

AZIDE ION: THE BEST BRIDGING LIGAND TO SYNTHETIC CHEMIST

Dr. Subrata Naiya

SushilKar College, Ghoshpur, Champahati, Baruipur, 24 Parganas (S), West Bengal
743330, India

Abstract: Ligand is a Lewis base and Metal atom or ion is a Lewis acid. Ligands donate their electron pairs to metal atom or ion to form coordinate bond. Various types of ligands like monodentate, polydentate, ambidentate, chelating, bridging etc. are known. Among these bridging ligand is more important to synthetic chemist because it connects two or more metal atoms or metal ions to form polynuclear complexes. Among various bridging ligands azide ion is best because of its various bridging modes. Here, different bridging modes of azide ion have been described.

Key words: Ligand, polynuclear, ambidentate

Introduction:

At the beginning of the 20th century, inorganic chemistry was not a prominent field for researchers. After discovery of metal-amine complexes such as $[\text{Co}(\text{NH}_3)_6\text{Cl}_3]$ by Alfred Werner, inorganic chemists and researchers got a sunshine and motivation to enrich their research in inorganic field.^[1-2] Now, research on coordination chemistry becomes a hot topic for synthetic chemists. A variety of synthetic strategies have been applied to synthesize 1D, 2D, 3D polynuclearsupramolecular metal complexes with different bridging ligands like oxalato ($\text{C}_2\text{O}_4^{2-}$), cyano (CN^-), azido (N_3^-), nitrate (NO_3^-), Nitrite (NO_2^-) and carboxylate (COO^-).^[3-11] Among the bridging ligands, pseudohalides are very important, due to their versatile coordination behaviour that generates polynuclear complexes. However, azido ligand has been extensively used to synthesize polynuclear complexes of transition metal ions.^[12-15]

Among all bridging ligands azide ion is more important to inorganic chemist to synthesize polynuclear metal complexes due to different modes of bonding as it acts as a terminal ligand (mono-dentate) or bridging ligand with several types of bonding modes. Furthermore, the azide complexes may contain more than one of these modes of bonding

in the same compound. Dori and Ziolo, have divided the azide complexes into three main groups (terminal, end-on bridging, end-to-end bridging).^[16] Now, many versatile azido bridged transition metal complexes have been investigated.^[12- 14]

Structure of azide ions

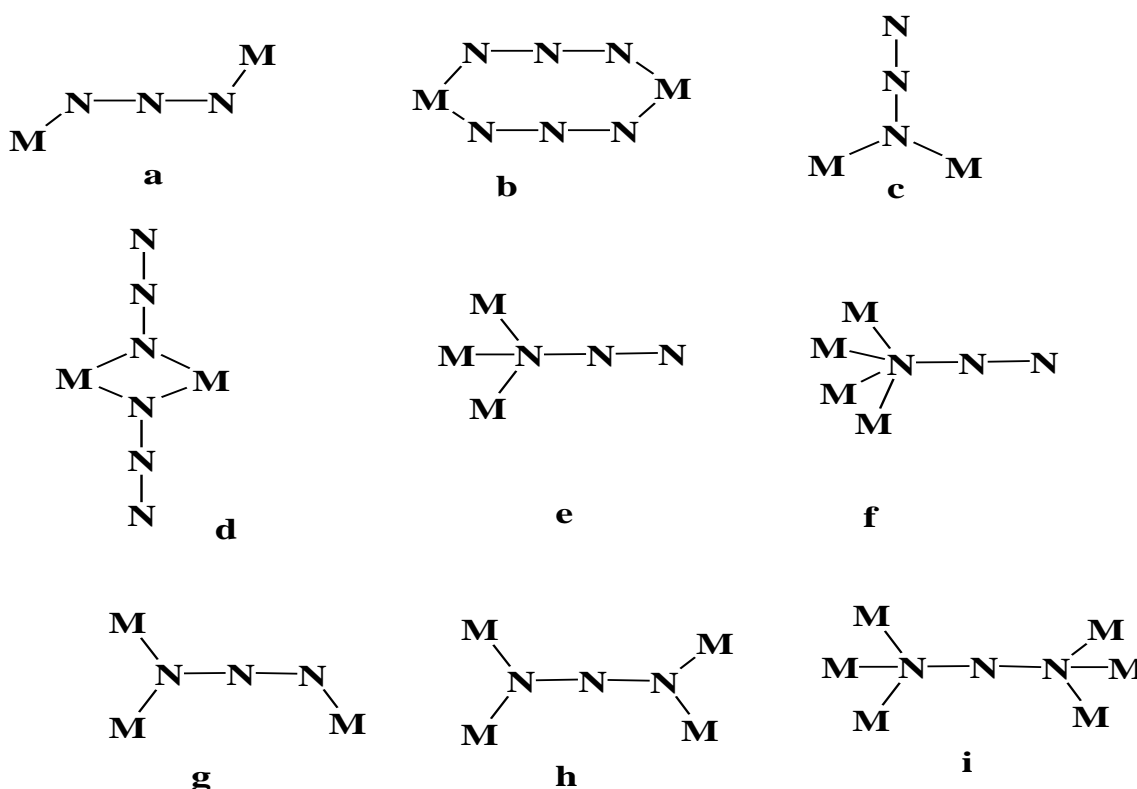
Azide is a polyatomic ion that is composed of three nitrogen atoms that together have a charge of -1 and N-N bond order is 2. Azide forms both ionic and covalent compounds with metals. Structure of azide ion (N_3^-) is linear and symmetric having equal N-N distances (Fig-1) whereas covalent azides are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



Fig -1: Structure of azide ion

Different bridging modes of Azide ions

Among all bridging ligands azide is an excellent and versatile ligands because it exhibits 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).



Scheme 1: Different bridging modes of azide ion

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]

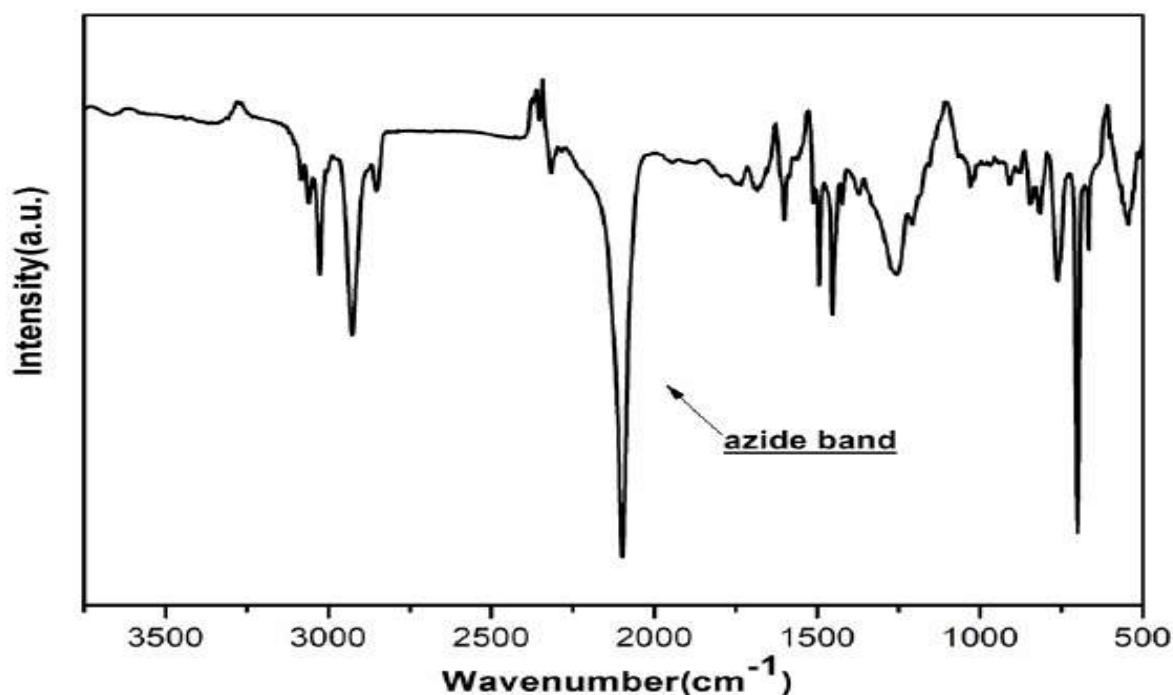


Fig. 2: IR Spectra of NaN_3

Hazards of azide

In most of the cases sodium azide is used to synthesize azido bridged metal complexes. But it is highly toxic.^[19] Ingestion of 100 to 200 mg can result in headache, respiratory distress, and diarrhea. Sodium azide in solution is rapidly absorbed through the skin. It rapidly hydrolyzes in water and acids, forming hydrazoic acid (HN_3), a highly toxic and volatile liquid solution that poses a serious inhalation hazard. It also decomposes violently when heated to 275°C . It reacts violently with carbon disulfide, bromine, nitric acid, and dimethyl sulphate. It reacts with halogenated organics (e.g., dichloromethane), forming explosive organic azides.

When sodium azide or its solutions come into contact with metal surfaces such as lead, copper, zinc, silver, or brass, heavy metal azides are formed. These metal azides are highly explosive. Even dilute solutions can accumulate enough azide salts over time to cause a serious explosion. Mixing sodium azide solutions with heavy metal salts including mercuric chloride can lead to explosions.

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.

Acknowledgments

I thank to University Grants Commission, India for funds provided through Minor Research Project No. F. PSW150/11-12 (ERO). I am also thankful to Sushil Kar College for research in beautiful environment.

References

1. Huheey, E. James Inorganic Chemistry (3rd ed.). PP. 360, 1983
2. J.Bjerrum, J. P. McReynolds, Inorg. Synth.Vol. 2, PP. 216–221, 1946
3. O.Kahn, , Molecular Magnetism, VCH, Weinheim, 1993.
4. M.Pilkington, S.Decurtins, J.A.McCleverty, T.J., Meyer (Eds.) Comprehensive Coordination Chemistry II.From Biology to Nanotechnology, Elsevier, vol. 7, pp. 177-184, 2004.
5. M.Verdaguer, A.Bleuzen,V.Marvaud, J. Vaissermann,M.Seuleiman, C.Desplanches, A.Scuiller, C. Train, R.Garde, G.Gelly, C.Lamenech, I.Rosenman, P.Veillet, C. Cartier, F.Villain, Coord. Chem. Rev., vol. 1023, pp. 190-192, 1999.
6. M. Ohba,H., Coord. Chem. Rev. vol. 198, pp. 313-328, 2000.
7. S.Naiya,H.S. Wang, M. G. B. Drew,Y. Song, A.Ghosh, vol. Dalton Trans., vol-40, pp. 2744- 2756, 2011

8. M. S. E. Fallah, R. Vicente, J. Tercero, C. Elpelt, E. Rentschler, X. Solans and M. Font-Bardia, *Inorg. Chem.*, 2008, 47, 6322;
9. E. Colacio, J.-M. D. Vera, J.-P. Costes, R. Kivekas, J.-P. Laurent, J. Ruiz and M. Sundberg, *Inorg. Chem.*, 1992, 31, 774;
10. M. S. Ray, A. Ghosh, A. Das, M. G. B. Drew, J. Ribas-Arino, J. Novoa and J. Ribas, *Chem. Commun.*, 2004, 1102
11. S. Naiya, S. Biswas, M. G.B. Drew, A. Ghosh, *Vol. 34*, pp. 67-73, 2012
12. S. Naiya, C. Biswas, M. G. B. Drew, C. J. Gomez-Garcı, J. M. Clemente-Juan, A. Ghosh, *Inorg. Chem.*, *Vol. 49*, PP. 6616–6627, 2010.
13. C. Adhikarya, S. Koner, *Coord. Chem. Rev. Vol. 254*, PP. 2933–2958, 2010
14. G.S. Papaefstathiou, S.P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans, *Angew. Chem. Int. Ed. vol.40*, pp. 908-910, 2001.
15. F. Meyer, P. Kircher, H. Pritzkow, *Chem. Commun.* pp. 774-775, 2003.
16. Z. Dori, R. F. Ziolo, *Chem. Rev.*, *Vol. 73*, PP. 247–254, 1973.
17. Fehlhammer, W. Peter, Beck, Wolfgang *Allgem. Chem. Vol. 639*, PP 1053–1082, 2013.
18. R.T.M. Fraser, *Anal. Chem. Vol. 31*, PP. 1602–1603, 1959
19. P.G. Urben (Ed.), *Bretherick's Handbook of Reactive Chemical Hazards 6th Ed.*, Oxford, Butterworth-Heinemann, 1999.