

Exploring Uncommon Space Groups in Cadmium Azide Compounds: A Mini-Review with Examples in $I41/acd$, $R\bar{3}$, $Pcca$, and $C2/m$ Crystal Systems

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ABSTRACT

The CCDC statistics reveal that the $P21/c$ space group is the most common space group found in Cadmium Azide complexes. However, there are several rare space groups present in these compounds, which have not been explored in detail. This mini-review aims to shed light on these uncommon space groups in cadmium azide compounds, including $I41/acd$, $R\bar{3}$, $Pcca$, and $C2/m$. Each space group is described in detail, and an example is presented for each to provide a better understanding of their unique properties. For instance, the $I41/acd$ space group has a tetragonal crystal system with a unique four-fold symmetry axis, while the $R\bar{3}$ space group belongs to the trigonal crystal system and has a three-fold axis of symmetry. $Cd(N_3)_2$ is used as an example for each space group to illustrate their characteristics. These findings offer valuable insights into exploring uncommon space groups in cadmium azide compounds, which could lead to the creation of new materials with unique properties. This research could have significant implications for the development of advanced materials in various fields, including electronics, optics, and catalysis.

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1. Introduction

In recent years, there has been a significant focus on the study of coordination polymers due to their unique properties. The azide group is renowned for its high energy content and remarkable reactivity, endowing it with versatility across various fields such as chemistry and material science^{1,2}. The azide group exhibits remarkable chemical reactivity, attributed to its exceptional ability to serve as a leaving group for molecular nitrogen. Azides display versatility in their role as electrophiles, nucleophiles, and radical acceptors, making them suitable for a wide range of reaction pathways involving highly reactive intermediates². The energy properties of azide compounds are influenced by their electronic structure. The presence of negative charges on the terminal nitrogen atoms is associated with lower ionization energies, whereas the central atom positive charge exhibits a higher ionization energy³. The electronic structure of compounds containing the azide group significantly influences their energy transfer and reactivity. Cadmium azide complexes have been particularly interesting because of their potential applications in areas such as photocatalysis and luminescence^{4,5}. Additionally, Cadmium (II) complexes of thioureas have been used to create CdS nanoparticles, which have potential applications in the microelectronic industry⁶. Cadmium azide has also shown promise as a potential candidate for micro-initiating explosives due to its sensitivity, detonation ability, and high-temperature resistance⁷. Nanostructure zinc and cadmium azide and thiocyanate complexes have been synthesized and characterized for their thermal, antimicrobial, and DNA interaction properties⁸. All reported applications are for very broad structures. The group spaces of these structures, particularly in cadmium azide complexes, are quite diverse. While the most common space group for these complexes is $P2_1/c$, there are also some uncommon space groups present in these structures, which is the focus of this mini-review. According to CCDC statistics, these structures have low abundance, with most of them being below 1%.

2. $I4_1/acd$

The space group $I4_1/acd$, also known as $I4(1)/acd$, is part of the tetragonal crystal system and has 16 symmetry operators (as shown in **Figure 1**). It is characterized by a four-fold rotation axis and a perpendicular mirror plane. This space group is commonly found in materials that exhibit negative thermal expansion, such as Ca_2MnO_4 and Ca_2GeO_4 , as well as in the three-dimensional Dirac semimetal Cd_3As_2 . The International Tables Volume A provides diagrams and data tables for all 230 space groups, including $I4_1/acd$ ⁹. In the compounds of cadmium azide, this space group is present in less than 1% of the cases.

One example of a molecule with this space group is $Cd_4(N_3)_4\{(py)_2C(OCH_3)(O)\}_2$ ¹⁰.

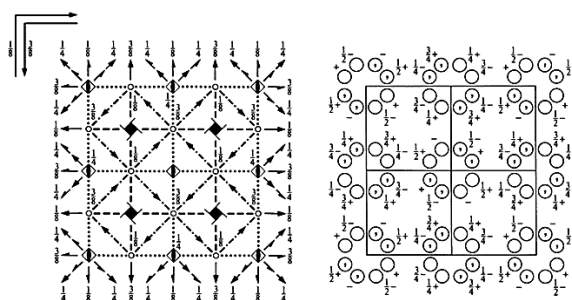


Figure 1. $I4_1/acd$ (International Tables for Crystallography (2016). Vol. A 142, pp. 494-497.)

The compound has a specific shape known as octahedral geometry, and the azide is located at the end of its structure. The structure of the compound is shown in **Figure 2**, and it consists of a symmetrical tetranuclear structure with double open cubane-like shapes that have two missing vertices. The dicubanelike cores are held together by a hydrogen bond between O (4) and H(4A) and O (1). The crystallographically related Cd (1) and Cd(1a) atoms are connected through deprotonated oxygen atoms, O (3) and O(3a), of the monoanion $(py)_2C(OH)O^-$. These atoms also act as triple bridges, connecting to Cd (2) and Cd(2a) atoms, respectively. Additionally, Cd (1) atoms are bridged to Cd (2) through the deprotonated oxygen atom O (1) of the monoanion $(py)_2C(OCH_3)O^-$ and to Cd(2a) through the nitrogen atom N (99) of the end-to-on N_3^- ion. The monoanions $(py)_2C(OH)O^-$ and $(py)_2C(OCH_3)O^-$ coordinate to the metal centers asymmetrically. The local environment around Cd centers can be described as a highly distorted octahedral. Cd (1) atoms are coordinated to two μ_3 -oxygen atoms of the monoanions $(py)_2C(OH)O^-$, one μ_2 -oxygen of $(py)_2C(OCH_3)O^-$, two pyridine nitrogen atoms, and a nitrogen donor of $\mu_{1,1}$ - N_3 bridge. The coordination sphere of Cd (2) atoms is composed of the μ_3 -oxygen atom of the monoanion $(py)_2C(OH)O^-$, μ_2 -oxygen atom of $(py)_2C(OCH_3)O^-$, two pyridine nitrogen atoms, and two nitrogen donors of the terminal and bridging ions, N_3^- . The angles between the Cd atoms and other atoms are also provided in the text, including Cd- N_{azide} -Cd (101.37(13) °) and Cd- $NNCO$ -Cd (100.0(3) °).

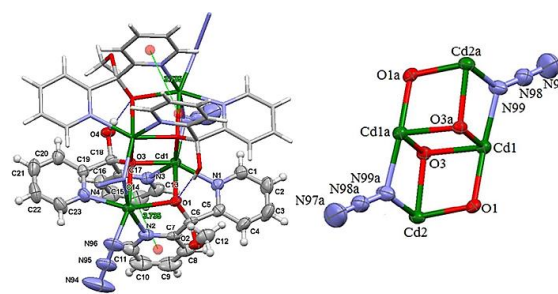


Figure 2. Molecular structures of $[Cd_4(N_3)_4\{(py)_2C(OH)(O)\}_2\{(py)_2C(OCH_3)(O)\}_2]$

3. $R\bar{3}$

The $R\bar{3}$ space group is a crystallographic space group that describes the symmetry of a crystal. It is also known as space group No. 146 and belongs to the trigonal crystal system (Figure 3). The $R\bar{3}$ space group has a three-fold rotation axis and three mirror planes.

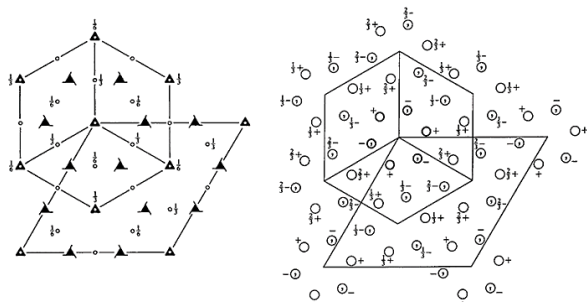


Figure 3. $R\bar{3}$ (International Tables for Crystallography (2016). Vol. A 142, pp. 500.)

It is a subgroup of the hexagonal space group $H\bar{3}$ and is related to the space group $R3$ by a change of origin. The space group symbol $R\bar{3}$ can be used to describe the symmetry of crystals with a rhombohedral unit cell. The International Tables for Crystallography Volume A contains diagrams and tables of data for the 230 space groups, including $R\bar{3}$. The $R\bar{3}$ space group is used to describe the symmetry of various materials, including minerals such as calcite and dolomite^{9,11,12}.

$[Cd_7(pyridine)_6(N_3)_6] (NO_3)_{1.33}(N_3)_{0.66} \cdot 12H_2O$ is contained in this space group with azide bridging. The azide has μ 1,1 mode in this structure¹³. Cadmium is coordinated with six atoms and has octahedral geometry (Figure 4).

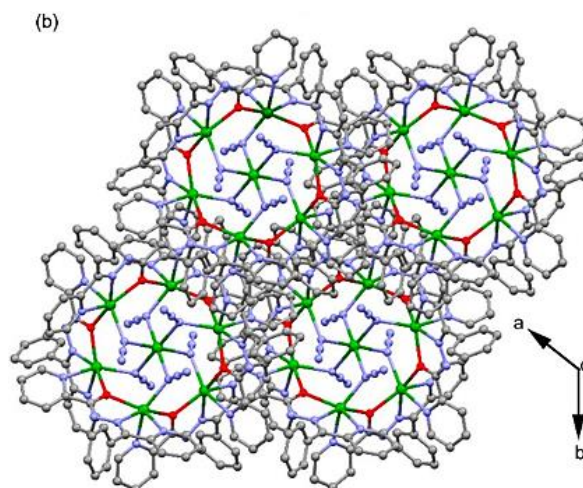
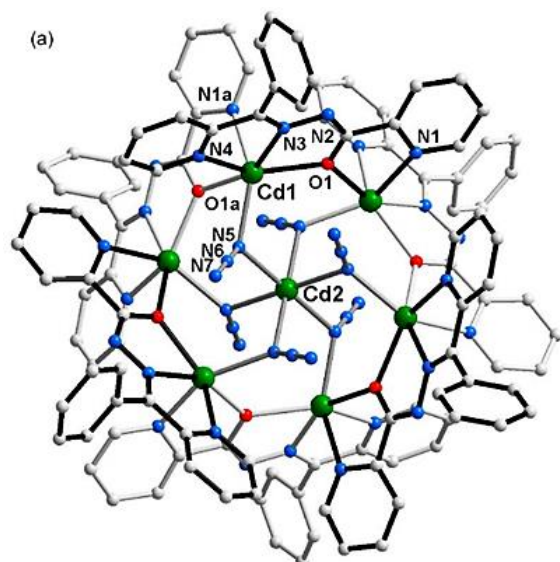


Figure 4. Crystal structure of the cation of $[Cd_7(pyridine)_6(N_3)_6] (NO_3)_{1.33}(N_3)_{0.66} \cdot 12H_2O$ with atom label scheme of the independent unit (primed atoms at $x-y+1/3$, $x-1/3$, $-z+2/3$) (a), and the packing of four molecules of 3 (b). (European Journal of inorganic che

The structure of the compound, crystallizing in trigonal space group $R\bar{3}$, contains a cationic cluster $[Cd_7L_6(\mu_{2-1,1}-N_3)_6]^{2+}$, having an S_6 symmetry, two disordered NO_3^-/N_3^- anions and lattice water molecules. The metal complex is shown in Figure 4. The Cd_7 unit is made up of six $\mu_{2-1,1}-N_3$ ligands that connect the Cd_6 hexagon with the central metal, and six carbonyl μ_2-O atoms that connect the metals at the periphery. The central cadmium atom Cd_2 is located 0.92 Å from the planes defined by the two sets of three coplanar cadmium atoms (Cd_1)₃, with the six L ligands arranged as two open hemispheres surrounding three N_3^- anions in each case. Three N atoms from symmetry-related ligands L complete the distorted octahedral coordination around the Cd_1 metallic core, resulting in an N_4O_2 donor environment. The central Cd_2 has an N_6 donor set built by six azide ligands in an octahedral environment, with bond angles that do not deviate by more than 2° from ideal values. The Cd_1-O coordination bond lengths involving the μ_2-O carbonyl are 2.288(2) and 2.325(2) Å, with a bridging Cd-O-Cd angle of $123.76(9)^\circ$. The Cd-N bond distances relative to the bridging azide ligands are 2.283(2) (Cd1-N) and 2.314(2) Å (Cd2-N), with a Cd1-N5-Cd2 bond angle of $109.06^\circ(10)$. The other Cd1-N bond distances are similar, ranging from 2.340(3) to 2.351(2) Å. The intermetallic distances are 4.0679(2) Å ($Cd_1 \cdots Cd_1$) and 3.7436(2) Å ($Cd_1 \cdots Cd_2$). Figure 4b shows the packing of four molecules. While similar complexes with metals bridged by azide anions have been reported, such as wheel-shaped Co_7 and heteronuclear Ni_4Na_3 ¹⁴ and Co_4Na_3 ¹⁵ clusters, all of which have $\mu_{3-1,1,1}-N_3$ connecting ligands, no example of a Cd_7 member bridged by azido ligands has been reported to date.

4. $Pcca$

The $Pcca$ space group is a crystallographic space group that describes the symmetry of a crystal. It is also

known as space group No. 69 and belongs to the orthorhombic crystal system⁹. The Pcca space group has a glide plane perpendicular to a four-fold rotation axis. The space group symbol Pcca can be used to describe the symmetry of crystals with an orthorhombic unit cell. The International Tables for Crystallography Volume A contains diagrams and tables of data for the 230 space groups, including Pcca. The Pcca space group is commonly found in materials such as LiCoO₂ and LiNiO₂. The combination of all symmetry operations in the Pcca space group results in a total of 16 different space groups describing all possible crystal symmetries in the orthorhombic system (Figure 5).

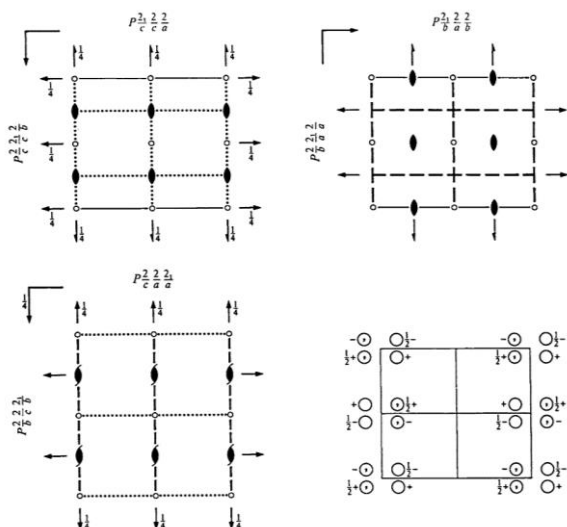


Figure 5. Pcca (International Tables for Crystallography (2016). Vol. A 142, pp. 280.)

The complex [Cd(pypz)₂(dca)₂]_n was synthesized in this space group¹⁶, with the cadmium having octahedral geometry and being coordinated by six atoms as shown in Figure 6. The azide acts in a terminal position in this structure. In the former case, the half-occupied metal ion is coordinated by two half-pypz ligands with C₂ symmetry, while in the latter case, it is coordinated by one independent pypz ligand. The metal centers are bridged by the pypz linkers via terminal pyridyl groups to form 2D (4,4) coordination layers with large square grids. These wavelike layers display a parallel stacking with layer-to-layer separations of approximately 4.1-4.2 Å. The anionic side arms in these structures have extended lengths, typically around 6.4 Å, defined as the distance from one metal center to the furthest terminal atom of the bound anion. For each layer, the dangling anionic pendants located at the axial sites of the octahedral metal centers penetrate the grid-like voids of two adjacent puckered layers up and down. As a result, in each case, three adjacent layers are entangled to produce a 3D polythreaded architecture. Weak interlayer C-H...N hydrogen bonds are found to reinforce such 3D supramolecular networks.

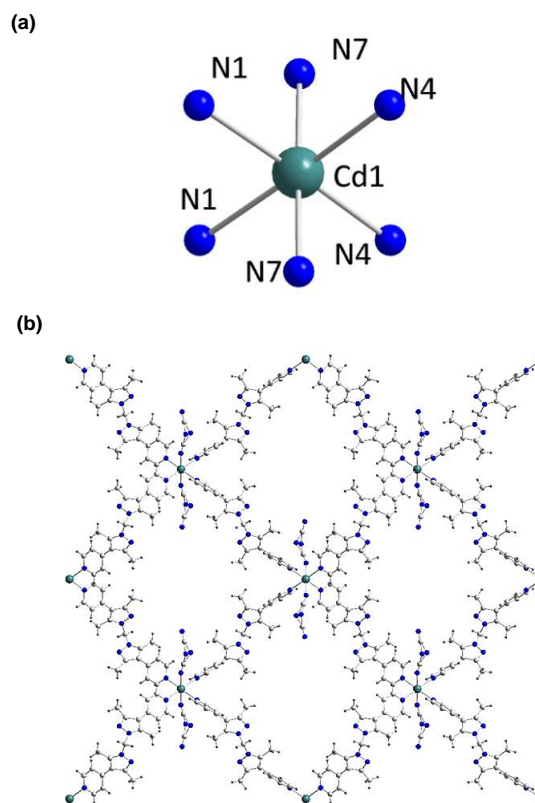


Figure 6. [Cd(pypz)₂(dca)₂]_{n16} (a) Perspective view with atom labeling scheme (b) Packing view

5. C₂/m

The C₂/m space group is a crystallographic space group that describes the symmetry of a crystal. It is also known as space group No. 12 and belongs to the monoclinic crystal system. The C₂/m space group has a two-fold rotation axis and a mirror plane perpendicular to it. The space group symbol C₂/m can be used to describe the symmetry of crystals with a monoclinic unit cell. The International Tables for Crystallography Volume A contains diagrams and tables of data for the 230 space groups, including C₂/m. The C₂/m space group is commonly found in materials such as molybdenum disulfide (MoS₂) and tungsten diselenide (WSe₂). The combination of all symmetry operations in the C₂/m space group results in a total of 15 different space groups describing all possible crystal symmetries in the monoclinic system (Figure 7).

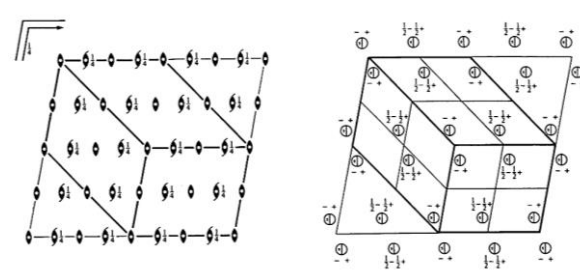


Figure 7. C₂/m (International Tables for Crystallography (2016). Vol. A 142, pp. 174.)

The compound $\{[\text{Cd}(\text{N}, \text{N}-(1,1\text{-methyl})\text{bis}(\text{imidazole}) (\text{L}1))_2(\text{N}3)_2]_n\}$ crystallizes in this space group and has an octahedral geometry with a coordination number of 6¹⁷. The complex consists of 1D neutral polymeric chains, where the Cd^{II} ion is coordinated to four different L1 ligands and two trans azide ligands. The two trans-Cd-N (azide) bond distances are 2.326(3) Å, which is shorter than the four Cd-N(L1) distances of 2.352(8) Å. The cis N-Cd-N bond angles deviate only slightly from Oh symmetry and range from 88.36(9) to 91.57(7) °. Each L1 ligand connects two CdII ions in the bis-monodentate bridging mode to form a linear 1D neutral polymeric double chain. Two Cd^{II} centers are bridged by two L1 ligands to form a 16-membered metallomacrocyclic with a Cd \cdots Cd separation of 9.346 Å. The 1D chains are cross-linked by weak hydrogen bonds between nitrogen atoms of the azide anions and the hydrogen atoms of the imidazole ring (Figure 8). The hydrogen-bonding bond lengths and bond angles are as follows: H \cdots N distances of 2.61, 2.54, 2.39 Å; C \cdots N separations of 3.451, 3.408, 3.345 Å, C-H \cdots N bonds angles of 150, 155, 170°, which are within the normal range of such weak interactions. These weak interactions extend the 1D chains into a 3D structure. It is worth noting that the coordination polymer is extended into higher dimensionality via hydrogen bonds between the 1D systems and not through hydrogen bonds between lattice/ coordinated water and/or anions. This provides an interesting example of supramolecular chemistry and crystal engineering.

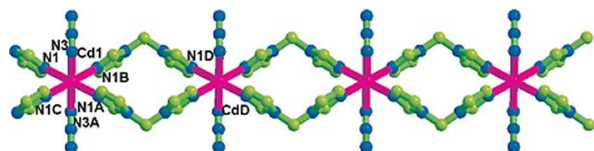


Figure 8. $\{[\text{Cd}(\text{N}, \text{N}-(1,1\text{-methyl})\text{bis}(\text{imidazole}) (\text{L}1))_2(\text{N}3)_2]_n\}$ (Reprinted (adapted) with permission from 17. Copyright (2005) American Chemical Society.)

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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