coordinate nickel(II) with oxygen donor atoms. Third, both I and II represent the planar, dianionic coordination of the triketonate ligand that we have observed to be exclusively the case for first-row transition-metal ions in our previous work.[2a,10,11] Fourth, there is ample literature precedence for type I complexation to form binuclear complexes[12] from mononuclear Schiff base chelates. Thus, although the structural details are not known with certainty, it is reasonable to assume that the three nickel(II) ions are in a linear array each with two bridging ketonic type oxygen atoms. In other words, there is a shared edge between adjacent pseudooctahedra in the complex.

The magnetic properties of $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$ are quite unexpected in view of the results obtained for the binuclear nickel(II) 1,3,5-triketonates. These complexes, which contain two nickel(II) pseudooctahedra sharing a common edge, exhibit antiferromagnetic exchange between the adjacent nickel ions with exchange constants, J, from about −10 to −30 cm^{-1}.

Acknowledgment. We wish to thank Dr. R. V. Thundathil for assistance with the low-temperature measurements. The financial assistance of the National Science Foundation through Grant CHE 80-10809 and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged.

Registry No. $Ni_3(TFDAA)_2(OH)_2(H_2O)_6$, 80502-89-2.

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Stabilities of Structures Related to the High-Pressure Form of GeP, Which May Be Derived from Rock Salt by Bond Breaking

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There are four different structures with a rock salt size cell which contain square-pyramidal coordination at each center and where the pseudo-fourfold rotors point in the same direction. One of these corresponds to the high-pressure form of the nine-electron compound GeP. We show how band structure calculations correctly predict this as the lowest energy structure and how the yellow form of TlI is by far the most stable arrangement among these structures for 10-electron compounds. The band structure energies of these systems can be successfully modeled by considering the energetics associated with variation of the apical–basal bond angle in five-coordinate square-pyramidal molecules. The chemical and electronic reasons behind this stability sequence may thus be simply understood.

Introduction

We have recently described a simple technique by which we may make progress in understanding why solid-state materials adopt the structures they do.[2] First, we enumerate the number of symmetry inequivalent ways we may distort a symmetrical parent structure to a daughter. Second, we calculate, via band structure computations, the energies of these alternatives and compare them with observed structure types. Last, we look for chemical reasons behind these energetics and hence qualitative arguments as to structural stability and preferences. One series which has succumbed to our treatment is the generation of structures related to those of arsenic or black phosphorus from that of rock salt (Figure 1) by scission of three mutually orthogonal linkages at each atomic site of the latter.[3] It turns out that there are 36 different ways of producing universal trigonal-pyramidal coordination in a cell of this size. Only a few of these are actually found in reality, and the reasons behind the adoption of the stable possibilities are fascinating ones.[4]

Electronically the distortion of the eight-electron rock salt structure to that of arsenic (or its derivative structure exhibited by GeTe) or black phosphorus (or its derivative structure exhibited by GeS) is understandable along lines which are established for viewing molecular geometries.[5] The extra two electrons per formula unit (for 10-electron GeS, GeTe) would have to occupy high-energy orbitals at the rock salt geometry. On distortion, as three linkages around each center are broken, these orbitals drop dramatically in energy to become lone-pair orbitals in the new structure. In this paper we are interested in the somewhat smaller group of structures which may be derived from rock salt by breaking a single linkage around each center and are typified by the high-pressure modification of the nine-electron species GeP[6] (Figure 2).

Structural Enumeration

In previous papers[3,7] using our theoretical philosophy we have made use of powerful combinatorial techniques, on the basis of Pôlya's theorem,[8] to derive the number of structurally related arrangements. For the present system however it is very easy just to write down the seven possibilities based on a rock salt-sized cell and square-pyramidal coordination at each site. These are shown in Figure 3 and divide naturally

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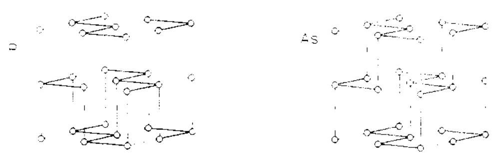

Figure 1. Generation of the structures of arsenic and black phosphorus by scission of three mutually orthogonal linkages around each center of rock salt.

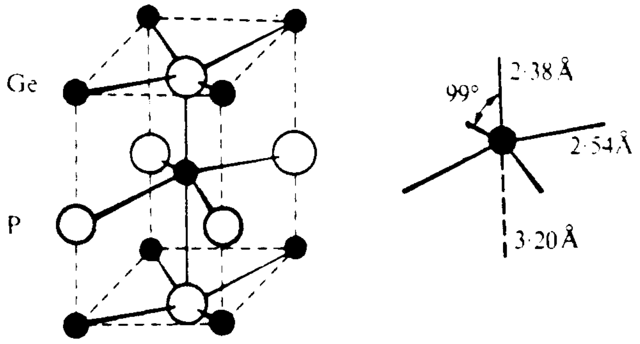

Figure 2. Structure of the high-pressure form of GeP.

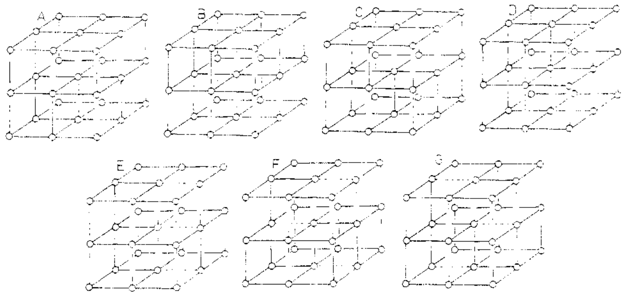

Figure 3. Two sets of structures (A–D and E–G) involving scission of a single linkage around each rock salt center.

into two sets: those four structures (A–D) where the broken bonds lie along the same direction and the remaining three (E–G) where the bond breaking occurs along two perpendicular directions. The latter give rise to extremely distorted geometries which try to accommodate square-pyramidal local geometries with pseudo-fourfold rotors which point in different directions on adjacent atoms. Our theoretical discussions will center on the first group of four structures where the local coordination geometry is still based on the square pyramid.

Calculations and Results

Calculations were performed on all four possibilities (A–D), the parent rock salt structure (R), and a rock salt structure appropriately elongated along the z axis (R′) with use of an extended Hückel based tight-binding method with the parameters described in the Appendix. With nine electrons per formula unit we find that in each case (A–D) the system is predicted to be metallic, in accord with the experimental evidence[6] for the high-pressure form of GeP itself. The energies of each alternative are shown in Table I. Satisfyingly the GeP structure A, the only structure out of A–D known at present to exist, is calculated to lie at lowest energy. All of the structures including the distorted structure R′ lie lower in energy than the rock salt geometry. This energetic stabilization occurs as a result of stabilization of the highest occupied orbital (band), which on distortion changed from antibonding to lone-pair character. The lone-pair band has electron density on both Ge and P atoms but is naturally more concentrated on the more electropositive Ge atoms. The energetic differences among the four structures A–D themselves lie, however, in the lower energy orbitals, and we need to search further for the electronic reasons behind their differential stabilization.

Table I. Energies[a] (eV) of the Rock Salt Structure (R), a Tetragonally Distorted Variant (R′), and Structures Related to GeP

structure	E (9 e)	E (10 e)	structure	E (9 e)	E(10 e)
R	−529.936	−521.861	C	−543.619	−542.527
R′	−541.443	−542.163	D	−541.403	−542.579
A	−544.300[b]	−543.968	D′	−544.390	−548.077[b]
B	−543.267	−543.080			

[a] Obtained from an 8 k point averaging procedure (see Appendix). [b] Experimentally observed structure.

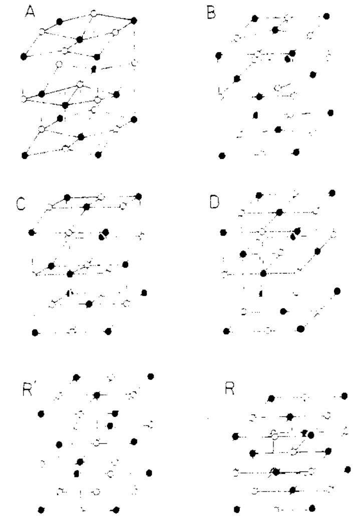

Figure 4. Local coordination in the structures A–D, R, and R′. There are eight structure **1**'s per unit cell in A, four **3**'s and two each of the **1** and **2** in B, eight **3**'s in C, and eight **2**'s in D.

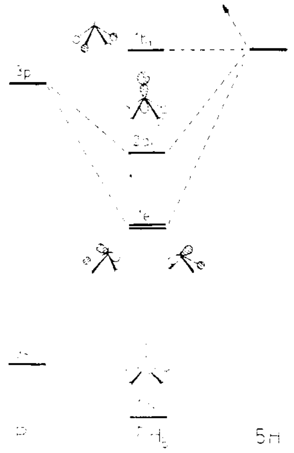

Figure 5. Orbital structure of a PH_5 molecule.

The four structures A–D may be categorized according to the local coordination environment in the crystal (Figure 4). A and D exclusively contain tetragonal-pyramidal sites of local C_{4v} symmetry with bond angles (θ) between axial and basal linkages of 99.5 and 90°, respectively (**1**, **2**). B and C contain

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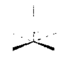

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distorted square pyramids with two angles of 99.5° and two of 90° (**3**). There are also small changes in the nearest-neighbor distances in the clusters (**1**–**3**). The two structures B and C are calculated to be close together in energy, and the numerical results of Table I indicate that the systems become increasingly less stable as the axial–basal angle decreases.

We have modeled this local behavior by looking at the results of molecular orbital calculations on AB_5 molecules with

Table II. Relative Energies of Local Square-Pyramidal Structural Units

structure	angles (θ), deg	E, eV	structure	angles (θ), deg	E, eV
1	all 99.5	−0.4558	3	half 90, half 99.5	−0.3210
2	all 90	0			

Table III. Relative Energies of the Nine-Electron Structures A–D

	E, eV[a]	E', eV[b]		E, eV[a]	E', eV[b]
A	−2.897 (−2.874)	−3.646	C	−2.216 (−2.310)	−2.568
B	−1.864 (−1.951)	−2.196	D	0 (0)	0

[a] From Table I energies evaluated with 8 k points (64 points in parentheses). [b] From Table II and Figure 4.

square-pyramidal geometries, following the results of Hoffmann, Howell, and Muetterties.[9] The level ordering of a simple PH_5 molecule and their orbital description is shown in Figure 5. It is extremely interesting to note that the calculated minimum energy geometry in these published computations on C_{4v} PH_5 and PF_5 occurs at a value of θ (**1**) of 99.8°. This value is virtually identical with the value of 99.5° found[6] in the high-pressure form in GeP. With four-electron pairs around each center, the orbitals through $2a_1$ are filled. Interestingly if the projection of the AB linkage perpendicular to the fourfold rotor is kept constant during the distortion, rather than the other obvious alternative of keeping the AB distance itself constant, then the energy of the $1b_1$ orbital does not change during the distortion. This arises simply because the B–B nonbonded distances do not vary during the distortion, and this orbital contains no central atom character by symmetry. Around each Ge atom and around each P atom in these GeP-like structures there are an average four and one-half electron pairs. The extra half an electron pair is not important in determining the angular geometry, as we can see Figure 5, but of course is vital in generating the partially broken up solid-state structure from the rock salt structure in the first place, as we described above. We may average the energies of local "GeP_5" and "PGe_5" molecules as described in the Appendix in order to estimate and understand the relative energies of **1**–**3**. The values are given in Table II. We also show the relative energies of the structures A–D computed from these three building blocks and the calculated energy differences from the band structure calculations in Table III. Both qualitatively and quantitatively the agreement between the two is very good. The molecular analogy has thus enabled us to understand the chemical reasons behind these energetic differences. It also indicates why the highest occupied orbitals of the band structure calculations, the ones unoccupied for the octet configuration, do not appear to be important in determining the energies of these structures relative to each other. This is a rather surprising conclusion since at first glance one might expect lone-pair–lone-pair repulsions, information about which is contained in these orbitals, to play a major role in the energy differences among these structures. It is interesting that in the 10-electron structures related to As and black P as well, lone-pair orbitals contribute little to relative energies while providing the major driving force for the distortion of any of these structures from the rock salt parent.[4]

The Yellow TlI Structure

One obvious distortion of structure D which might be expected to result in an energetic stabilization is slippage of one slab of the structure with respect to its neighbors. An obvious route is along the 110 direction such that one of the atoms in the structure becomes pseudo-seven-coordinate (Figure 6).

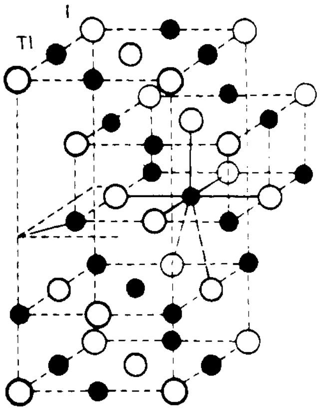

Figure 6. Structure of the yellow form of TlI.

Table I shows that this distorted structure (D′) is indeed considerably stabilized with respect to the parent structure (D). It is found experimentally[10] as the yellow form of the 10-electron compound TlI and in InBr and InI. The theoretical reasons behind this are not hard to find since the energy changes D → D′ are largely located in the HOMO at each **k** point for the 9-electron system and the highest two orbitals for the 10-electron system. These orbitals are largely lone-pair orbitals located at the ends of the severed bonds, and lone-pair–lone-pair repulsions are significantly reduced on the distortion. Accordingly a larger effect is found for the 10- as compared to the 9-electron systems. The structure D′ is calculated to be the lowest energy alternative in the series of Table I and is the only one of these structures actually experimentally observed for 10-electron systems. For 9 electrons as well, it is a little lower in energy (but not significantly given the sort of errors we expect in our averaging process) than the observed high-pressure GeP type, A.

Finally, it is interesting to note that although we have considered the generation of the yellow TlI structure and that of black phosphorus (GeS) via different (but clearly related) routes, there is another geometrical connection between these structures which is of interest. Hyde et al.[11] show how the distortion NaCl → GeS (SnS) → TlI lies along a smooth topological path, the result being a chemically twinned rock salt structure. These authors regard the distortion as arising via the "sizes" of the atoms present. In this paper of course we have focused on the driving force provided by the extra electrons: an electronic rather than steric effect, although the two are related[12] as we have shown elsewhere.

Discussion

Evidence is slowly building to indicate that many of the structural features of solids may be understood by extending molecular orbital ideas developed in the molecular field and that often the comparisons are good at the semiquantitative level. Our confidence in the analysis presented in this paper must be somewhat less however than that in our study on the arsenic, black phosphorus, and related systems[4] simply because of the smaller number of different structures which are possible in this problem. In our study on arsenic-like structures, the energies of the 36 possibilities were matched by a weighted sum of energetic contributions from four structural units. In the present case there are four (A–D) possibilities but three structural units used as building blocks. However, the excellent correlation with the molecular model does encourage the belief

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Table IV. Atomic Parameters for Atoms Si and P, and Pseudoatoms Ge′ and P′

	Si	P	Ge′	P′
Slater exponent	1.383	1.600	1.383	1.600
H_{ii} (3s), eV	−17.3	−18.6	−13.25	−16.3
H_{ii} (3p), eV	−9.2	−14.0		

that these really are the electronic reasons behind the stabilities of these structures.

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Appendix

Both crystal and molecular calculations in this paper used the extended Hückel method.[13] The band structure program was written by M.-H. Whangbo and used in ref 14. We are grateful to Dr. Whangbo for permission to use his program.

Because of the lack of well-established extended Hückel atomic parameters for Ge, we used parameters appropriate for Si, as listed in Table IV. The size of the observed unit cell of GeP was reduced accordingly to produce the nearest-neighbor distances shown in the representative fragment (**4**),

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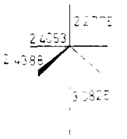

which should be appropriate for Si and P. Each of structures A–D had cell parameters $a = b = 4.8106$ Å and $c = 5.36$ Å. The P and Ge atoms were displaced from their ideal positions in a tetragonally distorted rock salt cell by moving them along c, a distance of $\pm 0.0376c$, the sign at each atom depending on the structure. The two "rock salt" structures considered were R′, a tetragonally distorted NaCl type with this unit cell, and R, an ideal NaCl type with $c = 4.8106$ Å corresponding to a situation in which no Ge–P bonds are broken and each atom has six neighbors at 2.4053 Å. The "TlI" structure D′ was obtained from structure D by doubling c and translating one of the layers normal to c by (a/4, b/4) relative to the other.

Energies of each of these structures except D′ were evaluated at the special points[4] $i/8, j/8, k/8$ [$i, j, k = \pm 1$, 3 (8 symmetry-inequivalent points)] and $i/16, j/16, k/16$ [$i, j, k = \pm 1$, 3, 5, or 7 (64 points)]. The Fermi level was computed by assuming each of these points represented an equal volume in the Brillouin zone, and the energy was obtained accordingly. As seen in Table III, the results of these two sets of calculations were essentially identical. In structure D′, only the first set of special points was used.

Molecular calculations were performed on GeP'_5 and PGe'_5 units. In both cases the apical bond distance was 2.2775 Å, and the basal distance was 2.4053 Å when the bond angle was 90°. The molecules were then distorted by increasing θ either with fixed bond distances or by moving the basal atoms parallel to the figure axis, thereby increasing the bond distances slightly, as in the crystals themselves. The average relative energies from this second distortion mode are in Table II. Because the HOMO (filled for 10 electrons per molecule and half-filled for 9) does not change in energy during this distortion, these results are insensitive to the exact electron count at each atomic center. Addition of p orbitals to the ligands does not qualitatively alter these conclusions.

Registry No. GeP, 25324-55-4.

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Electron Distribution and Bonding Patterns in Octahedral Organometallic Complexes of Co(III), Co(I), and Mn(I) with a Ligand Geometry of *fac*-a_3b_2c: A Nuclear Quadrupole Resonance Analysis

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Note is made of the fact that NQR signals of the metal frequently appear in organometallic complexes in which octahedral coordination of the metal occurs with the stoichiometry and structure of *fac*-a_3b_2c. An electrostatic model of the electric field gradient correctly describes the NQR data in $(\eta^5\text{-}C_5H_5)CoI_2c$ and $(\eta^5\text{-}C_5H_5)CoIc_2^+$ complexes (c = CO, $PO_3C_6H_{11}$, $P(OPh)_3$, PPh_3, $AsPh_3$, $SbPh_3$, NC_5H_5, NH_2CH_2Ph (Ph = C_6H_5) and c_2 = ethylenediamine, *o*-phenylenediamine, and bipyridyl). The electrostatic model is most suitable for predominantly σ-donor ligands and works less well for ligands with large π acidity. Comparison of NQR data for Mn(I) complexes of the type $(\eta^5\text{-}C_5H_5)Mn(CO)_2c$ and the above Co(III) complexes indicates the electric field gradient has the opposite sign in these two isoelectronic metals. The inversion is traceable to differences in the 3d orbital electron distribution between Co(III) and Mn(I) which are brought on by the difference in bonding of CO and I. These results help reconcile conflicting discussions that have appeared concerning the electric field gradient of Mn(I) organometallic complexes. The nature of bonding between Co(III) and an uncommon ligand, the phosphonate group, $P(O)(OCH_3)_2$, is revealed to be a weak σ donor with some π-acceptor ability.

Introduction

Compounds of Co(I) and Co(III) having three unique ligands a, b, and c in an octahedral arrangement of stoichiometry *fac*-a_3b_2c are prevalent in organometallic chemistry. There are several reasons why a determination of the ground-state electronic structure of this category of compounds is important.

First, 18e complexes of Co(I) with the formulation Cp(Co)b_2, where b = CO, $P(OR)_3$, and PR_3 (R = alkyl) and Cp = $\eta^5\text{-}C_5H_5$, exhibit strong basic character in the presence of a Lewis acid.[1,2] Similarly, 16e Cp(Co)b_2 complexes are Lewis

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