Atom-Type Assignment in Molecules and Clusters by Perturbation Theory—A Complement to X-ray Structure Analysis

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Abstract: An approach to distinguish elements with similar atomic numbers in molecules and clusters is presented and applied to experimentally synthesized and structurally characterized mixed-metallic compounds. By first treating a homogenized reference system constructed from the original compound and applying first-order perturbation theory it is possible to find the most stable distribution of the atom types to the atomic sites in a very efficient way. This work is focused on the appropriate choice of homogenized reference systems and on applications treating experimentally synthesized compounds. With these examples is shown that the method is a helpful complement to X-ray crystal structure analysis.

Keywords: cluster compounds • density functional calculations • perturbation theory • X-ray diffraction

Introduction

X-ray structure analysis is one of the most powerful and most widely used tools for the determination of crystal structures. Distances between atoms can be determined very accurately and reliably with this method. Nevertheless, it is a major obstacle that elements of similar atomic numbers usually are hardly to distinguish solely from X-ray data. In many cases the correct assignment of atom types to atomic sites can be found by chemical experience and intuition. Matters become difficult, if the systems investigated show more complex structures, which is usually the case for atom clusters, in particular if they consist of (different types of) metal atoms. For these systems the assignment of metal types to atomic sites sometimes is possible by a combination of X-ray data, chemical experience, and quantum-chemical calculations.[1] Chemical experience is of high importance for this kind of treatment, as the number of possible distributions of atoms to sites, which increases exponentially with the number of atoms, has to be reduced to a manageable size for quantum-chemical calculations.

A desirable alternative might be a more systematic and more economic method, using as input only the atomic coordinates from X-ray structure analysis and, if available, the stoichiometry or at least the total number of nuclear and electronic charges of the system yielding a prediction for the (most probable) assignment of atom types to atomic sites. Indeed, a very efficient estimation for the relative stabilities of different distributions is provided by first-order perturbation theory, as described in a previous work.[2] In the first step, the heteroatomic system, A_nB_m, is "homogenized" yielding M_{n+m}, for which the electron density is calculated by quantum-chemical methods. In the second step, the "heteroatoms" are re-introduced as perturbations of the homogenized system, causing energy changes that depend on the position of the perturbations and allow us to predict the atomic sites favorable for an increase/decrease of nuclear charge (i.e., of the atomic number) leading to a proposal for the assignment of atom types A and B to the atomic sites. It is known that any perturbation theory can be expected to give reasonable results only if the perturbation is not too large; this means 1) that the difference in the nuclear charge of the elements of interest must be small and 2) that the homogenized reference system, that is, the type of M, has to be chosen with care, as the real system is described as a perturbation of this system. After briefly explaining the theory we focus on the choice of suitable reference systems and investigate applicability and limits of the method. We apply the method to selected systems taken from literature; all systems selected consist (among others) of two types of elements that are close together in the periodic table, thus causing problems in assigning atom types to atom positions solely from X-ray data.

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Computational Methods

We consider an arbitrary molecule $A_mB_nL_k$. The elements A and B are of similar atomic numbers, L_k denotes the rest of the system, that is, the sum of all atoms (not necessarily all of the same type) that are neither of type A nor of type B. To identify the positions of A and B we pursued the following route. First, the homogenized system $M_{m+n}L_k$ is treated. M might be chosen, for example, as M = A, or as M = B, but other possible (and better) choices are discussed below. For the reference system $M_{m+n}L_k$ energy and electron density are calculated, for example, by means of density functional theory (or any other quantum-chemical method suited for the system), by using the atomic coordinates of $A_mB_nL_k$ determined, for example, by X-ray structure analysis (this usually is not exactly a local minimum structure for the quantum-chemical method used, but it is sufficient for our goal, namely the determination of atom types). In the next step we re-introduce the heteroatoms as perturbations of the (unperturbed) reference system $M_{m+n}L_k$ and compare the first-order energy change for different distributions of the m (n) atoms of type A (B) to the $n+m$ possible sites.

We briefly repeat the derivation of the first-order energy change as described previously.[2] Starting from the "homogenized" system $M_{n+m}L_k$, replacement of a single atom of type M by one of type A at site $\mathbf{R}_i$ means adding the nuclear charge $\Delta Z = Z_M - Z_A$ at $\mathbf{R}_i$ and changing the total electron number by the same amount. In this case, the first-order energy change ΔE_i is given by the derivative of the total energy of $M_{n+m}L_k$ (E) with respect to the nuclear charge (Z) at the corresponding site $\mathbf{R}_i$ and with respect to the change in the number of electrons (e) [Eq. (1)].

$$\Delta E_i = \frac{\partial E}{\partial Z}\Big|_{\mathbf{R}_i}(Z_A - Z_M) + \frac{\partial E}{\partial e}(Z_A - Z_M) \tag{1}$$

The second term in Equation (1) does not depend on the specific position of the perturbation ($\mathbf{R}_i$) as (expressed in term of molecular orbitals), independent from the specific position of $\mathbf{R}_i$, always the same orbitals, LUMO/HOMO, of the reference system are filled/emptied when adding/removing (differential) electronic charges. This term cancels when comparing the first-order energy change (ΔE_i) for different atom positions to obtain relative stabilities and does not need to be discussed any more. The first term consists of contributions from core–electron attraction (E_{Ze}) and core–core repulsion (E_{ZZ}). Carrying out the derivative of these contributions at $\mathbf{R}_i$ with respect to Z leads to energy change for $M_{m+n-1}A_1L_k$ in the first-order [Eq. (2)].

$$\begin{aligned}\Delta E_i &= \left[\frac{\partial E_{Ze}}{\partial Z}\Big|_{\mathbf{R}_i} + \frac{\partial E_{ZZ}}{\partial Z}\Big|_{\mathbf{R}_i}\right](Z_A - Z_M) \\ &= \left[-\int \frac{\rho(\mathbf{r})}{|\mathbf{R}_i - \mathbf{r}|}\mathrm{d}^3 r + \sum_{k=1,k\neq i}^{m+n} \frac{Z_M}{|\mathbf{R}_i - \mathbf{R}_k|}\right](Z_A - Z_M) \\ &= V_i \cdot (Z_A - Z_M)\end{aligned} \tag{2}$$

In Equation (2) V_i is the electrostatic potential (for the homoatomic system $M_{m+n}L_k$) at $\mathbf{R}_i$, arising from the total electron density, $\rho(\mathbf{r})$, and all nuclear charges except of that located at $\mathbf{R}_i$.

For $A_mB_nL_k$, in which atoms of type A are to occupy sites $\mathbf{R}_i$ and those of type B sites $\mathbf{R}_j$ we get the sum of single contributions, as energy contributions from interactions of "perturbed" centers are of higher order. For the definition of relative stabilities it is convenient to normalize the first-order energy changes by substracting the mean value. We finally obtain the estimated relative energy [Eq. (3)].

$$\begin{aligned}E_{est} &= (Z_A - Z_M)\sum_{i=1}^{m} v_i + (Z_B - Z_M)\sum_{j=1}^{n} v_j \\ v_i &= V_i - \sum_{l}^{m+n} V_l\end{aligned} \tag{3}$$

The value for E_{est} can be computed with very low computational effort, as it only requires calculation of the electrostatic potential at $m+n$ atomic sites. Thus, for $Z_B > Z_A$, the most stable distribution of A and B in $A_mB_nL_k$ (the lowest value for E_{est}) is obtained, if the m positions with lowest v_i are occupied by atom type B and the other ones by type A. These formulae are valid for any choice of M, but of course the quality of the results depends on the choice of M. Close-lying choices for M are M = A or M = B, that is, the systems $A_{m+n}L_k$ or $B_{m+n}L_k$, but we may also think of using an "averaged" (pseudo) atom $\bar{E}$ with a nuclear charge $Z_{\bar{E}} = (mZ_A + nZ_B)/(n+m)$. $Z_{\bar{E}}$ usually is not an integer number, but this choice has the advantage that the system $\bar{E}_{m+n}L_k$ has the same total number of nuclear (and electronic) charges as the original system $A_mB_nL_k$. Of course, this choice is possible only if m and n, that is, the stoichiometry, or at least the total number of nuclear and electronic charges of the system are known.

Before investigating the accuracy of the method, in particular the influence of M, and applying it to selected examples, we summarize the technical details of quantum-chemical treatments. All calculations were done with the program system TURBOMOLE by using methods of density functional theory[3] with the Becke–Perdew-86 functional.[4,5] For the Coulomb part the resolution-of-the-identity approximation (RI-J)[6,7] was used. We accounted for scalar relativistic effects by effective core potentials (ECPs);[8] for Rb–Cd ECPs included the inner 28 electrons, for In–Te the inner 46 electrons. Basis sets were of triple-zeta valence quality (TZVP),[7,9] except for the Ag–In cluster[1] (see below), for which split valence bases (SVP)[7,9] were used. For this system, phenyl rings of the experimental structure were replaced by H atoms leading to $[Ag_{26}In_{18}S_{36}Cl_6(H_2PCH_2PH_2)_{10}]^{2+}$, as done previously.[1] Convergence of the SCF procedure and obtaining the (usually) most stable orbital occupation was realized by using the approach of fractional occupation numbers (FON).[10] SCF procedures (spin-unrestricted) always started from an occupation showing some unpaired electrons (typically four); the initial electron "temperature" was set to 300 K and gradually lowered until it reached 30 K leading to integer occupations of all shells.

Results and Discussion

Applicability and limits of the method: In a previous work[2] the first-order perturbational method was shown to give reliable estimations for bare mixed transition-metal clusters, but "real" chemical systems usually are less homogeneous, as for example, complexes or clusters in which the metal atoms are bridged and/or covered by different kinds of ligands.

To investigate the applicability of the method to more general chemical systems, we treated the simplified model compounds OC-A-B-Cl shown in Figure 1; A and B denote selected combinations of elements Rb–Te, as specified below. In all cases, topology and structure parameters were fixed to the values given in Figure 1. For these idealized systems (in fact, for most choices of A and B the systems are nonlinear) we investigated the energy change when exchanging A and B obtained with the first-order method with respect to the difference of single-point energies of original and A–B interchanged system. At first, we calculated the energy difference between the situation in which A occupies position 1 (B occupies 2) and the situation with interchanged atoms A and B [Eq. (4)], for A and B being neighboring elements in the periodic table ($Z_B = Z_A + 1$), as well as for the case $Z_B = Z_A + 2$.

$$E_{swap}(1{,}2) = E(\text{OC-A-B-Cl}) - E(\text{OC-B-A-Cl}) \tag{4}$$

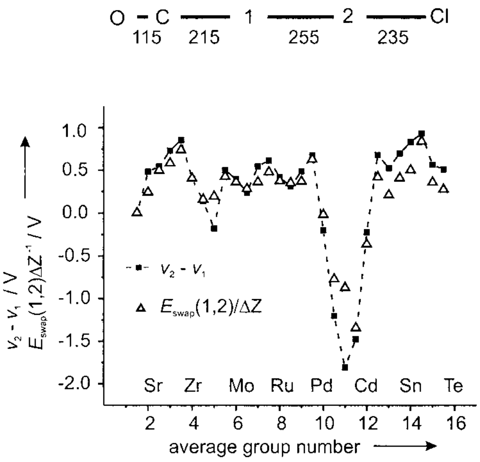

Figure 1. Geometry parameters for the model system OC-AB-Cl, single-point energy differences between A-B interchanged and original system, $E_{swap}(1,2)$ (divided by ΔZ), and difference of electrostatic potentials at positions 1 and 2, $v_2 - v_1$, for homogenized reference systems OC-MM-Cl, that is, first-order estimation for $E_{swap}(1,2)/\Delta Z$, Equations (3) and (4). Quantities are plotted versus the average group number of atoms A and B.

For clarity we note, that a negative value of $E_{swap}(1,2)$ indicates a preference for the situation "atom A (lower nuclear charge) at position 1 (left), atom B at position 2", whereas a positive value means, that the A–B-interchanged system is preferred. Figure 1 shows a plot of $E_{swap}(1,2)/\Delta Z$ versus the average group number of A and B (dividing by $\Delta Z = Z_B - Z_A$ ensures comparability of energy differences for the two cases $\Delta Z = 1, 2$). For the majority of element combinations, systems with the element left in the periodic table bonding to Cl ("B–A") are preferred versus the interchanged ones by 0.1 to 0.8 eV, but for Pd/Ag, Ag/Cd, Pd/Cd and Ag/In it is the other way around. We note in passing, that similar results are obtained for the previous period (K–Se), as well as for mixtures of both periods, for example, for Cu/Zn we obtain −1.25 eV, for Cu/Cd −1.33 eV, which are both close to the value for Ag/Cd of −1.34 eV.

Next we applied the first-order perturbation theory. We calculated the homogenized reference systems OC-M-M-Cl to compare the first-order expression $\Delta E = (v_2 - v_1)\Delta Z$ [Eq. (3)] and $E_{swap}(1,2)$ [Eq. (4)]. For M we used both "real" elements (nuclear charge $Z = 38, 39, \ldots, 51$) and "pseudo" elements with noninteger atomic charges ($Z = 37.5, 38.5, \ldots, 51.5$). In case of the latter, the orbital basis of the element to the right in the periodic table was used, for example, for $Z = 46.5$ (the pseudo element between Pd and Ag) the orbital basis for Ag was used. Values for $v_2 - v_1$, the first-order approximation for $E_{swap}(1,2)/\Delta Z$, are also shown in Figure 1. The connecting lines are mainly drawn to help the eye, but as one may vary the number of nuclear and electronic charges continuously, they are not completely artificial. Indeed, we observe a good correlation of the first-order estimated and explicitly correlated values, if we compare the value of $E_{swap}(1,2)/\Delta Z$ for a given heteroatomic system with the values for $v_2 - v_1$ obtained from the homoatomic system with the same number of electrons (i.e., the same average group number). Errors for $v_2 - v_1$ compared to $E_{swap}(1,2)/\Delta Z$ typically amount to 0.1–0.4 V, and reveal the effect of higher orders of perturbation theory describing redistribution of electrons due to the nonequivalence of the two nuclear charges. These errors are small enough to allow for the correct prediction of the assignment of A and B to sites 1 and 2 in all cases except for the combination Zr/Mo. The error for this system is in the usual range (0.4 V), but as estimated and calculated values are small in this case (0.2 V), we observe different signs for explicit calculation and first-order estimation in this case.

In previous work[4] we treated mixed metallic systems of neighboring elements Pt and Ir without using averaged nuclear charges; instead we averaged the values obtained from the pure Pt and pure Ir systems and this lead to very reasonable results. Also for the present case this appears to be a suitable procedure as well, at least as long as ΔZ is not too large. In the present example similar results are obtained for the two different averaging procedures, as one may see by connecting in Figure 1 one point with the next point but one and comparing the result to the point in-between. The two procedures do not always yield similar results, as the following example shows.

We consider the model compound H_2InSbH_2 shown in Figure 2. The C_s symmetric system shows a planar coordination for the In atom and a bent one for the Sb atom as the HOMO (a′) mainly represents the lone pair of Sb. Consequently, the In–Sb interchanged system is much less stable, $E_{swap}(1,2) \approx -4.0$ eV [for the sign see Eq. (4) and subsequent discussion]. The first-order perturbational method was applied by using as reference systems M = In, Sb, Sn. In case of Sn, two different occupations were considered; at

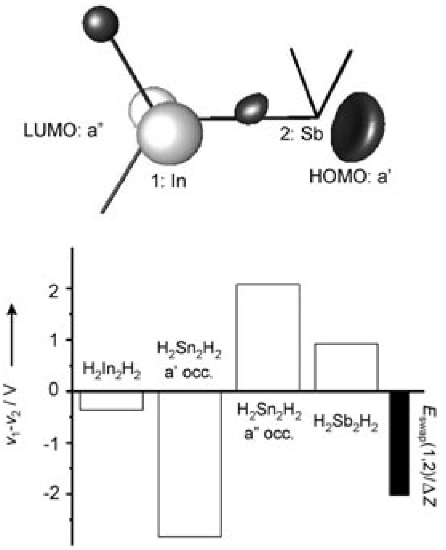

Figure 2. Molecular structure, and HOMO and LUMO orbitals for H_2InSbH_2. Electrostatic potentials v_i at positions 1 and 2 for different homogenized reference systems (see text) and single-point energy difference for interchanging In and Sb, $E_{swap}(1,2)$, divided by ΔZ (right hand side) to be compared with $v_2 - v_1$.

first the one identical to the original compound and secondly one in which the a″ (the LUMO of the original compound) instead of the a′ orbital was occupied; for all cases the results for $\nu_2-\nu_1$ are also shown in Figure 2. From the value for $E_{\mathrm{swap}}(1,2)$ one would expect (see above) $\nu_2-\nu_1 \approx E_{\mathrm{swap}}(1,2)/\Delta Z \approx -2$ V. A result in this range is obtained only for M = Sn and even for this choice only if the a′ orbital is occupied, but not if the a″ orbital is occupied instead. This is not too surprising, as for M = In both the HOMO and the LUMO of the original compound are not occupied, whereas for M = Sb both orbitals are occupied. In both cases the electronic situation of the homogenized system H_2MMH_2 is completely different from that in H_2InSbH_2, and values obtained for $\nu_1-\nu_2$ cannot be used to predict the preferred distribution of In and Sb to the two sites. Consequently, results are even worse for M = Sn, if the "wrong" orbital, that is, the LUMO of the original compound, is occupied. As a criterion to distinguish the "wrong" from the "correct" occupation, the total energy for each of them may be used. It is much lower for the latter (4.5 eV), and it is indeed the occupation found by the method of fractional occupation numbers (FON).[10]

From these results it is evident that the most appropriate reference system is constructed by averaging nuclear charges ($M=\bar{E}$, $Z_{\bar{E}}=(mZ_A+nZ_B)/(n+m)$) and determining the energetically best occupation of molecular orbitals by using the FON method.[10] Nevertheless, for less critical cases, qualitative results often are obtained correctly also when using M = A or M = B as reference, as in the previous study[2] and in the following example.

Complex $[Ru_3Rh(CO)_{13}]^-$,[11] Figure 3, is an experimentally synthesized comparably small system that contains two neighboring transition-metal-atom types. The authors proposed that Rh occupies position 1, because of the symmetry of the cluster core and due to arguments of local electron counting. The first-order perturbational method was applied by using $[Ru_4(CO)_{13}]^-$, $[Rh_4(CO)_{13}]^-$, and a system with averaged nuclear charge $[\bar{E}_4(CO)_{13}]^-$ with $Z_{\bar{E}}=44.25$ as reference systems; for Ē the orbital basis of Rh was used. The resulting quantities ν_i [Eq. (3)] for the four positions by using the three different reference systems are also shown in Figure 3. The assignment proposed previously[11] is confirmed independent of the reference system used. In all cases ν_1 is clearly negative, whereas ν_{2-4} exhibit positive values that are very similar for these three positions, as the system is of slightly disturbed C_{3v} symmetry. To determine the quality of the different reference systems, we compare the first-order estimation, $\nu_2-\nu_1$, and $E_{\mathrm{swap}}(1,2)/\Delta Z$ (= 1.75 V), that is, the energy difference (from single-point calculations) between the distribution proposed in reference [11] and a system in which Rh occupies position 2 instead of position 1. We observe increasing errors of the estimation with increasing difference in electron numbers (and electronic situation) between the original system and the homogenized reference case. Agreement is excellent for $M=\bar{E}$, $\nu_2-\nu_1\approx 1.8$ V, worse for M = Ru (Rh) differing by one (three) electrons from the reference; $\nu_2-\nu_1\approx 1.25$ (0.75 V) for these cases. Thus, for the following we only discuss results obtained by the reference system that has the same number of electrons as the original one.

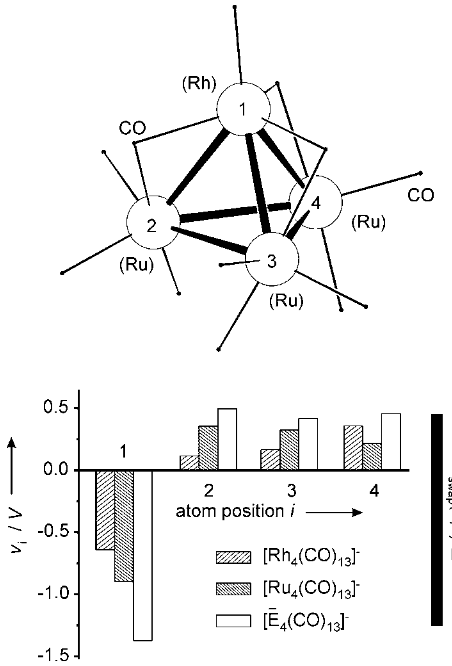

Figure 3. Molecular structure of $[Ru_3Rh(CO)]^-$ (distances in ring 2–3–4: 286–289 pm, remaining edges: 273–276 pm) and electrostatic potentials ν_i at positions 1–4 for different homogenized reference systems (see text). Ē denotes a nucleus carrying 44.25 elementary charges, the weighted average of Ru and Rh. At the right hand side, the difference of single-point energies for interchanging assignment for positions 1 and 2, $E_{\mathrm{swap}}(1,2)$, divided by ΔZ is plotted to be compared with $\nu_2-\nu_1$.

Application to a large system: For the cluster shown in Figure 4, $[Ag_{26}In_{18}S_{36}Cl_6(H_2PCH_2PH_2)_{10}]^{2+}$, the assignment of Ag and In to atomic sites was not possible solely on the basis of X-ray data.[1] In fact, the assignment proposed by the authors was achieved by a combination of X-ray data, quantum-chemical calculations, and chemical intuition or experience. First of all, the number of In/Ag atoms had been determined from the total mass of the cluster (under the assumption that the types and numbers of nonmetal atoms were correct). This means, one has to find the correct distribution among 497420 possibilities to distribute 13 Ag atoms and 9 In atoms to 22 sites (the other 22 position are determined by the C_i symmetry of the cluster). In reference [1] this problem was solved by reducing the number of possibilities dramatically by using arguments from chemical experience and many test calculations, finally leading to eight possible candidates. In a computationally demanding study, structure parameters were optimized for these isomers, for the two of lowest energy a comparison of calculated and measured distances finally lead to the proposed assignment.

We applied the first-order approach using $[\bar{E}_{44}S_{36}Cl_6(H_2PCH_2PH_2)_{10}]^{2+}$ ($Z_{\bar{E}}=47.818$) as the homogenized reference system. For Ē the orbital basis of Cd was

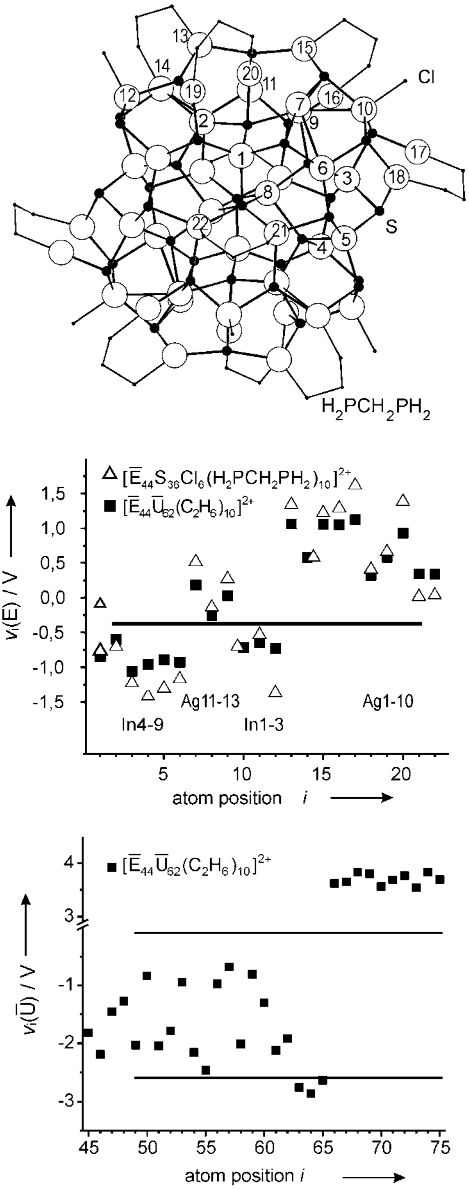

Figure 4. Molecular structure of $[Ag_{26}In_{18}S_{36}Cl_6(H_2PCH_2PH_2)_{10}]^{2+}$ (upper part). Middle part: Electrostatic potentials v_i at the 22 symmetry non-redundant metal atom sites using $[\bar{E}_{44}S_{36}Cl_6(H_2PCH_2PH_2)_{10}]^{2+}$ and $[\bar{E}_{44}\bar{U}_{42}(H_2\bar{U}CH_2\bar{U}H_2)_{10}]^{2+}$ as reference systems. Ē denotes a nucleus with the weighted average of nuclear charges of In and Ag (47.818 elementary charges), Ū analogously one with that of P, S, and Cl (15.774 elementary charges). The labeling "In4–9" and so forth is that of reference [1]. Lower part: Electrostatic potentials v_i at the 31 symmetry non-redundant P/S/Cl sites as obtained for $[\bar{E}_{44}\bar{U}_{42}(H_2\bar{U}CH_2\bar{U}H_2)_{10}]^{2+}$.

used, as nuclear charges of Ē and Cd are most similar ($Z_{Cd} = 48$). Moreover, we employed a second reference system. As not only Ag and In are of similar atomic numbers, but also P, S, and Cl, we used as reference $[\bar{E}_{44}\bar{U}_{42}(H_2\bar{U}CH_2\bar{U}H_2)_{10}]^{2+}$ ($Z_{\bar{U}} = 15.774$). In the middle part of Figure 4, the values for v_i at the 22 symmetry-distinct Ag/In positions are shown for both reference systems; in addition, in the lower part of the figure the values for v_i at the 31 symmetry distinct P/S/Cl positions are presented for the second reference system. For both reference systems the assignment due to the first-order estimation, done with comparably small computational effort (less than 1 % of that in reference [1]), and, in particular for the second reference system, without any assumptions from chemical intuition, is in line with that proposed in reference [1]. If In is assigned to the nine positions with lowest v_i (and to the symmetry images of these positions) and Ag to the remaining ones, one obtains the same assignment for In/Ag as in reference [1]. This is also true for the assignment of P/S/Cl. If we occupy the three positions with lowest v_i (and the three symmetry images) with Cl atoms, the next (2×)18 sites with S, and the remaining ones with P, we indeed get the assignment postulated in reference [1]. Let us discuss some details concerning the values of v_i. For position 8 (middle part of Figure 4), we observe a slightly negative value; despite this fact we assigned Ag to this position, as all available In atoms (their number is fixed due to the mass of the cluster) were already distributed to sites showing lower v_i. This assignment strictly speaking is not correct in the sense of Equation (3). Probably the averaging of nuclear charges lead to an electron density yielding slightly overestimated v_i for some of the sites binding to phosphine ligands (13–21), which lifted the average value of V leading to a slight negative shift of v_i for the other positions. Moreover the energetic sequence of less stable interchanged systems derived from the differences of the v_i in the present approach is different from that in reference [1]. This is not too surprising, as the present treatment neglects not only electronic relaxation, but also effects of geometry relaxation, which both were included in the previous treatment.[1] As noted above, also the occupation of the P/S/Cl sites is correctly predicted by the first-order approach. One observes a large difference of v_i for the P sites on the one hand and for the S/Cl sites on the other. Moreover, whereas the values for the P sites are nearly identical, those for the S/Cl sites show a large scatter, which may be rationalized as follows. The P sites always have the same environment, they are bound to two H, one C, and one Ē atom, but a great variety is observed for the environments of the S sites, which may in a simplified way be characterized by the number of neighboring atoms. This is two for sites 51 and 55, four for 53 and 59, and three for the others. We observe a (weak) correlation between connectivity of S sites and values for v_i at these sites. Positions with two neighbors show low v_i (within the S sites), such with four neighbors high v_i, those with three neighbors usually show values somewhere inbetween, but also values in the range of the two- as well as in that of the fourfold coordinated S sites. The three (Cl) sites with lowest v_i, 63–65, have only one neighboring atom. At this point we meet chemical experience and intuition: in the present work Cl was assigned to these three positions as they show lowest v_i; in the previous treatment the same was done because of the single coordination of these sites.

Conclusion

We have presented an economic method to propose the assignment of atoms of similar atomic numbers to atomic sites in experimentally synthesized and structurally characterized molecules. As this method is based on perturbation theory, the results are most reliable if the atomic numbers of the respective atoms are not too different (this makes the method an ideal complement to X-ray structure analysis) and if the reference system is constructed by averaging nuclear charges at atom positions of interest, so that the total number of electrons and nuclear charges is the same as in the original compound. Following this route reasonable proposals for the distribution of atom types to atomic sites are possible with comparatively low computational effort.

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