Buckled-layered Structure of Zinc Dicyanamide, $Zn^{II}[N(CN)_2]_2$

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Recently $M^{II}[N(CN)_2]_2$ (M = Co, Ni) have been identified as a new class of molecule-based magnetic materials.[1,2] Since dicyanamide, $[N(CN)_2]^-$, can bridge 2, 3, or 4 metal sites,[1−4] several solid-state motifs are known. $Ni[N(CN)_2]_2$ (T_c = 19.7 K) has an octahedral coordination geometry, while two polymorphs have been observed for $Co[N(CN)_2]_2$.[2] α-$Co[N(CN)_2]_2$ (T_c = 8.7 K) is isomorphous to $Ni[N(CN)_2]_2$, while β-$Co[N(CN)_2]_2$ shows two spin canting transitions (T_{c1} = 2.7; T_{c2} = 8.9 K) and, on the basis of the optical and magnetic properties, is assigned to a tetrahedral coordination geometry; however, the structure has not been determined.[2]

Herein we report the preparation,[5] single-crystal X-ray structure,[6] and infrared spectrum of $Zn[N(CN)_2]_2$, the first structurally characterized tetrahedral metal dicyanamide complex (Figure 1). The crystal structure consists of an extended 2-D layered network in which each Zn^{II} bonds to four $[N(CN)_2]^-$ in a nearly ideal square Zn···Zn metal array and each $[N(CN)_2]^-$ is μ-bonded to two Zn^{II} centers (Figure 2). $[N(CN)_2]^-$ maintains C_{2v} symmetry with C(1)−N(4) and C(2)−N(5) bond distances of 1.293 (8) and 1.289 (11) Å (averaging 1.29 Å) and C(1)−N(1) and C(2)−N(2) distances of 1.142 (8) and 1.138 (10) Å (averaging 1.14 Å), respectively, as is typical of the $[N(CN)_2]^-$ anion.[1−4] All atoms except C(1) and N(1) reside on the mirror plane parallel to the crystallographic *b* axis. Each Zn^{II} is four-coordinate with Zn−N(1) and Zn−N(2) bond distances of 1.969 (6) and 1.954 (8) Å, respectively, and averaging 1.96 Å. These Zn−N distances compare favorably to those found in related materials, but are significantly shorter (2.120 and 2.211 Å) than those observed in $Zn[C(CN)_3]_2$.[7] This is consistent with the trend that M−L

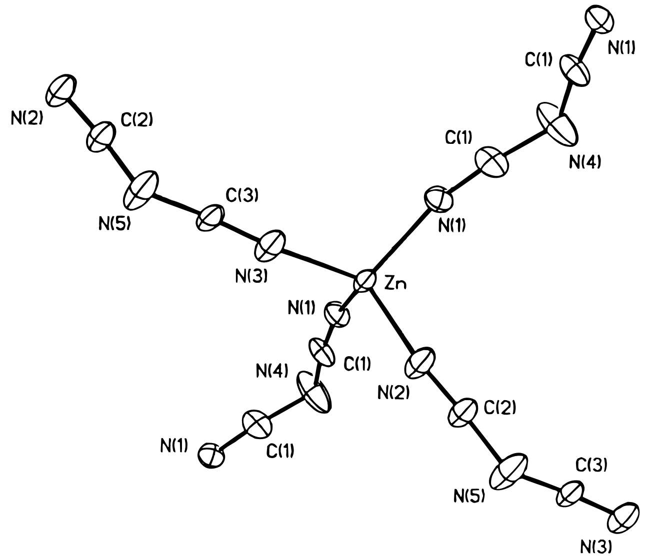

Figure 1. ORTEP diagram[9] (30%) with the atom labeling scheme showing the first coordination sphere of the tetrahedral Zn^{II} site: Zn−N(1) = 1.954 (8) Å, Zn−N(2) = 1.969 (6) Å, Zn−N(1)−C(1) = 156.7 (6)°, and Zn−N(3)−C(3) = 170.5 (7)°.

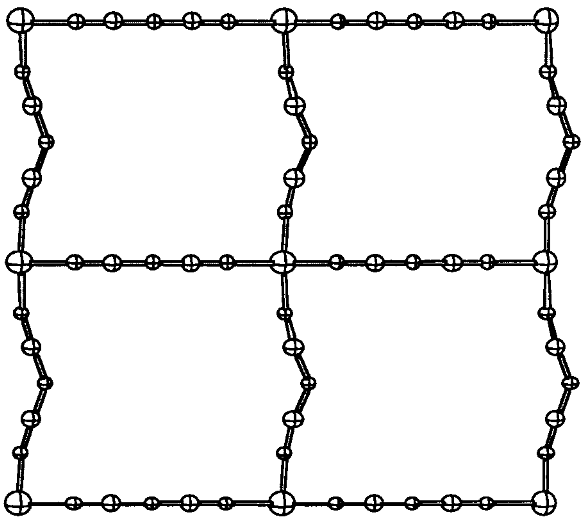

Figure 2. View normal to the crystallographic *ab* plane depicting the nearly ideal square array made up of Zn^{II} vertexes and $[N(CN)_2]^-$ edges.

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(5) A 5 mL aqueous solution of $Zn(NO_3)_2 \cdot 3H_2O$ (1.24 mmol, 0.3019 g) was added while stirring to a 10 mL aqueous solution of $Na[N(CN)_2]$ (2.48 mmol, 0.2204 g) giving immediate precipitation of a white powder. The material was collected by vacuum filtration and dried in vacuo over P_2O_5 for 2 h yielding 0.2188 g (90%). Colorless crystalline blades suitable for X-ray structure determination were grown by slow solvent evaporation of the filtrate over a 3 week period and accounted for the remaining 10% of the total yield. υ(CN) Nujol: 2458 w, 2386 m, 2298 s 2261 s, and 2206 s cm^{-1}. Decomposition occurs above 300 °C (DSC).

(6) Crystal data for C_4ZnN_6: $M = 197.46$, orthorhombic *Pnma*, $a = 7.6209$ (4) Å, $b = 7.5958$ (4) Å, $c = 12.0477$ (7) Å, $V = 697.65$ (7) $Å^3$, $Z = 4$, $D_c = 1.880$ Mg m^{-3}, $R(F) = 0.059$, $R_w(F^2) = 0.1479$, with a goodness-of-fit of 1.108. A colorless blade measuring 0.2 × 0.1 × 0.02 mm was used for the structure determination. Intensity data were collected in the $\theta-2\theta$ scan mode ($6 < 2\theta < 56°$) at −75 °C using a standard Siemens P4 X-ray diffractometer equipped with a SMART CCD area detector and a graphite monochromator ($\lambda = 0.710\,73$ Å). The limiting *hkl* indicies for the collected data were $-9 \leq h < 9$, $-9 \leq k \leq 9$, and $-14 \leq l \leq 15$. Of 4135 reflections collected, 881 were independent ($R_{int} = 0.0681$). All atoms were refined with anisotropic displacement coefficients. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and by full-matrix, least-squares procedures using the Siemens SHELXTL (Version 5.0) Software Package. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Center.

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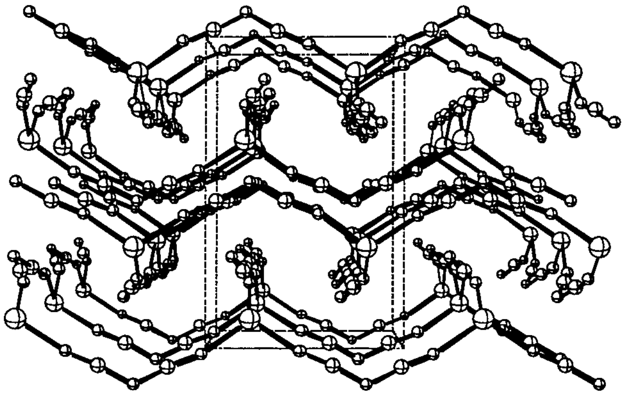

Figure 3. Adjacent tightly packed $Zn[N(CN)_2]_2$ 2-D layers offset by a/2 with respect to alternating sheets. The closest interlayer Zn···Zn separations are 6.335 and 6.673 between pairs and 4.492 Å between staggered pairs.

distances increase with increasing coordination number due to steric crowding. The N(1)−Zn−N(2) and N(2)−Zn−N(3) bond angles are 108.2 (2) and 112.1 (3)°, respectively, and represent a slight distortion from T_d symmetry.

Other examples of μ-bonded dicyanamide-based solids consist solely of 1-D chains, such as those found in $Mn[N(CN)_2]_2(py)_2$,[8] $Sn(CH_3)_2[N(CN)_2]$,[4] and $Ag[N(CN)_2]$.[3] $Zn[N(CN)_2]_2$ represents the first and only example where 1-D ribbons are not observed in the solid state. Two-dimensional buckled layers have been identified in $Zn[N(CN)_2]_2$ (Figure 3), however, two different sheet packings are found. In Figure 3, pairs of tightly packed sheets are generated where each alternating pair is offset 0.5a so as to afford a more efficient crystal packing. Solvent molecules are not intercalated in the structure and interpenetration of multiple 2-D layers does not occur. A density of 1.88 Mg m^{-3} is calculated for $Zn[N(CN)_2]_2$ and is comparable to the value found for $Zn[C(CN)_3]_2$ (1.96 Mg m^{-3}). Furthermore, it is interesting to note that $Zn[N(CN)_2]_2$ has tetrahedral metal sites in contrast to $Zn[C(CN)_3]_2$ which assumes an octahedral geometry and affords an interpenetrating structure. The shortest intralayer Zn···Zn separations are 7.599 and 7.621 Å, while the interlayer separations are significantly shorter at 6.335 and 6.673 Å. In addition, the closest Zn···Zn contact between adjacent sheet pairs is 4.492 Å. Figure 4 gives an alternate view of the sheet packing viewed down the a axis.

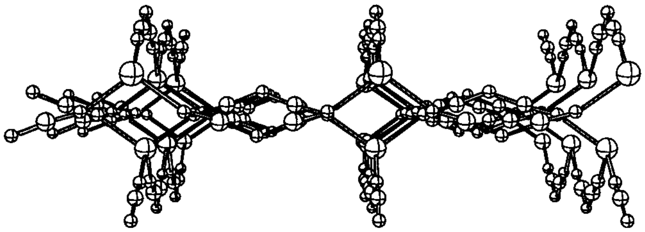

Figure 4. Perspective view of the sheet packing viewed down the a axis.

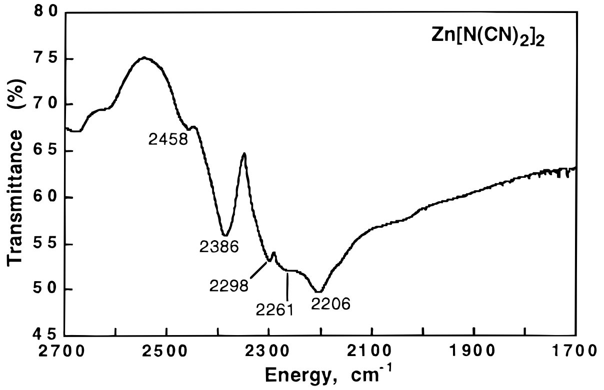

Figure 5. Infrared spectrum of $Zn[N(CN)_2]_2$ showing only the υ_{CN} region.

The infrared spectrum of $Zn[N(CN)_2]_2$ was obtained, and Figure 5 shows the cyano-stretching region. Strong bands at 2386, 2298, and 2261 cm^{-1} are observed, although slightly shifted with respect to other $M[N(CN)_2]_2$ materials, including β-$Co[N(CN)_2]_2$.

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Supporting Information Available: Tables of crystallographic details, positional and thermal parameters, interatomic distance and interatomic angles, and cation and anion labeling diagram for $Zn[N(CN)_2]_2$ (4 pages). Ordering information is given on any current masthead page.

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