A Spectroscopic Resolution of the Structure of Zn(CN)₂

EXECUTIVE SUMMARY

Two different cubic structures of the negative thermal expansion material zinc cyanide have been reported in the literature: one, an ordered structure (space group P43m) where ZnC₄ tetrahedra are linked to neighboring ZnN₄ tetrahedra with CN bonds and vice versa, and the other, a disordered structure (space group Pn₃m) where N and C sites are indistinguishable. We carried out group theoretical analyses to classify the phonons of different symmetries in the two structures, and also recorded and analyzed the Raman and infrared spectra to resolve the ambiguity about structure. Based on the number of Raman and IR modes expected and observed, we concluded that the compound exists in a disordered structure.

OUTLINE

The structure of Zn(CN)₂ was reported to consist of three-dimensional, inter-penetrating, tetrahedral frameworks of Zn-CN-Zn rods as shown in Fig. 1. Two different cubic structures have been reported to fit well to the diffraction patterns. In the ordered structure the CN ions lying along the body diagonal are orientationally ordered such that they form ZnC₄ and ZnN₄ coordination tetrahedra around alternate cations. The 'ordered' structure thus consists of a ZnC₄ tetrahedron (at the centre of the cell) linked to neighbouring four ZnN₄ tetrahedra (at the corners of the cell) with CN bonds. The remaining four Zn atoms at the corners of the cell are not bonded to atoms in the cell but only to atoms in the neighbouring cell. These Zn atoms of each unit cell form the second framework, and two such interpenetrating frameworks pervade the three dimensional lattice. The space group determined from single crystal X-ray diffraction analysis is P43m (a=4.44, c=4.366 Å). It was pointed out that exchanging C and N atoms did not significantly alter the refinement parameters, i.e., it was possible that C and N populate each other's site with a fractional occupancy of 0.5, giving rise to a disorder in the lattice. Since it is difficult to distinguish between C and N by X-ray diffraction, neutron diffraction was undertaken to unambiguously determine the structure, due to the vastly different neutron scattering lengths of C and N. It was found that a disordered structure with space group Pn₃m (a=4.44, c=4.366 Å) fits equally well to the diffraction pattern. In the disordered structure the CN bonds are orientationally disordered or flipped randomly such that both C and N sites are occupied by these atoms with a fractional occupancy of 0.5. Because of the indistinguishability of C and N in this structure the space group also has inversion symmetry. Fig. 2 shows the unit cell for the disordered structure where the origin is shifted by (a/4, a/4, a/4) with respect to the unit cell of the ordered structure. The values of the final refinement parameters of the 'ordered' and the 'disordered' structures were essentially the same. A disordered structure was argued to be appropriate because the fitted isotropic thermal parameters for C and N for the ordered structure were found to be quite different. However, this apparent difference was attributed to widely different neutron scattering powers of N and C. We attempted to resolve the ambiguity about the structure, from vibrational spectroscopic considerations. Factor group analyses of the phonon symmetries in both the possible structures of Zn(CN)₂ were carried out. Raman and infrared spectra of Zn(CN)₂ were recorded and the results are compared with those predicted from factor group analyses. The results point to a disordered structure with space group Pn₃m.

Zn(CN)₂ (>99.5%) was obtained from M/s. Alfa Aesar. Raman spectra were recorded in the backscattering geometry using the 488-nm line of an argon ion laser. Measurements at 10 K were carried out using an APD closed-cycle helium refrigerator. Scattered light from the sample was analyzed by a SPEX double monochromator, and detected with a photomultiplier tub. Scanning of the spectra and data acquisition were carried out using a home-built microprocessor-based data acquisition cum-control system. Subsequent to the completion of a scan, data were transferred to a personal computer for further analysis. IR spectra of the sample using (1) CsI pellet, (2) Nujol and (3) high density polyethylene were recorded using a BOMEM DA-8 FTIR spectrometer.

![Fig. 1: Ordered structure of Zn(CN)₂, space group P43m.](image1)

![Fig. 2: Disordered structure of Zn(CN)₂, space group Pn₃m.](image2)
**RAMAN AND IR SPECTROSCOPIC TECHNIQUES**

Raman spectroscopy and Infrared Absorption spectroscopy are vibrational spectroscopic techniques. They are also known as ‘finger printing’ techniques for molecules/solids since each molecule/material has its characteristic vibrational spectrum. They arise due to the vibrational motions of chemical bonds in the material, such as C-O, C-C, C-H, O-H, C≡C, etc. Since materials can have several different bonds differing in strength, one has in general several vibrational frequencies, corresponding to each of the bonds. IR is commonly employed by chemists for quick recording of spectra whereas Raman spectroscopy finds favor mainly with Physicists for the study of phase transitions in crystals, etc. Raman is a non-destructive technique but the instrumentation could be relatively expensive.

Raman and IR techniques are complementary to each other, and for a good understanding of a material both techniques should in general be employed. For a molecule with a centre of inversion (or a solid with an inversion symmetry), Raman and IR frequencies are mutually exclusive, i.e., they appear at different frequencies. This is the principle that has been useful in the present study to converge upon the disorder structure.

**FACTOR GROUP ANALYSIS AND EXPERIMENTAL MEASUREMENTS**

Zn(CN), has two formula units per unit cell. In the ordered structure, as shown in Fig. 1, the Zn(1) atom occupies the tetrahedral ‘a’ sites at $(0, 0, 0)$ and Zn(2) atom occupies the tetrahedral ‘b’ sites at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. C and N atoms occupy distinct 4e sites with C site symmetry. Four C atoms around Zn(2) form a coordination tetrahedron. Similarly the four N atoms around Zn(1) (three N atoms from the neighboring cells) form the other coordination tetrahedron. The 30 degrees of freedom arising from the 10 atoms in the cubic unit cell result in 3 acoustic phonons and 27 optical phonons. The 6 degrees of freedom corresponding to the linear molecular ion CN can be divided into 1-internal (stretching vibration), 3 rigid-translations and 2 rigid rotational degrees of freedom. Factor group analysis was carried out using Bhagavantam and Venkatarayudu method. The following irreducible representations of the acoustic and optical phonons were obtained:

$$\Gamma_{\text{optical}}(27) = 2A_{1}(R) + 2E(R) + 2F_{1} + 5F_{2}(R, IR)$$

The correlation method of Fateley and Dollish also gave identical results. Out of these, $A_{1}$, E and $F_{1}$ are Raman active, and $F_{2}$ is also IR active. $F_{2}$ modes are not optically active. Thus there are 9 optically active modes. All 9 modes are Raman active and 5 of them are IR active as well, for this ‘ordered’ structure.

Similar analysis of the ‘disordered structure’ results in 5 Raman active and 2 IR active modes. Comparison of experimental results with those expected from Factor group analysis (Table 1) establishes that the structure should be ‘disordered’.

<table>
<thead>
<tr>
<th>Number of modes expected from group theory</th>
<th>Observed mode frequencies (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>“Ordered”</td>
<td>Raman</td>
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<tr>
<td></td>
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<td>339</td>
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**CONVERGING ON THE STRUCTURE OF Zn(CN)$_2$**

The striking feature of Table 1 is the mutual exclusion of the observed Raman and IR frequencies, except for the high frequency mode about 2220 cm$^{-1}$. This mutual exclusion points to a structure with an inversion symmetry, i.e., the disordered structure. The IR frequency at 2218 cm$^{-1}$ is indeed expected here in spite of the arguments from factor group analysis to the contrary, since the CN has a strong dipole moment that should give rise to IR activity. Taking this into account, the structure is still concluded to be disordered, since the ‘mutual exclusion’ is a strong indication of a centrosymmetric structure, in this case the disordered one. It is noteworthy that several other cyanides such as CuCN, AgCN and AuCN also are known to have this ‘head to tail’ disorder of the CN ion.

**ACHIEVEMENT**

We have addressed a long standing controversy in the structure of Zn(CN)$_2$, and using spectroscopic techniques, resolved the structure to be disordered. It is noteworthy that this problem could not be satisfactorily solved using X-ray diffraction or neutron diffraction techniques earlier by other research groups.

**PUBLICATIONS ARISING OUT OF THIS STUDY AND RELATED WORK**


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