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of the metal d orbitals. Thus, the accidentally degenerate HOMOs in this species contain two unpaired electrons that can be removed without rupturing the complex.

Cyclic voltammetric and EPR studies of **1** clearly indicate the presence of two one-electron reduction processes that strictly are quasi-reversible. Quasi-reversibility most often is an indication of slow electron transfer, which can be caused by geometrical or conformational changes in the molecule before, during, or after electron transfer.[52] Fenske-Hall calculations were performed on the anions of **1**. The reduction of **1** to its monoanion results in an electron being added to the LUMO, which is primarily metal-based (84%) with some Cp (14%) and C_2S_4 (2%) character. This metal-based orbital is not strongly antibonding and could accommodate an extra electron.

Calculations on the dianion indicate that a geometrical arrangement may be occurring in the molecule. We are continuing to investigate the intriguing reduction chemistry of the C_2S_4-bridged titanium dimer with hope of isolating these anions for structural investigation.

Acknowledgment. This research was generously supported by the National Science Foundation. We are particularly pleased to acknowledge Professor Dick Fenske for several helpful discussions and Dr. Gary Wesenberg for his assistance with the VAX 8650 computer system. H.A.H. is especially grateful to Dr. Kimberly A. Schugart for her assistance in the initial use of the Fenske-Hall MO program. D.R.K. thanks Professor Frank Weinhold for fruitful discussions related to the natural bond orbital (NBO) procedure developed by him and his co-workers.

Registry No. 1, 109242-42-4; **2**, 78452-81-0; $C_2O_4^{2-}$, 338-70-5; $C_2S_4^{2-}$, 78906-82-8; $[(Cp_2Ti)_2(\mu\text{-}C_2Su)]^{2+}$, 136236-70-9; $[(Cp_2Ti)_2(\mu\text{-}C_2O_4)]^{2+}$, 136236-69-6.

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Elemental Structures of the Heavy Main Group Atoms and the Second Moment Scaling Hypothesis

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Abstract: We show that Hückel calculations, used in conjunction with second moment scaling, correctly predict the structure types in a given row of the main group atoms. We accurately predict the structure types of Cu, Zn, Ga, Ge, As, Se, Ag, Cd, In, Sn, Sb, Te, Tl, Pb, Bi, and Po. Only one significant error is observed in this series.

Introduction

The structure of the elements is a fundamentally important issue in solid-state chemistry and physics.[1] For this reason theoretical methods have been developed which quite accurately account for these structures. One particular theoretical triumph has been the use of pseudopotential methods.[2] Pseudopotential calculations are able to accurately predict the elemental phase transitions caused by increasing pressure. It has been found that pressure often induces elements to adopt the structure type of a heavier element which belongs to the same column of the periodic table. For example Si under pressure first adopts the white-Sn (w-Sn) structure and later under very high pressure adopts the fcc structure of Pb.[3] Therefore, pseudopotential calculations have generally been used in comparing elemental structure types which are found in a given column in the periodic table.

Much less work has been carried out in comparing the structure types found in a given row of the periodic table. One more recent exception to this is to be found in the work of Pettifor.[4] Pettifor has shown the tightbinding (or Hückel) method can resolve the structural preferences of the transition-metal series (from group 3 to group 10). One especial advantage of these Hückel calculations is that due to their calculational simplicity it is possible to determine the geometric origins of Hückel energetic effects.[5] However, the Hückel method has not been very widely applied to main group elemental structures. The principal difficulty is associated with coordination number (i.e., the number of near neighbors an atom possesses). The three main transition metal structure types (fcc, hcp, and bcc) all have uniformly high coordination numbers. This changes upon leaving the transition-metal block. For instance, while Cu and Zn are 12 coordinate, their neighbors Ga, Ge, and As are respectively 7, 4, and 3 coordinate. The problem is that in Hückel theory, coordination number is approximately proportional to Hückel band width, and band width directly affects Hückel energies. The results of a direct comparison of the Hückel energies of the Cu, Zn, Ga, Ge, and As structures would therefore be senseless.

Scaling Hypothesis

These difficulties in Hückel theory can be directly traced to the absence of repulsive terms in the Hückel Hamiltonian. As there are no repulsive energy terms, there are no forces in Hückel theory which keep the atoms away from one another. Unfortunately accurate calculation of repulsive interactions between the electrons in a system requires the use of multideterminental wave functions.[6] It is therefore difficult to devise a method which accurately calculates the effects of these inter-

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Table I. Main Group Elemental Structures and Their Rings[1]

element	Cu	Zn	Ga	Ge	As	Se
structure types	fcc	hcp	Ga	diamond	As	Se
geometric features	tetrahedra	tetrahedra	triangles	hexagons	hexagons, squares	chains, squares
element	Ag	Cd	In	Sn	Sb	Te
structure type	fcc	hcp	In	w-Sn, diamond	As	Se
geometric features	tetrahedra	tetrahedra	tetrahedra	hexagons, squares, hexagons	hexagons, squares	chains, squares
element			Tl	Pb	Bi	Po
structure type			hcp	fcc	As	simple cubic
geometric features			tetrahedra	tetrahedra	hexagons, squares	squares

actions and at the same time maintains the simple form of Hückel theory.

A number of years ago a suggestion was made in work by Podloucky and Pettifor and independently in work of Burdett and myself.[7] We suggested that one should keep the variance at a fixed value. Variance follows the formula

$$\text{variance} = \frac{1}{n}\sum_{i=1}^{n}(E_i - E_{\text{avg}})^2$$

where n is the number of molecular orbitals, E_i are the individual molecular orbital energies, and E_{avg} is the average of all the E_i's. By keeping the variance constant one keeps the atoms at an average fixed distance apart from one another. We therefore avoid the fictitious correlation which Hückel theory places between bond length and total energy. We have recently shown that this hypothesis can be used to rationalize the structure of both intermetallic and alloy structures.[7] In this paper we show that this same method can be applied to the main group structures of the heavier elements. In practice we use our scaling hypothesis in the following manner. We compare the total electronic energies of several different structure types. We fix the second moment, μ_2 ($\mu_2 = \sum_{i=1}^{n} E_i^2$), to a single fixed value. This is equivalent to fixing the variance to a fixed value (see formula above) as the average molecular orbital energy, E_{avg}, is a constant in Hückel theory for a given atom type. We generally choose a second moment which corresponds to that calculated for one specific compound. We then scale the overall density, leaving all bond angles unchanged, so that all the structure types under consideration have the same second moment.

Other than this change due to the scaling hypothesis, we use standard Hückel theory in our band calculations. These methods are well reviewed.[8] We use the Wolfsberg–Helmholz approximation[9] for our off-diagonal elements of the Hamiltonian, H_{ij}, $H_{ij} = KS_{ij}(H_{ii} + H_{jj})$ where S_{ij} are the overlap integrals, H_{ii} and H_{jj} are the Coulombic integrals for the ith and jth atomic orbitals, and K is a proportionality constant. We use Hückel theory and not extended Hückel theory.[10] In other words we solve the equation $H\psi = E\psi$ and not $H\psi = ES\psi$. Finally we use Slater-type orbitals and in general a set of atomic parameters which were originally developed by Hoffmann and his co-workers.[10] Only in the case of contracted orbitals do we have to alter the extended Hückel parameters for our Hückel calculations.

Elemental Structures

In Table I we list the elemental structures for the last three rows of groups 11 through 16. We include groups 11 and 12 for three reasons. First, this corresponds to the electron counting scheme of the Hume–Rothery rules;[11] second, Pettifor's transition-metal calculations were unsuccessful in treating the group 11 structure types;[4] third, this corresponds to the elements used

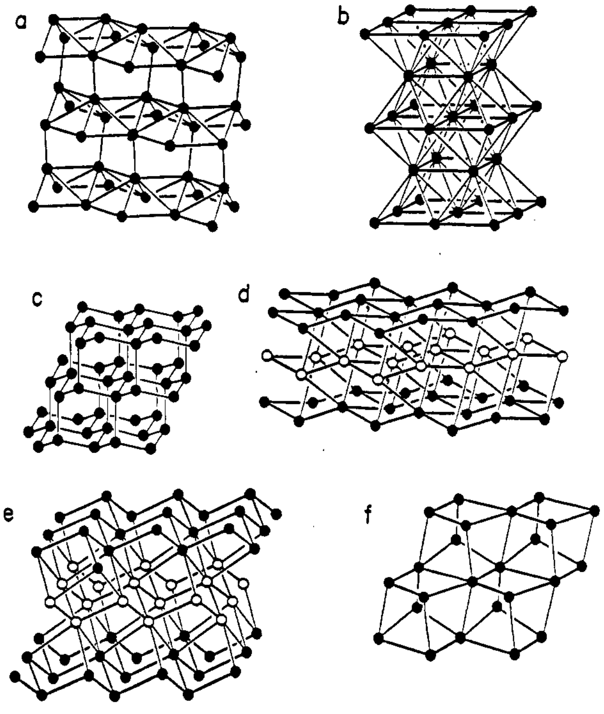

Figure 1. The crystal structure of (a) Ga, (b) In, (c) Ge and g-Sn, (d) w-Sn, (e) Bi (As structure type), and (f) Te. Thick lines indicate shorter bonds; thin lines longer bonds. In (d) and (e) open and filled circles have been used to emphasize the hexagonal chair sheets present in these structures. In the In structure short bonds are 3.25 Å while the long bonds are 3.38 Å. Note that both (e) and (f) are distortions of the simple cubic structure.

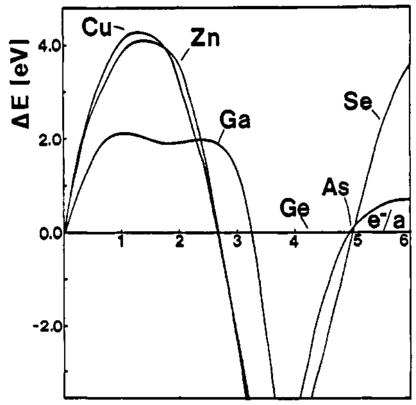

Figure 2. The difference in energy between the Cu, Zn, Ga, Ge, As, and Se structures as a function of electron count. The difference in binding energy between a given structure and the Ge structure is plotted. Thus Ga is the most stable structure from 2.5 to 3.25 e$^-$/atom. The energy plotted is in eV/atom. For the band calculations, k-point (kp) meshes based on the primitive cubic, hexagonal, and orthorhombic cells were used. For the cubic cells 165 kp were used, for hexagonal cells 252 kp (Zn, Se) and 90 kp (As) were used, and for orthorhombic cells 27 kp (Ga) were used.

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(7) Early applications of the second moment scaling hypothesis (a) for AB (main group and transition metal) phases are given by Pettifor and Podloucky (Pettifor, D. G.; Podloucky, R. *Phys. Rev. Lett.* **1984**, *53*, 1080) and (b) for the Peierls distortion by Burdett and Lee (Burdett, J. K.; Lee, S. *J. Am. Chem. Soc.* **1985**, *107*, 3063). More recent work includes: (c) Cressoni, J. C.; Pettifor, D. G. *J. Phys. Cond. Matter*, submitted for publication. (d) Lee, S. *J. Am. Chem. Soc.* **1991**, *113*, 101. (e) Recent work for alloy structures: Hoistad, L.; Lee, S. *J. Am. Chem. Soc.*, in press.

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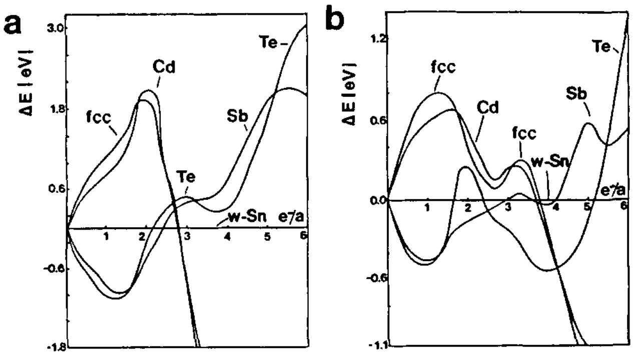

Figure 3. The difference in energy between the fcc, Cd, In, w-Sn, Sb, and Te structures as a function of electron count. Differences were plotted between a given structure and that of w-Sn. To the resolution of this figure, there is nearly no difference between the fcc and In curves. Therefore, only the fcc curve is shown. See Figure 2 for figure conventions and k-point meshes. In addition, for the tetragonal In and w-Sn structures a primitive cell, 126 kp mesh was used. In (a) $H_{ii}(4s) = 16.0$ eV, $\zeta(4s) = 2.16$; $H_{ii}(4p) = -9.0$ eV, $\zeta(4p) = 1.85$. In (b) 4s parameters were changed. $H_{ii}(4s) = -23.0$ eV, $\zeta(4s) = 3.00$. The volumes were adjusted to give the same second moment as Ge.

in our previous work.[7] It may be seen in Table I that for the 16 elements, 9 different structure types are normally adopted.[1] In this paper, for reasons that will be made clear, we will not discuss the Au and Hg structures. In Figure 1 we illustrate the Ga, As, Se, In, and w-Sn structure types. From the perspective of the moments method[5] we consider the smallest size rings of bonded atoms present in these structures. These are displayed in Table I. In the case of triangles we have divided the structures into two categories: those which contain tetrahedra and those which do not. The general rule is that the more triangles a system contains, the greater is the tail in the DOS.[5c,12] The energetic effects of this have previously been discussed. For us, all we need recall is that tetrahedral systems are stable at a lower electron count than systems with fewer triangles.

Calculations on the Third Row

It may be seen that in the third row, the structure types proceed in an order which corresponds to that predicted by a moment method ring analysis. In Figure 2 we show the results of a Hückel band calculation on these six structure types. In this calculation, we have adjusted the density of all six structures so that their calculated DOS have a second moment equal to that of experimentally determined Ge.[1] Ge literature parameters[10h] were used in the band calculations for all six structure types. It may be seen that agreement between Figure 2 and Table I is excellent. Only in the case of Ge vs As is there a perceptible error. It would appear that the As curve is energetically lower than it ought to be.

Heavier Main Group Elements

It is well-known that the fourth and fifth row main group atoms exhibit different chemical behavior than the lighter elements. Generally, the elements behave as if they have one pair less of valence electrons. It has been demonstrated that this inert pair effect is due to relativistic contraction of the s orbital.[13] The 5s and 6s orbitals have shrunk in size and therefore exert less stereochemical control. For example, the bond angles in Bi and Po are respectively nearly 90° and exactly 90°.[1] These are the bond angles one would expect in an element whose only valence electrons are p electrons. We therefore study the six structure types found in the fourth row: Ag(fcc), Cd, In w-Sn, Sb, and Te. In Figure 3a, we compare these six structure types using the sample parameters as were used in Figure 2. It may be seen that agreement between Figure 3a and Table I is not good. The In structure, which energetically is almost identical with the fcc structure, is not favored at 3 e⁻/atom by 1.3 eV/atom. Similarly, w-Sn is not the preferred structure at 4 e⁻/atom by 0.8 eV/atom. These are sizable errors. In Figure 3b, we use our chemical understanding of the inert pair effect and artificially contract the 4s orbital. This contraction corresponds to what we believe takes place in 5s orbitals. In Figure 3b, the 4s orbital H_{ii} (Coulombic value) has been lowered to −23.0 eV and the Slater-type orbital exponent was set so that $\zeta = 3.0$. It may be seen that several dramatic changes occur. The sequence of structures is now fcc, Cd, fcc, w-Sn, Sb, and finally Te. We note the fcc curve is always within 0.02 eV/atom of the curve for the In structure type. Therefore, to the level of accuracy of our calculations we cannot distinguish between the fcc and In structure types. We therefore see that the observed sequence of structure types (fcc, Cd, In, w-Sn, Sb, Te) is quite accurately portrayed in our calculation. In Figure 4 we compare the In, g-Sn (grey tin or diamond), Sb, and Te structures. Here, we see that there is one error. The Sb structure is 0.4 eV/atom less stable than the g-Sn structure. This error may be attributed to two factors. First, by contracting the s orbital, the valence band becomes increasingly of p only character. In the limit of complete s-orbital contraction, the half-filled band is found at 5 e⁻/atom. Hence, the zone of stability of the diamond structure shifts to the right. Second, there appears to be a systematic error in our calculation of the energy differences between the diamond and As structure types. This may be seen in both Figures 2 and 4. Finally, we note two points of interest. Grey tin is found to be of lower energy than white tin by 1.7 eV/atom. Although grey tin is more stable (at 0 K) than white tin,[14] this difference in energy is overestimated. This shows that the Hückel method does not produce reliable results when comparing structure types which belong to the same column of the periodic table. In other words, Hückel theory works best in rationalizing structure features which depend on the number of valence electrons. Second, it should be noted that the hcp and fcc curves in Figure 3b are bimodal, whereas the hcp and fcc curves in Figure 3a have only one mode. The second and smaller mode occurs at an electron count where the hcp and fcc structures would be more stable were the s orbitals to be entirely contracted.

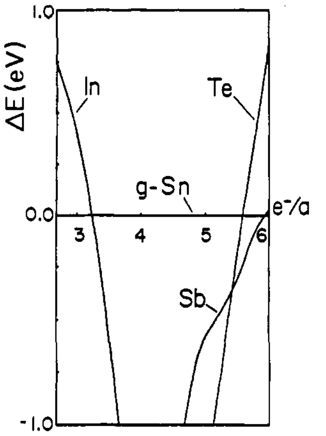

Figure 4. The difference in energy between the In, g-Sn, Sb, and Te structure as a function of electron count. The same parameters as those of Figure 3b were used. Differences in energy between a given structure and g-Sn are plotted. See the captions of Figure 2 for calculational details and figure conventions.

We now turn to the bottom row of the main group atoms. We contract the s orbital even further and compare the energies of the hcp, fcc, Bi, and Po structures in Figure 5. The energetic pattern corresponds to results we have previously published in which the s orbital is entirely excluded.[5c] As we noted before, the agreement between experiment and theory is excellent. We must however exclude Au and Hg from our calculation as it is not clear what electrons should be used in our model.

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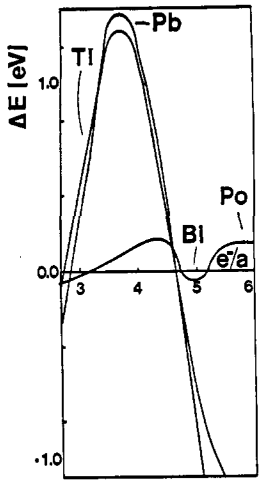

Figure 5. The difference in energy between the Tl, Pb, bi, and Po structures as a function of electron count. Parameters used were $H_{ii}(4s) = -30.0$ eV, $\zeta(4s) = 3.5$; $H_{ii}(4p) = -9.0$ eV, $\zeta(4p) = 1.85$. Differences in energy between a given structure and the Bi structure are plotted. See Figures 2 and 3 for figure conventions and calculational details.

One general trend is clear. In the case of two or three types of electrons (s, p, or d) the energetically lowest band exerts relatively little stereochemical control. For example, were Pettifor to have contracted the d orbitals in his calculation on the later transition elements, he would have found that Cu should indeed be in the fcc structure type as is known to be experimentally correct. Similarly, we have contracted the s orbitals more than standard literature values would lead us to believe in the case of the heavier main group atoms.[13]

This difference can be traced to the use of Hückel and not extended Hückel theory. In the Hückel theory of extended solids the most bonding molecular orbital is calculated to be at an unrealistically low energy. As we wish to place the s band near the bottom of the p band we must therefore place the H_{ii} Coulombic value of the s orbitals at a rather low energy. This choice of a low energy for the H_{ii} value of the s orbital in turn has an effect on the overall size of the s orbital. This is so as we use the Wolfsberg–Helmholz approximation for the off-diagonal H_{ij} elements. In this approximation an increase in the magnitude of H_{ii} directly increases the value of H_{ij} (see preceding section). As we have used unrealistically low H_{ii} values to compensate for the deficiencies of Hückel theory, we must therefore rely on small overlap integrals, S_{ij}, so that the overall magnitude of the off-diagonal elements H_{ij} is correct. In order to have small S_{ij} values we use overly contracted Slater exponents, ζ, in describing our Slater-type orbitals.

In our work we have used an average set of atomic parameters to resolve the trends that occur within a given row of the periodic table. One drawback of this method is that we are unable to introduce element-specific features into our calculations. However, it has been previously shown that several element-specific distortions are found in structures such as Zn, Cd, Ga, and In. As such distortions do not greatly change the ring structures of the systems it is generally not possible for our generic elemental model to resolve these distortions. For example, we were unable to explain why In has distorted from the fcc structure.

Finally, it should be noted that the energetic results of a Hückel calculation are unable to explain the stability of the P_4 or As_4 tetrahedron. See ref 5 for a discussion of this problem.

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Theoretical Study on the Electronic Spectra of Model Compound II Complexes of Peroxidases

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Abstract: A quantum chemical study of the electronic structure and spectra of four compound II iron porphyrin complexes with varying axial ligands, Cl^- (Hemin), pyridine, imidazole, and imidazolate (model peroxidase), has been carried out using the INDO/S method. These calculations confirm the nature of the triplet ground state as one in which the two unpaired electrons occupy the Fe–O π^* orbitals that are primarily Fe(IV) $3d_{xz}$ and $3d_{yz}$. About 20% of the unpaired spin density is calculated to be on the oxygen atom, in agreement with the experimental estimate of about 25%. The calculated spectra show that charge-transfer (CT) transitions exist for all compound II complexes. The excitation energies for these CT transitions are estimated to be between the Q and B (Soret) bands and to have moderate oscillator strengths. Although a description of the CT excited state for each of the model systems is complex, an electron transition from the porphyrin π orbitals to the Fe–O π^* orbitals is a common component. For Hemin-II, an additional component of the CT transition wave function is an excitation from the Cl $3p_z$ orbital to the porphyrin $4e_g$ orbitals. For the pyridine and imidazole complexes, there is a mixing in the CT of an excitation from the porphyrin π to a ligand π^* orbital. For the complex with an imidazolate ligand, mixing of porphyrin $\pi \rightarrow \pi^*$ excitations was found. The fact that the model compound II complexes with both a neutral imidazole and a deprotonated imidazolate ligand have CT transitions between Q and B does not allow us to use spectral properties to predict the actual form of this intermediate in the reaction mechanism of protein.

Introduction

Iron–oxo compounds are proposed to participate in the biochemical cycles of several different kinds of heme enzymes to perform essential oxidations in various biochemical pathways.[1-5] For instance, cytochrome c peroxidase (CCP), horseradish per-

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