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Pressure Tuning Spectroscopy as a Diagnostic for Pressure-Induced Rearrangements (Piezochromism) of Solid-State Cu(II) Complexes

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The chemical, optical, electrical, and magnetic properties of materials[1] depend on the arrangement of atoms, ions, or molecules in the system, the nature of the energy levels available to the outer electrons, and the accessibility of low-lying excited states of the system. The observed state of a given system is determined by a balance of many different and oftentimes opposing interactions. In the solid state, which is the focus of this Account, important interactions include anion-cation interactions, hydrogen bonding, steric effects, van der Waals forces, and lattice interactions. Frequently the balance of forces defining a system and its properties is delicate. The basic effect of compression in this context is to alter the balance by varying the contributing interactions unequally. In extreme cases the balance is altered sufficiently so that the system undergoes an electronic transition and a new ground state is adopted. Compression changes the interactions that determine the state of a particular system and necessarily perturbs the energy levels of the system. Both the relative energy and orbital composition of each level are affected. We refer to perturbation of energy levels by compression as "pressure tuning" and to the experimental observation of the effect as "pressure tuning spectroscopy".

In this Account we examine the effect of high pressure on several solid-state Cu(II) complexes. We shall see that high pressure can change the molecular configuration of the complexes. We refer to a change in the molecular configuration of a system as a rearrangement. Our goal is to understand the nature of pressure-induced rearrangements. In particular we are interested in the range of geometric configurations adopted by species in the solid state, the way in which these configurations may be altered, and how these configurations are related to each other.

Electronic absorption spectroscopy has proven to be an invaluable probe of the geometry of Cu(II) complexes.[2,3] The appearance of the electronic absorption spectrum is frequently highly characteristic of the geometry about the copper center. We shall use pressure tuning electronic absorption spectroscopy to assess changes in the configuration of three classes of Cu(II) complexes: (1) $CuCl_4^{2-}$, (2) Cu(diethylenetriamine)-

(di-2-pyridylamine)copper(2+), and (3) bis(N,N'-diethylethylenediamine)copper(2+). In each case, a series of counterions is used to provide a range of geometries for the copper moieties in each class at ambient pressure. The different geometries in each class may be characterized quantitatively by internal structural parameters (e.g., bond lengths and/or angles). The electronic absorption spectrum is sensitive to changes in structural parameters induced by pressure.

Before discussing specific examples, we present three general findings of our experiments. First, the differences in geometry among the members of each of the three classes at ambient prssure become less distinct upon compression. The range of values for the structural parameter of each class decreases with increasing pressure, indicating that all members of the class tend toward a common molecular configuration.

Second, the changes observed in molecular configuration in each class with pressure appear to follow structural pathways.[4,5] A stereochemical structural pathway may be defined as those distorted configurations of a complex (or complexes) that represent a progressive change from one reference geometric form to another. Position along a pathway can be defined in terms of the value of a characteristic structural parameter, and the limiting values are defined by the two reference geometries. In a sense, a structural pathway represents "allowed" configurations of a species in the solid state. Our results indicate that as members of each class pass from an initial ambient pressure configuration to new configurations at higher pressure, the configurations adopted by different members at different pressures are similar. That is, the configuration of one member at a given pressure is similar to that of other members at different pressures. This indicates that different members pass through a common series of configurations upon compression. In this context, the members of each class at ambient pressure represent different points on a structural pathway particular to the class, and pressure induces a movement of each member along its pathway by changing the molecular configuration.

Finally, our studies indicate that progress along a structural pathway can occur in several ways. In some systems, the molecular rearrangement occurs continuously over all pressures, indicating a stochastic process;

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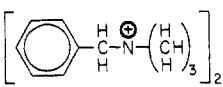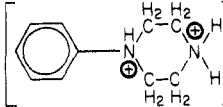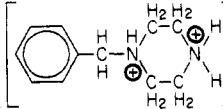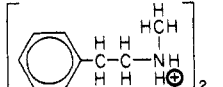(5) Hathaway, B. J. Struct. Bonding (Berlin) 1984, 57, 55.

Figure 1. Cations, dihedral angles, and approximate anion symmetry of the tetrachlorocuprate complexes discussed in this Account.

in others, the rearrangement involves a discontinuous process (a first-order phase transition); and in still others, the rearrangement possesses intermediate characteristics and is consequently best described as partially cooperative.

CuCl₄²⁻

We first consider a series of five tetrachloro-cuprates.[6,7] The cations of the five complexes are shown in Figure 1. The different configurations of the tetrachlorocuprate ion may be regarded as intermediate points along a stereochemical structural pathway extending from a regular tetrahedral to a square-planar geometry. We characterize the position of a given configuration along this pathway by its dihedral angle. This is the angle formed by two planes, each of which contains the copper center and a different pair of chlorides.[4] Thus, the dihedral angles of regular tetrahedral and square-planar complexes are 90° and 0°, respectively. Figure 1 lists the dihedral angle and approximate symmetry of the tetrachlorocuprate ion at ambient pressure in its complexes with the five cations.[8-10] In this Account, we use the one-electron designation as an approximate description indicating the major or root component of a molecular orbital which, in a nonregular geometry, may be composed to some degree of mixed d orbitals possibly with significant ligand contribution. In parentheses we indicate the appropriate one-electron energy levels of Figure 2 which have been established for four of the five complexes at ambient pressure by polarized absorption measurements.[11-14] Since the energy levels of (NphpipzH₂)-

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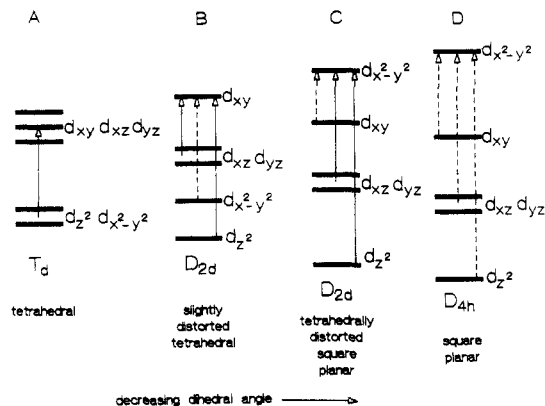
Figure 2. One-electron energy levels of the tetrachlorocuprate ion in various geometries.
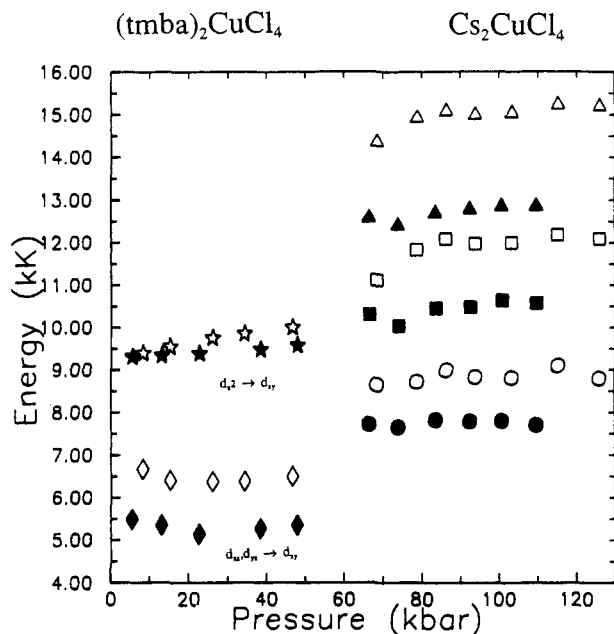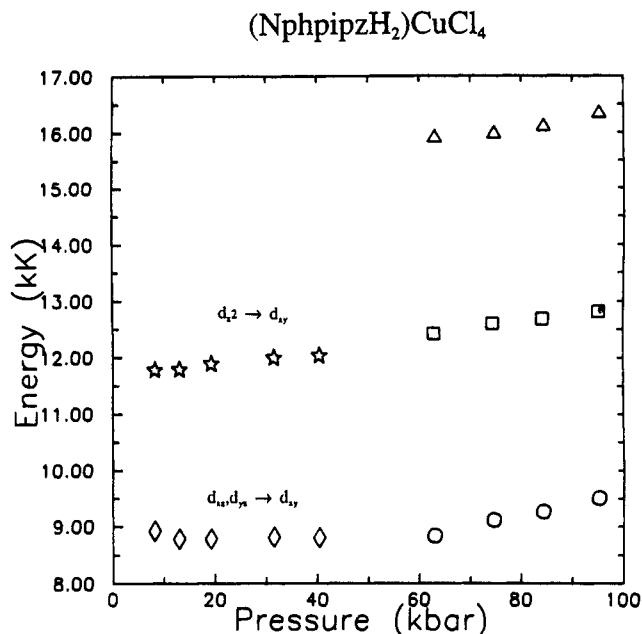

Figure 3. Pressure dependence of the energies of the electronic transitions in (tmba)₂CuCl₄ (open symbols) and Cs₂CuCl₄ (filled symbols).

CuCl₄ have not been rigorously determined, we shall assume that the levels of Figure 2B apply. In Figure 2 we also show which transitions are dipole allowed (solid arrows).

Our experiments consisted of measuring the electronic absorption spectrum of each complex as a function of pressure. The experimental techniques are described in detail elsewhere.[7] The spectra were then resolved into Gaussian components corresponding to the transitions shown in Figure 2. The low-pressure spectra were fit with bands corresponding to the two dipole-allowed transitions shown in Figure 2B. Polarized absorption experiments done by others[11,12] have shown that the dipole-forbidden transition is of very low intensity, and consequently, we have excluded it from the fits. The high-pressure spectra demonstrate the dramatic change in the spectrum after molecular rearrangement of the complexes has occurred. For reasons discussed in the original paper, it was necessary to fit the high-pressure spectra with three bands. The spectra of Cs₂CuCl₄ are similar to those of (tmba)₂CuCl₄.

The pressure dependence of the energies of the resolved d–d transitions in Cs₂CuCl₄, (tmba)₂CuCl₄, and

$(NphpipzH_2)CuCl_4$

Figure 4. Pressure dependence of the energies of the electronic transitions in $(NphpipzH_2)CuCl_4$.

$(NphpipzH_2)CuCl_4$ is shown in Figures 3 and 4. Three regions are indicated by the data for each complex. At low pressure, the configuration of the tetrachlorocuprate ion in the three complexes is similar to that at ambient pressure. At high pressure, a new configuration of the tetrachlorocuprate ion for each complex is present. At intermediate pressures, the anion in each of the three complexes undergoes a rearrangement from the low-pressure form to the high-pressure form. The high-pressure spectra reveal the nature of the rearrangement involved. Most notably, at high pressure, ligand field absorption occurs at much higher energy than at low pressure. This implies a much greater ligand field strength at high pressure in each of the complexes, indicating a smaller dihedral angle for the tetrachlorocuprate ion (Figure 2). In fact, correlations have been presented in the literature that relate the highest energy d–d transition in tetrachlorocuprate complexes at ambient conditions to the dihedral angle of the anion.[8,15] These correlations show that the lower the dihedral angle, the higher in energy a d–d transition appears. The greater width of the absorption envelope at high pressure is also consistent with a rearrangement involving a decreased dihedral angle.

The significant changes in transition energy and bandwidth mentioned above suggest a sizeable decrease in dihedral angle. On the basis of our study of $(NbzpipzH_2Cl)_2CuCl_4$ (Figure 1) (vide supra), it is clear that the dihedral angle at high pressure in Cs_2CuCl_4, $(tmba)_2CuCl_4$, and $(NphpipzH_2)CuCl_4$ is greater than 19°. Thus we are able to conclude that the dihedral angle in each of the three complexes is less than 51.6°, greater than 19°, and probably not close to either limit. The high-pressure situation is consequently somewhere between those depicted in parts B and C of Figure 2. We can furthermore conclude, on the basis of the relative energies shown in Figures 3 and 4, that the dihedral angles after rearrangement decrease as Cs_2CuCl_4 > $(tmba)_2CuCl_4$ > $(NphpipzH_2)CuCl_4$. Lastly, the

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greater resemblance of the spectra of Cs_2CuCl_4 and $(tmba)_2CuCl_4$ at high pressure to the spectrum of $(NphpipzH_2)CuCl_4$ and the greater similarity in component band energies at high pressure suggest that the spread of dihedral angles present for the three complexes is smaller at high pressure than at low pressure. The rearrangements observed in Cs_2CuCl_4, $(tmba)_2CuCl_4$, and $(NphpipzH_2)CuCl_4$ are examples of systems that exhibit intermediate rearrangement order (a significant extent of cooperativity). In each complex, the rearrangement occurs over a pressure range of about 20 kbar.

The remaining two tetrachlorocuprates, $(NbzpipzH_2Cl)_2CuCl_4$ and $(nmpH)_2CuCl_4$ (Figure 1), possess much smaller dihedral angles at ambient pressure than the three complexes considered above. The energy levels of $(NbzpipzH_2Cl)_2CuCl_4$ at ambient pressure are depicted in Figure 2C. It has been demonstrated[13] that the dipole-forbidden transition is of very low intensity, and we therefore resolved the low-pressure spectra into two components. In contrast to the previous three complexes, the spectrum of $(NbzpipzH_2Cl)_2CuCl_4$ exhibits only minor changes upon compression. The main effect of compression is reflected in intensity changes of the bands (Figure 9, ref 7). Beginning at about 25 kbar, the high- and low-energy bands simultaneously and continuously gain and lose intensity, respectively. The intensity effect continues steadily up to about 80 kbar, after which the trend slows and appears to level off. Both bands shift to higher energy in the first 40 kbar. Between 40 and 60 kbar, both bands shift abruptly but only by about 300–500 cm⁻¹ to lower energy, and above 60 kbar, slight and continuous shifts to lower energy are observed.

The relatively subtle spectral changes observed for $(NbzpipzH_2Cl)_2CuCl_4$ make it more difficult to determine the behavior of this complex upon compression. We discuss the possibilities more completely in the original paper.[7] The important point for the purposes of this Account is that any change induced in the geometry of the anion with pressure is slight. This is in contrast to the previous three complexes as well as to the remaining complex in this series.

$(nmpH)_2CuCl_4$ is square planar (dihedral angle = 0°) at ambient pressure (Figure 1), and the energy levels of Figure 2D apply. Although none of the three transitions are dipole allowed in square-planar (D_{4h}) symmetry, each is vibronically allowed.[14] The pressure dependence of the energies of the transitions is shown in Figure 5. At low pressures, the three d–d transitions shift to slightly higher energies due to a small increase in ligand field strength which ordinarily occurs upon compression. Between about 50 and 70 kbar, the complex undergoes a rearrangement, which is reflected in the distinct change in the appearance of the spectrum. After rearrangement, the spectrum no longer exhibits three discernible transitions. The overall bandwidth is also greatly reduced, and there is a distinct absence of the ligand field absorption initially present between 16×10^3 and 19×10^3 cm⁻¹. The overall absorption profile has also moved to much lower energy. These observations imply that the rearrangement that occurs involves an increase in the dihedral angle of the tetrachlorocuprate anion. The energy levels of the rearranged complex are no longer described by Figure 2D.

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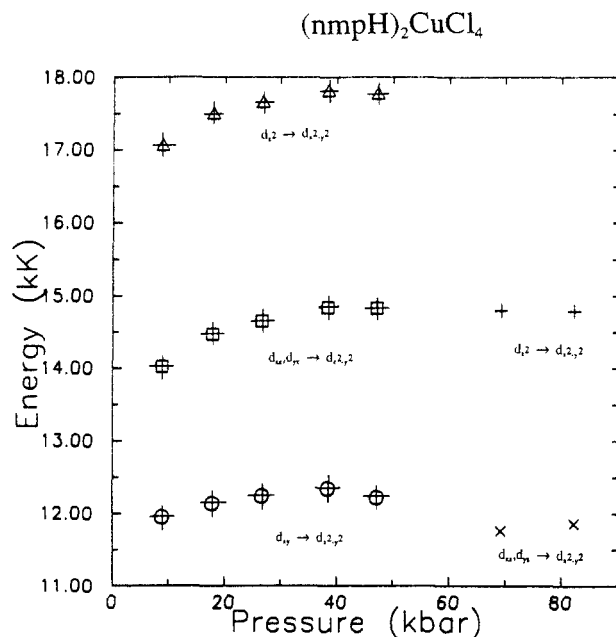
(nmpH)₂CuCl₄

Figure 5. Pressure dependence of the energies of the electronic transitions in (nmpH)₂CuCl₄.

Figure 6. (a) Schematic structure of [Cu(dien)(bipyam)]²⁺ (adapted from ref 17) and (b) one-electron levels of [Cu(dien)-(bipyam)]²⁺ in distorted square-pyramidal and distorted trigonal-bipyramidal geometries. From ref 16.

Instead, Figure 2C best applies and we have a situation similar to that of (NbzpipzH₂Cl)₂CuCl₄. Consequently we adopted resolution of the spectra after rearrangement into two components.

We can qualitatively assess the extent of the rearrangement by comparing the high-pressure spectrum of (nmpH)₂CuCl₄ (Figure 8b, ref 7) with the low-pressure spectra of (NbzpipzH₂Cl)₂CuCl₄ (Figure 7a, ref 7). These spectra indicate that the high-pressure configuration of the anion in (nmpH)₂CuCl₄ has a dihedral angle somewhere near 20°. Since the energies of the two transitions in (nmpH)₂CuCl₄ at high pressure (Figure 5) are lower than the corresponding transitions in (NbzpipzH₂Cl)₂CuCl₄ at low pressure, we believe that the high-pressure dihedral angle in (nmpH)₂CuCl₄ is slightly higher than 19°.

If we consider the five tetrachlorocuprate complexes collectively, we have the result that neither regular geometry (tetrahedral or square planar) is the pressure-stabilized configuration of the tetrachlorocuprate ion. Our experiments indicate that all five tetrachlorocuprate complexes seem to progress toward a common pressure-stabilized configuration. This configuration, if ultimately attained at sufficiently high pressures, would possess a dihedral angle of about 25–45° (compared to 0–67.9° at low pressure) and consequently would best be described as a strongly tetrahedrally distorted square plane.

Cu(dien)(bipyam)²⁺

As our second example, we consider the complexes [Cu(dien)(bipyam)]X₂·nH₂O (dien = diethylenetriamine; bipyam = di-2-pyridylamine; X = Cl⁻, n = 2, α_3 = 159.0°; X = ClO₄⁻, n = 1, α_3 = 151.9°; and X = NO₃⁻, n = 0, α_3 = 137.2°).[16] These complexes form a series of cation distortion isomers that represent different points on a structural pathway defined by regular trigonal-bipyramidal (α_3 = 120°) and regular square-pyramidal (α_3 = 165°) geometries.[17] The chloride and

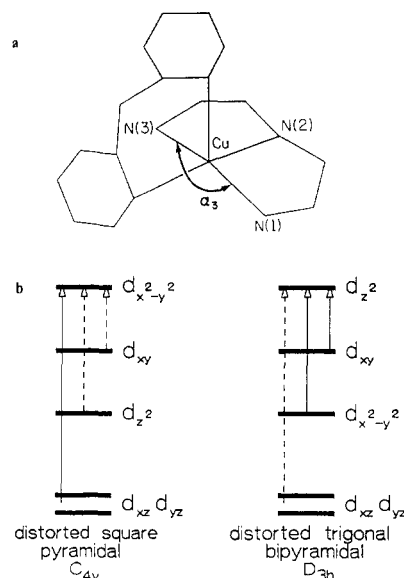perchlorate complexes are best described as distorted square pyramids and the nitrate complex as a distorted trigonal bipyramid. The position of the complexes along the pathway may be characterized by the internal angle α_3 (Figure 6a). The energies of the one-electron levels of the copper(II) ion are a function of α_3.[17] In Figure 6b we show the relative ordering of the one-electron levels in distorted square-pyramidal and distorted trigonal-bipyramidal geometries. We also show whether a given d–d transition is dipole allowed using selection rules based on the symmetry (C_{4v} (square pyramid) or D_{3h} (trigonal bipyramid)) of the corresponding undistorted configuration. Polarized absorption measurements on complexes of geometries similar to those of the three complexes considered here have shown that all three d–d transitions are of nonnegligible intensity.[3] Consequently we adopted resolution of the spectra of all three complexes into three Gaussian components corresponding to the appropriate transitions of Figure 6b.

The pressure dependence of the relative intensities of the three transitions for the chloride and perchlorate complexes (Figure 7) provides the best indicator of the effect of pressure on these two complexes. The high and low intensities of the d$_{xz}$,d$_{yz}$ → d$_{x^2-y^2}$ and d$_{xy}$ → d$_{x^2-y^2}$ transitions in both complexes at low pressure, respectively, are consistent with the dipole selection rules of Figure 6b. The high intensity of the d$_{z^2}$ → d$_{x^2-y^2}$ transition is not. Apparently the intensity of this transition is most sensitive to the distortion from strict C_{4v} symmetry present in the two complexes at low pressure. Two observations are noteworthy: (a) in both complexes, the intensity of the d$_{z^2}$ → d$_{x^2-y^2}$ transition decreases with increasing pressure (Figure 7) relative to the other two transitions, and (b) the intensity of the d$_{z^2}$ → d$_{x^2-y^2}$ transition in the perchlorate complex at low pressure relative to the other two transitions is greater than in the chloride complex. Observation a indicates that with increasing pressure both complexes approach

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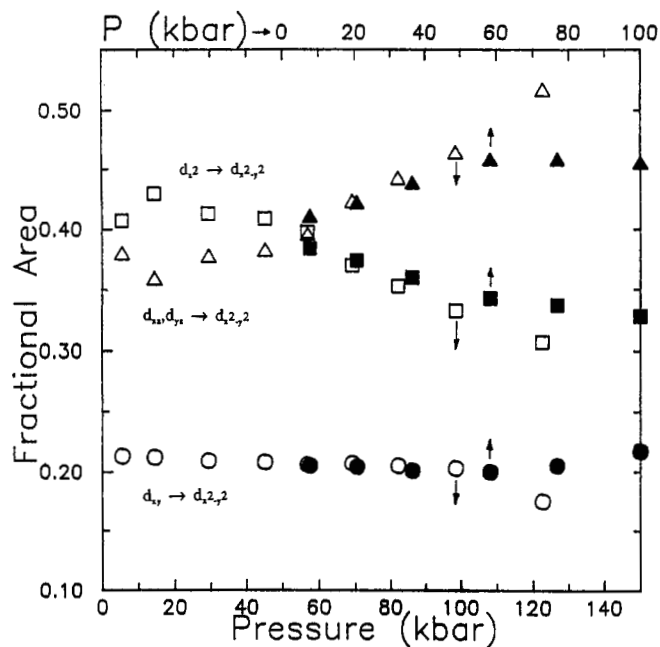
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Figure 7. Pressure dependence of the fractional areas of the electronic transitions in [Cu(dien)(bipyam)](ClO$_4$)$_2$·H$_2$O (open symbols, lower scale) and [Cu(dien)(bipyam)]Cl$_2$·2H$_2$O (filled symbols, upper scale).

Figure 8. Pressure dependence of the fractional areas of the electronic transitions in [Cu(dien)(bipyam)](NO$_3$)$_2$ (open symbols, lower scale) and [Cu(dien)(bipyam)]Cl$_2$·2H$_2$O (filled symbols, upper scale). From ref 16.

a more regular square-pyramidal geometry; i.e., α_3 increases, and both complexes become less distorted with increasing pressure resulting in stricter adherence to C_{4v} selection rules (Figure 6b). Observation b is consistent with the greater distortion from regular square-pyramidal geometry present in the perchlorate complex (smaller α_3) at ambient pressure than in the chloride complex.

Figure 7 also demonstrates another important point. Notice that the intensities seen in the perchlorate complex at approximately 60 kbar (the pressure at which we begin to overlap the data) are similar to those seen in the chloride complex at a much lower pressure. Also, the behavior seen in the perchlorate complex above about 60 kbar is qualitatively the same as that seen in the chloride complex beginning at low pressure. These results indicate that the molecular configuration in the perchlorate complex at about 60 kbar is very similar to that of the chloride complex at ambient pressure and thereby provide supporting evidence for the conclusion that a more regular square-pyramidal geometry is induced in these complexes with increasing pressure.

The remarkable similarity in the behavior of the two complexes beginning at the point of data overlap (Figure 7) indicates that the change in configuration induced in the two complexes by pressure is orderly and follows a well-defined pathway. The energies of corresponding transitions in the two complexes are very similar in the overlapping pressure region as well. The transformation of both complexes to more regular square-pyramidal configurations occurs in a stochastic (continuous) manner.

For [Cu(dien)(bipyam)](NO$_3$)$_2$, a distinct increase in the intensity of the high-energy transition and simultaneous decrease in the intensity of the low-energy transition are observed upon compression. The changes observed in the electronic spectrum are due to a rearrangement of the nitrate complex from a distorted
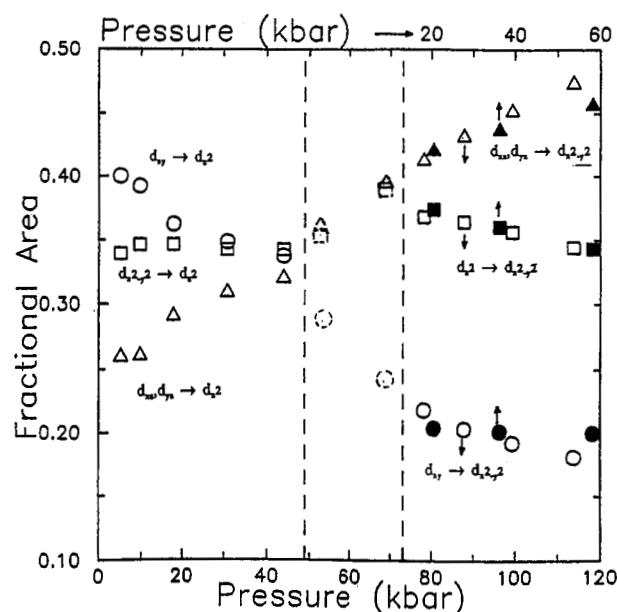
trigonal-bipyramidal geometry ($\sim D_{3h}$) at low pressure to a distorted square-pyramidal ($\sim C_{4v}$) geometry at high pressure. The variation in approximate symmetry associated with the rearrangement is responsible for a modification of electronic selection rules consistent with the intensity changes observed in the nitrate complex upon compression.

Figure 8 shows the pressure dependence of the fractional areas of the three transitions in the nitrate complex and compares them with the data obtained for the chloride complex. The vertical dashed lines define the primary region over which the rearrangement of the nitrate complex, including the change in ground state, occurs. The rearrangement indicated by the vertical dashed lines is another example of a change in configuration that is neither purely stochastic nor cooperative. Figure 8 indicates that immediately after rearrangement (78 kbar) the configuration of the nitrate complex is similar to that of the chloride complex at approximately 20–30 kbar. Comparison with Figure 7 shows that this configuration is also similar to that of the perchlorate complex at about 70 kbar. The similarity seen for the nitrate and chloride complexes in the data overlap region suggests a further and primarily stochastic transformation of the nitrate complex to a more regular square-pyramidal configuration. The progress of the transformation after rearrangement is much like that observed in the chloride and perchlorate complexes, suggesting that all three complexes proceed along the same pathway toward a regular square-pyramidal geometry. Finally, the three complexes possess configurations that are more similar at high than at low pressure.

Cu(dieten)$_2^{2+}$

As a final example, we consider the complex [Cu(dieten)$_2$](BF$_4$)$_2$ (dieten = N,N'-diethylethylenediamine).[18] At ambient pressure, the symmetry about

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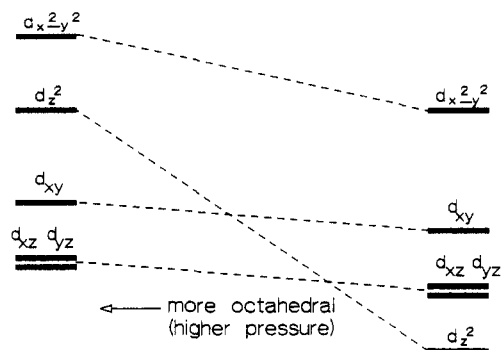
Figure 9. Splitting of the one-electron energy levels of the Cu^{2+} cation in D_{4h} symmetry. Reprinted with permission from ref 18. Copyright 1989 American Chemical Society.
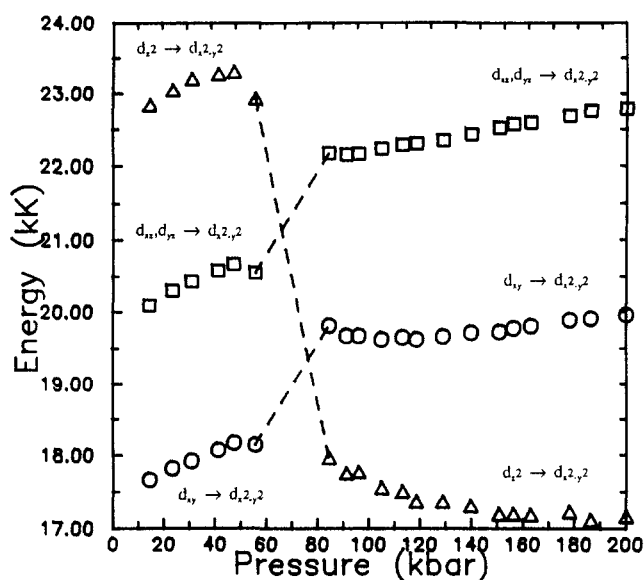
$Cu(dieten)_2(BF_4)_2$
(polycrystalline)

Figure 10. Pressure dependence of the energies of the electronic transitions in $[Cu(dieten)_2](BF_4)_2$. From ref 18.

the copper ion in this complex is square planar with no significant axial interaction between the anions and the copper center. The anions are more than 3 Å away from the copper center, positioned in symmetric positions above and below the molecular CuN_4 plane near ethyl groups of the chelate ligands and consequently displaced from the normal to the CuN_4 plane. The two ethyl groups in one of the chelate ligands extend above the CuN_4 plane, and the two ethyl groups of the other chelate ligand extend below this plane.[19] The one-electron levels applicable to the ambient- and low-pressure configurations are shown on the right side of Figure 9. The $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions are of comparable intensity and are about twice as intense as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition.[20] These intensities remain essentially constant with pressure.

The energies of the transitions (Figure 10), however, are affected dramatically by pressure. The striking changes seen in the transition energies are due to a molecular rearrangement induced in the complex by

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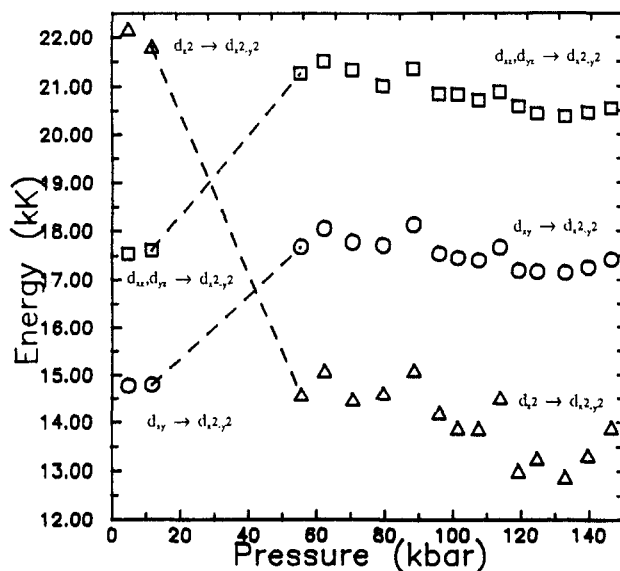
$Cu(dieten)_2(BF_4)_2$ in 2VYPY

Figure 11. Pressure dependence of the energies of the electronic transitions in $[Cu(dieten)_2](BF_4)_2$ in a poly(2-vinylpyridine) environment. From ref 18.

pressure, and this involves a marked increase in the axial interaction between the anions and copper center. The complex transforms from a square-planar (highly octahedrally distorted) configuration at low pressure to an elongated octahedral (moderately octahedrally distorted) configuration at high pressure. Pressure has induced progress of the complex along a structural pathway connecting elongated and compressed octahedral geometries.[21] The energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is a measure of the distortion present in these complexes.[20] The higher the energy of this transition, the greater the octahedral distortion. The dramatic red shift observed for this transition is due to the increased out-of-plane covalent interaction between the anions and the copper d_{z^2} orbital which occurs upon rearrangement to a less distorted octahedral configuration. The increase in this covalent interaction leads to an increase in the energy of the d_{z^2} level relative to the $d_{x^2-y^2}$ level (Figure 9) and hence to a decrease in the energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The abrupt nature of the rearrangement in the complex suggests a process that possesses a high extent of cooperativity.

We were also interested in the effect of the solid-state environment on the rearrangement of $[Cu(dieten)_2](BF_4)_2$. We examined the effect of pressure on the complex dissolved in poly(2-vinylpyridine). A low concentration of the complex was used in order to minimize complex–complex interactions. The complex is essentially isolated in the polymer as ion triples. In this way the effect of a non-ionic solid-state environment on the rearrangement could be explored. The resolved spectrum of the dissolved complex at low pressure is similar to that of the polycrystalline complex at low pressure. We report the pressure dependence of the transition energies in the polymer in Figure 11, which shows that the rearrangement described for the polycrystalline complex occurs in the complex when

(21) Gazo, J.; Bersuker, I. B.; Garaj, J.; Kabesova, M.; Kohout, J.; Langfelderova, H.; Melnik, M.; Serator, M.; Valach, F. *Coord. Chem. Rev.* 1976, *19*, 253.

dissolved in the polymer. Three differences are observed in the polymer: the rearrangement (1) starts at a lower pressure, (2) extends over a much larger pressure range, and (3) is complete at a lower pressure. The rearrangement is essentially cooperative for the polycrystalline material, and it is more nearly stochastic for the complex dissolved in the polymer. This study shows the potential for tuning the extent of cooperativity of molecular rearrangements by altering characteristics of the solid-state environment.

Conclusion

While the examples here all involve complexes of Cu(II), the mechanisms discussed in the introduction should apply much more generally to solid-state reactions including geometrical changes in complexes involving other metals, e.g., Ni(II) or Co(II), in metal cluster compounds, and to geometrical changes (e.g., cis–trans or keto–enol) in organic molecules in the solid state.