

Synthesis and Magnetic Properties of Polynuclear Complexes of 1st Transition Metals: A Mini Review

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Abstract

The design and synthesis of multinuclear complexes has attracted considerable interest for their utility in small memory devices and quantum phenomena. The studies of magnetic studies of those complexes are very important to know their behavior in presence of magnetic fields. Now a days, ongoing interest is to synthesis single molecule-based magnets (SMMs) that can be derived from transition metals with different ligands. Majority of the metals that are used for the synthesis of such single-molecule magnets are Co(II/III), Mn(II/III), Cu(II) and Ni(II). Different synthetic routes and ligands have been used to get multinuclear 1st transition metal complexes, especially bridging ligands such as azide, thiocyanate, cyanate, hydroxyl, carboxylates etc. along with phenol-based Schiff base ligands are widely used. The exchange coupling between the unpaired electrons of two metal centers connected through bridging ligands depends on several factors, such as metal metal distance, bridging angles, geometry, etc.

Keywords: *3d Metal Complex; High Nuclearity; Polynuclear; Single Molecule Magnet (SMM)*

Introduction

The polynuclear transition metal complexes are of ongoing interest for their relevance to biological systems (Messerschmidt *et al.*, 2001) due to their utility for designing active sites of metalloproteins, in molecular magnetism, especially for the single molecular magnets (SMM) (Miyasaka *et al.*, 2004; Sahu *et al.*, 2023; Dey *et al.*, 2023), and for devising nano-materials (Weiss, 2010) for their potential use in nanoscience and technology. Most importantly, the magnetic properties of the multinuclear complexes containing paramagnetic centers have taken great attention for their wide range of technological applications. The literature survey reveals that the coupling constant (J) depends on the M-A-M (M = metal, A = bridging atom) angle and M-A bond lengths (Nanda *et al.*, 1994). The coupling between the metal centers can be modulated by changing the geometry of the complex around the metal center or by changing the bonding parameters that are associated with the interaction of the metal centers along with the bridging ligands. Therefore, appropriate metal ions as well as bridging ligands are vital for the formation of desired multinuclear complexes (Mukherjee *et al.*, 2009). Various synthetic methods have been developed for obtaining multinuclear transition

Exploration of Chemical Complexity

metal complexes. The synthetic strategies sometimes make it difficult to get predicted structure, but the targeted complexes that behave as single-molecule magnets (SMM's) are always a subject of extensive investigation. The large spin ground state and a significant negative (easy-axis) magneto anisotropy make the system an intrinsic bistability with very slow thermal relaxation of the magnetization at very low temperatures in the molecular magnets (Das *et al.*, 2011) that are widely used for their possible applications in small memory devices as well as in quantum computing (Thomas *et al.*, 1996).

Review of Literature

Polynuclear metal clusters with high nuclearity by using a variety of poly-pyridine and poly- β -diketonate ligands and 3d metals V to Cu have gained attention for single-molecule magnets (SMMs). Many of these, specially $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CR})_{16}(\text{H}_2\text{O})_4]$ and $[\text{Mn}_4\text{O}_3\text{Cl}_4(\text{O}_2\text{CEt})_3(\text{py})_3]_2$ compounds, can be given as examples of nanoscale magnets (Sessoli *et al.*, 1993; Sieber *et al.*, 2005). Various polynuclear clusters form nanoscopic architectures with interesting magnetic properties (Gole, Mondal & Mukherjee, 2014). Mukherjee *et al.* (2003) also designed polynuclear complexes with bridging carboxylate groups and studied their magnetic properties. The magnetic nature of 1st transition metal complexes is shown in Table 1.

Table 1: Some selective 1st transition metal complexes with their magnetic nature

Compound	Magnetic Nature	J (cm ⁻¹)	Ref.
$[\text{Cu}(\text{L})(\mu_{1,1}\text{-N}_3)(\text{ClO}_4)]_2$	Antiferromagnetic	-7.2	Nandy <i>et al.</i> , 2015
$[\text{Cu}(\text{L})(\mu_{1,1}\text{-NCO})(\text{ClO}_4)]_2$	Ferromagnetic	+0.41	Nandy <i>et al.</i> , 2015
$[\{\text{Cu}(\text{L})(\text{CF}_3\text{COO})\}_2]_n$	Antiferromagnetic	-0.47±0.01	Shit <i>et al.</i> , 2016
$[(\text{maleate})_2\text{Ni}_3(\text{bpe})_4(\text{H}_2\text{O})_4](\text{NO}_3)_2\cdot\text{H}_2\text{O}$	Ferromagnetic	+1.74	Mukherjee <i>et al.</i> 2003
$[(\text{adipate})\text{Mn}(\text{bpe})]$	Antiferromagnetic	-1.84 (0.015)	Mukherjee <i>et al.</i> , 2003
$[\text{Mn}_2\text{O}_2(\text{O}_2\text{CCH}_3)(\text{bpea})_2](\text{ClO}_4)_3$	Antiferromagnetic	-124	Pal, Chan & Armstrong, 1992
$[\text{Mn}_3\text{O}_4(\text{OH})(\text{bpea})_3](\text{ClO}_4)_3$	Antiferromagnetic	-76	Pal, Chan & Armstrong, 1992
$[\text{Cu}_2\text{L}_2(\text{N}_3)]_2$	Antiferromagnetic	-8.5	Koner <i>et al.</i> , 2004
$[\text{Cu}(\text{L}^1)(\text{N}_3)]_n(\text{ClO}_4)_n$	Ferromagnetic	+2.15	Mukherjee <i>et al.</i> , 2002
$[\text{Cu}(\text{L}^2)(\text{N}_3)]_n(\text{ClO}_4)_n$	Ferromagnetic	+3.61	Mukherjee <i>et al.</i> , 2002
$[\text{Ni}_2\text{L}_2(\text{N}_3)_2(\text{H}_2\text{O})_2]$	Ferromagnetic	+23.5	Mukherjee <i>et al.</i> , 2009
$[\text{Ni}_2\text{L}_2(\text{NO}_3)_2]$	Antiferromagnetic	-24.27	Mukherjee <i>et al.</i> , 2009
$[(\text{CuL}^1)_2\text{Mn}(\sigma\text{-}(\text{NO}_2)\text{C}_6\text{H}_4\text{CO}_2)_2]$	Antiferromagnetic	-7.027(2)	Ganguly <i>et al.</i> , 2023

$[(\text{NiL})_2\text{Mn}(\text{NCS})_2(\text{CH}_3\text{OH})_2] \cdot \text{CH}_3\text{OH}$	Antiferromagnetic	-4.84	Maity <i>et al.</i> , 2021
$[(\text{NiL})_2\text{Mn}(\text{N}(\text{CN})_2)_2(\text{CH}_3\text{OH})_2] \cdot \text{CH}_3\text{OH}$	Antiferromagnetic	-5.23	Maity <i>et al.</i> , 2021
$[\text{Mn}_4\text{L}_2(\mu_3\text{-Cl})_2\text{Cl}_2]$	Antiferromagnetic	-0.19(J_1), -6.87(J_2), -0.70(J_3)	Das <i>et al.</i> , 2019
$[\text{Mn}_4\text{L}_2(\mu_{1,1,1}\text{-N}_3)_2(\text{N}_3)_2]$	Antiferromagnetic	+0.11(J_1), -0.64(J_2), +0.11(J_3)	Das <i>et al.</i> , 2019
$[\text{Ni}_4(\text{L}^2)_2(\mu_3\text{-OCH}_3)_2(\text{NO}_3)](\text{NO}_3) \cdot \text{CH}_3\text{OH}$	Ferromagnetic	+0.64(J_1), +8.41 (J_2)	Ghosh <i>et al.</i> , 2019
$[\text{Ni}_6(\text{L}^2)_2(\text{o-van})_2(\mu_3\text{-OH})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	Antiferromagnetic	-5.60(J_1), -9.39 (J_2), -5.18(J_3), +3.72(J_4)	Ghosh <i>et al.</i> , 2019
$[\text{Cu}^{\text{II}}_2(\text{L}^7)_2(\mu\text{-Cl})_2][\text{ClO}_4]_2$	Ferromagnetic	+6.0(1)	Singh, Lloret & Mukherjee, 2014
$[\text{Cu}^{\text{II}}(\text{L}^6)(\mu\text{-Cl})][\text{ClO}_4] \cdot \text{CH}_3\text{CN}$	Antiferromagnetic	-0.20(1)	Singh, Lloret & Mukherjee, 2014
$[(\mu_{1,3}\text{-N}_3)\{\text{Co}^{\text{II}}(\text{L}^1)(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{NO}_2)\text{Co}^{\text{III}}(\text{N}_3)_2\}_2]\text{PF}_6$	Antiferromagnetic	-13.07	Banerjee <i>et al.</i> , 2019
$[\text{Mn}_2\text{L}_2(\text{ClO}_4)_2]$	Ferromagnetic	+1.95(2)	Seth, Giri & Ghosh, 2015
$[\text{Mn}_2\text{L}_2(\text{NCS})_2]$	Ferromagnetic	+0.44(1)	Seth, Giri & Ghosh, 2015
$[\text{Ni}_2\text{L}_2(\text{NO}_2)_2]$	Antiferromagnetic	-39	Biswas <i>et al.</i> , 2017
$[\text{Ni}_3\text{L}_3(\text{OH})(\text{NO}_2)] \cdot \text{ClO}_4$	Ferromagnetic	+18.2	Biswas <i>et al.</i> , 2017
$\{[(\text{NiL})_2\text{Co}(\text{NCNCN})_2] \cdot \text{CH}_3\text{CN}\}_\infty$	Ferromagnetic	+4.1	Ghosh <i>et al.</i> , 2013
$\{[\text{CuL}^2]_2\text{Co}\{\text{dca}\}_2\} \cdot \text{H}_2\text{O}$	Antiferromagnetic	-18.6	Biswas <i>et al.</i> , 2014

Multinuclear complexes with Schiff bases and coligands have shown interesting magnetic properties. The combined effect of phenoxide and carboxylate on magnetic properties of bridged complexes has also been studied (Nanda *et al.*, 1994). Salen type Schiff base ligands form Co(II/III) mixed valence complexes in *cis* and *trans* form by varying the solvent. Moreover, by changing the anionic coligands e.g. perchlorate, thiocyanate, dicyanamide etc., various phenoxido bridged Mn(III) complexes have been synthesized (Biswas *et al.*, 2011). The magnetic coupling between the metal centers was ferromagnetic in some of these complexes and antiferromagnetic in the others, which have been rationalized by DFT calculations and/or considering the structural parameters (Seth, Giri & Ghosh, 2015). The tridentate N₂O-donor Schiff base/reduced Schiff base ligands were utilized for the syntheses of complexes of Ni(II) and Cu(II) having various nuclearities. The magnetic measurements showed that the coupling between the metal centers can be ferro- or antiferromagnetic depending upon the bridging angles and bond distances (Biswas *et al.*, 2017). The supramolecular robustness of $\{[\text{ML}]_2\text{M}\}$ type building blocks derived from N₂O₂ ligands has also been explored. Firstly, the linear-bent flexibility of the basic trinuclear structural unit $\{[\text{NiL}]_2\text{M}\}$

Exploration of Chemical Complexity

was evaluated with dicyanamide by varying $M = \text{Ni}, \text{Zn}$ and Cd (Das, Gómez-García & Ghosh, 2015). Secondly, the use of flexible trinuclear metallatecton $\{(\text{CuL})_2\text{Co}\}$ as a building block to construct coordination complexes with ortho-, meta-, and para-benzenedicarboxylates for evaluating positional isomeric effects of the ligand. Both the results showed that the trinuclear units could conveniently be used as nodes for the synthesis of polynuclear complexes (Biswas *et al.*, 2014). Trinuclear heterometallic $\text{Cu}^{\text{II}}-\text{Mn}^{\text{II}}$, $\text{Cu}^{\text{II}}-\text{Co}^{\text{II}}$ complexes have been prepared by N,O donor ligands with o-nitro benzoate anion (Ganguly *et al.*, 2023). The anionic coligands cyano, oximato, azido, dicyanomido, and thiocyanato are excellent for the formation of bridged one-dimensional, two-dimensional or three-dimensional dinuclear, trinuclear or tetranuclear complexes and these complexes play important role in understanding molecular magnetism. Among these pseudohalide anions, azide is the excellent for superexchange pathway between the paramagnetic centers of 3d transition metal ions (Adhikary & Koner, 2010). Azide containing μ -1,1 (end-on, EO) and μ -1,3 (end-to-end, EE) bridging Ni(II) and Mn(II) complexes have shown excellent magneto-structural correlations. Unprecedented end-on double azido bridged low Cu–N(azide)–Cu angles copper(II) complex have been reported with their magnetic properties (Koner *et al.*, 2004). Mukherjee *et al.* (2002) reported magnetic properties of three novel end-to-end single azido-bridged ferromagnetic copper(II) chains. Magneto-structural studies have been performed for the chlorido bridged coordination polymers (Singh, Lloret & Mukherjee, 2014). A rare defective dicubane tetranuclear μ_3 -chlorido and a $\mu_{1,1,1}$ -azido bridged Mn(II) complex have been reported and coupling constant values of the complex are rationalized by DFT calculations (Das *et al.*, 2019). Mixed bridged azido/cyanato copper(II) complexes have been studied with their magnetic studies (Nandy *et al.*, 2015).

Discussion

Different polynuclear 3d transition metal complexes have been prepared by using different types of ligands, most of them are Schiff bases derived from salicylaldehyde derivatives and diamines, phenoxido-bridged Cu(II) complexes are most frequent ones. The magnetic properties of the Cu_2O_2 core of these phenoxido-bridged complexes depend on several factors, such as coordination geometry of the metal centers, Cu–O bond lengths, Cu–O–Cu bond angles, Addition parameters, Cu...Cu distances, which are the parameters that have been shown to influence coupling constants (J) values (Biswas *et al.*, 2011). Thompson *et al.* (1996) observed that the J values strongly vary for μ -hydroxido, μ -alkoxido and μ -phenoxido bridged Cu(II) complexes. In general, larger the Cu–O–Cu angle favours large antiferromagnetic coupling between two paramagnetic centers. Simultaneously, Ni–O–Ni angles larger than 98° favour antiferromagnetic interactions for double alkoxido or hydroxido bridges Ni(II) complexes but the antiferromagnetic coupling becomes more strong for phenoxido bridged Ni(II) complexes whereas ferromagnetic coupling appears for angles close to 90° . The

presence of an additional *syn-syn* carboxylato bridge contributes weak or moderate antiferromagnetic coupling (Mukherjee *et al.*, 2009). The magnetic coupling of heterometallic phenoxido-bridged Ni(II)–Mn(II) complexes is linearly dependent on the bridging angles. Antiferromagnetic exchange interaction increases with increasing Ni–O–Mn angles and the cross over angle is about $\sim 98^\circ$ for ferro- to antiferromagnetic exchange couplings (Maity *et al.*, 2021). The exchange coupling interaction of thiocyanato-bridged Ni(II) complexes depends on various factors such as bridging bond distances, bond angles and Ni–N–S–Ni torsion angle. The Ni–S–C and Ni–N–C angles which are close to 100° and greater than 160° respectively, are usually weak ferromagnetically coupled (Escuer *et al.*, 1996) and the antiferromagnetic coupling decreases with greater bridging bond distances. The bridging mode azide coligand influences the structure of the transition metal complexes and in general, end-on and end-to end coordination modes of azide ligand favour ferromagnetic and antiferromagnetic coupling between the paramagnetic metal centers, respectively (Adhikary & Koner, 2010). Most of the reported $\mu_{1,3}$ -azido bridged Co(II) complexes are antiferromagnetic (Banerjee *et al.*, 2019).

Conclusion

This review shows the utility of different ligands for the assembly of multiple metal centers (whether homometallic or heterometallic) in a predetermined fashion. The factors that are responsible for determining the nuclearity and shape of the resultant clusters have been identified and monitored to get the desired products. The resultant polynuclear homometallic or heterometallic complexes were also utilized as a structural building block for the synthesis of coordination polymers. With the judicious variation of the ligands and metal ions, different research groups were able to synthesize complexes having wide variation of phenoxido bridging angles, which helped to draw magneto-structural correlations in different coordination complexes of 1st transition metals.

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