(Table I) seem to be too large; calculated amplitudes for the corresponding distances in C_3O_2 are 0.038 and 0.043 Å, respectively.[41] If they bear any reality and are not merely results of parameter correlation, the large values might indicate some propensity for dissociation. Cl_2CCO decomposes at lower temperatures[28] than ketene itself. l(SP) of Cl_2CCO should be treated with caution, too, because of the small number of available experimental frequencies.[7] Our l(SP) for Cl4$\cdots$Cl5, e.g., is too small compared to the calculated value 0.0691 Å in Cl_2CO.[31b]

The parameters of Cl_3CCOCl fit well the trends observed[13] in the series of chlorosubstituted acetyl chlorides (Table IV): the C—C bond lengthens and the Cl—CO bond and the carbon–chlorine bonds on the average shorten as the number of chlorine substituents increases from acetyl chloride to its trichloro derivative. The bond angle C—C═O decreases in the same series.

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Registry No. Cl_3CCOCl, 76-02-8; Cl_2CCO, 4591-28-0.

Supplementary Material Available: Tables of total experimental electron diffraction intensities (2 pages). Ordering information is given on any current masthead page.

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Piezochromism: Pressure-Induced Rearrangements of Thermochromic and Related Cu(II) Complexes Containing Asymmetrically Substituted Ethylenediamine

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Abstract: The effects of high pressure on the thermochromic and related complexes $[CuL_2]X_2$ [L = *N,N*-diethylethylenediamine (dieten), X = BF_4^-, ClO_4^-, Cl^-; L = *N,N*-dimethylethylenediamine (dimeen), X = BF_4^-; L = ethylenediamine (en), X = BF_4^-] are described. Electronic and infrared spectroscopies indicate an increase in the interaction between anion and molecular CuN_4 plane of all complexes with increasing pressure. For both the electronic and infrared spectra, the similarity between the high-pressure spectra of the dieten complexes and the low-pressure spectra of the en and dimeen complexes indicates that the former transform to a geometry similar to that of the latter with pressure. A color change is associated with the transformation. The short pressure range over which the rearrangement occurs in the crystal indicates that it is a highly cooperative process. Studies of some of the complexes in polymeric environments [sodium polystyrenesulfonate and/or poly(2-vinylpyridine)] show that the rearrangement occurs at lower pressure and is much less cooperative in the polymers.

Many of the complexes $[Cu(dieten)_2]X_2$, where X is an anion and dieten is *N,N*-diethylethylenediamine, exhibit interesting behavior with temperature and have been the subject of a number of physical investigations.[3-8] When X is BF_4^-, ClO_4^-, or NO_3^- the complex exhibits a dramatic color change from a red low-temperature form to a blue form at a well-defined higher temperature.[4,9] This thermochromic behavior was originally attributed by Lever et al.[4] to a temperature-dependent axial interaction between the anion and the CuN_4 plane and later was demonstrated to be due to a weakening of the in-plane ligand field strength as a result of the onset of dynamic disorder of the chelate rings as the temperature is raised.[7,8]

Ferraro et al.[5] studied the effect of pressure (0–48 kbar) on the infrared and electronic band maximum of these complexes and concluded that no significant change in axial interaction occurs with increasing pressure. These workers argue that the primary effect of pressure is to contract the in-plane copper–nitrogen distances, thereby minimizing the axial interaction causing no color change.

In this paper we investigate the effect of pressure to 150–200 kbar on the electronic and infrared spectra of the complexes $[CuL_2]X_2$ [L = *N,N*-diethylethylenediamine (dieten), X = BF_4^-, ClO_4^-, and Cl^-; L = *N,N*-dimethylethylenediamine (dimeen), X = BF_4^-; L = ethylenediamine (en), X = BF_4^-). Gaussian resolution of the electronic spectra are reported. In addition to the polycrystalline studies, the electronic spectra of some of the complexes were studied as dopants in a sodium polystyrenesulfonate (L = dieten, X = BF_4^-, ClO_4^-) or poly(2-vinylpyridine) (L = dieten, X = Cl^-, BF_4^-) environment.

Experimental Procedure

Sample Preparation. The ligands en, dimeen, and dieten were obtained from Aldrich and used without further treatment. The en complexes were prepared by the method of Procter,[10] while the dimeen and dieten

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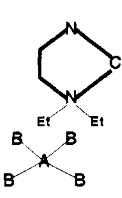

Figure 1. Schematic structure of $[Cu(dieten)_2](AB_4)_2$.

complexes were prepared by the method of Pfeiffer and Glaser.[9] The en complexes were recrystallized from methanol, while the dimeen and dieten complexes were recrystallized from methanol–ethanol mixtures. Satisfactory elemental analysis was obtained for each complex.

Polymeric samples containing doped complexes (3.5 mol % based on the monomer) were prepared by dissolving both the complex and polymer in an appropriate solvent followed by spin coating of the solution on glass plates to form films upon solvent evaporation. Water and ethanol were used as solvents for samples doped in sodium polystyrenesulfonate and poly(2-vinylpyridine), respectively.

Physical Measurements. The electronic spectra ($8-25 \times 10^3$ cm^{-1}) of all samples were recorded as absorption spectra. Polycrystalline spectra were recorded as Nujol mulls, and polymeric samples were used neat. The samples were illuminated by light from a 100-W tungsten–halogen lamp (powered by an Oriel 6329 ac power supply) passing through a Kratos GM252 monochromator ($^1/_4$ m) equipped with a 450 [$(13-25) \times 10^3$ cm^{-1}] or 1000 [$(8-13) \times 10^3$ cm^{-1}] blaze diffraction grating. The light passing through the sample was detected by an EMI 9558QA [$(13-25) \times 10^3$ cm^{-1}] or 9684QB [$(8-13) \times 10^3$ cm^{-1}] photomultiplier tube which was connected to an Ortec photon-counting system. Details of the optical equipment may be found elsewhere.[11] The data was extracted point by point without varying the monochromator slit widths. Gaussian resolution of the electronic spectra was accomplished by a nonlinear least-squares curve-fitting algorithm.

The infrared spectra (polycrystalline samples only) were recorded as Nujol mulls in the range 4000–700 cm^{-1} with a Nicolet 7199 FTIR.

Results and Discussion

Polycrystalline Studies. Electronic Spectra. Crystallographic data are available for some of the complexes[7,12] and for some similar complexes.[13-16] These data show that the complexes $[CuL_2]X_2$ adopt an elongated tetragonal octahedral configuration with an approximately planar $Cu-N_4$ arrangement and the anions occupying symmetric sites above and below the molecular CuN_4 plane. When L = en, the nearest out-of-plane anion atoms lie directly on the perpendicular to the CuN_4 passing through the copper cation. To our knowledge no structures for L = dimeen complexes have been reported. The structure of $[Cu(dieten)_2](ClO_4)_2$ (shown schematically in Figure 1) indicates perchlorate anions which lie off of this perpendicular. The oxygens closest to the copper center are nearly 2 Å off the perpendicular.[16] In the course of our studies we performed a powder XRD on $[Cu(dieten)_2](BF_4)_2$ which showed that this complex is isostructural to the perchlorate analogue (Figure 1). The ethylene linkages (regardless of L) adopt a symmetrical-skew gauche configuration in which one carbon is above and the other below the molecular plane. Although the strict molecular symmetry of these complexes is C_i, ESR and polarized electronic spectra suggest that the tetragonal distortion present overrides the strict ligand field symmetry and that an approximate D_{4h} symmetry is suitable.[10,17-19] The splittings of the one-electron energy levels of the copper(II) ion in D_{4h} symmetry as a function of tetragonal distortion are shown in Figure 2.[19] If the small differences in the in-plane copper–nitrogen bond lengths are taken into account, the symmetry of the CuN_4 plane is D_{2h}. The primary effect of lowering the symmetry from D_{4h} to D_{2h} is to remove the degeneracy shown for the d_{xz} and d_{yz} levels. Since this splitting is expected to be small[10] and for the reasons cited above, we shall analyze the electronic spectra on the basis of D_{4h} molecular symmetry.

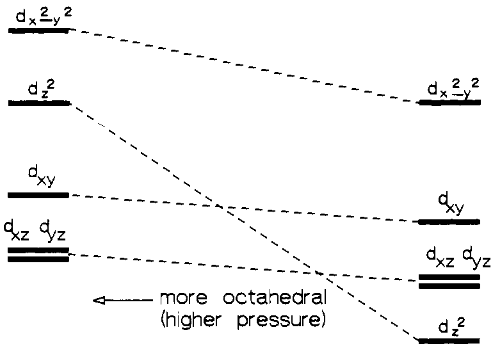

Figure 2. Splitting of the one-electron energy levels of the d^9 Cu^{2+} cation in D_{4h} symmetry.

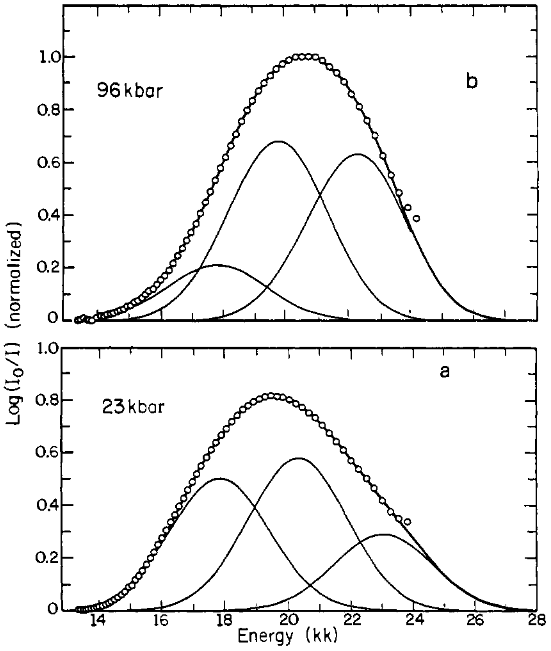

Figure 3. Resolved electronic absorption spectrum of polycrystalline $[Cu(dieten)_2](BF_4)_2$ at (a) 23 kbar and (b) 96 kbar.

In D_{4h} symmetry three electronic transitions are predicted for the d^9 Cu^{2+} cation (Figure 2). Based on polarized single-crystal electronic studies of copper–ethylenediamine complexes[15,17] the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition appears as a low-intensity band and the remaining transitions, with the $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ transition higher in energy than the $d_{xy} \rightarrow d_{x^2-y^2}$ transition (Figure 2), as similarly more intense bands. These results are consistent with the results we obtained when resolving the electronic spectra of the complexes studied into Gaussian components. At all pressures [except those during which we believe a molecular rearrangement occurs in the dieten complexes (vide infra)] it was mandatory, for all of the complexes, to resolve the electronic spectrum into two high-intensity components and one low-intensity component. It was not possible to obtain a fit to the data otherwise.

Representative resolved electronic spectra at low and high pressure for $[Cu(dieten)_2](BF_4)_2$ are shown in Figure 3. It is important to note that it was not possible to obtain acceptable

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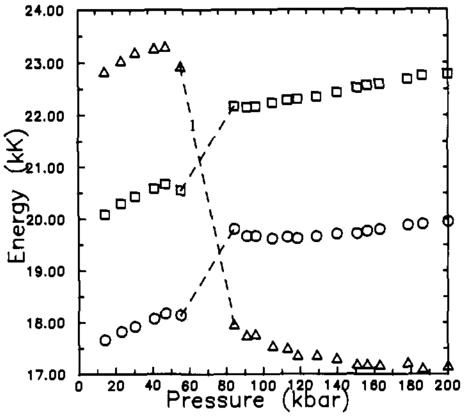

Figure 4. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions in polycrystalline [Cu(dieten)$_2$](BF$_4$)$_2$.

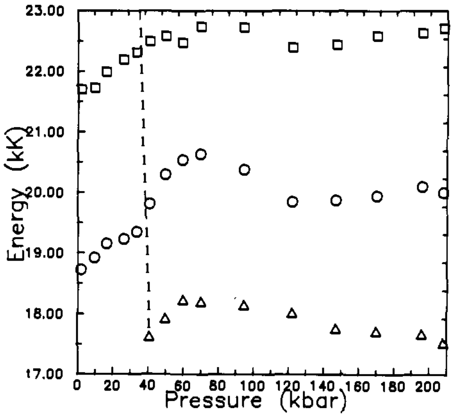

Figure 5. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions in polycrystalline [Cu(dieten)$_2$](ClO$_4$)$_2$.

Gaussian fits at low pressure by fitting the spectra with a low-intensity band at low energy. Only by placing a low-intensity band at high energy were successful fits obtained. This is qualitatively consistent with the shape of the envelope at low energy. At low pressure (e.g., Figure 3a) the initial rise of the curve at low energy is much steeper than the corresponding rise at high pressure (e.g., Figure 3b), indicating the presence of a lowest energy band at low pressure that is significantly more intense than the lowest energy band at high pressure. On the other hand, it was essential at high pressure to have a low-intensity band at low energy and to have the two highest energy bands of high intensity to obtain a fit to the data. A similar series of resolved spectra was observed for [Cu(dieten)$_2$]Cl$_2$. The high-pressure electronic spectra for the dieten complexes very much resemble the low-pressure spectra of the en and dimeen complexes, as demonstrated later in the paper.

For [Cu(dieten)$_2$](ClO$_4$)$_2$, it was not possible to clearly resolve the low-intensity high-energy $d_{z^2} \rightarrow d_{x^2-y^2}$ band at low pressure because of the presence of a high-intensity high-energy charge-transfer band. This band is present in all complexes studied, but only in the case of [Cu(dieten)$_2$](ClO$_4$)$_2$ at low pressure does the charge-transfer band sufficiently interfere with the ligand field bands to affect Gaussian spectral resolution. Unsuccessful attempts were made to fit the low-pressure [Cu(dieten)$_2$](ClO$_4$)$_2$ spectra with a low-intensity ligand field band at low energy, suggesting that this band occurs at high energy at low pressure. Above ~40 kbar we found that it was not possible to obtain acceptable fits without including the low intensity $d_{z^2} \rightarrow d_{x^2-y^2}$ band at low energy, suggesting that a dramatic red shift of this band occurs in the vicinity of 40 kbar similar to what we observed in the other dieten complexes (vide infra).

In Figures 4–6 we show the pressure dependence of the electronic transition energies obtained by Gaussian resolution of the electronic spectra of the three dieten complexes. The most striking feature observed is a dramatic red shift in the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition energy over a rather small pressure range for all three dieten complexes. Significant blue shifts are seen in the energies of the $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$, and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions over the same pressure range. The regions in the electronic energy plots indicated by the dashed lines represent pressures over which the significant changes in component band energies described above occur. As discussed later, we believe the shifts are a consequence of a molecular rearrangement in the dieten complexes. The pressures subtended by the dashed lines represent situations in which two equilibrium molecular configurations are present (in varying proportions), and consequently, the recorded electronic spectra represent superpositions of the spectra from two distinct molecular configurations: low- and high-pressure forms. The spectra obtained at the pressures indicated by the dashed lines should in reality be fit with six bands. Aside from purely computational complications, a six-band resolution is not particularly meaningful since the relative amounts of each molecular configuration over this pressure range are unknown. Consequently, we do not report band positions for the rearrangement pressure range, but rather we use dashed lines to denote the transformation from one molecular configuration to the other.

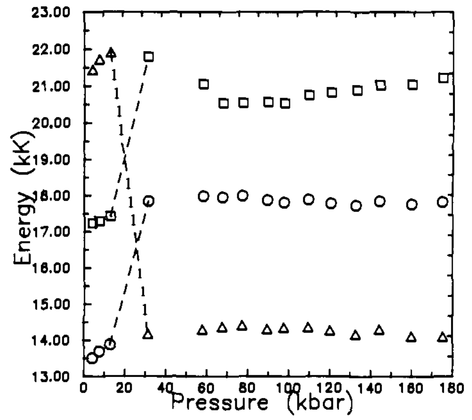

Figure 6. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions in polycrystalline [Cu(dieten)$_2$]Cl$_2$.

The energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is a measure of the tetragonal distortion present in these complexes.[17] The higher this energy, the greater is the distance between the anion and molecular plane. Thus, our resolved spectra indicate that at atmospheric pressure the three dieten complexes are highly distorted. This observation is consistent with X-ray data available for [Cu(dieten)$_2$](ClO$_4$)$_2$[7,16] which shows a Cu–O distance of 3.65 Å.

The dramatic red shift observed in the energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition in the three dieten complexes suggests the occurrence of a molecular rearrangement in these complexes in which a marked decrease in the anion–molecular plane distance results from application of pressure. An increased out-of-plane covalent interaction between the anion and the copper d_{z^2} orbital occurs simultaneously with a decreased distortion. It is this increased interaction that leads to an increase in the energy of the d_{z^2} level relative to the $d_{x^2-y^2}$ level (Figure 2) and hence to a decrease in the energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition.

Supporting evidence for a rearrangement involving a decrease in the anion–cation distance is found in our studies of [Cu(en)$_2$](BF$_4$)$_2$ and [Cu(dimeen)$_2$](BF$_4$)$_2$. Resolved electronic spectra at low pressure for these two complexes are shown in Figure 7. The bandwidths resulting upon spectral resolution are similar to those of the three dieten complexes. The high-pressure (100+ kbar) spectra of the en and dimeen complexes are nearly identical with the 96-kbar spectrum of the dieten complex (Figure 3b). It is clear from Figure 7 that in both complexes the low-intensity $d_{z^2} \rightarrow d_{x^2-y^2}$ transition occurs at low energy; that is, these spectra at low pressure resemble the spectra of the rearranged dieten complexes. Since the primary difference between the en

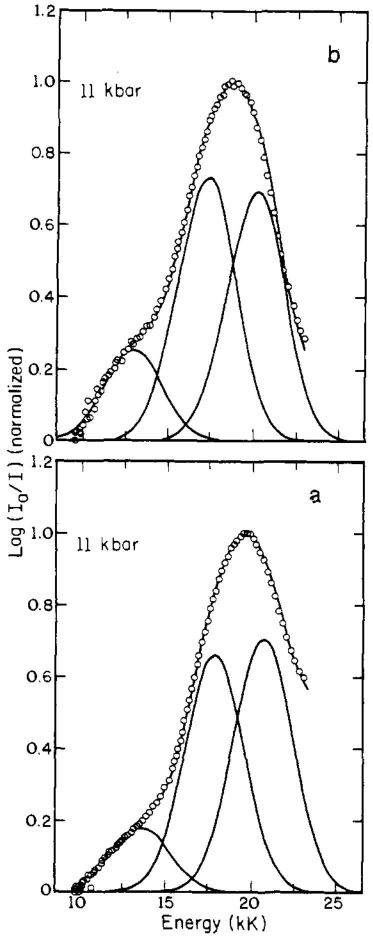

Figure 7. Resolved electronic spectrum of (a) $[Cu(en)_2](BF_4)_2$ and (b) $[Cu(dimeen)_2](BF_4)_2$ at 11 kbar.

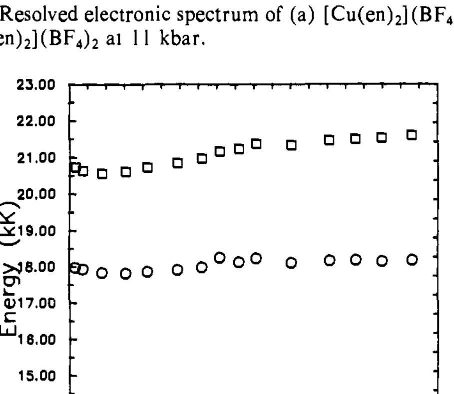

Figure 8. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions in polycrystalline $[Cu(en)_2](BF_4)_2$.

and dimeen complexes and the corresponding dieten complex is the cation–anion distance [the Cu–F distance is $[Cu(en)_2](BF_4)_2$ is known to be 2.56 Å,[12] and although the corresponding distance in $[Cu(dimeen)_2](BF_4)_2$ is unknown, it is expected to be much less than that in the dieten analogue due to significant steric differences between methyl and ethyl substituents], these studies suggest that an important part of the molecular rearrangement that occurs in the three dieten complexes is a decrease in the cation–anion distance. No molecular rearrangement is suggested by the resolved electronic spectra of $[Cu(en)_2](BF_4)_2$ and $[Cu(dimeen)_2](BF_4)_2$ upon application of pressure (Figures 8 and 9).

In the pressure region of the dieten complexes below the rearrangement (Figures 4–6), there is a distinct shift to higher energy of the ligand field bands with pressure. This is undoubtedly due

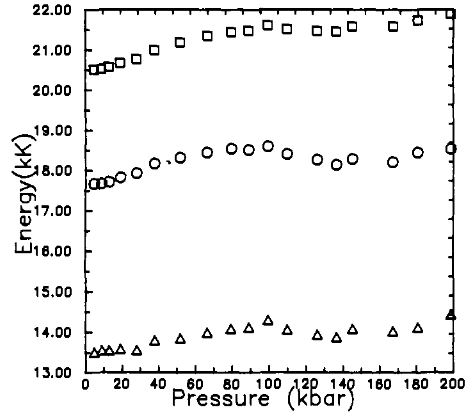

Figure 9. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions in polycrystalline $[Cu(dimeen)_2](BF_4)_2$.

to an increase of the ligand field strength resulting primarily from compression of the in-plane Cu–N bonds. The effect of compression on ligand field splitting has been thoroughly documented.[20] After rearrangement there are only modest changes in component band energy with pressure. The behavior is very much similar to that observed for the en and dimeen complexes at all pressures (Figures 8 and 9). X-ray measurements at ambient pressure for a variety of axial (out-of-plane) groups have demonstrated that as the axial group–copper distance decreases below ~3.1 Å there is a distinct tendency for the Cu–N distance to increase,[21] which indicates a significant electronic interaction. At the higher pressures this expansion of the Cu–N distance due to a decrease of the axial group–copper distance with pressure apparently roughly balances the direct compression effect on the Cu–N bond. Also, at low pressure the axial electronic interaction is not strong enough (due to the sufficiently large anion–cation distance) to cause a red shift of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition energy upon increasing pressure. Only upon molecular rearrangement is the interaction increased sufficiently to observe the red shift.

Our analysis differs from that of Ferraro et al.,[5] who examined the electronic spectra (0–48 kbar) of $[Cu(dieten)_2]X_2$ ($X = ClO_4^-$, BF_4^-, NO_3^-). These authors report shift data only for the maximum of the electronic absorption spectrum. In their study they observe no color change for the complexes and conclude that the anion–cation interaction is not increased upon application of pressure up to 48 kbar. Our studies over a much larger pressure range show that the resolved electronic spectra (not simply the d–d envelope maximum) are important in detecting a significant increase in the anion–cation interaction. (Later we present infrared data consistent with such an increase prior to rearrangement.) We observed color changes in the three dieten complexes we studied (anion, color before rearrangement, color after rearrangement): Cl^-, blue, purple; ClO_4^-, red, orange; BF_4^-, red, orange-yellow. The effects observed in the five complexes of this study were reversible upon release of pressure.

Molecular rearrangements in the gas phase or in (dilute) solution are stochastic processes, i.e., the probability of a given molecule rearranging at some temperature and pressure depends only on the free energy difference between the two molecular geometries. As a limiting case, in a perfect crystal where the molecules are strongly interacting, all molecules must rearrange simultaneously. This is a totally cooperative process—a first-order phase transition. If the molecules interact only weakly in the crystal, the probability of a given molecule rearranging if its neighbor rearranges may be less than one but greater than that predicted by the free energy difference between structures. Grain

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boundaries, surfaces, and other crystal defects may contribute to this situation. We use the phrase "extent of cooperativity" to describe the situation lying between the stochastic and first-order extremes. We regard this aspect as one of the more interesting possibilities of solid-state chemistry.

A related description is that in the gas phase there is no cooperativity, in ordinary liquids there is highly localized (nearest neighbor) cooperativity, while in a crystal of strongly interacting molecules the cooperativity is macroscopic. In very viscous liquids, polymers, glasses, or weakly bound molecular crystals, the extent of cooperativity may be anywhere between the nearest neighbor limit and the macroscopic limit.

It should be noted that in the situation where there is significant molecular interaction in the crystal a molecule may rearrange to a structure that would not be the lowest free energy of the "free molecule" at a given temperature and pressure provided that this rearrangement allows the assembly of molecules to assume a configuration that sufficiently lowers the free energy of the crystal.

A further aspect is that the driving force for pressure-induced molecular rearrangements in solids is as likely to be differences between the configurations with respect to intermolecular forces and packing as it is to be associated with changes of bond length within the molecule. This aspect has implications also for pressure-induced rearrangements in solution, where differences between molecular configurations (isomers) in polarizability, dipole moment, and in degree and kind of solvation may frequently dominate over purely intramolecular considerations, both with regard to chemical equilibrium and reaction rates.

It is interesting to note that the molecular rearrangement in each of the three dieten complexes occurs over a small pressure range, suggesting a high extent of cooperativity. This is in contrast to the results obtained in the polymeric environment studies (vide infra). The data indicate that the degree of cooperativity in the dieten complexes increases in the order $Cl^- < ClO_4^- < BF_4^-$. This is reasonable given that the pressure range over which the molecular rearrangement occurs increases in the same order. Assuming the three complexes are of similar compressibility, at higher pressure the lattice is more compressed and stiffer (higher bulk modulus); thus, it is more difficult for the molecules to undergo independent internal rearrangements.

Infrared Spectra. The infrared spectra of the complexes studied were measured up to 120 kbar. The anion–copper cation distance in $[Cu(dieten)_2](ClO_4)_2$ is large (3.65 Å) at ambient pressure, and only minor structural deviations of the perchlorate anion from free ion T_d symmetry are observed.[7,16] Based on the XRD obtained in the course of this work, a similar situation is expected for $[Cu(dieten)_2](BF_4)_2$. It is therefore not surprising that at ambient pressure the infrared spectra of the anions in these two complexes resemble those of the free anions. Hatfield et al.[22] reached a similar conclusion in their studies of the perchlorate complex.

An increase in the anion–copper cation interaction, as indicated by the electronic study, when we raise the pressure should lead to a breakdown of the original near T_d symmetry of the anions in $[Cu(dieten)_2]X_2$ ($X = ClO_4^-, BF_4^-$). An increased copper–oxygen (copper–fluorine) interaction is expected to increase the bond length of the interacting oxygen (fluorine) and chlorine (boron) atoms in the anion. The other three Cl–O (B–F) bond lengths are not expected to be significantly affected. Thus, an increased anion–cation interaction is expected to lower the anion symmetry to C_{3v}.[23] This reduction of symmetry results in a splitting of the degenerate modes ν_3 and ν_4 of the free anion, with the previously forbidden ν_1 and ν_2 modes becoming infrared allowed.[23] The ν_2 and ν_4 modes are found at energies below our lower detection limit (700 cm^{-1}) and the ν_3 mode appears in a region where strong in-plane ligand absorption is normally found. Thus, the totally symmetric mode ν_1, appearing in less complicated regions of the spectrum, is expected to be the most informative direct infrared probe of the anion–copper cation interaction.

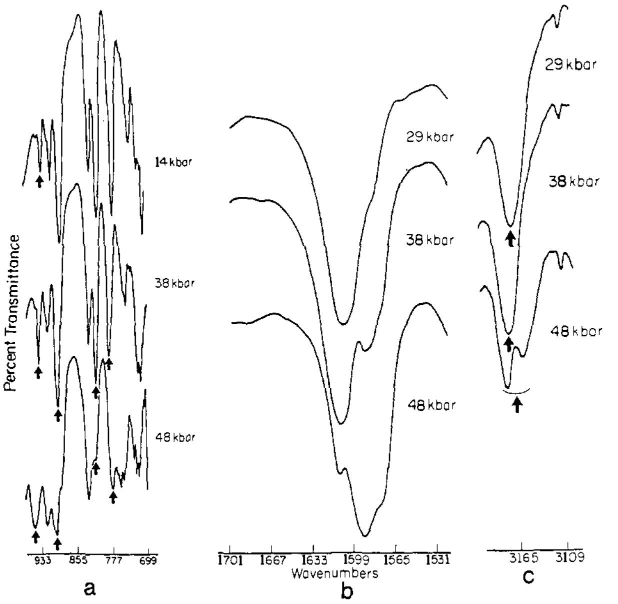

Figure 10. Infrared spectrum of polycrystalline $[Cu(dieten)_2](ClO_4)_2$: (a) 700–950 cm^{-1}, (b) 1530–1700 cm^{-1}, and (c) 3100–3200 cm^{-1}.

The ν_1 mode in ClO_4^- has been assigned in several perchlorate complexes[24,25] and is expected to appear at ~930 cm^{-1}. At low pressure this mode appears as a weak band at 935 cm^{-1} in $[Cu(dieten)_2](ClO_4)_2$ (Figure 10a). Upon application of pressure the $\nu_1(ClO_4^-)$ mode gains considerable intensity up to ~38 kbar, at which point its intensity remains essentially constant up to 120 kbar. The observed intensity increase is consistent with the symmetry change anticipated above for the perchlorate anion upon increased interaction with the copper cation.

Supporting infrared evidence for a decreased anion–copper cation distance is found in the NH_2 scissoring mode at 1600 cm^{-1} (Figure 10b). Initially this band appears as a single sharp, strong peak consistent with little or no out-of-plane interaction.[26] At 38 kbar the band is split into two components (1609 and 1588 cm^{-1}), indicating an increased interaction between the perchlorate anions and the molecular plane.[26]

The electronic absorption spectrum study of $[Cu(dieten)_2](ClO_4)_2$ indicates that a cooperative rearrangement occurs over a small pressure range near 40 kbar; it is interesting to examine how the infrared spectrum changes as the pressure is raised above 40 kbar. Figure 10 shows the infrared spectra of $[Cu(dieten)_2](ClO_4)_2$ as we pass through the rearrangement pressure range (approximately 38–48 kbar). Several changes are noteworthy: (1) the $\nu_1(ClO_4^-)$ mode appearing at 937 cm^{-1} broadens considerably and shifts blue ~15 cm^{-1}. The blue shift over the rearrangement pressure range is roughly twice that observed in the first 38 kbar; (2) the bands near 900, 810, and 780 cm^{-1} (Figure 10a) are drastically reduced in intensity. The IR spectra in this region at lower and higher pressure than those shown resemble the spectra at 29 and 48 kbar, respectively; only minor changes outside the rearrangement pressure range were observed. Since the infrared spectrum of $[Cu(en)_2](ClO_4)_2$ shows no bands between 889 and 705 cm^{-1},[24] the bands at 810 and 785 cm^{-1} are most likely associated with ethyl substitution of the chelate ring. The band at 900 cm^{-1} at 38 kbar is present at 887 cm^{-1} at ambient pressure and consequently is assigned as a chelate band.[24] The dramatic intensity loss of the three bands therefore suggests that the molecular rearrangement that takes place involves a repositioning and/or reorientation of the ethyl groups and chelate rings; (3) additional broadening and splitting of the NH_2 band near 1600 cm^{-1} develops between 38 and 48 kbar (Figure 10b); and (4)

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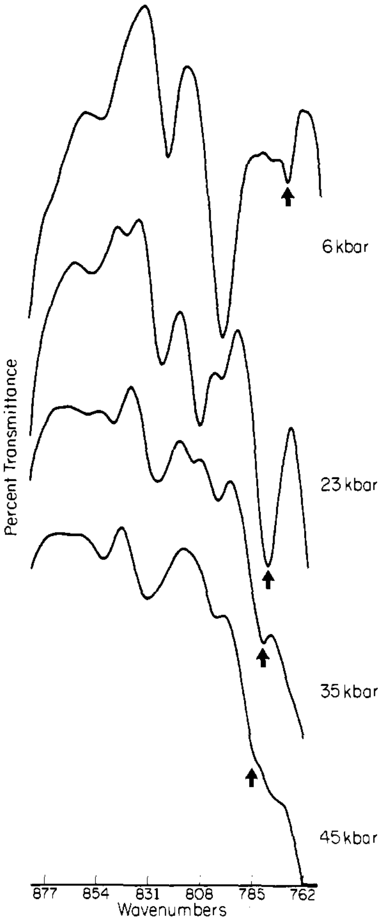

Figure 11. Infrared spectrum (760–860 cm^{-1}) of polycrystalline [Cu(dieten)$_2$](BF$_4$)$_2$ at different pressures.

considerable splitting develops in the 3200–3400 cm^{-1} region, with a new band appearing at 3250 cm^{-1} (not shown). Two bands originally at 3250 and 3310 cm^{-1} (not shown) have each shifted blue roughly 30 cm^{-1} between 38 and 48 kbar. This shift is double that observed in the first 38 kbar. Also, the band (originally unsplit) near 3170 cm^{-1} (Figure 10c) at 38 kbar is split into two components and is much less intense at 48 kbar. Since this region of the spectrum is the C–H and N–H stretching region, these changes support the proposed participation of the ethyl groups and chelate rings in the cooperative rearrangement. Much less dramatic changes were seen in this region of the IR spectrum outside of the rearrangement pressure range.

The pressure-dependent behavior of the ν_1(BF$_4^-$) mode is less informative due to interference by chelate bands. The ν_1(BF$_4^-$) mode is expected[10] to appear at ~770 cm^{-1} and is found at 769 cm^{-1} at atmospheric pressure in our study. Upon application of pressure the band gains considerable intensity (Figure 11). It is, however, not possible to monitor its intensity above ~35 kbar due to interference from bands originally at lower energy that move blue and broaden to obstruct it. The ν_1(BF$_4^-$) band between 35 and 70 kbar is detectable as a high-energy shoulder on a broad band, and although it is difficult to determine its exact intensity, the shoulder becomes more intense with increasing pressure. Above 70 kbar it is no longer possible to detect the shoulder due to broadening of the entire band. The broadening effects mentioned above also preclude analysis of lower intensity bands, originally present near 800 cm^{-1}, believed to be due to the ethyl groups. These bands, absent in the infrared spectrum of [Cu(en)$_2$](BF$_4$)$_2$, are observable at low pressure but are obscured before the rearrangement pressure of the complex is reached.

Also obscured before rearrangement is the band at ~3170 cm^{-1}. At low pressure, analogous to the perchlorate complex discussed above, the band is not split. Due to the higher rearrangement pressure in [Cu(dieten)$_2$](BF$_4$)$_2$, however, the band is masked before rearrangement by Nujol bands which shift blue.

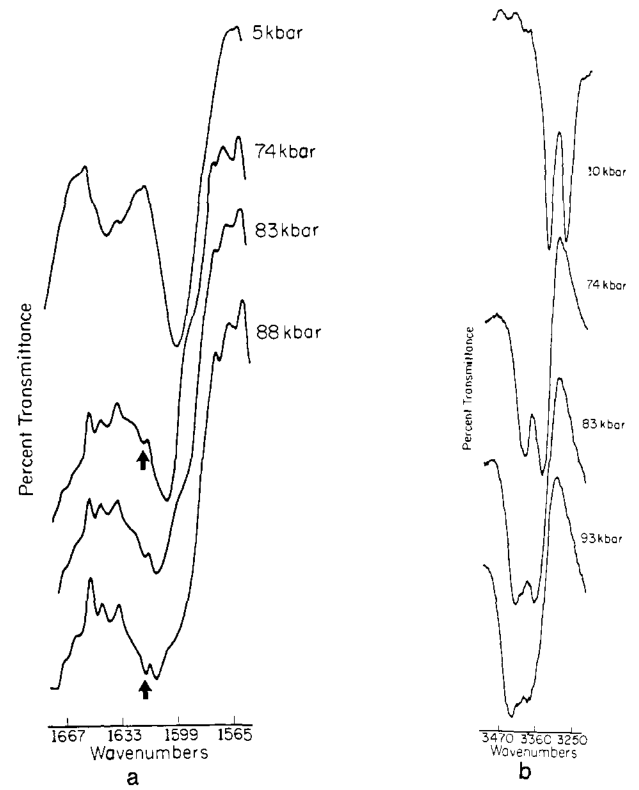

Figure 12. Infrared spectrum of polycrystalline [Cu(dieten)$_2$](BF$_4$)$_2$ at different pressures: (a) 1560–1700 cm^{-1} and (b) 3200–3500 cm^{-1}.

At atmospheric pressure the NH$_2$ scissoring mode in [Cu(dieten)$_2$](BF$_4$)$_2$ appears as a medium-intensity unsplit band at 1600 cm^{-1} (Figure 12a). At 74 kbar the band has shifted blue slightly (7 cm^{-1}) and is still unsplit. Between 74 and 83 kbar the band exhibits considerable broadening and a second component of comparable intensity develops. The two components are located at 1620 and 1613 cm^{-1}. Also of significance in the 74–83-kbar range is the dramatic broadening and splitting of the two bands present in the C–H and N–H stretching region (Figure 12b). At 10 kbar these two bands appear at 3338 and 3285 cm^{-1}. At 74 kbar both bands have broadened only slightly and have shifted blue 65 cm^{-1}. Above 74 kbar substantial splitting develops, and by 92 kbar the two bands have coalesced into one another. The above changes are similar to changes described in the perchlorate analogue and are consistent with a sudden increase in the BF$_4$–molecular plane interaction over the pressure range 74–83 kbar and provide evidence for the participation of the ethyl groups and/or chelate rings in the molecular rearrangement of the dieten–BF$_4$ complex.

Supporting evidence for a rearrangement involving an increased anion–cation interaction is found in the infrared spectrum of [Cu(en)$_2$](BF$_4$)$_2$ (Figure 13). The splittings after rearrangement discussed above (Figures 10b,c and 12) for the NH$_2$ scissoring mode (ca. 1600 cm^{-1}) and the band at ca. 3170 cm^{-1} are already present at low pressure in [Cu(en)$_2$](BF$_4$)$_2$. Also, the ν_1(BF$_4^-$) mode (not shown) appears as an intense band at ca. 766 cm^{-1} in [Cu(en)$_2$](BF$_4$)$_2$ at low pressure. These observations provide further evidence for the similarity of the high-pressure dieten and low-pressure en cases.

Analogous comments apply to the infrared spectrum of [Cu(dimeen)$_2$](BF$_4$)$_2$ (not shown). No unusual effects were seen in either the en or dimeen complexes upon application of pressure.

Although the chloride anion has no pure modes, several features seen in the infrared spectrum of [Cu(dieten)$_2$]Cl$_2$ at low pressure resemble features seen in the infrared spectra of the other two dieten complexes at higher pressures. At 15 kbar there is already a considerable amount of splitting in the C–H and N–H stretch region (3300–3500 cm^{-1}) and the NH$_2$ scissoring band is split into two components (1583 and 1629 cm^{-1}). Both of these features (not shown) are consistent with an initially stronger anion–mo-

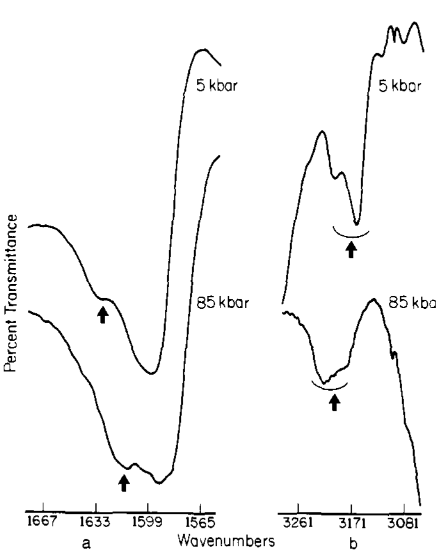

Figure 13. Infrared spectrum of polycrystalline [Cu(en)$_2$](BF$_4$)$_2$ at low and high pressure: (a) 1550–1700 cm^{-1} and (b) 3050–3300 cm^{-1}.

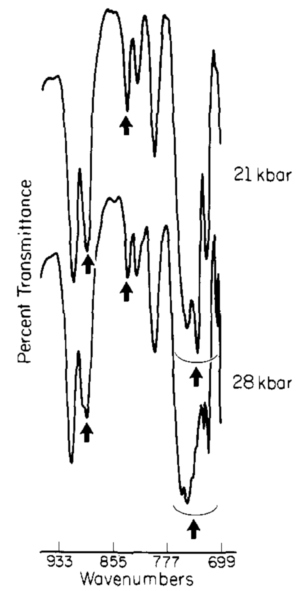

Figure 14. Infrared spectrum (700–950 cm^{-1}) of polycrystalline [Cu(dieten)$_2$]Cl$_2$ at different pressures.

lecular plane interaction in [Cu(dieten)$_2$]Cl$_2$ than in the other two dieten complexes. The implied smaller initial anion–cation separation is reasonable given the significantly smaller size of the chloride anion and the lower rearrangement pressure suggested by the electronic study. The primary effects of pressure are seen between 14 and 28 kbar (Figure 14). The band at 834 cm^{-1} experiences a dramatic intensity decrease and noticeable splittings occur in the band at 893 cm^{-1}. Both of these bands are absent in the spectrum of [Cu(en)$_2$]Cl$_2$[24] and are therefore believed to be a consequence of ethyl substitution of the chelate ring. Other effects in this pressure range include an increase in the splitting of the C–H stretching bands (not shown), an increase in the energy difference of the two components of the NH$_2$ scissoring band (not shown), a dramatic decrease in the intensity of the band at 735 cm^{-1} (Figure 14), and the development of additional band splitting in the 700–750-cm^{-1} region (Figure 14). Only minor changes of these types are seen above 28 kbar and the observations noted above provide evidence for a marked increase in the interaction between the chloride anion and the molecular plane between 14 and 28 kbar.

Summary of Crystalline Studies. In the low-pressure region the dieten complexes exhibit a behavior consistent with some continuous shift of the axial ligand nearer the copper cation and an increase in ligand field due to compression of the Cu–N bond. At some pressure there is a discontinuous decrease of the anion–copper cation distance. The low intensity $d_{z^2} \rightarrow d_{x^2-y^2}$ excitation shifts from high to low energy and there are changes in the infrared spectra of both the axial ligand and the NH$_2$ moieties (as well as vibrations associated with the ethyl groups) consistent with a considerable distortion of both the cation and anion due to this closer association.

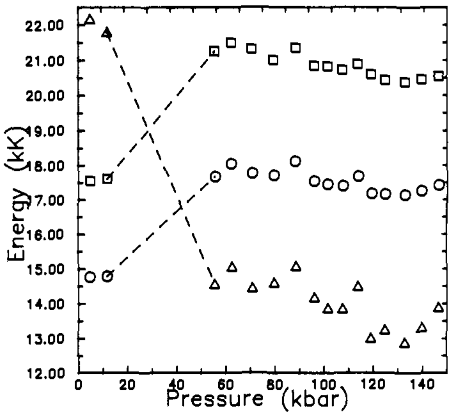

Figure 15. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions of [Cu(dieten)$_2$](BF$_4$)$_2$ in a 2VYPY environment.

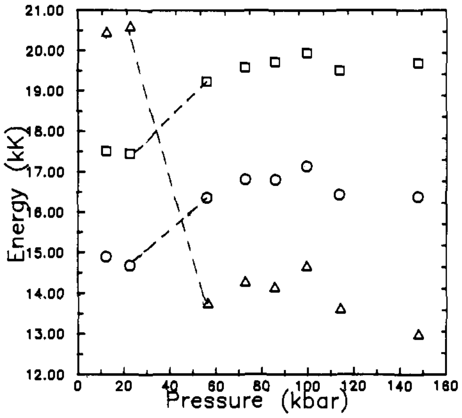

Figure 16. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions of [Cu(dieten)$_2$](BF$_4$)$_2$ in a PSS environment.

It is not possible to establish from our data the exact geometry of the assembly at high pressure or the path along which the rearrangement occurs. However, the high-pressure electronic spectra of the dieten complexes closely resemble the low-pressure spectra for the en and dimeen complexes, and the pressure shifts for the dieten compounds above the rearrangement pressure are very similar to those observed throughout the pressure range for the en and dimeen complexes. In addition, the IR spectra for the dieten spectra above the rearrangement pressure closely resemble the low-pressure IR spectra for the en and dimeen complexes. It is thus reasonable to assume that the cation–anion arrangement for the dieten complexes at high pressure is quite similar to that observed for the en complex at ambient pressure.

At 25 °C and ambient pressure these crystals are already in the low-temperature "motion-inhibited" phase. Thus, the transformations we observe with increasing pressure at ambient temperature cannot be simply related to the thermochromic transitions[3,4] observed at higher temperature and ambient pressure.

Studies in Polymeric Environments. [Cu(dieten)$_2$](BF$_4$)$_2$ was studied as a low concentration (~3.5 mol %) dopant in a poly(2-vinylpyridine) (2VYPY) and a sodium polystyrenesulfonate (PSS) environment. Only electronic spectra were recorded. Band positions are shown in Figures 15 and 16. The resolved spectra indicate that the same process occurs in both polymers and that this behavior is similar to the behavior observed in the crystal. Two major differences are found in the polymeric environments:

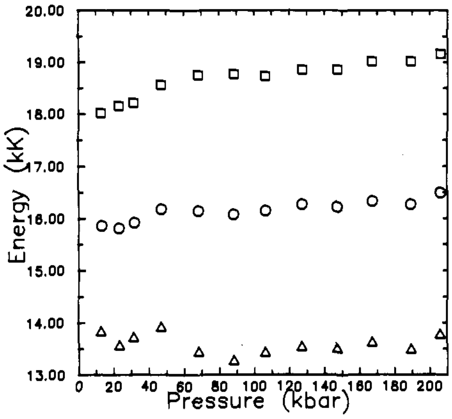

Figure 17. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions of $[Cu(dieten)_2](ClO_4)_2$ in a PSS environment.

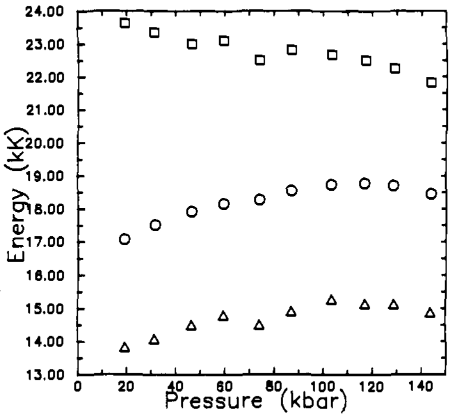

Figure 18. Pressure dependence of the energies of the $d_{z^2} \rightarrow d_{x^2-y^2}$ (△), $d_{xz},d_{yz} \rightarrow d_{x^2-y^2}$ (□), and $d_{xy} \rightarrow d_{x^2-y^2}$ (○) electronic transitions of $[Cu(dieten)_2]Cl_2$ in a 2VYPY environment.

(1) the pressure range over which the molecular rearrangement occurs is greatly expanded and (2) the rearrangement initiates at lower pressure in both polymers. The effects observed in the polymer studies were also reversible.

In PSS the resolved electronic spectra at pressures less than 25 kbar resemble those of the crystal before rearrangement (Figure 3); the low-intensity $d_{z^2} \rightarrow d_{x^2-y^2}$ band appears at high energy. At 56 kbar the $d_{z^2} \rightarrow d_{x^2-y^2}$ band has shifted to low energy, with the spectrum resembling that shown at 96 kbar in Figure 3. The resolved spectra between 25 and 56 kbar represent, in varying proportions, superpositions of the spectra which define the extremes of the rearrangement pressure range (25–56 kbar). This observation is consistent with the presence of two (equilibrium) configurations of the doped system in the polymer environment. In order to monitor the continuous changes taking place, we continued to fit the spectra between 25 and 56 kbar with three bands. We must emphasize that the three bands resulting from these fits do not represent pure electronic transitions but rather combinations of different electronic transitions in the two molecular configurations. We therefore do not report values obtained from these fits. We report instead a qualitative description of the results; namely, as we increase the pressure above 25 kbar a continuous increase in the intensity of the high-energy Gaussian occurs concomitant with a continuous decrease in the intensity of the low-energy Gaussian. This process is complete at 56 kbar. This indicates an absence of significant cooperativity in the polymer and a site-dependent rearrangement process. No dramatic changes were observed in the spectra above 56 kbar. In 2VYPY a similar situation arises, with the transition pressure range extending from 12 to 47 kbar. No significant effects were seen outside of this pressure range.

$[Cu(dieten)_2](ClO_4)_2$ and $[Cu(dieten)_2]Cl_2$ were studied as low concentration (~3.5 mol %) dopants in PSS and 2VYPY, respectively. In both cases, at ambient pressure the resolved spectra resemble those of the respective crystals after the molecular rearrangement had taken place. In neither case were any significant effects observed upon an increase in pressure over the range studied. The band locations are shown in Figures 17 and 18.

The polymer studies collectively show that the polymeric environments used are capable of facilitating the molecular rearrangement process in the sense that these environments reduce the pressure required to induce rearrangement, the extremes being $[Cu(dieten)_2](ClO_4)_2$ and $[Cu(dieten)_2]Cl_2$, which are already transformed at low pressure. The lower rearrangement pressures suggest that anion–copper cation distances are contracted in the polymers.

In 2VYPY, a nonionic polymer, we would expect intramolecular axial anion–copper cation interactions to be stronger than in the crystal because intermolecular interactions are no longer ionic in nature. Thus, a shorter axial distance is not unreasonable.

Although PSS chains possess ionic side groups, our results suggest that intermolecular ion(copper complex)–ion(PSS side group) interactions in the polymer are weaker than those in the crystal, consequently implying stronger intramolecular ion–ion interactions and shorter axial distances in PSS relative to the crystal. This merely indicates a smaller number of charged sites per unit volume in the polymer than in the crystal; a reasonable conclusion given the nonionic nature of the PSS backbone.

The semiionic nature of PSS is, however, possibly responsible for the higher upper limit of the transition pressure range found in PSS than in 2VYPY. The greater ionic character of intermolecular interactions in PSS than in 2VYPY possibly leads to a slightly longer axial distance in PSS and thereore a slightly higher rearrangement pressure.

The polymer studies in conjunction with the crystal studies suggest that ion–ion forces are important in determining the anion–copper cation distance and consequently the rearrangement behavior of $[Cu(dieten)_2]X_2$ ($X = BF_4^-, ClO_4^-, Cl^-$) systems with pressure. Ionic media, via electrostatic forces of attraction and repulsion, appear to result in larger anion–copper cation distances than nonionic media and lead to higher pressures of rearrangement.

The polymer and crystal studies also demonstrate how a given molecular rearrangement can be primarily stochastic in some environments and cooperative in others. Our results show that between the ideal limits of purely stochastic processes and purely first-order phase transitions there exists an intermediate region in which processes of varying extents (or degrees) of cooperativity may be found. We feel that these ideas may have important consequences in solid-state chemistry and merit further consideration.

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