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Formation and Structure of a 2,3,9,10,16,17,23,24-Octacyanophthalocyanine–Potassium Complex in Thin Film

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Abstract

Dipotassium 2,3,9,10,16,17,23,24-octacyanophthalocyaninate [$K_2Pc(CN)_8$] has been synthesized as a thin film by reaction of tetracyanobenzene with KCl at 623 K in an evacuated sealed tube. The film was produced on a cleavage face of KCl crystals and is composed of slender tentacle-like crystallites. The molecular image of the crystal is observed by high-resolution electron microscopy and indicates that the crystal is an $H_2Pc(CN)_8$–K complex. The crystal structure of the complex is determined from electron diffraction patterns and high-resolution electron micrographs. The unit-cell dimensions are $a = b = 1.57$ nm, $c = 0.674$ nm, and the space group is *P4/mcc*. The molecular arrangement in the crystal is determined directly from the molecular images. The planar molecules of $H_2Pc(CN)_8$ are in a layer normal to the c axis and are located at the corners of the square lattice. The molecules are packed along the c axis and rotate alternately from the a axis by 27.4°. K atoms are surrounded at the center of the square by eight nitrile groups from octacyanophthalocyanine molecules in two successive layers. The crystal structure proposed from the molecular image is confirmed by comparison with a computer-simulated image.

Introduction

Since the molecular image of chlorinated copper phthalocyanine was observed by Uyeda, Kobayashi, Suito, Harada & Watanabe (1972), high-resolution electron microscopy (HREM) has been used, not only for the direct imaging of organic crystal structures (Kobayashi, Fujiyoshi & Uyeda, 1982), but also for determining molecular structure at the atomic level (Uyeda & Ishizuka, 1974; Uyeda, Kobayashi,

Ishizuka, Fujiyoshi, 1980). However, high-resolution information is very difficult to obtain from most organic crystals because of their sensitivity to radiation damage by the electron beam. In order to reduce the radiation damage, HREM of organic crystals has been carried out by the minimum dose method (Fujiyoshi, Kobayashi, Ishizuka, Uyeda, Ishida & Harada, 1980), in a cold stage, or by encapsulating the specimen (Fryer & Holland, 1984). The interpretation of high-resolution electron micrographs of complex structures is greatly facilitated by comparison with computer-simulated images (O'Keefe, Fryer & Smith, 1983). The high-resolution image of chlorinated copper phthalocyanine has been interpreted completely on the basis of computer simulation of the crystal structure (Uyeda, Kobayashi, Ishizuka & Fujiyoshi, 1978–79). In the studies carried out so far, the major function of HREM has been to detect the regular structures of crystals. One of the ultimate objectives for HREM is the determination of the molecular structure in crystalline and amorphous states of products of chemical reactions.

1,2,4,5-Tetracyanobenzene (TCNB) has been used as a bifunctional monomer for the synthesis of polymeric metal phthalocyanines (poly-MPc's) (Norrell, Pohl, Thomas & Berlin, 1974; Bannehr, Meyer & Wöhrle, 1980; Lin & Dudek, 1985). The reaction of TCNB with metals or metal salts in the solid state produces poly-MPc's (Wöhrle, Marose & Knoop, 1985). In a paper by Ashida, Ueda, Yanagi & Sayo (1988) thin films were produced on KCl and metallic copper substrates by reaction of TCNB with the substrate material in an evacuated tube. The resulting films were monomeric or polymeric metal octacyanophthalocyanines [MPc(CN)$_8$] depending on the reaction temperature. The metal octacyanophthalocyanine molecules are planar with D_{4h} symmetry as shown in Fig. 1. The films produced on copper have crystalline structure (Fryer & Kinnaird, 1983). MPc(CN)$_8$ complexes were also synthesized by Wöhrle, Meyer & Wahl (1980), but their molecular dimensions and crystal structures have not been investigated yet.
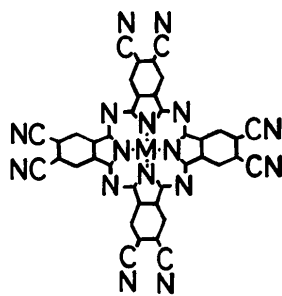
Fig. 1. Molecular structure of a metal octacyanophthalocyanine complex.

The present study is concerned with the structural elucidation of films produced from TCNB and KCl. The molecular image of the product was observed by atomic level resolution in an HREM. The molecular arrangement and crystal structure of the product are discussed on the basis of computer simulation of the proposed crystal structure.

Experimental

Tetracyanobenzene was heated with a (100) cleavage face of a KCl crystal in an evacuated sealed tube at 623 K for 5–24 h. The film produced on the KCl crystal was separated from the substrate in water and mounted on a microgrid coated with evaporated gold particles. High-resolution electron micrographs were obtained with a JEM-200CX electron microscope equipped with a minimum exposure device. The electron miscroscope was operated at 200 kV with a microscope parameter of spherical aberration coefficient of 2·0 mm. The (111) lattice image from gold ($d = 0·235$ nm) provided an accurate magnification calibration. The unit-cell lengths were accurately determined from electron diffraction patterns, using the lattice spacings of gold as reference.

To interpret the experimental images, computer simulation was performed, assuming particular molecular dimensions and arrangements in the crystal. The multislice method was adopted for the calculation of scattering amplitudes using the algorithm developed by Ishizuka & Uyeda (1977). Contrast transfer functions (CTF) were calculated with attenuation by a chromatic defocus spread of 10 nm and a beam convergency α_c of 0·1 mrad, and the cut-off frequency of the objective aperture was chosen to be 2·05 nm^{-1} ($\sin\theta/\lambda$). Crystal data of phthalocyanine obtained by Robertson (1936) and those of TCNB obtained by Prout & Tickle (1972) were used for the simulation of the image.

Results and discussion

The film formed on the substrate KCl crystal by reaction with TCNB is composed of slender tentacle-like crystallites, as shown in Fig. 2. The product was identified as dipotassium octacyanophthalocyaninate [K$_2$Pc(CN)$_8$] by means of infrared and visible spectra and elemental analysis (Ashida et al., 1988). In the case of very thin films (about 5 nm in thickness), many of the crystallites with grating structure are surrounded by an amorphous phase, as shown in Fig. 3(a). The selected-area electron diffraction pattern from the crystallite is a single net pattern with C_{4v} symmetry, corresponding to a spacing of 1·57 nm, as shown in Fig. 3(b). The optical diffraction pattern from the micrograph shows C_{4v} symmetry composed of square lattice points of 1·57 nm spacing (Fig. 3c). This pattern is in good agreement with the corresponding electron

diffraction pattern. The optical transform confirms that the real image of Fig. 3(a) was recorded near the Scherzer focus of 85 nm, since the scattering band from the carbon film superimposed on the crystalline pattern shows no visible intensity rings. On the other hand, the selected-area diffraction pattern from the lamellar crystallite shown in Fig. 4(a) represents the fiber pattern which indicates the fiber period of 0·337 nm and the

spacing of 1·57 nm, as shown in Fig. 4(b). From the features of growing crystals, it appears that the crystal planes shown in Figs. 3 and 4 correspond to the planes normal and parallel to the direction of growth, respectively.

From the above relations, the unit-cell dimensions of the crystal can be deduced: $a = b = 1·57$ nm and the interplanar distance is 0·337 nm; thus all the expected reflections appear in the diffraction patterns.

Fig. 5(a) shows a high-resolution micrograph, corresponding to Fig. 3(a), which was noise-reduced photographically by a translational multiple-exposure technique. Figs. 5(b) and 5(c) show the optical densities measured along the lines XX' and YY' in the image. The symmetry of the image and each of its intensity peaks are confirmed accurately from the figures. The structure image indicates many characteristic features: the square network with a distance of 1·57 nm is composed of two nearly parallel lines with a spacing of 0·44 nm and high-contrast circles of diameter 0·56 nm are situated at each corner of the square. High-contrast dots are located at the center of each square and four short rods link the corners to the central dot. Fig. 6 shows a high-resolution micrograph corresponding to Fig. 4(a). The structure image indicates that parallel bars pile up along the column axis with a distance of 0·337 nm and that adjacent bars are in a line. The figure shows the molecular layers projected on a plane parallel to the column axis. According to Berlin & Sherle (1971), the poly-MPc's synthesized from TCNB and metals have two Pc units linked *via* a peripheral benzene ring, and extend to either a ribbon or a sheet of parquet pattern. Assuming such a structure, the phthalocyanine repeating unit in poly-MPc should have a size less than 1·1 nm. Therefore, this finding also shows that the product is not a polymer but a monomer of $K_2Pc(CN)_8$.

Consequently, the planar molecules of $K_2Pc(CN)_8$ in the crystal pile up parallel to each other along the c axis.
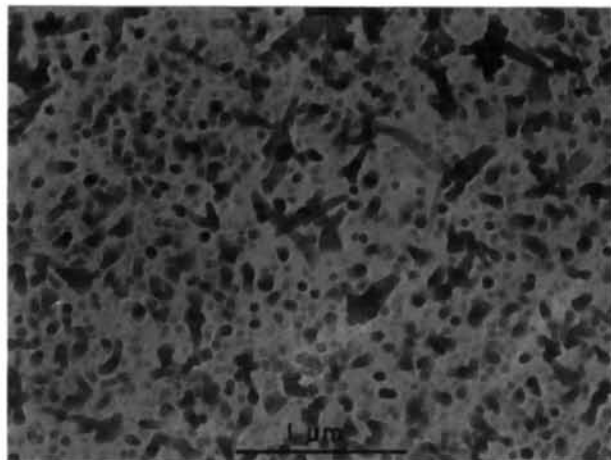

Fig. 2. Electron micrograph of a thin film produced on a KCl crystal.
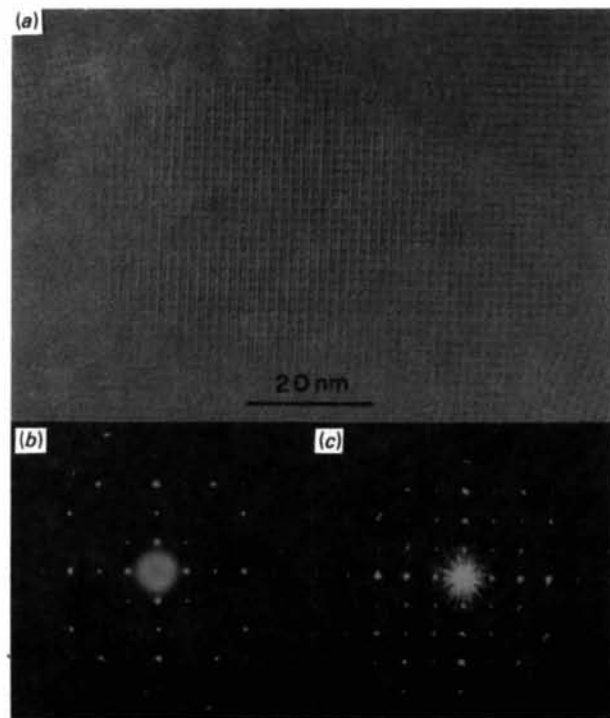

Fig. 3. (a) Electron micrograph of a very thin film produced on a KCl crystal, (b) selected-area diffraction pattern and (c) optical diffraction pattern from a crystallite.
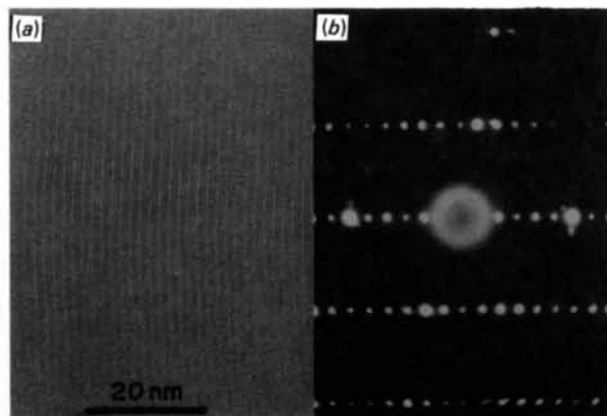

Fig. 4. (a) Electron micrograph and (b) selected-area diffraction pattern of a lamellar crystal.

The high-contrast circles are presumed to be tetra-azaporphyrin rings because of the coincidence of the diameter, although no pattern exists in the circles. It is well known that alkali-metal-containing Pc's are readily demetalized in dilute acid solutions and water (Barrett, Dent & Linstead, 1936). The specimens for electron microscopy were separated from the substrate in water. It is reasonable to assume that $K_2Pc(CN)_8$ would form $H_2Pc(CN)_8$ without any change of structure when the specimen comes into contact with water.
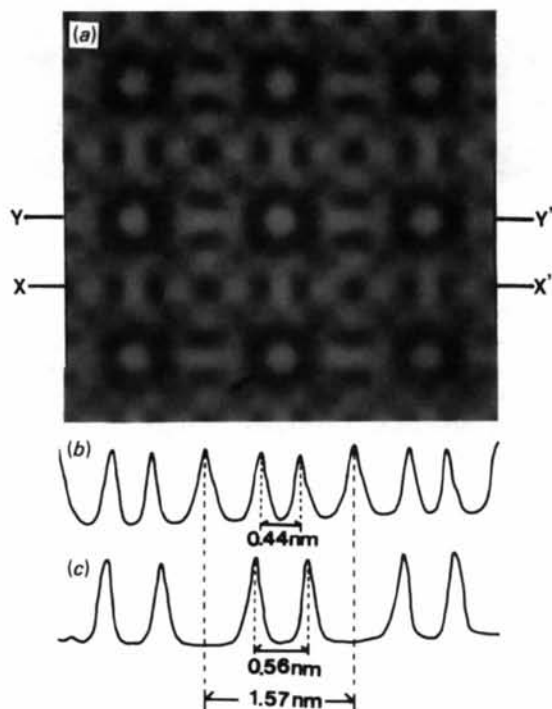

Fig. 5. (a) High-resolution structure image of the crystal of Fig. 3(a), and optical density along the lines XX' (b) and YY' (c) in the image.
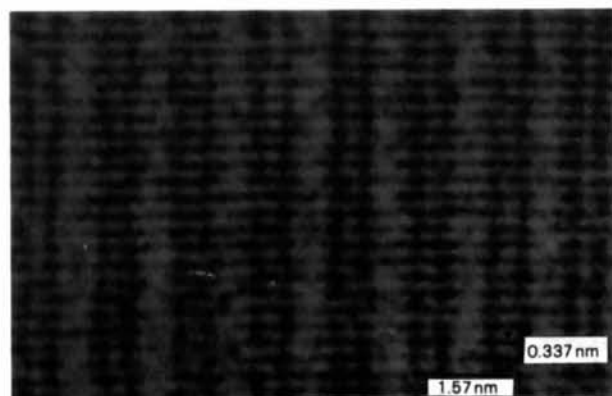

Fig. 6. High-resolution structure image of the crystal of Fig. 4(a).

In most MPc crystals, the planar molecules are aligned parallel to each other in a column, with a constant intermolecular distance of 0·34 nm. The molecular plane makes a given angle with the column axis that passes through all the central metal atoms. In the case of MPc's with sandwich structures, such as $U(Pc)_2$ (Gieren & Hoppe, 1971), $Th(Pc)_2$ (Kobayashi, Fujiyoshi & Uyeda, 1983) and $Sn(Pc)_2$ (Bennet, Broberg & Baenziger, 1973), a metal atom is sandwiched between two parallel Pc planes, which have interplanar spacing of less than 0·34 nm and which are staggered with respect to each other. This staggering of parallel molecules has also been found for a cofacial $[Si(Pc)O]_n$ polymer (Dirk, Inabe, Schoch & Marks, 1983). The eclipse conformation, in which the staggering angle is near $0°$, has only been observed in cases of relatively large interplanar spacing, for instance 0·353 nm in $[Ge(Pc)O]_n$. According to Ciliberto, Doris, Pietro, Reinser, Ellis, Fragala, Herbstein, Ratner & Marks (1984), the angle at which the planes are staggered in the Pc−O−Pc system is a sensitive function of interplanar spacing and macrocycle substituents. An alternate rotation was observed for the $NiPcI_{1·0}$ complex (Schramm, Scaringe, Stojakovic, Hoffman, Ibers & Marks, 1980), in which the angular difference between successive molecules was $39·5°$ and the separation of molecular planes was 0·324 nm. These findings suggest that molecular staggering takes place when the planar molecules are packed in a column with an interplanar spacing shorter than about 0·35 nm. The interplanar spacing of the molecular layers in Fig. 6 is less than 0·34 nm, and it is probable that the $H_2Pc(CN)_8$ molecules rotate alternately around the column axis.

It is noted that a high-contrast dot appears in the center of the square lattice, as shown in Fig. 5. The intensity peak at this position could not be caused by $H_2Pc(CN)_8$ molecules, because the spot pattern is different from the circular pattern of azaporphyrin rings and an extra molecule cannot be interposed in the molecular arrangement described above. In the previous paper (Ashida et al., 1988), the films produced on a KCl substrate by reaction of TCNB with KCl were found to include more K atoms than would be required for coordination in Pc rings. The well-defined charge-transfer complex, TCNQ−K, is considered a suitable example for the present case. According to the structure analysis of Konno, Ishii & Saito (1977), a K atom in crystalline TCNQ−K is at the center of a distorted cube of eight N atoms and the K−N distance is 0·293 nm. In addition, Richard, Zanghi, Guedon & Hota (1978) have reported that a K atom is octahedrally surrounded by eight TCNQ groups in which the K−N distance is either 0·286 or 0·297 nm. Therefore, it is presumed that the dots correspond to the extra K atoms situated in the channel between phthalocyanine columns. On the basis of these considerations, the

molecular arrangement in the crystal is illustrated schematically in Fig. 7. The planar molecules of $H_2Pc(CN)_8$ are in a layer normal to the c axis and are located at the corners of the square at a distance of 1·57 nm; the molecules are rotated alternately from the a axis by $\pm\omega$ in successive layers, as shown in Figs. 8(a) and 8(b). When these molecular layers are packed along the c axis and a K atom is surrounded at the
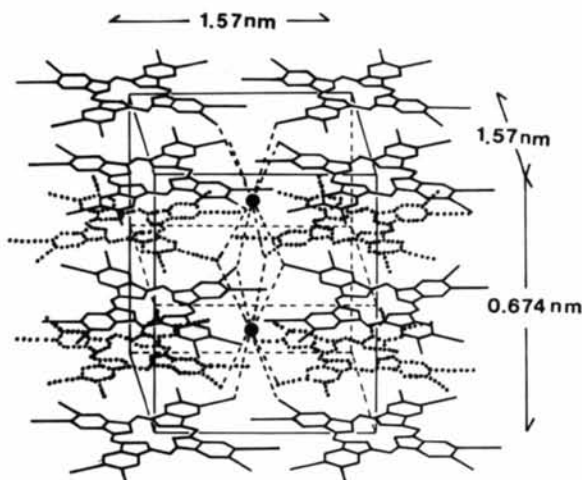

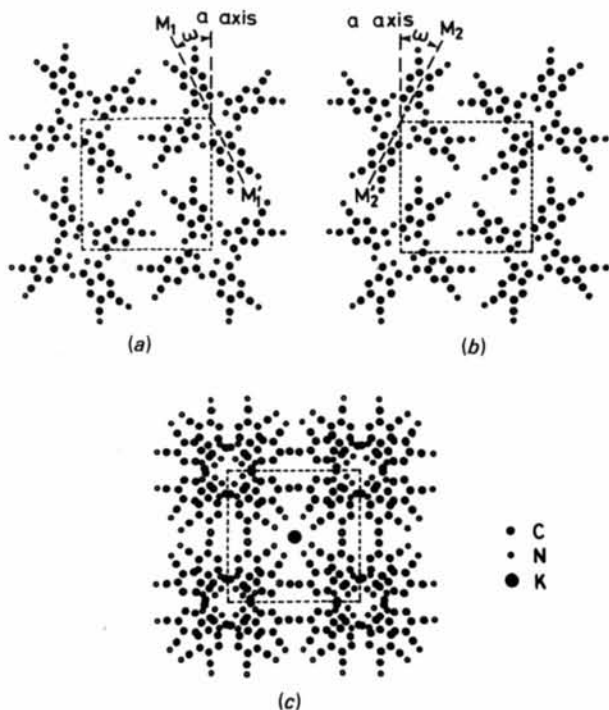Fig. 7. Perspective view of the octacyanophthalocyanine–potassium complex.

Fig. 8. Molecular arrangements projected along the c axis: (a), (b) molecules in two successive layers; (c) schematic diagram of the crystal structure projected along the c axis.
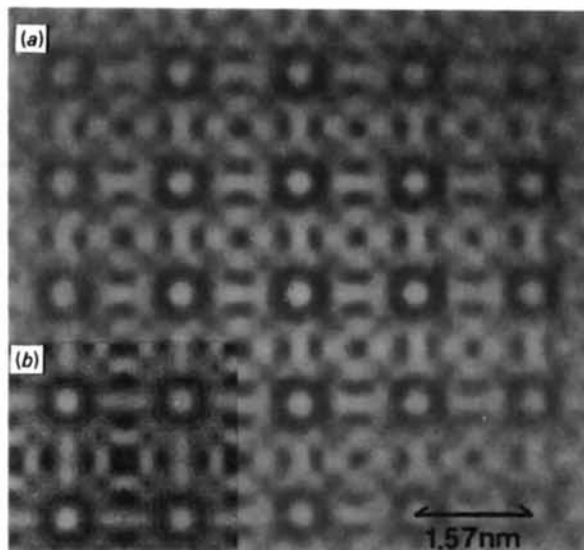

Fig. 9. (a) Molecular image and (b) multislice computer-simulated image of the complex.

center of the square by eight nitrile groups of two successive layers, both molecules and atoms projected along the c axis are superimposed as shown in Fig. 8(c). When the angle ω is approximately 27°, eight nitrile groups of individual $H_2Pc(CN)_8$ extend from the corner to the centre and other nitrile groups are superimposed giving rise to pairs of links between neighboring $H_2Pc(CN)_8$. Because of the alternate rotation of the molecules in a column, it is concluded that the c axis spacing is 0·674 nm, twice that of successive molecular planes, and that the crystal belongs to space group $P4/mcc$. The image shown in Fig. 5(a) is quite similar to the superimposed pattern of the $H_2Pc(CN)_8$–K complex projected along the c axis. On the basis of this model a computer simulation was carried out taking account of the staggering angle ω (about 30°), the underfocus near the Scherzer focus and the crystal thickness (about 5 nm). The staggering angle ω was found to be 27·4°. Fig. 9 shows the computer-simulated image at 70 nm underfocus for a crystal of thickness 4 nm and the corresponding real image; both images coincide well. Thus, the high-resolution image of $H_2Pc(CN)_8$–K is interpreted completely by the proposed crystal structure. The simulated images of $H_2Pc(CN)_8$–K will be described in detail elsewhere.

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A Mean-Square Displacement Amplitude Analysis of Terminally Bound CO Groups in Transition-Metal Clusters

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Abstract

Mean-square displacement amplitudes (m.s.d.a.'s) obtained from conventional room-temperature and low-temperature X-ray diffraction, and from neutron diffraction studies of metal carbonyl clusters are analyzed for the terminally bound CO groups. The relationships between m.s.d.a.'s of M, C and O atoms are investigated by applying the 'rigid-body' test along the M—C, M—O and C—O vectors, and are examined on the basis of simple vibrational motion models. Results of this analysis show that the C-atom m.s.d.a.'s are substantially affected by bonding electron density deformation. The relationship with the 'sliding effect' observed on passing from isotropic to anisotropic treatment of the C-atom thermal motion is also discussed.

Introduction

Carbon monoxide as a ligand plays a central role in metal cluster chemistry and certainly represents one of

the most studied molecules in the organometallic field. The extraordinary geometrical versatility shown by CO is demonstrated in the results of scores of structural studies on metal carbonyl complexes and clusters both in solution and in the solid state (Band & Muetterties, 1978; Evans, 1977). As a matter of fact, while spectroscopic techniques have provided most information on the dynamic processes related to CO fluxionality in solution (Adams & Cotton, 1985), thus far solid-state aspects of CO structural chemistry mainly have been investigated by single-crystal X-ray and neutron diffraction (Raithby, 1980). More recently the borderline between static and dynamic implications of CO structural chemistry has become more and more narrow as migrational processes have been claimed to occur for some metal carbonyl clusters in the solid state (mainly by solid state NMR techniques) (Hanson, Lisic, Petty & Iannacone, 1986; Hanson & Lisic, 1986) and X-ray solid-state data have in turn been used to provide correlations with dynamic processes occurring in solution (Benfield & Johnson, 1980; Braga & Heaton, 1987). Moreover, the availability of large amounts of both experimental and theoretical informa-

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