Compressibility and High-Pressure Phase Transition of a Metalloporphyrin: (5,10,15,20-Tetraphenyl-21H,23H-porphinato)cobalt(II)

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Introduction

Hazen and Finger1 recognized three principal compression mechanisms in solids: nearest neighbor bond compression, reduction of bond angles, and intermolecular compression. Bond compression and bond angle bending are well documented in numerous high-pressure structure studies of minerals and mineral-like compounds,2 but little work has been done to elucidate compression or high-pressure structures of molecular crystals. The metalloporphyrin (5,10,15,20-tetraphenyl-21H,23H-porphinato)cobalt(II), C_{44}H_{28}N_{4}Co (here abbreviated CoTPP), is available in euhedral, stable crystals that are particularly well-suited for such high-pressure investigations. Its unit cell is relatively small (a = 15.05 Å, c = 13.97 Å, V = 3167 Å³), its symmetry is high (tetragonal, space group I42d), and the presence of the relatively heavy element cobalt enhances the X-ray scattering efficiency of the crystals.

The original objectives of this study were to measure compressibility of CoTPP and to relate this compression to the molecular structure. During the course of the experiments a reversible phase transition was observed. A secondary objective, therefore, is to describe this new transition and to relate it to possible transitions in other molecular crystals.

Under the high-pressure conditions used in this study, only the space group and size of the unit cell could be measured by X-ray diffraction. Supplementary high-pressure studies of the CoTPP infrared spectra were conducted in order to learn of possible changes in intermolecular distances and configuration, with relatively little distortion of the intramolecular structure.

Experimental Section

Specimen Description. Euhedral 100 × 100 × 40 μm crystals of CoTPP were handpicked under a binocular microscope from synthetic material (Aldrich Chemical Co., Milwaukee, WI; catalog no. 25,219-0).

Room-Pressure Unit-Cell Parameters. A single crystal was mounted on a glass fiber for preliminary room-pressure X-ray study. Unit-cell parameters were determined from data collected on an automated four-circle diffractometer with monochromatized Mo Kα radiation. Diffractometer parameters were measured for 28 reflections, each of which was measured in eight equivalent positions.5,6 Unit-cell parameters were refined initially as triclinic; lattice parameters were refined to conform to tetragonal dimensionality and final values were refined with tetragonal constraints (Tables I and II).

Swanson et al.7 noted that systematic errors result in refined unit-cell parameters that differ, depending on the range of reflection 2θ used in the refinement. This phenomenon is evident in the present data. Reflections in the range from the 9° to 13° 2θ result in a calculated cell volume of 3166.3 Å³; from 12° to 15° a volume of 3164.8 Å³; and from 18° to 21° a volume of 3162.5 Å³ (Table I). Higher angle data thus yield significantly smaller unit-cell volumes. It is essential when results at different pressures are compared that the same range of 2θ be employed.

High-Pressure Unit-Cell Parameters. All high-pressure data were collected on a crystal of CoTPP mounted in a Merrill-Bassett type diamond-anvil cell.8 Glycerin was employed as the hydrostatic pressure medium and several 5-10-μm diameter chips of ruby were added for pressure calibration.7

Lattice parameters at each pressure were refined from diffractometer angles of 10–14 reflections with 2θ < 14°. Higher angle reflections would have been more desirable for lattice parameter measurements, but no reflections with 2θ > 14° have sufficient intensity. Even the low-angle reflections employed in this study have an average intensity of only 40 count s⁻¹, which is minimal for satisfactory peak centering.

All lattice parameters were refined initially as triclinic (Table I). Parameters for CoTPP up to 5.0 kbar conformed to tetragonal dimensionality and were also refined with tetragonal constraints (Table II).

Infrared Spectra. Spectra were measured in a diamond-anvil cell similar to that described by Mao and Bell.9 A Nicolet 7199 Fourier transform infrared optical bench equipped with a liquid nitrogen cooled mercury cadmium telluride detector for the mid-IR and a liquid helium cooled bolometer (Model HD-3; Infrared Laboratories Inc., Tucson, AZ) for the far-IR were employed. A Nicolet 1280 data processing unit was used for spectral acquisition. An all-reflecting 4X beam condenser was used as described by Hofmeister et al. (in press).

Pressures were gauged by the shift of the R1 fluorescence line of ruby powder covering the sample. Small crystals of the porphyrin were placed in the diamond-anvil cell and squeezed to form


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TABLE I: Unit-Cell Parameters of meso-(Tetraphenylporphinato)cobalt(II) Refined as Pseudotetragonal without Symmetry Constraints (i.e., as Triclinic); 9–13° Data Unless Otherwise Noted

<table>
<thead>
<tr>
<th>press., kbar</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>(\alpha), deg</th>
<th>(\beta), deg</th>
<th>(\gamma), deg</th>
<th>(V_0), Å(^3)</th>
<th>(V/V_0)</th>
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<tbody>
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<td>0.001 (a)</td>
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<td>15.058 (4)</td>
<td>13.974 (9)</td>
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<td>90.00 (3)</td>
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<tr>
<td>0.001 (b)</td>
<td>15.062 (4)</td>
<td>15.055 (4)</td>
<td>13.957 (2)</td>
<td>89.99 (2)</td>
<td>90.01 (2)</td>
<td>90.02 (2)</td>
<td>3164.8 (13)</td>
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<tr>
<td>0.001 (c)</td>
<td>15.053 (3)</td>
<td>15.053 (3)</td>
<td>13.957 (2)</td>
<td>90.02 (1)</td>
<td>90.01 (1)</td>
<td>90.02 (2)</td>
<td>3162.5 (10)</td>
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<td>(\sim 0.1)</td>
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<td>15.076 (7)</td>
<td>13.972 (11)</td>
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<td>14.839 (7)</td>
<td>13.208 (12)</td>
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<td>88.31 (7)</td>
<td>90.01 (5)</td>
<td>2905.4 (38)</td>
<td>0.918</td>
</tr>
</tbody>
</table>

\(^a\)Crystal in air; 9–13° data. \(^b\)Parenthesized figures represent esd's. \(^c\)Crystal in air; 12–15° data. \(^d\)Crystal in air; 18–21° data. \(^e\)Crystal in cell with air bubble.

A least-squares fit of unit-cell volume as a function of pressure gives:

\[ V = V_0 + \frac{1}{1 - \beta_0} \left( \sum P \cdot \Delta V \right) \]

where \(\beta_0\) is the axial compressibility.

\[ \beta_0 = \frac{1}{V_0} \left( \frac{1}{\gamma} - 1 \right) \]

The \(\beta_0\) and \(\gamma\) values were used to refine the unit-cell parameters (Table I). Both axes display significant curvature as reflected in the second-order terms in eq. 1 and 3.

The \(\beta_0\) value is 3.4 times more compressible than \(\alpha\) (Table I), resulting in a steadily decreasing \(c/a\) with increasing pressure (Table I). Both axes display significant curvature as reflected in the second-order terms in eq. 1 and 3.

The 5-kbar unit cell deviates significantly from tetragonal symmetry (see Table I; \(\beta = 89.84° \pm 0.04°\)).

It is not possible to maintain pressures below about 25 kbar with the lever-arm design of the diamond-anvil cell used in infrared experiments. Spectra were initially measured, therefore, at a minimum pressure of 25 kbar, after which spectra at increasing then decreasing pressure were obtained.

Results

Compression from 1 bar to 5 kbar. Lattice parameters and unit-cell volume vary smoothly as a function of pressure below 5 kbar. Tetragonal unit-cell edges as a function of pressure and average compressibilities (1 bar to 5 kbar) are:

- \(a = 15.057 (2) - [0.0025 (2)] P + [0.0007 (3)] P^2\) (1)
- \(\beta_0 = 0.00147 (4) kbar^{-1}\) (2)
- \(c = 13.967 (7) - [0.080 (6)] P + [0.002 (1)] P^2\) (3)
- \(\beta_0 = 0.0050 (2) kbar^{-1}\) (4)

The \(\beta_0\) value is 3.4 times more compressible than \(\alpha\) (Figure 1), resulting in a steadily decreasing \(c/a\) with increasing pressure (Table I). Both axes display significant curvature as reflected in the second-order terms in eq. 1 and 3.

A least-squares fit of unit-cell volume as a function of pressure to a Birch–Murnaghan equation of state

\[ P = 1.5K_0\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{2/3} \times \left[ 1 - 0.75(4 - K') \left(\frac{V_0}{V}\right)^{2/3} - 1 \right] \]

yields a bulk modulus \(K_0 = 108 (7)\) kbar and \(K' = 7 (4)\), with initial volume \(V_0 = 3167.1\) Å\(^3\).

The High-Pressure Phase. At 5 kbar and higher pressures the unit-cell parameters deviate significantly from tetragonal di-

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Figure 2. Unit-cell parameters and volume of CoTPP vs. pressure. Average unit-cell errors are smaller than the data symbols. A distortional phase transition from tetragonal to triclinic dimensional symmetry occurs at 4.9 ± 0.2 kbar.

Equation-of-state parameters for the high-pressure phase were calculated from eight pressure–volume points (Table I). Zero-pressure bulk modulus is 85 (12) kbar, with $K' = 1 (1)$. Thus, the high-pressure CoTPP is significantly more compressible than the low-pressure phase.

Infrared Spectra to 141 kbar. Normal coordinate analysis of tetraethyl metalloporphyrins substituted by various metals has been carried out by Ogoshi et al. Many of their vibrational assignments could be correlated for the tetraphenyl compound used in this study. Vibrations due to the peripheral phenyl groups could be identified as well. The peak positions of all bands except two increase slightly with pressure. The magnitude of the positive pressure shift is, to a first approximation, correlated with band assignments. Bands near 3000 cm$^{-1}$ attributed to C–H stretching have the greatest slopes of about 1 cm$^{-1}$ kbar$^{-1}$. The far-IR bands associated with ring deformations and metal–nitrogen stretching motions have modest slopes of about 0.7 cm$^{-1}$ kbar$^{-1}$. The majority of bands associated with the phenyl groups and the porphine ring (for example, the ring-deformation band at a frequency of about 1000 cm$^{-1}$; Table III) had smaller slopes between 0.2 and 0.5 cm$^{-1}$ kbar$^{-1}$ although a few values ranged from 0 to 0.7 cm$^{-1}$ kbar$^{-1}$.

The slight negative pressure shift of the band at 900 cm$^{-1}$ associated with ring deformation indicates that the distortion from the low-pressure to high-pressure is altering the bonding within the ring. A moderate negative pressure shift of an unassigned 1800-cm$^{-1}$ feature indicates that this band is a fundamental, because no bands of lower energy can combine to give the correct frequency and pressure derivative.

Certain high-frequency bands, such as the ones at 3035 and 3070 cm$^{-1}$, due respectively to C–H in-plane vibrations of the porphine ring and C–H vibrations of the phenyl groups, have a pronounced broadening with increasing pressure. This effect is enhanced over that for lower frequency bands and practically obliterates the high-frequency components above 20 kbar. This observation argues that pressure gradients across the sample are not the sole cause of spectral broadening.

Discussion

Structural Inferences: The Low-Pressure Phase. The structure of CoTPP was elucidated by Madura and Scheidt. Stevens subsequently presented detailed crystal structure information, including high-resolution electron density distribution. The CoTPP molecule consists of a planar grouping of four interconnected pyrine rings, with four branching benzene rings in a "paddlewheel" orientation.

Figure 3. CoTPP molecule, consisting of four interconnected pyrine rings in planar conformation with four benzene rings in a paddlewheel orientation.

Table III: Changes in Selected Infrared Absorption Maxima of CoTPP with Increasing Pressure

<table>
<thead>
<tr>
<th>press., kbar</th>
<th>$\nu$, cm$^{-1}$</th>
<th>press., kbar</th>
<th>$\nu$, cm$^{-1}$</th>
</tr>
</thead>
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<td>Absorption Maxima of “Quadrant Stretching” of Phenyl Groups</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1600</td>
<td>23</td>
<td>1612</td>
</tr>
<tr>
<td>6.4</td>
<td>1603</td>
<td>40</td>
<td>1619</td>
</tr>
<tr>
<td>12</td>
<td>1605</td>
<td>69</td>
<td>1632</td>
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<tr>
<td>Absorption Maxima of In-Plane Ring-Deformation Frequencies of the Porphine Ring</td>
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<tr>
<td>0</td>
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<td>23</td>
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<td>1028</td>
</tr>
</tbody>
</table>


Compressibility and Phase Transition of CoTPP

Figure 4. Structure of CoTPP, after Stevens.9 (A) A (001) projection shows how CoTPP molecules occupy lattice points of a body-centered tetragonal unit cell. Six molecules at the corners lie at z = 0, whereas the two centered molecules are at z = 1/2. (B) A (100) projection reveals how the CoTPP molecules lie in the (001) planes. Intermolecular distances are greater between molecules parallel to c than in the (001) plane.

Complete three-dimensional structure refinements of CoTPP at high pressure were precluded by the weak intensities of diffraction maxima. Several lines of evidence, however, lead to the inference that almost all compression of CoTPP is intermolecular. First, the anisotropy of compression, with c 3.4 times more compressible than a, reflects the planar aspect of the molecules. Intermolecular regions constitute most of the distance parallel to c but only about a fourth of the distance parallel to a. Second, the magnitude of axial compression, on the order of 0.005 kbar\(^{-1}\) parallel to c, is typical of intermolecular compression in graphite, boron nitride, and SnS\(_2\).11 Axial compressibilities greater than 0.001 kbar\(^{-1}\) are uncommon in compounds with no intermolecular bonds. Third, the significant curvature of axial length vs. pressure plots (Figure 1) and the large \(K'\) of 7 are characteristic of intermolecular compression. Forces controlling intermolecular compression differ from forces controlling cation-anion-type bonding characteristic of most minerals, for which \(K'\) is typically 4.

Structural Inferences: The High-Pressure Phase. Structural aspects of the high-pressure phase may be inferred, in part, from two notable properties of CoTPP above 5 kbar. First, this high-pressure phase is more compressible than the topologically related low-pressure phase. This seemingly paradoxical behavior is typical of reversible phase transitions in which the high-pressure phase has more "compressional degrees of freedom" than the low-pressure phase. Rhenium trioxide, ReO\(_3\), is one of the most dramatic examples of this phenomenon.13,14 At low pressure the compound is cubic and Re-O bond compression is the only compression mechanism; the bulk modulus is greater than 2 Mbar. At about 5 kbar the oxide transforms reversibly to a lower symmetry form in which bending of Re-O-Re angles is added as a compression mechanism; the bulk modulus drops to about 200 kbar. The high-pressure phase is an order of magnitude more compressible than the low-pressure phase because distortion to a lower symmetry introduces a new compression mechanism. The same situation appears to obtain in CoTPP. Intermolecular compression at low pressure conforms to the tetragonal symmetry constraints. The benzene rings lie above molecules in adjacent layers, while molecules in alternate layers exactly superimpose. Above 5 kbar no such constraints obtain, and molecules may adopt more staggered superpositions.

Of special note is the 4-fold dimensional symmetry of (001) planes in the high-pressure phase. It might at first appear that each layer of the structure, and by inference each molecule that composes the layer, retains the symmetry of the low-pressure phase. However, in spite of the retention of a dimensionally square net, the a and b axes are significantly more compressible in the high-pressure phase than in the low-pressure phase. It would seem, therefore, that some subtle, but important, structural change has occurred within, as well as between, the layers, even though this change produces no obvious effects on the infrared spectra.

Conclusions

The behavior of CoTPP may be representative of many other high-symmetry molecular solids at high pressure. Intermolecular bonds typically compress by 0.005 kbar\(^{-1}\), resulting in large volume changes at relatively low pressures. Crystals composed of small molecules (with a correspondingly large intermolecular volume) are thus expected to have bulk moduli on the order of 100 kbar. Most constituent molecules, on the other hand, should be fairly rigid. If molecular conformation does not change significantly, then intramolecular compression will contribute little to the crystal’s pressure-volume response, a conjecture that is borne out by the infrared studies.

Distortional phase transitions, in which the arrangement of rigid molecules is slightly altered, may be an energetically favorable mode of compression in many organometallics. An increase in the number of compressional degrees of freedom may result from a decrease in symmetry; high-pressure phases of molecular solids, consequently, may commonly display greater compressibility than their low-pressure counterparts.

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