IJARSCT

International Journal of Advanced Research in Science, Communication and Technology

International Open-Access, Double-Blind, Peer-Reviewed, Refereed, Multidisciplinary Online Journal

ISSN: 2581-9429

Volume 2, Issue 1, September 2022

Impact Factor: 6.252

Nitrite Ion (NO_2^-) is a Good Bridging Ligand: A Short Review

Dr. Subrata Naiya
Department of Chemistry
Sushil Kar College, Champahati, Baruipur, South 24 Parganas, West Bengal, India

Abstract: *A bridging ligand is a ligand that coordinates to two or more metal atoms or ions in a coordination complex, effectively connecting them. These ligands can be either monoatomic or polyatomic. In coordination chemistry, various types of bridging ligands are recognized. Among them, the nitrite ion (NO□ $^-$) is a notable bridging ligand due to its ability to link two or more metal atoms or ions through its different donor atoms. This text describes the various bridging modes of the nitrite ion and its associated chemistry.*

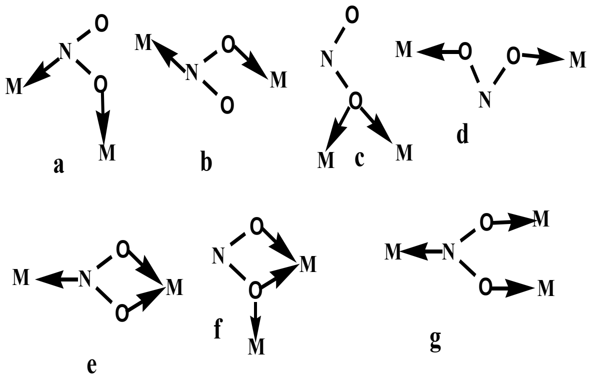
Keywords: Ligand, monoatomic, bridging, coordination

I. INTRODUCTION

The term "ligand" originates from the Latin word meaning "to tie or bind." In coordination chemistry, a ligand functions as a Lewis base, donating lone pair electrons to a metal atom or ion, this acts as a Lewis acid (lone pair electron acceptor). This electron donation results in the formation of a coordination complex [1]. Ligands are classified into various types, including ambidentate, chelating, and bridging ligands. Among these, synthetic chemists often favour bridging ligands for synthesizing polynuclear complexes due to their diverse bridging modes. Commonly used bridging ligands are NO_2^-, N_3^-, SCN^-, OH^-, CO_3^{2-}, CO, and Cl^-.

In recent years, researchers have shown growing interest in synthesizing polynuclear metal complexes using the nitrite ion (NO_2^-) due to its unique properties [2]. The nitrite ion is a small, ambidentate anion with versatile coordination capabilities, making it significant in transition metal chemistry. It can act as either a terminal or bridging ligand, with its bridging behavior being particularly valuable. This versatility enables the formation of diverse structural motifs [3], influencing the electronic, magnetic, and catalytic properties of metal complexes [3-6].

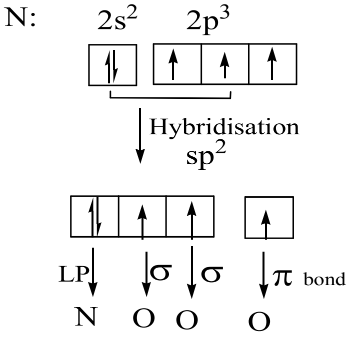
The bridging capability of the nitrite ion (NO_2^-) is particularly distinctive due to its wide range of coordination modes with metal ions. Seven distinct bridging modes of the nitrite ion have been identified in polynuclear compounds [3 - 10] (**see Scheme 1**).



Scheme 1

II. STRUCTURE OF NITRITE ION

The nitrite ion (NO_2^-) carries a negative charge of -1. It consists of a central nitrogen atom covalently bonded to two oxygen atoms. The nitrogen atom undergoes sp^2 hybridization, forming three equivalent sp^2 hybrid orbitals. Two of these orbitals form sigma (σ) bonds with the p orbitals of the two oxygen atoms, while the third sp^2 orbital contains a lone pair of electrons. Additionally, the nitrogen atom has an unhybridized p orbital that participates in pi (π) bonding with one of the oxygen atoms, resulting in a double bond (one σ bond and one π bond) with one oxygen and a single bond (one σ bond) with the other oxygen. (**Scheme -2**)



Scheme-2

Due to presence of one lone paired electron on central nitrogen atom the molecular geometry of the nitrite ion is bent (or V-shaped), with a bond angle of approximately 115°, rather than trigonal planar. (**Fig.-1**)

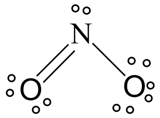


Fig-1

III. COORDINATION MODES OF NO_2^-

The nitrite ion can coordinate in several ways:

a) Monodentate (terminal):

i) Nitro (N-bound): $M–NO_2$

ii) Nitrito (O-bound): M–ONO

b) Bidentate (chelating or bridging):

i) Bridging via both oxygen atoms (μ-O,O')

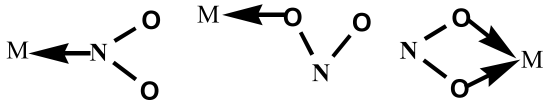
ii) Asymmetric bridging (μ-N,O)

c)Tridentate (bridging or chelating with bridging):

i) Tridentate via both oxygen atoms and nitrogen atom (μ-N,O,O')

3.1.**Monodentate Behavior**

The nitrite ion (NO_2^-) is a versatile ligand in coordination chemistry, capable of binding to metal centers as a monodentate (terminal) ligand. As a monodentate ligand, it typically coordinates through one of its oxygen atoms (O-binding, forming M–O–N=O) or the nitrogen atom (N-binding, forming $M–NO_2$) (**Scheme 3a & 3b**). This single-point attachment distinguishes it from its bidentate or bridging modes. The nitrite ion's coordination mode depends on factors like the metal's electronic properties and the reaction conditions, making it a flexible ligand in forming coordination complexes [1].



Scheme -3

3.2 Bridging Behavior

3.2.1Bidentate (chelating or bridging):

The nitrite ion (NO_2^-) is a versatile bidentate ligand in coordination chemistry. It can coordinate to a metal via:

a) Chelating Mode: Both oxygen atoms of NO_2^- bind to the same metal ion, forming a stable, cyclic chelate complex, often a four-membered ring [3]. **(Scheme -3)**

b) Bridging Mode: Each oxygen or the nitrogen and an oxygen of NO_2^- binds to different metal ions, linking them together in polynuclear complexes.

3.2.2 μ-N,O Bridging

In μ-N,O Bridging mode, the nitrogen atom coordinates to one metal and one oxygen atom to another**(Scheme 1a & 1b)**. This mode is commonly found,[2,11-12] and it can introduce asymmetry and fluxional behavior in the complex.

3.2.3 μ-O,O' Bridging

In this mode, both oxygen atoms of NO_2^- coordinate to two different metal centers(**Scheme 1c & 1d)**. This is the rare bridging mode and leads to the formation of dinuclear or polynuclear complexes [4,13-14]. The O,O'-bridging mode typically supports relatively rigid, planar structures.

3.3 Tridentate Behavior

3.3.1 tridentate (μ-N,O,O') Bridging

The tridentate bridging modes in which the NO_2^- ion is chelatedto one metal through the two oxygen atoms and bridged to a secondmetal ion either through the nitrogen atom [13-14]**(Scheme 1e)** orthrough one of the chelating oxygen atoms [15] **(Scheme 1f)**.Thesemodes of bridging are very uncommon in coordination chemistry.

IV. STRUCTURAL CONSEQUENCES

Magnetic properties

Bridging NO_2^- ions often result in metal-metal communication, which is important in magnetic and electronic materials. O/N-bridging mode (**Scheme 1a,b**) is most commonly found,[2-3,11-12] and it usually shows moderate antiferromagnetic interactions.[2-3,12] The two-atom O/O' bridging mode (**Scheme 1d**) of the nitrite ion is known to provide ferromagnetic coupling but examples are very rare.[4,8-9] The tridentate bridging modes in which the NO_2^- ion is chelated to one metal through the two oxygens and bridged to a second metal ion either through the nitrogen atom [15] (**Scheme 1e**) or through one of the chelating oxygen atoms [4-5] (**Scheme 1f**) are also uncommon and they usually mediate antiferromagnetic interactions.[5]

Bioinorganic relevance

Nitrite bridging—particularly via μ-nitrito or μ-oxo coordination—plays a pivotal role in metalloenzyme catalysis, especially in copper-containing nitrite reductases (CuNiR). It enables **efficient intramolecular electron transfer** from the Type-1 (T1) to the Type-2 (T2) copper centers by way of a conserved **Cys–His covalent bridge**, which couples redox sites and facilitates rapid turnover of nitrite to nitric oxide.[16-17]

Catalysis

Nitrite bridges are commonly observed in transition metal complexes involved in nitrogen cycle reactions, including nitrite reduction and NO_x transformations. The mode of coordination (e.g., O,O'-bridging or N,O-bridging) and the flexibility of the nitrite ligand allow for dynamic changes in the catalyst structure, which can facilitate electron transfer and substrate activation. These features make nitrite-bridged systems valuable models for metalloenzymes and promising components in synthetic catalytic systems for environmental and energy applications.[18]

IR spectra

In IR spectroscopy, nitrite bridging can be identified by characteristic vibrational bands, particularly in the N–O stretching region. Bridging nitrite ligands typically show two or more N–O stretching vibrations due to asymmetric coordination between metal centers. In μ-nitrito (O,O'-bridging) complexes, symmetric and asymmetric N–O stretches usually appear in the range of 1200–1400 cm^{-1}, often split due to different bonding environments [3]. In contrast, N-bound (nitro) or O-bound (nitrito) terminal ligands have more distinct single bands. The presence of multiple N–O stretches and their shifts relative to free nitrite provide evidence of bridging coordination [2-3]. Additionally, M–O and M–N vibrations may appear in the far-IR region (below 600 cm^{-1}), supporting the bridging nature. Overall, IR spectroscopy is a useful tool to distinguish between bridging and terminal nitrite ligands in metal complexes.

V. CONCLUSION

Nitrite is a flexible and functionally rich bridging ligand with significant structural and electronic implications. Its ability to adopt multiple coordination modes makes it a valuable component in designing novel coordination compounds with potential applications in catalysis, magnetism, and materials science.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to the Department of Chemistry, Sushil Kar College, for their invaluable support throughout this project. I am especially thankful to my Principal for his encouragement, insightful suggestions, and for providing access to the necessary resources and laboratory facilities.

REFERENCES

[1] C. E. Housecroft, &A. G. Sharpe, (2012). Inorganic Chemistry (4th ed.). Pearson Education Limited.
[2] P. Mukherjee, M. G. B. Drew, C. J. G´ omez–Garc´ ıa and A. Ghosh, Inorg. Chem., 2009, 48, 5848;
[3] S. Naiya, H. S. Wang, M.G.B.Drew, Y. Song and A. Ghosh, Dalton Trans., 2011, 40, 2744
[4] T. Liu, Y.-H.Chen, Y.-J.Zhang, Z.-M. Wang and S. Gao, Inorg. Chem., 2006, 45, 9148; [5] A. Gleizes, A. Meyer, M. A. Hitchman and O. Kahnsl, Inorg.Chem., 1982, 21, 2257.
[6] U.Fl¨ orke, H.-J. Haupt and P. Chaudhuri, J. Chem. Soc., Dalton Trans., 1998, 3801
[7] L.-K. Chou, K. A. Abboud and D. R. Talham, Chem. Mater., 1994, 6, 2051.
[8] V. Vo, Y. Kim, N. V. Minh, C. S. Hong and S.-J. Kim, Polyhedron, 2009, 28, 1150
[9] J. C. Byun, W. H. Lee and C. H. Han, Inorg. Chem. Commun., 2006, 9, 563.
[10] A. Escuer, M. Font-Bard´ ıa, E. Pe˜ nalba, N. Sanz, X. Solans and R. Vicente, J. Chem. Soc., Dalton Trans., 1999, 3115.
[11] U.Fl¨ orke, H.-J. Haupt and P. Chaudhuri, J. Chem. Soc., Dalton Trans., 1998, 3801
[12] L.-K. Chou, K. A. Abboud and D. R. Talham, Chem. Mater., 1994, 6, 2051.
[13] V. Vo, Y. Kim, N. V. Minh, C. S. Hong and S.-J. Kim, Polyhedron, 2009, 28, 1150
[14] J. C. Byun, W. H. Lee and C. H. Han, Inorg. Chem. Commun., 2006, 9, 563.
[15] A. Escuer, M. Font-Bard´ ıa, E. Pe˜ nalba, N. Sanz, X. Solans and R. Vicente, J. Chem. Soc., Dalton Trans., 1999, 3115.
[16] Kataoka, K., Furusawa, H., Takagi, K., Yamaguchi, K., & Suzuki, S. Journal of Biological Chemistry, (2000), 11, 8237
[17] E. I. Tocheva, L. D., Eltis, & M. E. P. Murphy, Nature, (2008), 455, 376.
[18] A. J. Timmons, M. D. Symes, Chem. Soc. Rev., 2015, 44, 6708

DOI: 10.48175/IJARSCT-8349N