, Ag13, and Ag11, with deviations in bond lengths up to 220 pm (In6-S11, Figure 3). It is obvious that experiment and calculation cannot be reconciled. Even In–X bond lengths (up to 270 pm) show too large deviations. It is gratifying that energetic ordering and distance statistics lead to the same conclusion: only the assignment in Figure 1 a agrees with the calculations.

The combination of various investigative approaches employed in this work opens new perspectives for similar cases in which a single method alone would not allow one to reach conclusions with confidence.

Experimental Section

$[Ag_{26}In_{18}S_{36}Cl_6(dppm)_{10}(thf)_4][InCl_4(thf)]_2$ **1.** $PhCO_2Ag$ (silver benzoate; 65 mg, 0.284 mmol) and dppm (43 mg, 0.112 mmol) were added to a solution of $InCl_3$ (50 mg, 0.226 mmol) in THF (20 mL). After the addition of $S(SiMe_3)_2$ (0.085 mL, 0.407 mmol) at −50 °C the suspension was allowed to warm up to room temperature while stirring, the precipitate dissolved, and the solution became orange. The solution was left to stand for several days, which resulted in the formation of yellow single crystals suitable for X-ray diffraction analysis. Yield: 50 %.

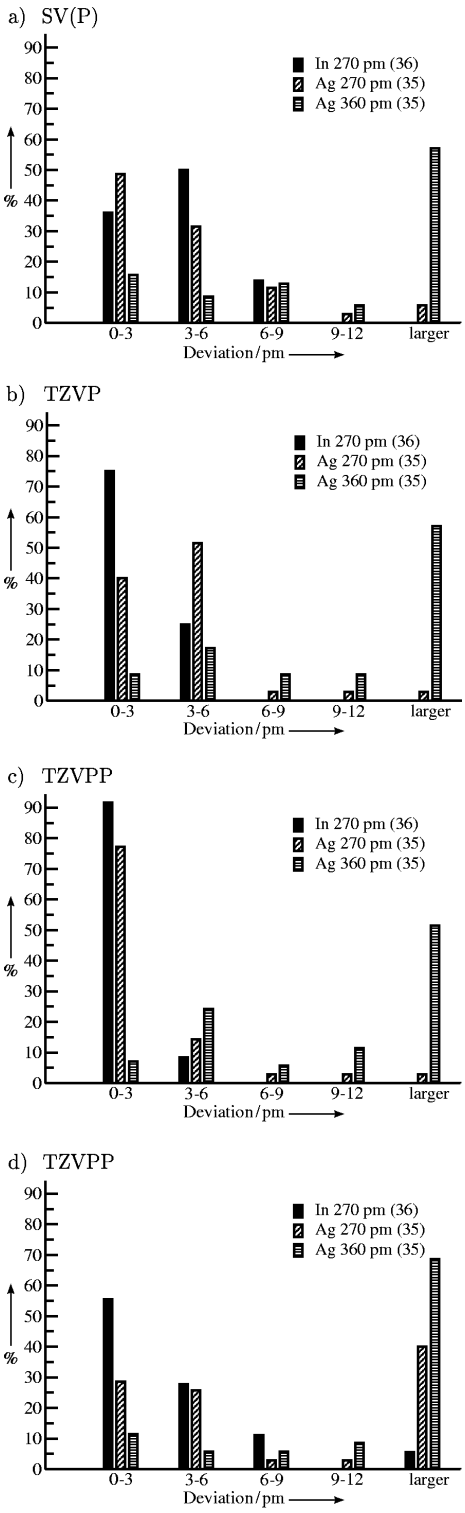

Figure 3. Histograms showing statistics of deviations (pm) between experimental and computed interatomic distances. The column height gives the percentage of cases with deviations indicated on the abscissa. Three classes are considered: In–X up to 270 pm, Ag–X up to 270 pm, and Ag–X between 271 and 360 pm, X = P, S, Cl, Ag, In. The number of cases in each class is indicated in parentheses as an inset. a), b), and c) refer to the most stable structure computed with SV(P), TZVP, and TZVPP respectively. d) refers to the second most stable structure (TZVPP) in which In6 was interchanged with Ag13, labeling of Figure 1a.

ESFTMS: Mass spectra were recorded on a Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonics, APEX II) equipped with an electrospray ion source modified by a home-built ion funnel for improved sensitivity.

Received: March 19, 2004 [Z460052]

Keywords: cluster compounds · density functional calculations · mass spectrometry · X-ray diffraction

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[14] X-ray analysis: STOE-IPDS II on a SCHNEIDER rotating anode ($Mo_{K\alpha}$-radiation; data collection and refinement (SHELX97, SHELXL93); numerical absorption correction. CCDC-233798 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). **1**: $C_{250}H_{220}Ag_{26}Cl_{14}In_{20}P_{20}S_{36}\cdot 18\,C_4H_8O$, triclinic, space group $P\bar{1}$ (Nr. 2), $Z=1$, lattice constants (190 K): $a=2002.2(4)$, $b=2361.6(5)$, $c=2624.3(5)$ pm, $\alpha=104.54(3)$, $\beta=104.78(3)$, $\gamma=111.62(3)°$, $V=10299\times10^6$ pm^3, $\mu(Mo_{K\alpha})=2.697$ mm^{-1}, $2\theta_{max}=55°$, 66322 reflections of which 33751 are unique (R(int) = 0.070) and 27994 with $I>2\sigma(I)$, 1832 parameters (Ag, In, Cl, S, P and C anisotrope, H atoms of the dppm ligands included in calculated positions. O and C of THF isotrope). Residual electron density 2.4 e Å^{-3}, $R1(I>2\sigma(I))=0.0480$; $wR2$ (all data) = 0.1847.

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[21] By interchanging Ag11 with In atoms from various other positions, energies increase by more than 250 kJ mol^{-1}.
[22] The basis and the auxiliary basis sets were a SV(P) (split valence with a set of polarization functions for each atom with the exception of H), a TZVP (triple-valence basis with a set of polarization functions), and a TZVPP, taken from the standard TURBOMOLE basis set file. TZVPP includes for example, (2d1f) polarization functions for p-block elements. a) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571 – 2577; b) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829 – 5835; c) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119 – 124; d) ftp://ftp.chemie.uni-karlsruhe.de/pub/.
[23] We could not afford calculations that included either Ph or Me (instead of H) for dppm in connection with a TZVPP basis for the cluster core. However, putting Ph or Me on selected dppm reduced the Ag–Ag distance by about 20 pm, thus reducing deviations to the experiment by 50 %.

