

A Short Review on Different Bridging Mode of Azide Ion

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Abstract: The azide ion (N_3^-) serves as a versatile bridging ligand in coordination chemistry, particularly in transition metal complexes, due to its diverse coordination modes. The most common are end-on (EO or $\mu-1,1$), where it binds through one nitrogen atom to two metals, and end-to-end (EE or $\mu-1,3$), linking metals via terminal nitrogens. Less frequent modes include $\mu-1,1,1$, $\mu-1,1,3$, and higher denticity variants. These modes enable formation of polynuclear structures, from dinuclear to 2D/3D networks. Magnetically, EO bridging typically induces ferromagnetic coupling, while EE promotes antiferromagnetic interactions (though angle-dependent reversals occur). This review highlights different bridging modes of azide ion.

Keywords: Ligand, polynuclear, bridging.

I. INTRODUCTION

At the beginning of the 20th century, inorganic chemistry was not a prominent field of research. The discovery of metal-ammine complexes, such as $[Co(NH_3)_6]Cl_3$ by Alfred Werner, provided significant impetus and motivation for inorganic chemists to advance the field.[1-2] Today, coordination chemistry is a highly active area of research among synthetic chemists. A wide range of synthetic strategies has been employed to prepare 1D, 2D, and 3D polynuclear supramolecular metal complexes using various bridging ligands, including oxalato ($C_2O_4^{2-}$), cyano (CN^-), azido (N_3^-), nitrate (NO_3^-), nitrite (NO_2^-), and carboxylate ($RCOO^-$) groups.[3-11] Among these, pseudohalides are particularly important due to their versatile coordination behavior, which facilitates the formation of polynuclear complexes. The azido ligand (N_3^-), in particular, has been extensively utilized to construct polynuclear complexes of transition metal ions.[12-15]

The azide ion stands out among bridging ligands for its significance in inorganic chemistry, owing to its diverse bonding modes. It can coordinate as a terminal (monodentate) ligand or as a bridging ligand in multiple geometries. Moreover, a single compound may feature azide ligands in more than one coordination mode simultaneously. Dori and Ziolo classified azido complexes into three main categories: terminal, end-on bridging ($\mu-1,1$ or EO), and end-to-end bridging ($\mu-1,3$ or EE).[16] These two primary bridging modes—end-on (where both metal ions bond to the same terminal nitrogen atom) and end-to-end (where each metal ion bonds to a different terminal nitrogen atom)—are the most common and have been widely exploited. The choice of mode often influences the magnetic properties of the resulting complexes, with end-on bridging typically mediating ferromagnetic interactions and end-to-end bridging favoring antiferromagnetic coupling (though exceptions exist depending on bond angles and other factors). In recent decades, numerous versatile azido-bridged transition metal complexes have been reported, highlighting the ligand's utility in designing polynuclear assemblies with tailored structural and magnetic properties.[12-14]

Structure of azide ions

Azide is a polyatomic ion that is composed of three nitrogen atoms that together have a charge of -1 and N-N bond order is 2. Azide forms both ionic and covalent compounds with metals. Structure of azide ion (N_3^-) is linear and symmetric having equal N-N distances (Fig-1) whereas covalent azides are linear but asymmetric with unequal N-N distances. [17]

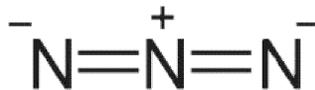


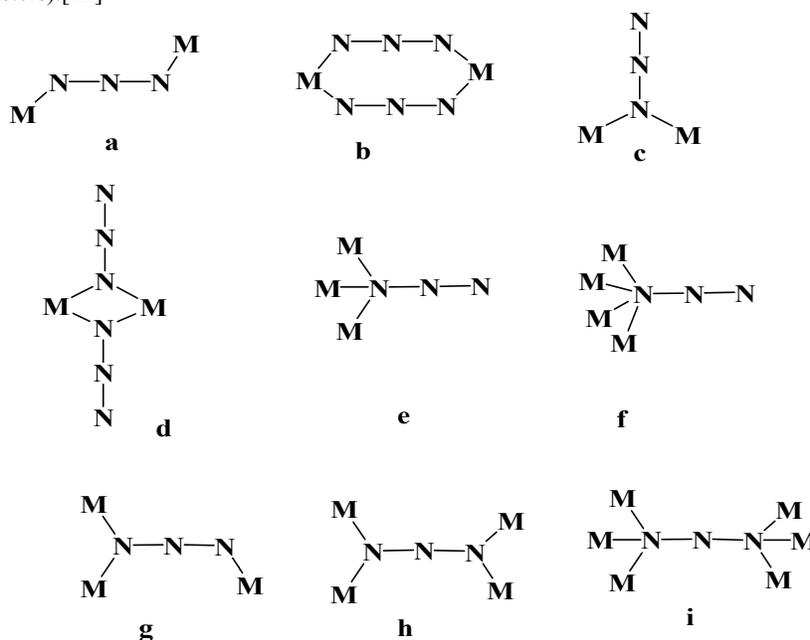
Fig -1: Structure of azide ion

Different bridging modes of Azide ions

The azide ion (N_3^-) stands out as one of the most versatile and effective bridging ligands in coordination chemistry. Its ability to connect multiple metal centers in diverse ways enables the construction of polynuclear complexes, clusters, and coordination polymers with intriguing magnetic properties. Its diverse bridging modes ranging from μ -1,1 (end-on, EO) and μ -1,3 (end-to-end, EE) to μ -1,1,1, μ -1,1,3, μ -1,1,1,1, μ -1,1,3,3, and μ -1,1,1,3,3,3 (Scheme 1).

The primary bridging modes include:

- μ -1,1 (end-on, EO):** The azide binds through one terminal nitrogen atom to two metal ions ($\text{M}-\text{N}-\text{N}_3-\text{M}$, sharing the same N) (Scheme - 1c). This mode typically induces ferromagnetic coupling between metals (e.g., in many Cu(II), Ni(II), and Mn(II) complexes) [16].
- μ -1,3 (end-to-end, EE):** The azide links metals via both terminal nitrogens ($\text{M}-\text{N}=\text{N}=\text{N}-\text{M}$) (Scheme - 1a). This usually results in antiferromagnetic coupling, though the sign can reverse with very large $\text{M}-\text{N}_3-\text{M}$ angles. [16-17]
Higher denticity modes expand versatility in high-nuclearity structures:
- μ -1,1,1 (triply bridging end-on):** One azide coordinates to three metals via the same terminal N (Scheme - 1e). (common in clusters, e.g., Cu(II) or Ni(II) systems with ferromagnetic interactions) [19].
- μ -1,1,3 bridging:** The azide bridges three metals—two via end-on at one end and one via end-to-end (Scheme - 1g). (seen in some Ni(II) or Cu(II) polymers).[20]
- μ -1,1,1,1 (quadruply bridging end-on):** Rare, with four metals sharing one terminal N (Scheme - 1g)..
- μ -1,1,3,3 bridging:** Bridges four metals (two end-on at each terminal N) (Scheme - 1h).[21]
- μ -1,1,1,3,3,3 bridging:** Extremely rare hexadentate mode, bridging six metals (Scheme - 1h). (reported in select high-nuclearity clusters).[22]



Scheme 1: Different bridging modes of azide ion

For example, in $[\text{Ni}(\text{N}_3)_2(\text{dmpd})] \square$ (dmpd = 2,2-dimethylpropane-1,3-diamine), azide adopts a mixed mode (μ -1,1,3-like), forming a 2D sheet with unusual magnetic behavior. In many Cu(II) chains like $\{[\text{Cu}(\text{N}_3)_3]^{-}\} \square$, both EO (μ -1,1) and EE (μ -1,3) modes coexist, yielding 1D structures.

These diverse modes (from bidentate to hexadentate) make azide ideal for tailoring magnetic exchange (ferro- vs. antiferromagnetic) and dimensionality in transition metal complexes, particularly with Cu(II), Ni(II), Mn(II), and Co(II).

IR spectra of azide ion

IR spectra analysis indicates that the free azide ion has stretching frequency 2040 cm^{-1} . [18] IR spectra of sodium azide is shown in Fig. 2. The peaks at $2041 - 2055 \text{ cm}^{-1}$ indicates terminal azide and $2060 - 2075 \text{ cm}^{-1}$ indicates μ -1,1 or μ -1,3 bridging azide. [12]

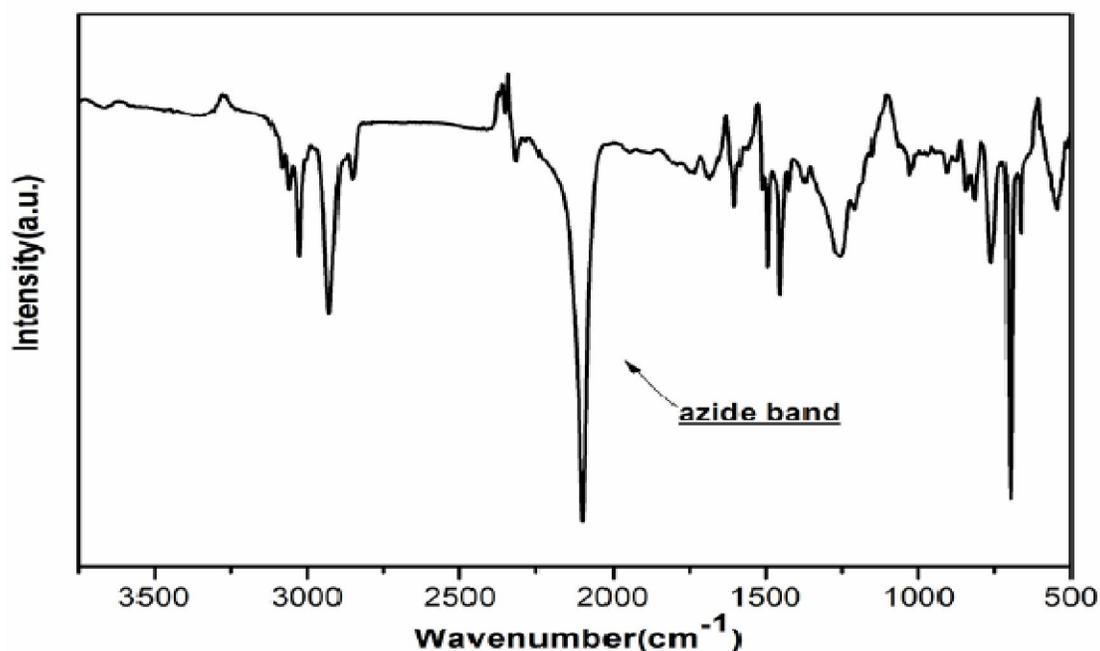


Fig. 2: IR Spectra of NaN_3

Hazards of azide

Sodium azide is commonly used as the azide source in the synthesis of azido-bridged metal complexes. However, it is highly toxic and presents significant health and safety hazards. [19]

Toxicity: Ingestion of as little as 100–200 mg can cause symptoms such as headache, respiratory distress, and diarrhea. Sodium azide in solution is rapidly absorbed through the skin, potentially leading to systemic toxicity. It readily hydrolyzes in water or acidic conditions to form hydrazoic acid (HN_3), a highly toxic, volatile compound that poses a severe inhalation hazard.

Physical and reactivity hazards: Sodium azide decomposes violently (with explosive potential) when heated to approximately $275 \text{ }^\circ\text{C}$. It reacts violently with compounds such as carbon disulfide, bromine, nitric acid, and dimethyl sulfate. It can also react with halogenated organic solvents (e.g., dichloromethane) to produce explosive organic azides.

Explosion risk from metal azides: Contact between sodium azide (or its solutions) and metals such as lead, copper, zinc, silver, or brass can form heavy metal azides, which are highly shock-sensitive explosives. Even dilute solutions may gradually accumulate sufficient azide salts on metal surfaces to create a serious explosion hazard over time. Mixing sodium azide solutions with heavy metal salts (e.g., mercuric chloride) can also trigger explosions.

II. CONCLUSION

There is no doubt that azide ion is best versatile bridging ligand to synthesize polynuclear metal complexes. Recently and past few years azide ion has been employed to synthesize μ -1,1 μ -1,3 to μ -1,1,1, μ -1,1,3, μ -1,1,1,1, μ -1,1,3,3, and μ -1,1,1,3,3,3 transition metal complexes. So, azide ion is the best bridging ligand to synthetic Chemist.

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