

From Three- to Four-Coordination in Copper(I) and Silver(I)

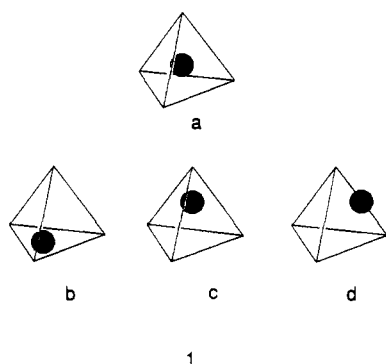
Jeremy K. Burdett*[†] and Odile Eisenstein*

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An orbital picture is presented of the factors influencing the choice of three- versus four-coordination for solids containing Cu(I) and Ag(I), of importance in appreciating the mobility of these ions in ionic conductors. The electronic preferences of both the nd orbital manifold and the $(n+1)(s+p)$ orbital manifold are for the regular tetrahedral arrangement, but mixing between the occupied nd and unoccupied $(n+1)s$ orbitals on distortion, via a second-order Jahn-Teller effect, as in Orgel's model for Hg(II), favors the lower coordination number. This balance is shown by calculation to be particularly sensitive at the end of the transition metal series.

Introduction

The coordination chemistry exhibited by Cu(I) and Ag(I) in their solid chalcogenides and halides is remarkable, and almost unique, in that low-energy barriers seem to separate two-, three-, and four-coordination. This property manifests itself in the widespread occurrence of ionic conduction,¹ the behavior of AgI being prototypic. Diffraction results often show a variety of coordination sites for these elements, frequently associated with large thermal parameters. For example, in a recent study² of the structure of CuVP_2S_6 , three sites were found for copper. The first is in a tetrahedral hole, the second is in a face joining tetrahedron to octahedron, and the third is a pair of sites in the octahedron. All three sites are populated, and the thermal parameters are quite large, that for the three-coordinate site resembling a cigar perpendicular to the face of the tetrahedron, indicating either dynamic or static disorder in this direction. In either case, a soft motion of the Cu(I) species is indicated. In many of the sulfides of Cu(I), similar structural features are found. Covellite, CuS , contains some copper atoms which are three-coordinated.³ In the hexagonal form of chalcocite, Cu_2S , the metal atoms are distributed among three sites.⁴ There are copper atoms in sites of three-coordination ($\text{Cu-S} = 2.28 \text{ \AA}$), distorted tetrahedral coordination ($3 \text{ Cu-S} = 2.59 \text{ \AA}$, $\text{Cu-S} = 2.15 \text{ \AA}$), and even two-coordination ($\text{Cu-S} = 2.06 \text{ \AA}$). We can visualize these geometries as arising via distortion of the ideal tetrahedral arrangement as in 1. The copper atom



may move from the tetrahedral site toward a face (eventually becoming three-coordinate), in the opposite direction, leading to one short Cu-S distance and three longer ones, or to an edge of the tetrahedron, resulting eventually in two-coordination. In the nonstoichiometric sulfide djurleite, $\text{Cu}_{1.96}\text{S}$, all of the copper atoms occupy trigonal holes⁵ but are slightly displaced toward the tetrahedral site. In many systems, that of chalcopyrite, CuFeS_2 , for example, the copper atom lies in a regular tetrahedral site. The sulfur atoms are arranged in a close-packed array in all of the compounds we have mentioned. In the molecular chemistry of Cu(I), a similar structural dichotomy is found. Chalcogenide and halide compounds of Cu(I) are known with regular tetrahedral coordination,⁶⁻⁸ as in the $\text{Cu}_4\text{X}_4\text{L}_4$ cubanes, with distorted tet-

rahedral coordination ($\text{L} = \text{olefin}$) with three short distances and one long distance, and with three-coordination as in the "step" complexes built from edge-sharing square Cu_2X_2 units. The soft motion connecting the trigonal planar CuL_3 geometry to a T-shaped one containing a linear two-coordinate CuL_2 moiety attached via a long bond to a third ligand has recently been studied theoretically.⁹ The oxide chemistry of Cu(I) is quite different¹⁰ from that described for the sulfides. Here, in solids the linear two-coordinate structure is the dominant structural unit, found in cuprite, Cu_2O , $\text{YBa}_2(\text{Cu}^{II}\text{O}_2)_2(\text{Cu}^I\text{O}_2)$, a compound structurally very similar to the 1-2-3 high-temperature superconductor,¹¹ and the copper delafossites, CuMO_2 , for example. Recently, however, a three-coordinate unit with a long distance to the third atom has been identified¹² in CuLaW_2O_8 (the distances are 1.89, 1.95, and 2.36 \AA) and tetrahedral four-coordination is known for a few systems, among them $\text{Cu}_6\text{Mo}_5\text{O}_{18}$.¹³ Two-, three-, and four-coordination are found too in Ag(I) chemistry. In Ag_3AsS_3 , for example,¹⁴ the silver atoms are present in both planar and pyramidal trigonal environments.

This interesting behavior of copper and silver in their chalcogenide and halide chemistry is unique. The structural chemistry of the isoelectronic Zn(II) is pedestrian by comparison, four-coordination being the rule. Neither do we find such widespread structural plasticity on moving to the left of copper in the periodic table. Although both trigonal planar $d^{10} \text{ML}_3$ (16 electrons) and tetrahedral ML_4 (18 electrons) compounds are known of course, this is only the case for organometallic systems such as $\text{Pt}(\text{PPh}_3)_3$. The case of four- versus six-coordination found for Ni(II) is readily understood in terms of a change of spin state. The rather special behavior of Cu(I) and Ag(I) seems to be due to their unique periodic table location, at the very end of the transition metal series.

Our attention was drawn to this problem by the result shown in Figure 1, which displays computed energy profiles for the movement of a metal atom along a 3-fold axis of a tetrahedral

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[†] Permanent address: Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, IL 60637.

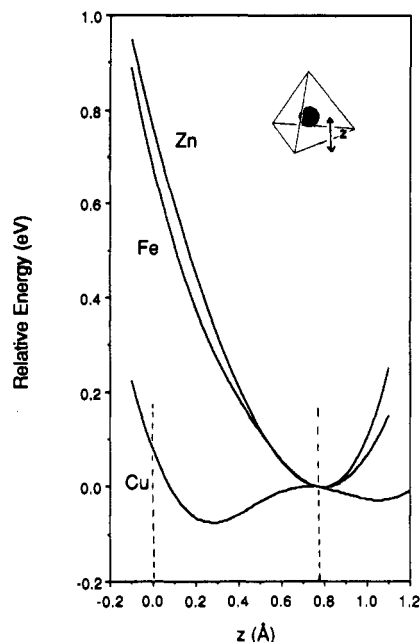


Figure 1. Computed energy profiles for the movement of a single metal atom per M_4S_4 unit cell of the wurtzite surface. The motion is along a 3-fold axis of the tetrahedron. The regular tetrahedral geometry (4 Cu-S = 2.30 Å) corresponds to $z = 0.767$, the metal lies in a site of planar trigonal coordination plus one long bond for $z = 0$ (3 Cu-S = 2.17 Å, Cu-S = 3.10 Å), and for $z > 0.767$, the geometry is one with one short and three long M-S distances (at $z = 1.1$ this corresponds to 3 Cu-S = 2.43 Å, Cu-S = 1.97 Å). The tetrahedral and planar trigonal geometries are indicated by dashed lines.

hole in a hexagonal close-packed lattice of sulfur atoms. The calculations used the extended Hückel implementations of tight-binding theory with standard orbital parameters for the metal atoms and a S-S distance of 3.75 Å, leading to a metal-S distance of 2.3 Å. The regular tetrahedral geometry (1a) occurs at $z = 0.767$ Å; the atom is located in a face (1b) for $z = 0$ and displaced toward one sulfur atom (1c) when $z > 0.767$ Å. Three curves are shown corresponding to Zn(II), d^{10} Cu, and d^{10} Fe, the last being a hypothetical system which uses the orbital parameters appropriate for iron but the electron count appropriate for copper. Notice the rather dramatic result which shows the stability of distorted structures 1b and 1c (both geometries found in high chalcocite as noted above) relative to the tetrahedral arrangement 1a for copper but the strong preference for the tetrahedral geometry for the other two systems. Not shown are results for movement of the metal atom to an edge of the tetrahedron. An analogous stabilization results for Cu but not for d^{10} Fe or Zn.

Before going any further, we have to comment on the problems inherent in one-electron models such as ours in viewing problems where bond lengths and coordination numbers change, and also the unreliability in an absolute sense of the orbital parameters used. Invariably, calculations designed to study distortions in molecules keep bonded interatomic distances equal and vary just the angles to avoid this problem, and distortions in solids are usually constrained to be small. However, there is no doubt that the model well captures the essence of this structural problem as shown in Figure 1, and so, bearing in mind these caveats, we proceed to analyze the orbital problem in the usual way to uncover the orbital factors which lead to this behavior.

Electronic Stability of Tetrahedral Metal Coordination

The results shown in Figure 1 are from a calculation on a solid with the wurtzite structure in which one metal atom is moved in a unit cell containing four MS_4 units. 2 shows two layers of the

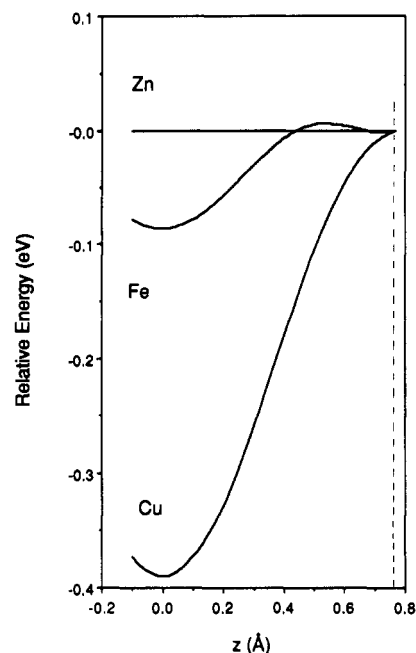
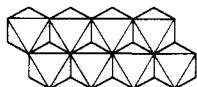


Figure 2. Computed energy profiles similar to those of Figure 1, except that here all four metal atoms of the wurtzite M_4S_4 unit cell move together. The tetrahedral geometry is indicated by a dashed line. The planar trigonal structure occurs at $z = 0$.

hcp structure and the octahedral and tetrahedral holes which are generated. A similar set of curves are found for the case where all four metal atoms of the unit cell move together. As before, zinc and iron are resistant to distortion but the tetrahedral structure is a local-energy maximum for copper. These curves are related energetically to those of Figure 1 by an approximate factor of 4. Here, though, an energy minimum is found in the copper calculation at $z = 0$. Thus this calculation shows the stability of the structure where all the metal atoms occupy trigonal holes in the lattice. This is the arrangement described above for djurleite, $Cu_{1.96}S$. Another interesting result is illustrated in Figure 2, which also shows movement of the metal atom along the 3-fold axis of the tetrahedron, but in this case for a solid of stoichiometry MS_4 , the unit cell containing a single metal atom. Notice in this case the almost flat surface for zinc, the slight preference of the trigonal structure for the hypothetical Fe (d^{10}) system, and the much stronger preference for the trigonal structure for copper. The origin of the difference between the two sets of curves is an interesting one to pursue. Crystal chemists, strongly influenced by the ideas of Pauling over the years, have concentrated on changes in cation coordination number and geometry. However, as we have pointed out elsewhere,¹⁵ changes in anion coordination are also important and figure in controlling the energetics of various ordering patterns in solids. Here, in the solid of stoichiometry MS_4 with the wurtzite structure, each metal is tetrahedrally coordinated by sulfur, but so too is each sulfur tetrahedrally coordinated by metal. Movement of a single metal atom in the unit cell toward a face destroys this stable sulfur coordination geometry, leading to an energetic penalty. In the solid of MS_4 stoichiometry, each sulfur is coordinated to a single metal and so there is no change in angular geometry on distortion. Thus, two ingredients (at least) go into the plots of Figure 1. Not only are there energy changes associated with changes in the local CuS_4 geometry, but an extra destabilization of the trigonal planar geometry is found for the case where coordination around sulfur is important. That we are dealing with a local effect is shown by calculations on the molecular cluster $MS_4(M_{12})$ where, in this fragment of the solid, each sulfur atom is tetrahedrally coordinated by copper, 12 metal atoms surrounding the tetrahedral MS_4 unit. Energy diagrams quantitatively very similar to those of Figure

1 result. We now study the energy levels of this unit to extract an electronic understanding of this energetic behavior.

The Electronic Details

Figure 3a shows the energy changes for the d orbitals of the central copper atom in the $\text{CuS}_4(\text{Cu}_{12})$ fragment used to simulate the behavior of the solid. These particular copper energy levels lie the highest in energy of all the metal d levels because the central copper atom, which moves within the confines of the S_4 tetrahedron, has the highest number of sulfur ligands. They are occupied and energetically control the functional form of the total energy on distortion. We have used the symmetry labels for the trigonal planar geometry to distinguish the two sets of e levels. Figure 3b shows an analogous picture but one for the CuS_4 molecule where all the Cu-S distances are kept fixed and only the angle θ is allowed to change. The range of geometrical distortions of the two plots are similar; the axial-basal angle in Figure 3a for $z = 1.2$ is 119° , and of course $z = 0$ corresponds to $\theta = 90^\circ$. Notice that the orbital behaviors of the two plots are quite similar around the tetrahedral geometry and are in accord with the energies expected on the basis of the angular overlap model¹⁶ (Figure 3c). We can see rather clearly the effect of performing the calculation with the two different sets of constraints. The only large difference is associated with the behavior of the a_1 orbital. This is most pronounced on moving toward the trigonal planar structure. For $z < 0.6$, the a_1 orbital is dramatically stabilized but continues to rise in energy for $\theta < 105^\circ$. Similar, but less striking, is the much steeper descent for $z > 0.767$ than for $\theta > 109.5^\circ$. This difference in behavior is very important. In contrast to the results for the solid, calculation of the total energy for copper using the results of Figure 3b shows a strong energy minimum at the tetrahedral structure (and even more so for the analogous system using iron parameters). This dominating behavior of the a_1 orbital in the solid, which clearly leads to the minima away from the tetrahedral geometry shown in Figure 1 for copper, is in accord with the suggestion¹⁷ that a second-order Jahn-Teller effect is behind the observation of nontetrahedral geometries in this system. We shall have more to say about this below. Of course, the detailed orbital explanation behind the different behaviors of the two plots of Figure 3a,b must involve a subtle balance of the variation in the relevant overlap integrals with distance.

Having identified the key player in this structural problem, an analysis of the d-orbital levels around the tetrahedral geometry for the cases of Cu and Fe should lead to clues as to the difference between the two sets of calculations. Some energy differences are shown in Figure 4. Plotted are the sum of the energies of the two sets of e levels and the energy of the a_1 level. The behaviors of the a_1 levels are quite similar for the two cases. Such a result would suggest very similar behaviors for copper and iron, which is not the case. The difference between the two systems lies in the much stiffer potential seen for the e level sum for the case of iron compared to copper. A perturbation analysis of these energy changes is enlightening. Both first- and second-order energy changes were calculated for the geometries at $z = 0.5$ and $z = 1.1$ relative to the tetrahedral structure. The first-order energy changes are always larger for iron than for copper for both a_1 and e orbitals. This is associated with, among other things, a larger overlap between iron 3d and ligand orbitals compared to the case of copper. Second-order energy changes are dominated by s/d mixing for the case of orbitals of a_1 symmetry, and this is always stabilizing for the a_1 (d) orbital. It is larger for copper than for iron due to the proximity of the 4s orbital. The overall effect is a similar change in the energy of the a_1 orbital for both iron, with the larger first-order change, and copper, with the larger (negative) second-order change. In contrast, there is no available empty e set to provide a second-order stabilization of the two pairs of occupied d orbitals of this symmetry. Overall, they are ener-

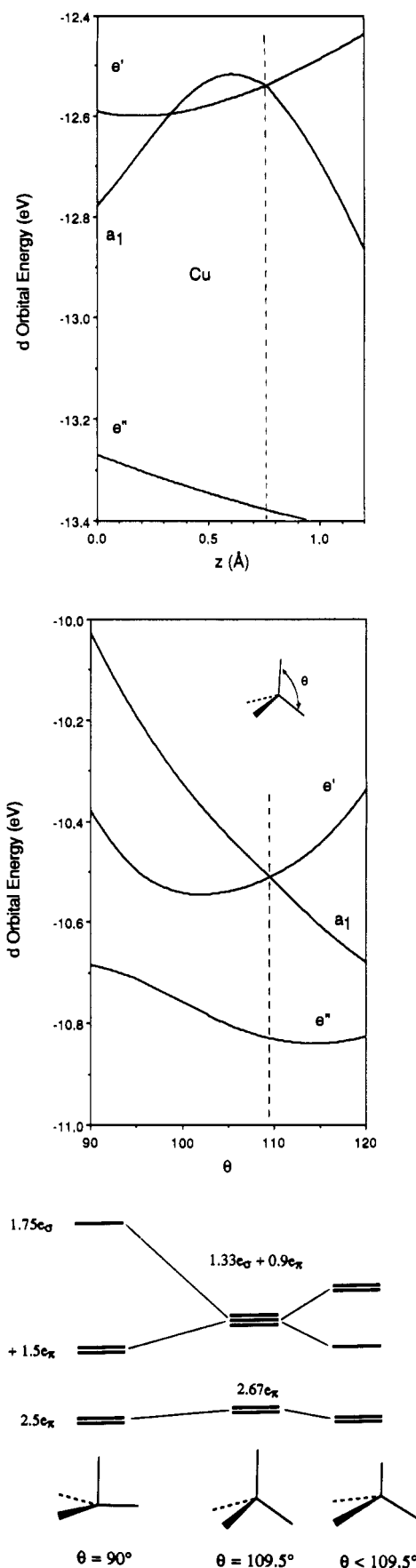


Figure 3. (a) Top: Computed d-orbital energies for the distortion used in Figures 1 and 2 for a $\text{CuS}_4(\text{Cu}_{12})$ cluster. (b) Middle: Computed d-orbital energies for the distortion of a CuS_4 molecule with all Cu-S distances kept constant. The tetrahedral geometry is indicated by a dashed line in both panels. (c) Bottom: Energy changes expected for (b) from the angular overlap model.

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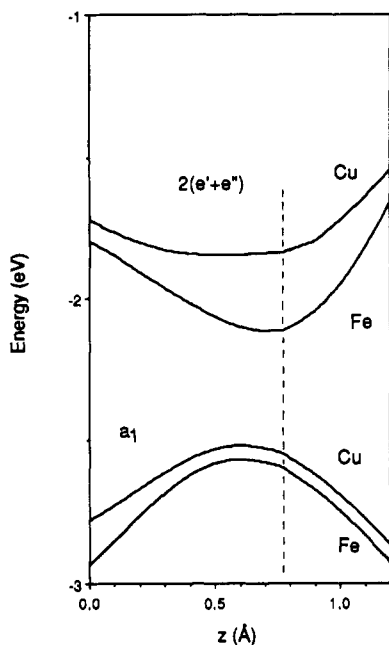


Figure 4. Variation in orbital energies and orbital energy sums for the distortion of Figure 3a for both the $\text{CuS}_4(\text{Cu}_{12})$ and $\text{FeS}_4(\text{Fe}_{12})$ clusters. Shown are the variations in the energy of the a_1 orbital and the sum of the e-orbitals taking into account their degeneracy. The tetrahedral geometry is indicated by a dashed line.

getically destabilized on distortion as they mix together. This effect is larger for iron than for copper, reflecting the stronger metal-ligand interactions for the former. Energetically (Figure 4) a much stiffer distortion for the e symmetry levels results for iron than for copper. From angular overlap considerations,¹⁶ the most stable structure for a system with this electron count (i.e., the closed d shell) is the one where the orbital interactions are as symmetric as possible (namely, the tetrahedral structure), and the energetic penalty for nontetrahedral geometries shows up in our calculations as this strong second-order repulsion between the two sets of e levels on distortion. Clearly, it is the behavior of the a_1 orbital which provides the driving force for distortion away from tetrahedral.

The picture which emerges is thus the following one. The 3d orbitals are energetically more important in iron than in copper. This manifests itself in the generally larger first-order energy changes for iron described above. The total destabilization energy associated with the e orbitals shows a much more pronounced minimum at the tetrahedral structure for iron than for copper. The second-order Jahn-Teller stabilization is present for both iron and copper a_1 orbitals but is larger by calculation for the latter. Such stabilization is sufficient to overcome the energetic demand of the d-orbital manifold alone for the tetrahedral structure in the case of copper but not for iron. In zinc, where the 3d orbitals are not available, the energetic preference of the 4s and 4p orbitals is for the tetrahedral structure.

We could envisage too an argument based on the "size" of the two atoms. The 3d orbitals for iron are more diffuse than those for copper, suggesting that the larger iron atom fits into the S_4 cavity well whereas the smaller copper atom seeks to move to a site of lower coordination. However, contracting the valence orbitals of zinc (to simulate a smaller atom) diminishes the destabilization associated with movement away from tetrahedral but does not lead in our calculations to the generation of a stable nontetrahedral structure. Importantly, the double-minimum behavior found for copper in Figure 1 is replaced by a single minimum at the tetrahedral geometry when the average Cu-S distance is shortened to 2.15 Å. In terms of "size" arguments of course, the trigonal hole is now too small to allow the copper atom to pass through. In terms of orbital interactions, the d-orbital manifold is now stereochemically much more active at this shorter distance as a result of the increase in Cu-S overlap integrals.

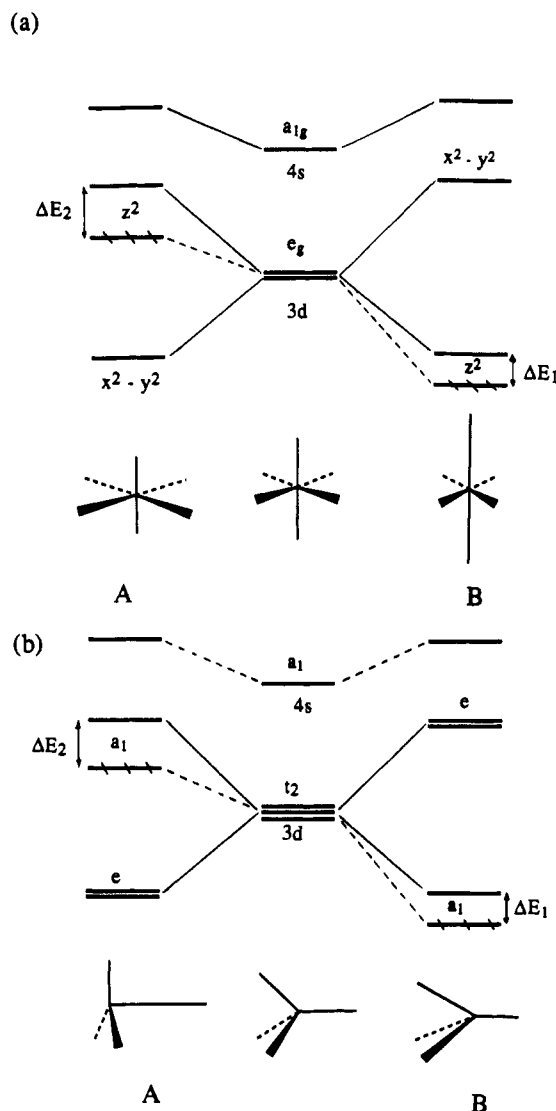


Figure 5. Effect of second-order Jahn-Teller considerations on the distortion of (a) octahedral and (b) tetrahedral systems. The effect of d/s mixing is shown by the dashed tie-lines and hatched orbital levels. In both cases, $|\Delta E_2| > |\Delta E_1|$, reflecting the smaller energy separation between the z^2 orbital (of a_1 symmetry) and the metal s orbital for cases A compared to B. For the d^{10} system the model suggests that case A should be prevalent, which is indeed the case. (The diagrams are of course schematic only.)

The observation of these structural features in this part of the periodic table has an interesting electronic origin. We know that nd and $(n+1)(s+p)$ orbitals are important for transition metal chemistry, and main group chemistry is dominated by the valence $s+p$ orbitals. The presence of judiciously located nd orbitals relative to the $(n+1)(s+p)$ set and a closed d shell sets up the electronic requirements for this structural behavior, namely a relatively weak set of metal d-ligand interactions but effective s/d mixing. This leads to a fascinating structural chemistry at the junction between the transition metals and the main group elements.

Effect of s/d Mixing

The ideas of the first-order Jahn-Teller effect have been used for many years to understand the nonoctahedral geometry of Cu(II), but only relatively recently has the second-order Jahn-Teller mixing of 3d and 4s orbitals^{16,18} been used to show why it is arrangement B with four short and two long distances which is favored over arrangement A, with two long and four short distances. The argument (Figure 5) centers on the fact that the

Table I. Orbital Parameters Used in the Calculations

element	orbital	H_{ii} , eV	ζ
Cu	4s	-11.4	2.2
	4p	-6.06	2.2
	3d ^a	-14.0	5.95 (0.5933), 2.30 (0.5744)
Fe	4s	-9.10	1.9
	4p	-5.32	1.9
	3d ^a	-12.6	5.35 (0.5505), 2.00 (0.6260)
Zn	4s	-12.41	2.01
	4p	-6.53	1.70

^a A double- ζ expansion, with coefficients in parentheses.

z^2 orbital, by symmetry the only one of the d set which is stabilized in this way, is doubly occupied for case B and only singly occupied in case A. For the d^{10} configuration then, distortion A is favored since $|\Delta E_2| > |\Delta E_1|$ on the basis of energy gap arguments. Such an argument allows access to the observation of linear two-coordination found for the Hg(II), Ag(I), and Cu(I) systems. These structural features have been described for many years in terms of Orgel's model¹⁹ of s/d mixing. Thus the structure of cinnabar (HgS) may be regarded as one containing octahedral coordination around mercury with two short bonds and four very long ones. The structures of the heavier mercuric halides are of the cadmium halide type, but instead of six-coordination, the geometry with two short plus four long distances is found. Figure 5b shows the extension of the argument to the distortion of the tetrahedron. The distortion (A) toward the trigonal plane (a_1 highest in energy as in Figure 3c) should be energetically favored over the distortion (B) to the structure with one short and three long bonds since, as in the octahedral case, $|\Delta E_2| > |\Delta E_1|$ on the basis of energy gap arguments. Although our calculation (Figure 1) shows this to be true, it is perhaps more appropriate to note that this is the distortion which appears most frequently in the examples we have found in the literature. By calculation, we find an s/d ratio in the a_1 orbital of Figure 3c of 0.18 for $z = 4.33$ and 0.14 for $z = 1.1$, two equal distortions from the tetrahedral geometry to quantitatively support this claim.

Mixing of 4s and 3d orbitals plays a role in influencing coordination number in molecular Cu(I) chemistry, as shown in a recent study⁸ of some cubane type systems. We need only look at some other "unusual" chemistry in this part of the periodic table to find other examples where such orbital effects are important. Interactions between Cu(I) atoms,²⁰ of importance in the assembly

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of many Cu(I) complexes, electronically are very similar to those associated with Pt(0)-Pt(0) interactions.²¹ Mixing between the nd and $(n+1)s$ orbitals is of crucial importance for both. Such effects are doubly important in cuprite, Cu_2O . The structure of this material consists of two interpenetrating Cu_2O lattices each containing linear two-coordinate copper and tetrahedral oxygen atoms in an ice-like arrangement. The Madelung energy is less favorable for the two separate lattices than for the observed structure. The presence of a stabilizing Cu(I)-Cu(I) interaction is sufficient to hold the structure together. (The interaction energy of the two lattices has been calculated²² to be of the order of 1 kcal/mol). Thus s/d interactions are responsible here both for the linear O-Cu-O unit in the ice-like structure of each lattice and for the interaction which holds them together.

Orbital mixing of a related type is also important at the beginning of the transition metal series. It can be used to understand the bent structures²³ of some of the AX_2 molecules ($A = \text{group 2 element}$, $X = \text{group 17 element}$) and also allows access²⁴ to the unusual geometries of several d^0 transition metal systems.

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Appendix

A metal-sulfur distance of 2.30 Å was used for all calculations of the tetrahedral geometry, except where stated. This leads to a distance of 2.169 Å for the corresponding trigonal planar geometry. (See ref 25 for a compendium of Cu(I)-S distances.) From considerations of the bond valence sum, the difference between three- and four-coordinate distances should be 0.106 Å, irrespective of the nature of the atoms. Table I shows the orbital parameters used in the calculations.

Registry No. Cu, 7440-50-8; Ag, 7440-22-4.

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Contribution from the Department of Chemistry,
University of Illinois, Chicago, Illinois 60680

Magnetic Ordering in $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$: Specific Heat Measurements

Roey Shaviv, Mary E. Redmond, and Richard L. Carlin*

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The specific heat of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ is reported over the temperature interval 1.6-40 K. A λ -feature, characteristic of a magnetic phase transition, is observed at 3.925 ± 0.005 K. Only 23% of the magnetic entropy is acquired below T_c , which is indicative of substantial short-range order.

Introduction

The substance $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ is one of a series of bimetallic compounds that are of current interest.¹ The various physical properties of this material have been summarized earlier.²

The compound is cubic at room temperature, but it undergoes a structural transition to a tetragonal phase as it is cooled below 280 K.³ We illustrate here the utility of specific heat measurements for the determination of the character of systems with magnetic interactions. This paper marks the first report of the specific heat of a copper-containing bimetallic coordination

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