

Coordination Polymers Containing Dicyanamide as Bridging Ligand: A Review

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Abstract

Dicyanamide $[\text{N}(\text{CN})_2]^-$, dca] bridged multinuclear metal complexes are described from the perspective of their structure and magnetism. It has been observed from several reports that dicyanamide can bind one, two or more metal centres with different bridging modes like $\mu_1, \mu_{1,3}, \mu_{1,5}, \mu_{1,1,5}, \mu_{1,3,5}$ modes and end up with a diverse range of 1D, 2D and 3D coordination polymers. Variable temperature magnetic study shows that depending on the nature of the metal centres some of these compounds show very interesting magnetic interaction through dcabridge. As for example, the neutral binary systems, $\text{M}(\text{dca})_2$, form three-dimensional rutile-like structures that exhibit ferromagnetic ($\text{M} = \text{Co}$ and Ni), antiferromagnetic ($\text{M} = \text{Cr}$, Mn and Fe) or paramagnetic ($\text{M} = \text{Cu}$) ground states. Among the different bridging modes $\mu_{1,5}$ bridging is occurred in most of the cases and a weak antiferromagnetic interaction is operating in these compounds.

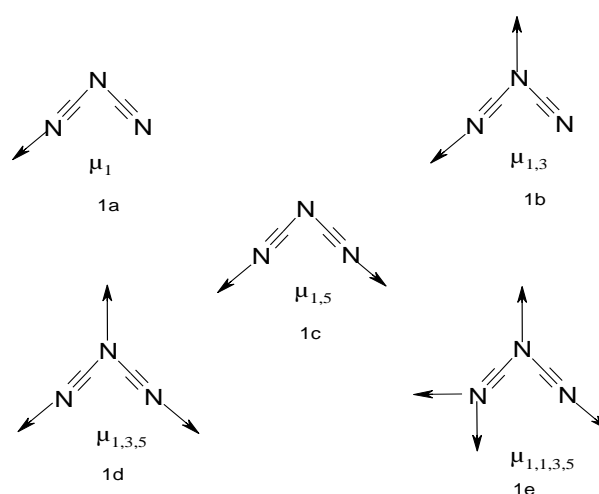
Key words: Coordination polymers, dicyanamide, magnetic properties

1. Introduction

The recent development in designing the novel solid-state structures and preparation of polynuclear complexes with one-, two- or three-dimensional homo- or heterometallic infinite frame-work and also mono- and dinuclear complexes are the subject of great interest due to

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their widespread applications in various fields like molecular magnetism, photochemical activity, inter-valence electron transfer reaction, catalytic reactions, biosynthesis etc. Additionally, the field of molecular magnetism has undergone quite impressive progress in the last decade¹. The magnetic exchange phenomenon within a molecule was first discovered by Guha et al. in year of 1951² and then by Bleaney and Bowers³, on a compound Cu(II) acetate monohydrate. These interactions may arise by the direct overlapping of magnetic orbitals of two connected metal centres or via super exchange through bridging atoms like O, N, S etc. Such interactions either decrease or increase the magnetic moment of the complex as a whole. In this connection, pseudohalide bridged polynuclear and dinuclear complexes continues to be subject of much interest, and intensive investigations have taken place as a result of their divers structures and potential applications in magnetic materials. Among the pseudohalides, dicyanamide $[\text{N}(\text{CN})_2]^-$, bridged polynuclear systems are a fast growing research field due to the large variety of topologies and magnetic properties that may be obtained from this ligand. Here my discussion is focussed only on the structures and magnetic properties of some dicyanamide bridged manganese, nickel and copper complexes.



Scheme 1. Different bridging modes of dicyanamide ligand

2. Different coordination modes of dicyanamideligand

The versatility of the dicyanamide as a ligand is well illustrated by its five structurally characterised coordination modes shown in Scheme¹⁻⁸, monodentate coordination through nitrile nitrogen atom (1a), bis-monodentate bridging through one nitrile and one amide nitrogen atoms (1b), end-to-end bridging through two nitrile nitrogen atoms (1c), tris-

monodentate bridging of three metal atoms (1d) and rarer μ_4 coordination where one of the two nitrile nitrogen atoms is coordinated to two metal ions (1e).

3. Different geometry of the coordination polymers containing dca ligand and their magnetic properties

It has been observed from the reported crystal structures that most synthetic efforts have apparently focused on Mn^{2+} ion⁹⁻¹¹. Escure et al. reported two new one-dimensional compounds, *trans*-[Mn(4-bzpy)₂(N(CN)₂)₂]_n and *cis*-[Mn(bpy)(N(CN)₂)₂]_n, (4-bzpy = 4-benzoylpyridine; bpy = 2,2'-bipyridyl) (Figure 1). Both the compounds exhibit weak antiferromagnetic coupling¹².

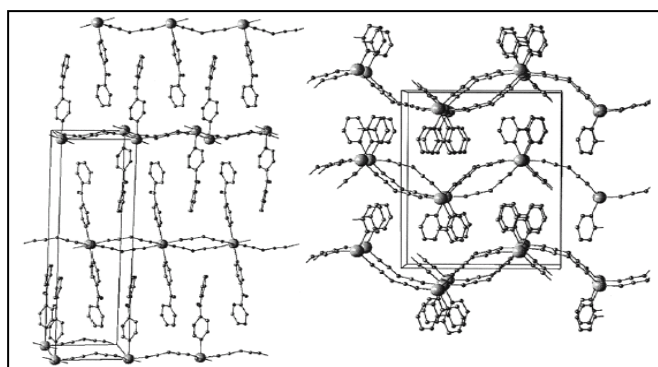


Figure 1. View along (001) direction of the unit cell of *trans*-[Mn(4-bzpy)₂(N(CN)₂)₂]_n and *cis*-[Mn(bpy)(N(CN)₂)₂]_n showing the packing of the chains¹²

Over the past years or so, several new binding modes have been identified although the $\mu_{1,5}$ -mode seemingly appears on a more regular basis and the manganese and nickel complexes with $\mu_{1,5}$ -dicyanamide bridging generally shows weak antiferromagnetic interaction⁹⁻¹². The neutral, binary systems, $M(dca)_2$, form three-dimensional rutile-like structures that exhibit ferromagnetic ($M = Co$ and Ni), antiferromagnetic ($M = Cr, Mn$ and Fe) or paramagnetic ($M = Cu$) ground states¹³. A 2D nickel(II) coordination polymer $Ni(dca)_2(H_2O) \cdot phz$ [$phz = phenazine$] (Figure 2) containing both bi- and tri-dentate dicyanamide bridges and intercalated phenazine was reported by Murrey and co-workers. Magnetic study indicates the complex displays long-range order ($T_c = 5.7 K$)¹⁴.

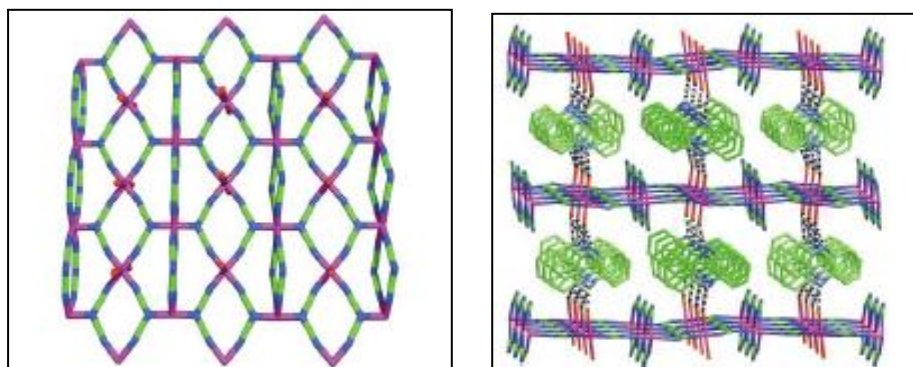


Figure 2. (a) 2D coordination polymer sheet structure of $\text{Ni(dca)}_2\text{-(H}_2\text{O).phz}$; (b) the alternate stacking of 2D $\text{Ni(dca)}_2\text{(H}_2\text{O)}$ coordination polymer sheets¹⁴

Fewer studies have utilised with Cu^{2+} ions and a handful of molecular and polymeric structures are known. The copper (II) ion is often known to adopt five-coordinate geometry, and a number of chain compounds have been reported in which such copper atoms, which are also coordinated to chelating ligands, are bridged by $\mu_{1,5}$ -dca ligands into 1D chains, $\text{Cu(dca)}_2\text{L}$, $\text{L} = 2,2'$ -bipyridine¹⁵ or $2,2'$ -dipyridylamine¹⁶ also have monodentate μ_1 -dca ligands, and show zigzag and linear geometries, respectively. No significant magnetic coupling was observed for the former compound, while weak intra-chain antiferromagnetic coupling ($J = -0.10 \text{ cm}^{-1}$ for a $-JS_1 \cdot S_2$ model of Hall)¹⁷ was reported for the latter. The most interesting compounds, atleast from a perspective of magnetism, are the α - and β -forms of $[\text{Cu(dca)}_2(\text{pyz})]$ {pyz = pyrazine} that have three-dimensional (3D) and two-dimensional (2D) frameworks, respectively, and 3D $[\text{Cu}_3(\text{dca})_6(\text{pym})_2]$ {pym = pyrimidine} that consists of an intricate self-penetrating lattice. While there was hints of weak spin-coupling in α - Cu(dca)_2 having rutile(TiO_2) like topology¹⁸, it is only recently that ferromagnetic order has been observed by means of field dependent specific heat measurements¹⁹. Additionally, supramolecular structure with intermolecular hydrogen bonding through dicyanamide nitrogen atom are also found in some reported complexes²⁰⁻²².

4. Structural modification by incorporation of different coligands

Modification of structures and the magnetic properties of the coordination polymers of dca ligand is possible by incorporation of coligands into the structures. As for example Escureet, *et.al.* reported²³ two one dimensional dicyanamide bridged derivatives with formula $[\text{Mn(ac)(terpy)}(\mu_{1,5}\text{-dca})]_n$ and $[\text{Mn(pdz)}_2(\mu_{1,5}\text{-dca})_2]_n$ {ac = acetate; terpy = $2,2':6'2''$ -terpyridine; pdz = pyridazine} having single and double dca bridges respectively. The first

complex contains heptacoordinated manganese(II) central atom with MnN_5O_2 pentagonal bipyramid environment, where as in the second complex manganese atom is hexacoordinated and both the complexes show weak antiferromagnetic coupling. Similarly there are several reports of dca complexes where the geometry and magnetic properties of complexes depend on the nature of the coligand used²⁴⁻²⁷.

5. Conclusion

Dicyanamide is a very good bridging ligand which gives a wide range of interesting polynuclear architectures with various transition metal ions. Some of these complexes also exhibit very interesting magnetic properties. The structural variation of the complexes can be possible by changing the coligand. Among all possible coordination modes of dca the $\mu_{1,5}$ -dca bridged complexes are very common and generally characterised by antiferromagnetic interactions among the so-linked metal ions.

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