2021 Sl. No. 1 Anangamohan Panja

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Proton controlled synthesis of two dicopper(II) complexes and their magnetic and biomimetic catalytic studies together with probing the binding mode of the substrate to the metal center†

Narayan Ch. Jana, [a] Pravat Ghorai, [a,b] Paula Brandão, [c] Zvonko Jagličić [d] and Anangamohan Panja [a,e]

This paper describes the synthesis, and structural and spectroscopic characterizations of two doubly bridged dicopper(II) complexes, $[Cu_2(\mu-H_2L)(\mu-OMe)](ClO_4)_2 \cdot 2H_2O$ (1) and $[Cu_2(\mu-L)(\mu-OH)](ClO_4)_2$ (2), with a binucleating ligand (HL) derived from the Schiff base condensation of DFMP and N,N-dimethyldipropylenetriamine, and their biomimetic catalytic activities were related to CAO and phenoxazinone synthase using 3,5-di-tert-butylcatechol and o-aminophenol (OAPH), respectively, as model substrates. Structural studies reveal that the major differences in these structures appear to be from the distinct roles of the tertiary amine groups of the ligands, which are protonated in 1, whereas it coordinates the metal centers in 2. Magnetic studies disclose that two copper(II) centers are strongly antiferromagnetically coupled with slightly different J values, which is further interpreted and discussed. They exhibited very different biomimetic catalytic activities; whereas 2 is an efficient catalyst, complex 1 showed somewhat lower substrate oxidation. The higher reactivity in 2 is rationalized by the strong involvement of the tertiary amine group of the Schiff base ligand, where the substrate oxidation is favored because of the transfer of protons from the substrate to the tertiary amine group, showing the importance of the functional groups in proximity to the bimetallic active site. Emphasis was also given to probing the binding mode of the substrate using an electronically deficient tetrabromomocatechol (Br_4CatH_2) and the isolated compound $[Cu_4(\mu-HL)_2(\mu-OH)_2(Br_4Cat)_4](NO_3)_2 \cdot 4H_2O$ (3) which suggests that monodentate asymmetric binding of 3,5-di-tert-butylcatechol and OAPH occurs during the course of the catalytic reaction.

Introduction

The design and synthesis of di- and poly-nuclear transition metal complexes with various bridging ligands has been ongoing research interest worldwide mainly because of their significance in several fields including bioinorganic chemistry, catalysis, and molecular magnetism.[1-3] In this regard, bi-compartmental phenolate containing ligands with symmetrical and asymmetrical pendent arms at the 2- and 6-positions of the phenolic group deserve a special mention as they are involved in the vast development of coordination chemistry as is shown by the results reported in the literature.[4-7] These arms can accommodate two similar or dissimilar transition metal ions, and hence produce both homo- or hetero-metallic transition metal complexes in which the metal centers are simultaneously bridged by the endogenous phenolate group together with one or two exogenous groups, such as hydroxide, carboxylate or pseudohalide ions.[8-13] In these doubly or triply bridged dinuclear metal complexes, two metal ions are placed in close proximity in the range of 2.9–4.0 Å, and in many such compounds, the metal centers are coordinatively unsaturated or weakly bonded to substitutionally labile ions or groups.[8-13] These structural features made these compounds attractive targets for mimicking the active site structures of various metalloenzymes, such as catechol oxidase (CAO),[10,11] catalase,[12] urease,[13] purple acid phosphatases,[14] phosphoesterases and DNA nucleases,[15] to elucidate the mechanistic aspect of the metalloenzymes and to establish the structure-

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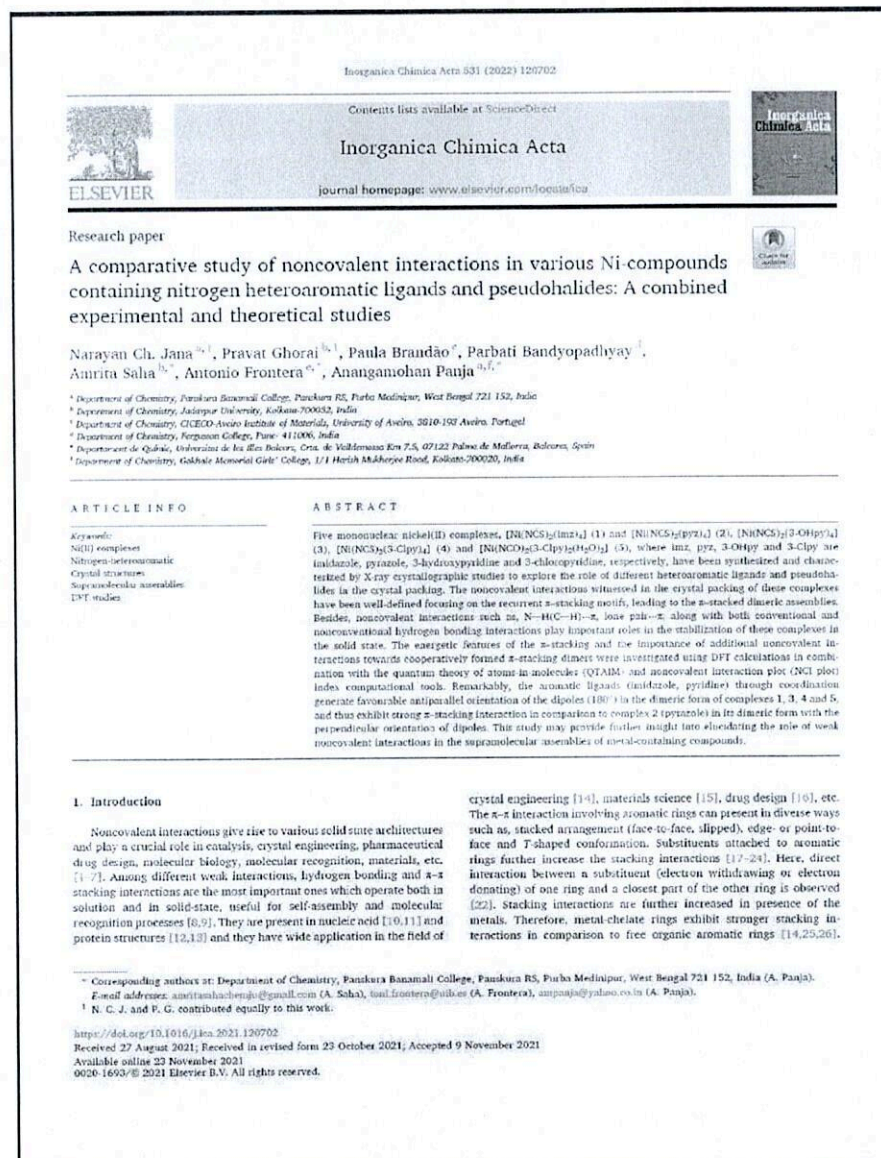[e] Department of Chemistry, Gokhale Memorial Girls' College, 1/1 Harish Mukherjee Road, Kolkata 700020, India

2021 Sl. No. 2 Anangamohan Panja

Research paper

A comparative study of noncovalent interactions in various Ni-compounds containing nitrogen heteroaromatic ligands and pseudohalides: A combined experimental and theoretical studies

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ABSTRACT

Five mononuclear nickel(II) complexes, $[Ni(NCS)_2(imz)_4]$ (1) and $[Ni(NCS)_2(pyz)_4]$ (2), $[Ni(NCS)_2(3-OHpy)_4]$ (3), $[Ni(NCS)_2(3-Clpy)_4]$ (4) and $[Ni(NCO)_2(3-Clpy)_2(H_2O)_2]$ (5), where imz, pyz, 3-OHpy and 3-Clpy are imidazole, pyrazole, 3-hydroxypyridine and 3-chloropyridine, respectively, have been synthesized and characterized by X-ray crystallographic studies to explore the role of different heteroaromatic ligands and pseudohalides in the crystal packing. The noncovalent interactions witnessed in the crystal packing of these complexes have been well-defined focusing on the recurrent π-stacking motif, leading to the π-stacked dimeric assemblies. Besides, noncovalent interactions such as, N—H(C—H)···π, lone pair···π along with both conventional and nonconventional hydrogen bonding interactions play important roles in the stabilization of these complexes in the solid state. The energetic features of the π-stacking and the importance of additional noncovalent interactions towards cooperatively formed π-stacking dimers were investigated using DFT calculations in combination with the quantum theory of atoms-in-molecules (QTAIM) and noncovalent interaction plot (NCI plot) computational tools. Remarkably, the aromatic ligands (imidazole, pyridine) through coordination generate favourable antiparallel orientation of the dipoles (180°) in the dimeric form of complexes 1, 3, 4 and 5, and thus exhibit strong π-stacking interaction in comparison to complex 2 (pyrazole) in its dimeric form with the perpendicular orientation of dipoles. This study may provide further insight into elucidating the role of weak noncovalent interactions in the supramolecular assemblies of metal-containing compounds.

1. Introduction

Noncovalent interactions give rise to various solid state architectures and play a crucial role in catalysis, crystal engineering, pharmaceutical drug design, molecular biology, molecular recognition, materials, etc. [1–7]. Among different weak interactions, hydrogen bonding and π-π stacking interactions are the most important ones which operate both in solution and in solid-state, useful for self-assembly and molecular recognition processes [8,9]. They are present in nucleic acid [10,11] and protein structures [12,13] and they have wide application in the field of crystal engineering [14], materials science [15], drug design [16], etc. The π-π interaction involving aromatic rings can present in diverse ways such as, stacked arrangement (face-to-face, slipped), edge- or point-to-face and T-shaped conformation. Substituents attached to aromatic rings further increase the stacking interactions [17–24]. Here, direct interaction between a substituent (electron withdrawing or electron donating) of one ring and a closest part of the other ring is observed [22]. Stacking interactions are further increased in presence of the metals. Therefore, metal-chelate rings exhibit stronger stacking interactions in comparison to free organic aromatic rings [14,25,26].

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CRYSTAL GROWTH &DESIGN

Article

Impact of Positional Isomers on the Selective Isolation of *cis-trans* Isomers in Cobalt-Dioxolene Chemistry and Solvation Effects on the Valence Tautomerism in the Solid State

Narayan Ch. Jana, Xing-Hui Qi, Paula Brandão, Corine Mathonière,* and Anangamohan Panja*

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ABSTRACT: Three new mononuclear cobalt compounds—*trans*-[Co(3,5-dbcat)(3,5-dbsq)(4-Etpy)$_2$]·CH$_3$CN (1), *cis*-[Co(3,5-dbcat)(3,5-dbsq)(3-NH$_2$py)$_2$]·DMF (2), and *trans*-[Co(3,5-dbcat)(3,5-dbsq)(4-NH$_2$py)$_2$]·2DMF (3) (where 3,5-dbcat^{2-} and 3,5-dbsq$^{•-}$ stand for 3,5-di-*tert*-butyl-catecholate and 3,5-di-*tert*-butyl-semiquinonate, respectively), derived from a redox-active *o*-dioxolene ligand in the presence of 4-ethylpyridine (4-Etpy), 3-aminopyridine (3-NH$_2$py), and 4-aminopyridine (4-NH$_2$py), respectively—have been synthesized and investigated with a view to examine possible influence of pyridine derivatives and solvation on the valence tautomeric (VT) process. Single-crystal X-ray diffraction data for all compounds at room temperature suggest Co(III)(3,5-dbcat)(3,5-dbsq) charge distribution in these complexes. Further insight into the crystal structures discloses the diverse non-covalent interactions offered by the isomers of aminopyridine in 2 and 3, leading to the first example of selective isolation of *cis* and *trans* isomers in cobalt-dioxolene chemistry induced by the positional isomers of the ancillary ligands. Variable temperature magnetic susceptibility data for all compounds between 2 K and 300 K are consistent with the structural studies. At elevated temperatures, complex 1 exhibits a VT interconversion from low spin Co(III)-(3,5-dbcat)(3,5-dbsq) to high spin Co(II)-(3,5-dbsq)(3,5-dbsq), triggered by the loss of lattice solvent molecules, while a partial interconversion is observed for complex 3, even heating up to 430 K. The present report overall highlights the impact of positional isomers on the selective isolation of *cis-trans* isomers in cobalt-dioxolene chemistry and solvation effects on the valence tautomerism in the solid state.
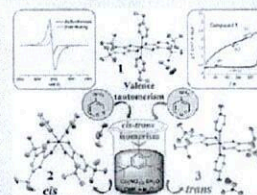
■ INTRODUCTION

Molecular materials that can be reversibly switched between distinguishable states are of great interest in the scientific community. The molecular switchable compounds are particularly attractive, because of the feasibility of fine-tuning in the chemical architecture, which allows tailor-made applications, such as sensors, information storage devices, or use in the field of molecular electronics.[1-10] Molecule-based systems that exhibit an intramolecular electron transfer (IET) phenomenon can be switched between isomers with different electronic states.[11-17] Valence tautomerism is also a specific phenomenon that involves a stimulated and reversible intramolecular electron transfer between a transition metal and a redox-active ligand.[18-20] So far, octahedral cobalt complexes with redox non-innocent dioxolene ligand are the most popular family of valence tautomeric (VT) complexes, particularly those involving 3,5-di-*tert*-butyl-dioxolene (3,5-dbdiox) and nitrogen-donor ancillary ligands.[21-33] In these systems, an intramolecular electron transfer occurs between two redox isomers that exhibit low-spin (ls) Co(III)-catecholate (cat^{2-}) at low temperature, while the high-spin (hs) Co(II)-semiquinonate (sq$^{•-}$) state is favored at higher temperatures.[21,34] Thermally and optically induced VT

transitions are the most common, while the influence of pressure,[35] soft X-rays,[36-38] and magnetic field[39] on VT transitions have also been reported but to a lesser extent.

After the discovery of the first VT cobalt-dioxolene complex,[40] [Co(III)(3,5-dbcat)(3,5-dbsq)(2,2'-bpy)] (where 2,2'-bpy is 2,2'-bipyridine), most of the other VT bis(*o*-dioxolene)cobalt complexes have been reported by replacing the 2,2'-bpy ligand with other bidentate N,N-donor ancillary ligands. Such complexes always adopt the *cis* orientation of the N-donor atoms, because of the structural restraints. By employing monodentate N-donor ligands in place of bidentate N-donor ligands, the *trans* arrangement of the ancillary ligands can be achieved and several such reports are available in the literature.[41-45] Most of these complexes exhibit VT transitions in the solid state, where intermolecular interactions between the chemical moieties, packing effect, and solvation effect

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Structural Analysis of a Biologically Active Glucan Isolated from the Alkaline Extract of an Edible Mushroom *Pleurotus sajor-caju*

Abstract: Polysaccharides from mushrooms have drawn the attention of chemists and immunobiologists on account of their immunomodulatory properties. Taking into account the usefulness of mushroom polysaccharides as immunomodulators and with a view to studying the immunological parameters, structural and some biological study of a glucan isolated from the fruiting bodies of *Pleurotus sajor-caju* were carried out. A polysaccharide was isolated from the fruiting bodies of the mushroom *Pleurotus sajor-caju* by hot alkaline extractions. The size exclusion chromatograms presented a single peak showing a molecular weight of 155 kDa. On the basis of acid hydrolysis, methylation analysis, and NMR analysis (^1H, ^{13}C, HMBC), the structure of the polysaccharide was established. The polysaccharide was composed of glucose and the methylation analysis showed that the units were $(1\rightarrow4)$, $(1\rightarrow6)$-linked. ^1H NMR spectroscopy revealed that the linkages were of β-type. The polysaccharide was composed of a repeating unit with a structure as below:

$$\rightarrow6)\text{-}\beta\text{-}D\text{-}Glc_p\text{-}(1\rightarrow6)\text{-}\beta\text{-}D\text{-}Glc_p\text{-}(1\rightarrow6)\text{-}\beta\text{-}D\text{-}Glc_p\text{-}(1\rightarrow$$
$$4$$
$$\uparrow$$
$$1$$
$$\beta\text{-}D\text{-}Glc_p$$
$$4$$
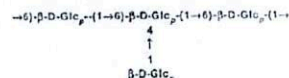
This polysaccharide possesses macrophage activity on mouse monocyte cell line.

Key words: *Pleurotus sajor-caju*; Polysaccharide; Structure; NMR, Macrophage activity.

Carbohydrates have demonstrated to possess interesting biological properties in terms of the prevention and treatment of common diseases. Several polysaccharides showing a β-glucan type structure are considered as valuable biological response modifiers (BRM) for their ability to enhance the immune cells and thereby help to prevent infections[1]. Mushrooms can be considered as a valuable source of bioactive carbohydrates. In this field, several polysaccharides and bioactive carbohydrates have been extracted[2]. Thus, the polysaccharides from several species, such as *Ganoderma*, *Lentinus*, *Agaricus* and *Pleurotus*, have been widely studied[3-6]. Different structural patterns have been found within the polysaccharides extracted from mushrooms. In this field, it is generally accepted that the β-$(1\rightarrow3)$, $(1\rightarrow6)$-linked carbohydrates play an important role in enhancing the antitumor and the immunomodulatory effects[5,7,8]. Furthermore, other structural features, such as the $(1\rightarrow4)$, $(1\rightarrow6)$ moiety found in several fungal species[1,9], have also demonstrated to enhance the immune system[10]. *Pleurotus sajor-caju* is commercially available in large scale near Midnapore city during the period of December-January. The alkaline extract (4% NaOH) of this edible mushroom was found to consist of D-glucose only. With a view to studying the structural as well as immunological properties of this macromolecule, a detailed structural characterisation of this polysaccharide, isolated from *P. sajor-caju* was carried out and described in this paper. The isolation and purification of polysaccharides are described together with the elucidation of the structural features by NMR analyses.

Results and Discussion: Polysaccharides were extracted from the fruiting bodies of the mushroom *Pleurotus sajor-caju* as previously described for other mushrooms[11,12]. The molecular weight of this fraction was estimated from a calibration curve prepared with standard dextrans[13] as 155 kDa. The determination of the chain composition by GC-MS after acid hydrolysis showed that the polysaccharide was composed of glucose, which indicated the presence of glucan-like polysaccharides. The results indicated the presence of 1,5,6-tri-O-acetyl-2,3,4-tri-O-methylglucose; 1,4,5,6-tetra-O-acetyl-2,3-di-O-methylglucose and 1,4,5-di-O-acetyl-2,3,4,6-tetra-O-methylglucose in a molar ratio 2:1:1. The methylation data suggested that the polysaccharide mainly consisted in a linear $(1\rightarrow6)$-linked polysaccharide with $(1\rightarrow4)$- linked side chains at O-4. In order to get more insight into the chemical structure of the polysaccharides extracted from the

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2021 Sl. No. 5 Moon Moon Dutta

Comparative Efficacy of Behavioural and Multimodal Interventions on Trait Anxiety and Parenting Style of Parents of Children With ADHD

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ABSTRACT

Objective: The study explored the comparative efficacy of behavioural and multimodal interventions in influencing trait anxiety and parenting style of parents of children suffering from Attention Deficit Hyperactivity Disorder (ADHD).

Method: 20 participating ADHD families consisted of biological parents and having one child meeting DSM-5 ADHD Combined Type criteria were selected. Children included aged between 6 and 10 years. Half of the participants received behavioural intervention (Group A) and rest received multimodal intervention (Group B). Initially baseline assessment was done, followed by intervention (10 sessions) and finally post-intervention assessment was conducted. Pre-post treatment change was then statistically analyzed.

Results: Statistical analysis using Wilcoxon-Signed Rank Test revealed both parents following multimodal intervention showed significant improvement from the baseline measures in the trait anxiety level. Mothers of ADHD children showed significant improvement in balanced parenting style following multimodal intervention. Fathers of ADHD children showed significant increase in 'perfectionistic supervisor' parenting style and decrease in the 'avoider' parenting style measure following multimodal intervention.

Keywords: ADHD; behavioural intervention; multimodal intervention; trait anxiety; parenting style

INTRODUCTION

Children's mental health covers a wide range of disorders. ADHD is the most commonly diagnosed neurodevelopmental disorder of childhood (Polanczyk et al. 2007). The core symptoms of the disorder include a developmentally inappropriate level of motor restlessness, inattention and impulsiveness that are present in childhood and can persist into adulthood (American Psychiatric Association, 2013). The high prevalence of ADHD is a growing public health concern because the behavioural symptoms of the disorder is a pervasive and debilitating condition that seriously affects learning and academic achievement as well as social functioning. Investigators have asserted that the child's ADHD is the primary determinant of parenting stress (Barkley et al., 1990). Living in a family with a child having ADHD impacts the whole family both inside the family sphere and socially (Moen et al., 2016). Foley (2011) described a higher level of family dysfunction in families with children having ADHD.

Parenting an ADHD child is a challenging task; parents often perceive their child's future as uncontrollable and unpredictable which increases parental anxiety level. Campbell et al., (1978) found a bidirectional interaction between the child's temperament and parenting behaviour; difficult to ascertain whether negative parenting causes ADHD or ADHD symptoms that caused difficult parenting. Parents of children with ADHD are more likely to adopt authoritarian parenting style (Yousefia et al., 2011) that make greater use of negative parenting strategies combined with low levels of emotional support and responsiveness (Khamis, 2006). A study conducted in India by Dutta and Sanyal (2016), found a significant positive correlation between trait anxiety and family pathology of parents of children with ADHD; mothers of children with ADHD had increased trait anxiety level and family pathology score compared to fathers of ADHD children.

Conventional treatments available for patients with ADHD other than medications includes educating family members about how to cope with symptoms to more formal behaviour modification interventions. However, several research findings suggest that since ADHD is a chronic, multifaceted disorder, such interventions must be lengthy and intensive, thus require a great deal of time and energy. Whereas, multimodal or multicomponent-behaviour therapy aimed to provide holistic-based care.

The present research focused on using both behavioural and multimodal therapeutic interventions to find out the pre-post treatment change of the two modes of interventions in influencing the trait anxiety and parenting style of parents having ADHD child which in turn might help in improving the family ambience and reducing the sufferings caused by the disorder.

Research Question 1:

How the two different modes of interventions affect the parental trait anxiety level?

Research Question 2:

Is there any pre-post treatment change on parenting style of parents of children with ADHD?

METHOD:

Participants:

This was a cross-sectional study involving parents having children diagnosed with ADHD. The 20 participating ADHD families consisted of biological parents and having one child meeting DSM-5 ADHD Combined Type criteria (APA, 2013) were selected. The Children included aged between 6 and 10 years; of average intelligence; referred from local Kolkata-based psychiatrists in private practice. They were matched in regard to the proportion of boys and girls. All children were diagnosed by the psychiatrist as well

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2021 Sl. No. 6 Saurabh Niyogi

Minimal and nonminimal universal extra dimension models in the light of LHC data at 13 TeV

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Universal extra dimension (UED) is a well-motivated and well-studied scenario. One of the main motivations is the presence of a dark matter (DM) candidate, namely the lightest level-one Kaluza-Klein particle, in the particle spectrum of UED. The minimal version of UED (mUED) scenario is highly predictive with only two parameters, namely the radius of compactification and cutoff scale, to determine the phenomenology. Therefore, stringent constraint results from the WMAP/PLANCK measurement of DM relic density (RD) of the Universe. The production and decays of level-one quarks and gluons in UED scenarios give rise to multijet final states at the Large Hadron Collider (LHC) experiment. We study the ATLAS search for multijet plus missing transverse energy signatures at the LHC with 13 TeV center-of-mass energy and 139 inverse femtobarn integrated luminosity. In view of the fact that the DM RD allowed part of mUED parameter space has already been ruled out by the ATLAS multijet search, we move on to a less restricted version of UED, namely the nonminimal UED (nmUED), with nonvanishing boundary-localized terms (BLTs). The presence of BLTs significantly alters the dark matter as well as the collider phenomenology of nmUED. We obtain stringent bounds on the BLT parameters from the ATLAS multijet plus missing transverse energy search.

I. INTRODUCTION

After almost a decade long running, the Large Hadron Collider (LHC) collected and analyzed 139 fb^{-1} integrated luminosity data along with a boasting discovery of the Higgs boson [1,2], confirming the mechanism behind masses of the weak gauge bosons and fermions of the Standard Model (SM). Numerous analyses of the LHC data in a variety of channels establish the predictions of the SM on firm footing [2]. Nonetheless, the existence of the Higgs boson brings forth other questions in terms of the stability of its mass, etc. On the experimental front, the evidence of neutrino oscillation, and hence the presence of tiny neutrino masses, casts a shadow over the SM. One can, in principle, solve this problem by incorporating right-handed gauge singlet neutrinos and assigning additional Yukawa terms in the SM, provided the mass hierarchy in the SM fermion sector is acceptable. A rather more daunting task is to incorporate the idea of a new weakly interacting massive particle in the theory in order to explain certain pressing cosmological as well as astronomical evidences in the name of dark matter (DM). Such inadequacies of the SM lead to plenty of novel theories that would come down to the SM at an appropriate limit.

The invocation of theories with extra spatial dimension(s) is of interest for a number of reasons. The most profound ones are the stability of the Higgs boson mass and the related hierarchy problems that were successfully explained by the Arkani-Hamed–Dimopoulos–Dvali model [3,4] and later by the Randall-Sundrum [5,6] model. Extra-dimensional theories can also achieve a light neutrino without introducing any heavy mass scale [7], the unification of gauge couplings [8], and can also account for hierarchies present in the SM fermion masses [9]. Among a variety of extra-dimensional frameworks, we confine ourselves to a particular variant, called the universal extra dimension (UED) model(s), where all the SM fields are allowed to propagate into the space(s) beyond the usual $3 + 1$-dimensional space-time [10–12]. Of course, there are other prospects of working with such frameworks, such as electroweak symmetry breaking without invoking a fundamental scalar [13], a cosmologically

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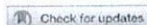
Tuneable structures and magnetic properties of pseudohalo-bridged dinuclear Ni(II) complexes derived from {N4} and {N3O} donor ligands†

Sarmistha Adak, ‡ªᶜ Yu-Chen Sun, ‡ᶜ Narayan Ch. Jana, ᵇ Paula Brandão, ᵈ Xin-Yi Wang *ᶜ and Anangamohan Panja *ªᵇ

Tetradentate ligands with {N4}-donor (L¹ and L²) and {N3O}-donor (HL³) groups prepared from a traditional Schiff base condensation reaction of N,N-dimethyldipropylenetriamine with pyridine-2-aldehyde or 2-acetylpyridine or 3-ethoxysalicylaldehyde, respectively, were used to react with Ni(II) salts in the presence of different pseudohalide ions, resulting in six new Ni(II) dimers with different bridging modes: [Ni₂(L¹)₂(μ₁,₃-N₃)₂](ClO₄)₂ (1), [Ni₂(L¹)₂(μ₁,₃-NCO)₂](ClO₄)₂ (2), [Ni₂(L¹)₂(μ₁,₅-N(CN)₂)₂](ClO₄)₂ (3), [Ni₂(L²)₂(μ₁,₃-N₃)₂](ClO₄)₂ (4), [Ni₂(L³)₂(μ₁,₁-N₃)₂]·0.5MeCN (5) and [Ni₂(L³)₂(μ₁,₁-NCO)₂]·0.5MeCN (6). Their structures and magnetic properties have been studied and discussed. Double end-to-end (EE) and end-on (EO) bridging modes were observed for both the azide and cyanate ions in these complexes. While the EE or EO azido-bridged Ni(II) compounds are quite common, the doubly EE or EO cyanato-bridged dimeric Ni(II) complex 2 was quite rare. Furthermore, we observed that in complex 4, the double azido bridges cross each other to form a rarely observed twisted boat-type arrangement of the (Ni(μ₁,₃-N₃)₂Ni) core, which leads to ferromagnetic interaction through the EE azide bridges. According to the present results, the introduction of different bridges and bridging motifs affords overall diverse magnetic interactions in these Ni(II) dimers, which has been discussed and rationalized in terms of previous literature reports.

Introduction

Synthesis of di- and poly-nuclear transition metal complexes with bridging pseudohalides is still attracting considerable research interest worldwide because of their structural diversities and rich magnetic properties.[1-6] In this context, the magnetochemistry of pseudohalo-bridged Ni(II) complexes has been extensively studied because of the presence of significant magnetic anisotropy in Ni(II) ions, arising from the second order spin-orbit coupling, in addition to the possible high spin ground states originating from the ferromagnetic coupling between the metal centres through the bridging

pseudohalides.[7-9] Among all the pseudohalides, the azide anion is of special interest. It is well established that the azide ion with an end-on (EO, μ₁,₁) bridging mode provides ferromagnetic (F) interaction, while end-to-end (EE, μ₁,₃) azide usually transmits antiferromagnetic (AF) coupling between Ni(II) ions.[10] Besides the azide anion, dicyanamide and cyanate ions are also frequently encountered in molecular magnetic materials. The μ₁,₅-dicyanamide (dca) bridges mediate mostly a very weak AF interaction between Ni(II) centres, while the μ₁,₃-mode of dca transfers moderate AF interactions, leading to some long-range magnetic materials.[11-15] The cyanate ion, on the other hand, propagates magnetic interaction between Ni(II) centres in a similar fashion to that of the azide ion but weakly and there is a scarcity of reports of such Ni(II) compounds in the literature.[16-22] In addition, unlike the azide ion, an experimental magneto-structural correlation is yet to be established for cyanato-bridged Ni(II) systems.[23,24]

Magnetically speaking for all these pseudohalides, their controllable specific bridging modes are of great value to dictate the desired magnetic properties of the resulting molecular compounds. A better understanding of the stereo-electronic factors governing the magnetic exchange interaction between metal ions through the bridging pseudohalides would enable us to design Ni(II) clusters with

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PAPER

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A novel triple aqua-, phenoxo- and carboxylato-bridged dinickel(II) complex, its magnetic properties, and comparative biomimetic catalytic studies with analogous dinickel(II) complexes†

Narayan Ch. Jana, [a] Zvonko Jagličić, [b] Paula Brandão, [c] Sarmistha Adak, [d] Amrita Saha [e] and Anangamohan Panja [*ad]

This paper describes the synthesis and structures of three dinickel(II) complexes, namely [Ni₂(μ-L)(μ-OH)](ClO₄)₂ (1), [Ni₂(μ-H₂L)(μ-OH)(NCS)₂]NCS (2), and [Ni₂(μ-HL)(μ-OBz)(μ-H₂O)(OBz)](ClO₄)₂·2.5H₂O (3) (where HOBz = benzoic acid), with an end-off compartmental ligand (HL) obtained via the Schiff base condensation of 2,6-diformyl-4-methylphenol and N,N-dimethyldipropylenetriamine in methanol. Structural characterization reveals that both 1 and 2 are phenoxo- and hydroxo-bridged compounds, while complex 3 is a unique triple aqua-, phenoxo- and carboxylato-bridged dinickel(II) complex. Although similar bridging patterns to that found in 3 are known, the combination of aqua-, carboxylato- and phenoxo-bridging in a dinickel(II) complex has not been reported in the literature. Variable temperature magnetic susceptibility analysis reveals that the two nickel centres are antiferromagnetically coupled, with J values ranging from −12 to −143 K, in these complexes. The phenoxazinone-synthase-like activities of these complexes have been investigated using o-aminophenol as a model substrate in a methanol medium, as this area is yet to be explored for nickel(II) systems. Mass spectrometry and EPR spectroscopic studies were further carried out to gain insight into the course of the reaction, and the reactivity trend has been further explored. The present work highlights the novel triply bridged dinickel(II) complex and its magnetic properties and demonstrates a comparative biomimetic catalytic study relating to phenoxazinone synthase.

Introduction

The synthesis and structural studies of transition metal complexes with a variety of bridging ligands still attract considerable research interest worldwide, mainly because of their relevance in biological systems, catalysis, and molecular magnetism.[1–3] The literature has witnessed the vast development of studies on the coordination chemistry of compartmental ligands that consist of two symmetrical or asymmetrical pendent arms at the 2- and 6-positions of a phenolic group. These ligands are capable of producing both homo- and hetero-metallic phenoxo-bridged dinuclear transition metal complexes in which metal centres are simultaneously bridged by the phenolate group.[4–7] In some cases, the presence of additional bridges, such as hydroxide, carboxylate, and pseudohalide ions, may lead to doubly or triply bridged dinuclear metal complexes in which two metal ions are placed in close proximity of 2.9–4.0 Å.[8–15] In many of these compounds, the metal centres are coordinatively unsaturated and/or bonded with substitutionally labile ions or groups, making these types of compounds attractive candidates for biomimetic studies; consequently, they have been extensively employed in the structural and functional modelling of various metalloenzymes, like catechol oxidase,[10,11] catalase,[12] urease,[13] purple acid phosphatases,[14] phosphoesterases, and DNA nucleases,[15] to gain insight into the mechanistic aspects of metalloenzymes. In addition to modelling the structures and functions of the active sites of metalloenzymes, these compounds could provide a large number of ferro-/antiferromagnetically coupled discrete dinuclear metal complexes; this could help to provide insight into the fundamental aspects of

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PAPER

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Two rhodamine–azo based fluorescent probes for recognition of trivalent metal ions: crystal structure elucidation and biological applications†

Jayanta Mandal,[a] Kunal Pal,[b] Sougata Ghosh Chowdhury,[b] Parimal Karmakar, [b] Anangamohan Panja, [c] Snehasis Banerjee [d] and Amrita Saha [*a]

Two rhodamine and azo based chemosensors (HL1 = (3',6'-bis(ethylamino)-2-((2-hydroxy-3-methoxy-5-(phenyldiazenyl)benzylidene)amino)-2',7'-dimethylspiro[isoindoline-1,9'-xanthen]-3-one) and HL2 = (3',6'-bis(ethylamino)-2-((2-hydroxy-3-methoxy-5-(p-tolyldiazenyl)benzylidene)amino)-2',7'-dimethyl-spiro[isoindoline-1,9'-xanthen]-3-one) have been synthesized for colorimetric and fluorometric detection of three trivalent metal ions, Al^{3+}, Cr^{3+} and Fe^{3+}. The chemosensors have been thoroughly characterized by different spectroscopic techniques and X-ray crystallography. They are non-fluorescent due to the presence of a spirolactam ring. The trivalent metal ions initiate an opening of the spirolactam ring when excited at 490 nm in Britton–Robinson buffer solution ($H_2O/MeOH$ 1 : 9 v/v; pH 7.4). The opening of the spirolactam ring increases conjugation within the probe, which is supported by an intense fluorescent pinkish-yellow colouration and an enhancement of the fluorescence intensity of the chemosensors by ~400 times in the presence of Al^{3+} and Cr^{3+} ions and by ~100 times in the presence of Fe^{3+} ions. Such a type of enormous fluorescence enhancement is rarely observed in other chemosensors for the detection of trivalent metal ions. A 2 : 1 binding stoichiometry of the probes with the respective ions has been confirmed by Job's plot analysis. Elucidation of the crystal structures of the Al^{3+} bound chemosensors (1 and 4) also justifies the 2 : 1 binding stoichiometry and the presence of an open spirolactam ring within the chemosensor framework. The limit of detection (LOD) values for both the chemosensors towards the respective metal ions are in the order of ~10^{-9} M which supports their application in the biological field. The biocompatibility of the ligands has been studied with the help of the MTT assay. The results show that no significant toxicity was observed up to 100 μM of chemosensor concentration. The capability of our synthesized chemosensors to detect intracellular Al^{3+}, Cr^{3+} and Fe^{3+} ions in the cervical cancer cell line HeLa was evaluated with the aid of fluorescence imaging.

Introduction

Colorimetric and fluorescent chemosensors which are designed for selective detection of metal ions play a crucial role in the development of medicinal and environmental

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research.[1-3] Various techniques such as atomic absorption spectroscopy,[4] inductively coupled plasma-mass spectroscopy,[5] plasma emission spectrometry,[6] neutron activation analysis,[7] chromatography[8] and voltammetry[9] are available for detection of different metal ions in food, biological systems, and environmental and industrial samples. Most of these detection techniques are expensive and users face challenges in sample preparation, instrument handling and their costly maintenance charges. In this regard, the fluorescence study is a highly sensitive, user friendly, low cost and real time monitoring process. Among different metal ions, trivalent metal ions, Al^{3+}, Cr^{3+} and Fe^{3+} deserve special mention. Extensive application of these metals in industry and daily life results in their diffusion and contamination in living systems and causes a wide variety of diseases.[10] Aluminium is the most abundant metal in the Earth's crust and used vastly for domestic purposes. The excessive concentration of Al^{3+} in the human body causes myopathy, encephalopathy, microcytic hypochromic

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Inorganic Chemistry

Magneto-structural Studies in Double Chloro- and Pseudohalo-bridged Isomorphic Dinickel(II) Complexes

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Anangamohan Panja*[a, d]

Four new complexes, [NiL(NO₃)]·CH₃OH (1), [Ni₂L₂(µ-Cl)₂] (2), [Ni₂L₂(µ₁,₁-NCO)₂] (3) and [Ni₂L₂(µ₁,₁-N₃)₂] (4) were synthesized from a tetradentate Schiff base (HL) prepared from the condensation reaction of N,N-dimethyldipropylenetriamine and 5-bromosalicylaldehyde. X-ray crystallography reveals that 2–4 are isostructural and isomorphic dinickel(II) compounds with bridging chloride or pseudohalides. All these three dinickel(II) complexes exhibit ferromagnetic interaction through bridging chloride or pseudohalides and their coupling constants are in the order 4 > 2 > 3, a replication of the average strength of exchange interactions found in such complexes characterised magnetically. Most importantly, compound 3 is a precious addition to the only four known examples of this family, and unprecedented high degree of structural and magnetic resemblances observed in 2–4 is the major achievement of the present work.

1. Introduction

Considerable attention has been directed towards the synthesis of di- and polynuclear transition metal complexes in recent years primarily because of their aesthetic structural diversity, relevance to the metalloenzymatic systems in biology[1–2] and fascinating magnetic properties.[3–8] In the field of molecular magnetism, Ni(II) ion is an automatic choice due to its large single-ion zero-field splitting, and as a consequence several di- and polynuclear Ni(II) complexes with interesting magnetic property have been developed.[9–11] The investigation of magnetic properties of binuclear Ni(II) complexes and correlating them with the structures are quite significant to gain insight into the fundamental aspects of the magnetic interactions as well as to integrate the derived ideas into the large clusters or extended systems to develop molecule-based magnetic materials with predictable magnetic properties. A common strategy to prepare such complexes is the utilization of a multidentate ligand along with judicial choice of a bridging ligand to transmit specific magnetic interactions between the paramagnetic metal centres.[12] The pseudohalide ligand particularly azide ion is the most attractive bridging ligand because of its diverse bridging modes, end-on (µ₁,₁) and end-to-end (µ₁,₃) modes being the most common ones, leading to the rich magnetic property in such compounds.[12] In contrast, the presence of two hetero-bridging atoms with polarizable π systems in other pseudohalides, namely cyanate, which can coordinate the metal ions through either of the heteroatoms, or both, are less versatile than the azide ion. Therefore, in contrast to the vast coordination chemistry of azido-bridged systems,[13–36] both structurally and magnetically interesting compounds with other pseudohalides are limited.[37] It is well known that halides and pseudohalides show great resemblances in several chemical and physical properties, but such similarity in coordination chemistry is quite limited, which is due to lack of coordinative versatility of one-atom halide ion compared to polyatomic pseudohalides. If pseudohalides bind the metal centre terminally or connect the metal centres through µ₁,₁ or µ₁,₃ bridging modes, then only it may have structural resemblance with halide analogues. Along with the rich coordination chemistry of azido-bridged complexes, sophisticated experimental and theoretical magneto-structural correlations are available for these complexes for better understanding the magnetic property of these systems, in which general tendency is that µ₁,₃ bridging mode exerts antiferromagnetic (AF) coupling, while µ₁,₁ coordination mode propagates ferromagnetic (F) exchange between the metal centres.[13–21] Cyanate ion transmits magnetic interaction between the metal centres almost in similar way as that azide ion does but weakly and a scarcity of reports of such Ni(II) compounds is available in the literature to establish a sophisticated magneto-structural correlation for cyanato-bridged Ni(II) systems.[19,23,24] When Ni(II) is five-coordinate, the magnetic coupling observed between the metal ions is usually dominantly AF in nature, while in octahedral or pseudo-

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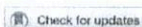Supporting Information for this article is available on the WWW under
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Macrocycle supported dimetallic lanthanide complexes with slow magnetic relaxation in Dy$_2$ analogues†

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Six dimetallic lanthanide complexes [Ln$_2$(L')(acac)$_2$] (1$_{Dy}$–3$_{Gd}$) (Ln = Dy (1$_{Dy}$), Tb (2$_{Tb}$) and Gd (3$_{Gd}$)) and [Ln$_2$(L')(tfac)$_2$] (4$_{Dy}$–6$_{Gd}$) (Ln = Dy (4$_{Dy}$), Tb (5$_{Tb}$) and Gd (6$_{Gd}$)) (H$_2$L = 1,9-dichloro-3,7,11,15-tetraaza-1,9 (1,3)-dibenzenacyclohexadecaphane-2,10-diene-1,9-diol), have been synthesized by the reaction of lanthanide nitrates with the HL ligand in the presence of acetylacetonate (acac) (or trifluoroacetylaceto- nate (tfac) and triethylamine (HL = 4-chloro-2,6-bis-[(3-((3-(dimethylamino)propyl)amino)propyl)imino) methyl)phenol). Ln-Assisted modification of the Schiff base HL occurred and led to the formation of a new macrocyclic ligand (H$_2$L'). X-ray crystallographic analysis revealed that the Ln^{III} ions of complexes 1$_{Dy}$–6$_{Gd}$ are all eight-coordinated in a square antiprismatic geometry with D$_{4d}$ local symmetry. Magnetic measurements of these complexes revealed that 1$_{Dy}$ and 4$_{Dy}$ show single-molecule magnet behaviour with energy barriers of 66.7 and 79.0 K, respectively, under a zero direct magnetic field. The orientations of the magnetic axes and crystal field parameters were obtained from theoretical calculations and an electrostatic model. The magneto-structural correlations of SMMs 1$_{Dy}$ and 4$_{Dy}$ are further discussed in detail.

Introduction

The design and synthesis of single-molecule magnets (SMMs) have attracted considerable attention in the fields of chemistry, physics and materials science because of their prospects and potential applications in high-density information storage, quantum computing, spintronics and magnetic refrigerators.[1] In recent years, there has been enormous interest in purely lanthanide-based SMMs, particularly using heavy lanthanide ions (Tb^{III}, Dy^{III}, Ho^{III} and Er^{III}), and this has progressively increased because of their significant uniaxial magnetic an- isotropy arising from the large unquenched orbital angular momentum along with a large ground-state spin, resulting in SMMs with higher relaxation energy barriers and blocking temperatures.[2] A large number of lanthanide-based SMMs with varying nuclearities have been developed.[3] Among them, binuclear lanthanide compounds are considered a very impor- tant class and have been extensively studied in the recent past as they have one of the simplest molecular architectures which allow a convenient study of the nature and strength of mag- netic coupling between two spin carriers, thereby elucidating magnetic relaxation mechanisms influenced by magnetic interactions.[4] Moreover, it is relatively convenient to determine the possible orientations of the magnetic anisotropy in the dimetallic system, leading to an understanding of the relation- ships between single-ion relaxation and relaxation in a mole- cular entity.

It is noted that organic ligands play a crucial role in the syn- thesis of discrete SMMs and modulation of SMM properties. Therefore, searching for suitable ligands is one of the key strat- egies for overcoming the difficulty in promoting magnetic interactions for purely lanthanide-based systems. Bulky organic ligands can encapsulate the metal centres, preventing intermolecular interactions by isolating molecular entities,

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† Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, ^{1}H NMR, PXRD and ESI-MS spectra, magnetic characteris- ation. CCDC 1967281–1967286 for 1–6 contain the supplementary crystallo- graphic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/D0DT02778B
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A facile biomimetic catalytic activity through hydrogen atom abstraction by the secondary coordination sphere in manganese(III) complexes†

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This paper describes the synthesis and structural characterization of four new manganese(III) complexes (1–4) derived from N_2O donor Schiff base ligands and their biomimetic catalytic activities related to catechol oxidase and phenoxazinone synthase. X-ray crystallography reveals that the Schiff bases coordinate the metal centre in a tridentate fashion, leaving the pendant tertiary amine nitrogen atom either protonated or free to balance the charge of the system, and these pendant triamines participate in strong hydrogen bonding interactions in the solid state. The hydrogen bonding ability of the pendant triamines at the second coordination sphere plays a crucial role in the substrate recognition and the stability of the complex–substrate intermediates. The effect of substitution at the phenolate ring towards the redox potential of the metal centre and the catalytic activity of these complexes has been observed. Detailed kinetic studies further disclose the deuterium kinetic isotope effect in which the transfer of the proton along the hydrogen bond from the substrates to the pendant triamine group at the secondary coordination sphere occurs at the key step in the catalytic reaction. The present reactivity nicely resembles the biochemical reactivities in the natural system in which a concerted electron and proton transfer to different species is usually observed. Remarkably, although some sort of influence of the secondary coordination sphere on catalytic activity has been reported mimicking the function of these metalloenzymes, such a direct participation of the secondary coordination sphere, particularly in modelling phenoxazinone synthase, has not been observed to date.

Introduction

The exploration of the coordination chemistry of manganese complexes has always been an area of interest due to their broad applications in catalysis in various organic reactions,[1–3] including bio-relevant catalysis, by complexes with varied nuclearities mimicking the functions of several metalloenzymes such as superoxide dismutase,[4] manganese dioxygenase,[5] catalases,[6–9] ribonucleotide reductase,[10] arginase[11] and the oxygen evolving complex.[12] Although there have been a lot of reports on polynuclear manganese complex analogues to biomolecules,[13] mononuclear manganese chemistry is still under continuous development[14,15] to shed light on the mechanistic pathway in which model complexes are expected to have the ability to exhibit the fascinating task of dioxygen activation[16–21] under mild conditions at the industrial level.[22] Thus, modelling an approach for devising a new coordination chemistry of manganese is indeed a realistic need to expose the structural and functional outcomes of enzymes.[23] In addition, for organic conversion in the presence of catalytic amounts of transition metal complexes, structure–function relationships have been investigated through the involvement of primary and secondary coordination spheres.[24–26] While the investigation of the influence of the primary coordination sphere is saturated,[27] the role of the secondary coordination sphere has not been explored enough in spite of its importance. Moreover, hydrogen bonding interaction, the most significant non-covalent interaction, is known to be highly demanding and effective in the regulation of metal-mediated reaction processes within the secondary coordination sphere

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† Electronic supplementary information (ESI) available: Fig. S1–S8, Scheme S1, Table S1 and data for DFT calculations. CCDC 2015236–2015239 for 1–4. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/D0DT02431G
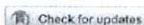
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The first report of a tetra-azide bound mononuclear cobalt(III) complex and its comparative biomimetic catalytic activity with tri-azide bound cobalt(III) compounds†

Narayan Ch. Jana,[a] Paula Brandão [b] and Anangamohan Panja [*ac]

Three new azide-bound cobalt(III) complexes, [Co(HL₂)(N₃)₄] (1), [Co(L₂)(N₃)₃] (2) and [Co(L₃)(N₃)₃] (3), where L₁, L₂ and L₃ are N,N-dimethyldipropylenetriamine, N⁴-isopropyldiethylenetriamine and N,N-diethyldiethylenetriamine, respectively, were synthesized and structurally characterised. X-ray crystallographic studies reveal that the structures of both 2 and 3 are very similar in which three terminal azide ions together with a triamine coordinate the metal centre. Complex 1 on the other hand is significantly different from the other two as the metal centre in 1 is bonded with four terminal azide ions and two donor sites of triamine L₁ leaving the tertiary amine group protonated. All the complexes are stabilized by rich hydrogen bonding interactions, leading to hydrogen bonded supramolecular chain structures. It is worth noting that complex 1 is the first example in cobalt(III) coordination chemistry in which all four azide ions coordinate the metal centre terminally. All these compounds exhibited efficient catalytic activity towards the oxidative coupling of o-aminophenols to phenoxazinone chromophores under aerobic conditions and the role of the structural factors in the catalytic activity has been explored. A mass spectrometry study was carried out to identify the products and important reactive intermediates and to support the mechanistic proposal.

Introduction

Dioxygen, a "green oxidant", is considered as an essential oxidant for the oxidation reaction of organic compounds, particularly to manufacture agrochemicals, pharmaceuticals, and other fine chemicals.[1,2] Utilization of this "green oxidant" is in great demand because it can oxidise organic molecules under mild conditions and the oxidation process is economically favourable. But this environmentally benign oxidant is kinetically inert due to its triplet ground state, and thus it is essential to activate triplet aerial oxygen to its active state to execute the oxidation process. However, metalloproteins can easily promote spin prohibited communication among dioxygen and organic matter for biochemical oxidation reactions by dioxygen activation.[3–5]

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† Electronic supplementary information (ESI) available: Fig. S1–S9 and Table S1. CCDC 2001493–2001495 contain the supplementary crystallographic data for 1–3. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0nj02339f

Thus, bioinorganic chemists have paid considerable attention to explore the mechanistic pathway of such enzymes by applying a simple model study to get insight into the enzymatic reaction.[6–8] Moreover, the development of new model catalysts that mimic the function of these enzymes may be utilized to achieve specific industrial transformation of organic substances[9,10] and therefore could be an alternative to traditional hazardous inorganic catalysts.[11–13]

We are presently working on first row transition metal complexes which can mimic the function of phenoxazinone synthase[14–16] and catechol oxidase.[17–19] The former is a multi-copper metalloenzyme[20] that catalyses the oxidative coupling of substituted o-aminophenols to produce the phenoxazinone chromophore in the final stage of biosynthesis of actinomycin-D.[21] This potent antineoplastic agent is known to be used clinically for the treatment of various cancers[22,23] through intercalation of the phenoxazinone chromophore into a DNA-base pair, thereby inhibiting the synthesis of RNA.[24] Apart from 2-aminophenoxazin-3-one (Phx-1) derivative, an oxygen transport enzyme, bovine hemoglobin, is capable of producing other phenoxazinone chromophores like 2-amino-4,4a-dihydro-4a-7-dimethyl-3H-phenoxazin-3-one (Phx-2) and 3-amino-1,4a-dihydro-4a-8-dimethyl-2H-phenoxazin-2-one (Phx-3) (Scheme 1), which can act as anti-bacterial agents.[25] Moreover, the phenoxazine chromophore itself

2020 Sl. No. 14 Anangamohan Panja

Nickel(II) Clusters

Syntheses, Structures and Magnetic Properties of Ferromagnetically/Antiferromagnetically Coupled Penta- and Hexanuclear Azido-Bridged Nickel(II) Coordination Compounds

Anangamohan Panja,*[a,b] Sarmistha Adak,[a,b] Paula Brandão,*[c] Ľubor Dlháň,[d] and Roman Boča*[e]

Abstract: The use of the Schiff base ligand (HL) derived from 2,6-diformyl-4-methylphenol and N,N-dimethyldipropylene-triamine in nickel(II) coordination chemistry has been investigated and two pentanuclear $[Ni_5(H_2L)_2(\mu_{1,1}-N_3)_4(N_3)_2(\mu_2-OH)_2-(H_2O)_2](NO_3)_4\cdot6H_2O$ (1), $[Ni_5(L)_2(\mu_{1,3}-OAc)_2(\mu_{1,1}-N_3)_4(\mu_2-OH)_2]\cdot12H_2O\cdot2CH_3OH$ (2) and one hexanuclear $[Ni_6(H_2L)_2(\mu_{1,1}-N_3)_4-(\mu_{1,3}-N_3)_2(N_3)_4(\mu_3-OH)_2(H_2O)_2](ClO_4)_2\cdot4H_2O$ (3) clusters were isolated under mild conditions. In these complexes, the nature of the anion and stoichiometry of the reactants seem to play important roles in directing the formation of the metal clusters. Their X-ray characterization shows that the Ni_6 cluster can be considered to be built from two triangular $[Ni_3(\mu\text{-phenoxido})-(\mu_3\text{-OH})(\mu N_3)_4]$ subunits with $bis(\mu_{1,3}\text{-}N_3)$ connectors, while bowtie-shaped Ni_5 clusters are formed by sharing a common vertex. Variable temperature magnetic properties of the penta- and the hexanuclear nickel(II) spin coupled clusters have been investigated and interpreted. According to the present results, although the core structures of triangular Ni_3 units are identical in these systems, the introduction of different bridges bring overall diverse magnetic interaction (antiferromagnetic to ferromagnetic) in these nickel(II) clusters.

Introduction

The last few decades witnessed rapid development of polynuclear coordination clusters with spin-coupled paramagnetic transition metal ions not only because of understanding of their fundamental magnetic phenomena but also for their potential applications as single-molecule magnets (SMMs)[1–9] and single-chain magnets (SCMs),[10–14] and in magnetic refrigeration and quantum computing and nanotechnological devices.[15,16] A rational approach to synthesize discrete exchange-coupled transition metal clusters depends on the synthetic strategy that involves the use of transition metal ions, multidentate blocking ligands in conjunction with the flexidentate bridging ligands to propagate specific magnetic interactions between the metal centers. In majority, the doubly or triply bridging anions like N_3^-, NCS^-, $N(CN)_2^-$, CN^-, $C_2H_3O_2^-$, $C_6H_5O^-$ and OH^- are used for the construction of magnetically interesting coordination clusters.[17] The sign and magnitude of the magnetic exchange interactions between the metal centers in coordination clusters depend on a number of factors; the most important of these are the type of bridging ligands and bridge angles. Among all, azido and hydroxo (phenoxido and alkoxido) bridges are the most versatile mediators of magnetic exchange interactions between paramagnetic ions due to their diverse coordination ability.[18] In most of the reported complexes, azido bridges propagate antiferromagnetic (end-to-end, $\mu_{1,3}$ bridges) or ferromagnetic interactions (end-on, $\mu_{1,1}$ bridges) depending upon the nature of the bridges.[19]

New ligands could provide us the opportunity to attain new structural types and spin topologies. Schiff-base ligands have been extensively used as blocking ligands in developing magnetically interesting compounds mainly because of their synthetic simplicity and tremendous structural diversities. The choice of ligands is always a major issue in the development of new synthetic routes to produce such type of coordination clusters.[20] Phenol-based dinucleating Schiff base ligands are needed to be special mentioned as they are capable to bind simultaneously two metal ions,[21] leading to the formation of

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2020 Sl. No. 15 Goutam Mahata
Anangamohan Panja

REGULAR ARTICLE

Iron(III) and cyano-bridged dinuclear copper(II) complexes: synthesis, structures and magnetic property of the copper(II) complex

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Abstract. This report describes the synthesis and structural characterizations of three new complexes: $[Na_3Fe_2(bbp)(Hbbp)(CN)_6(H_2O)_5]\cdot 4H_2O$ (1), $(Bu_4N)[Fe(bbp)_2]\cdot 3CH_3OH\cdot 2H_2O$ (2), and a cyano-bridged dinuclear copper(II) complex, $[Cu_2(tren)_2(CN)][Fe(bbp)_2]_2 \cdot 6CH_3OH\cdot 4H_2O$ (3), where H_2bbp = bis(2-benzimidazolyl)pyridine and tren = tris(2-aminoethyl)amine. X-ray crystallography reveals that the geometry of iron(III) centers in the complex anions of 1–3 is an octahedral, while it is a trigonal bipyramidal around copper(II) center in the complex cation of 3. Both bbp ligands meridionally coordinate iron(III) centers in the complex cations of 2 and 3, while three cyanide ions and bbp (or Hbbp) ligand occupied either of the meridional positions around the metal center in 1. In the dinuclear complex cation of 3, the Cu(II)-CN-Cu(II) bridging region is strictly linear as dictated by the symmetry with Cu⋯Cu separation of 5.084 (7) Å. Variable temperature magnetic susceptibility study shows that the cyano-bridge mediates the antiferromagnetic coupling between copper(II) centers with J value of -110 K in 3.

Keywords. Fe(III) and Cu(II) complexes; cyano-bridged dinuclear Cu(II); crystal structures; magnetic study.

1. Introduction

Transition metal cyanide complexes have attracted considerable interest due to their extraordinary variety of chemical and physical properties including color, magnetism, conductivity and hydrogen storage activity.[1–3] Recently, magnetic interactions between paramagnetic metal ions through the cyanide bridges have been extensively investigated.[4] In particular, the cyanide-bridged 3D bimetallic assemblies of Prussian-blue-type compounds have attracted great attention owing to the fact that many of them exhibit a long-range magnetic ordering above room temperature, photo-responsive behavior and slow relaxation of the magnetization.[4,5] It is well known that interaction between the metal centers through cyanide groups in an end-to-end fashion is the basis of all the interesting physical properties of such compounds. Therefore, dinuclear complexes in which a single cyanide ion bridges the metal centers can be served as model compounds for the study of exchange interaction between the metal centers.[6] Although a large number of cyanide-bridged 1D, 2D and 3D complexes were synthesized and their magneto-structural correlations have been established, simple M–CN–M(M') complexes containing one cyanide linkage were not much explored.[7] The simplest example in this regard is a dinuclear copper(II) complex with only one localized electron per metal center. It has been found that such complexes exhibit significant variation in the strength of antiferromagnetic coupling between two copper(II) centers depending upon the relative disposition of the bridging cyanide group and the type, and geometry of the metal centers.[7,8] In the complexes with tetradentate tripodal ligands, two trigonal bipyramidal (TBP) copper(II) centers are bridged by a cyanide at an axial coordination site and therefore, stronger antiferromagnetic interaction is expected in such complexes as the lobe of d_{z^2} orbital of the copper(II) ion containing unpaired electron is directed towards the σ orbitals of the cyanide ion, resulting in a greater overlap with the

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SYNTHESIS, CRYSTAL STRUCTURE, AND SUPRAMOLECULAR INTERACTIONS IN A BIS(TETRACHLOROCATECHOLATE) CHELATED MANGANESE(III) COMPLEX

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A mononuclear manganese(III) complex $[DABH_2][Mn_2(Cl_4Cat)_2(H_2O)_2]\cdot 4DMF$ (1) (DAB = 1,4-diaminobutane, Cl_4CatH_2 = tetrachlorocatechol) is synthesized by a one-pot reaction involving manganese(II) chloride tetrahydrate and tetrachlorocatechol in a 1:2 molar ratio in the presence of 1,4-diaminobutane in a DMF-water mixture under aerobic conditions, and is structurally characterized. X-ray crystallography reveals that the complex anion is constructed with two tetrachlorocatecholate ligands coordinated to the manganese(III) center in equatorial positions, and two axial positions are occupied by two water molecules. The crystal packing of 1 is stabilized by complex networks of hydrogen bonding interactions in which oxygen atoms of coordinated tetrachlorocatecholate ligands and lattice DMF molecules serve as hydrogen bond acceptors, while the axially coordinated water molecules together with doubly protonated 1,4-diaminobutane act as hydrogen bond donors. The solid state packing of 1 is further stabilized by Cl···Cl halogen bonding interactions within tetracholorocatecholate units and the C—H···π and π···π interactions involving DMF solvates and aromatic rings of the tetracholorocatecholate ligands. The complex is further characterized by IR spectroscopy and cyclic voltammetry, and the results are analyzed.

DOI: 10.26902/JSC_id61712

Keywords: manganese(III) complex, redox active ligand, crystal structure, hydrogen and halogen bonding, C—H···π and π···π interactions, cyclic voltammetry.

INTRODUCTION

Transition metal complexes with redox active organic ligands have attracted considerable attention because of their application in various fields, including bioinspired catalysis, C—H bond activation, and C—C cross coupling [1—7]. Furthermore, these compounds display several closely associated electronic states because of their close energy levels of the *d* and π orbitals of metal and the redox non-innocent ligand, respectively. These so-called valence tautomeric compounds can be switched by the influence of external stimuli such as heat and light, and therefore, these bistable materials are considered as potential candidates for the fabrication of memory storage devices [8—19]. Apart from the material perspective, several 1st row transition metal complexes with non-innocent ligands, such as dioxolenes, dithiolenes, and benzoquinonediimines, were synthesized for structural and/or functional models for various metallo-oxidases [20—25].

Weak non-covalent interactions, popularly known as supramolecular interactions, play important roles for the self-assembly of molecular systems of the highest relevance in both biological and che-

2020 Sl. No. 17 Newtan Biswas

Mental Health of the College and University Students in West Bengal during COVID 19 Pandemic and Lockdown

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Abstract

The world is going through panic, fear, anxiety, stress, worry and isolation because of COVID 19 pandemic and lockdown. Almost one third of the world population is living under some kind of quarantine or lockdown. All these things affect the mental health of any individual a lot. Researches in different countries in Europe stated that lockdown affects the mental health of individual severely. The concept of Mental Health in India is not new but people pay less attention or importance to it. It is a fact that staying mentally healthy is the key to live a good life. After completing 1st phase lockdown for 21 days, India started the 2nd phase lockdown. This 2nd phase will continue for 19 days that is till 3rd May, 2020. In West Bengal, Government has declared that all educational institutes will remain closed till 10th June, 2020. Studies in different parts of the world stated that even in normal time, depression, anxiety, stress among college and university students are high. Several reasons are there. This pandemic is increasing the intensity of those reasons. Experts of Economics have already predicted that unemployment, recession will increase rapidly, GDP growth rate of India may come down to 1.9% (IMF). All these predictions are creating an atmosphere of uncertainty about the future among the graduate and postgraduate students. These age group students are very vulnerable and sensetive to such environment.

In this situation the researcher wanted to carry out the study to find out the condition of the Mental Health of the college and university students of West Bengal, a state of Indian Republic, during lockdown and how they are facing this pandemic situation.

2020 Sl. No. 18 Newtan Biswas

Opinion of Undergraduate Students of Selected Districts of West Bengal about Online Classes During Lockdown

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(Abstract)

The entire world is going through the biggest crisis because of the Corona virus. Most part of the world is locked down. Most people are confined in their home. Corona virus attacked India in January 2020. After Janata Carfew on 22nd March, India officially declared lockdown on 24th March, 2020. To fight against the Corona virus, West Bengal government declared that all educational institutes will remain close from 16th Mach 2020, except the ongoing Higher Secondary Board exam. So, in West Bengal regular teaching learning stopped from that day. Large number of teachers as well as the government became worried. Then many teachers began to take class through different online platforms such as Edmodo, Google classroom, Zoom cloud meeting app etc.

Most of the teachers and students are using such online platform for the first time. The present research article tries to find out the experience and opinion of the under graduate students of West Bengal about these online classes. Are they really getting any benefit from such classes or not is also another topic of this research article.

Key words: *Corona virus, Lockdown, West Bengal, Education, Online Class Under graduate.*

INTRODUCTION

Online class is not a very new concept, but both for the students and many teachers of West Bengal this concept is quite new. The concept of online class is gaining popularity today mainly because of the threat of Corona Virus. India is going through a period of

2019 Sl. No. 19 Anangamohan Panja

Research paper

A rare flattened tetrahedral Mn(II) salen type complex: Synthesis, crystal structure, biomimetic catalysis and DFT study

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ABSTRACT

A new flattened tetrahedral high spin Mn(II) complex (1) has been synthesized using N_2O_2 donor Schiff base ligand. Complex 1 was characterized by X-ray diffraction and various spectroscopic techniques. For further understanding of electronic structure of the complex, DFT calculations and electrochemical studies have been performed. This is a rare example of a flattened tetrahedral Mn(II) salen type Schiff base complex. High-spin d^5 configuration of the metal center provides no crystal field stabilization energy to the system and that is the main reason behind the significant deviation of this salen-type ligand from planarity. Notably, the propylene linker in the ligand provides adequate flexibility so that such an uncommon binding mode of the salen type Schiff base ligand becomes possible. Complex 1 exhibits excellent catalytic property towards oxidation of o-aminophenols in aerobic condition. Detailed kinetic investigations together with the mass spectrometry studies reveal several important information relating to biomimetic catalytic activity of the present complex.

1. Introduction

Manganese is the 12th most naturally occurring trace metal found in the living systems. Coordination chemistry of manganese is driven by a part of its occurrence in the active sites of several enzymes in the biological systems [1–4]. For example, in photosystem-II (PS-II), manganese centers constitute oxygen evolving complex (OEC) which photolytically oxidizes water to oxygen. In the active site structures of Mn containing catalase [5–7] and peroxidase, the manganese centers are found to coordinate with N or O donor ligands [8,9]. It is clear that nature has chosen Mn in the active site of different metalloenzymes due to its rich redox properties and possibilities of presence of Mn ions in different geometries and stable oxidation states. This enzymatic activities of Mn inspired us to use its model complexes for selective oxidation of organic molecules. It is important to mention that synthesis of biologically-compatible, environment-friendly and energetically-efficient metal complexes is a challenging task for the development of new chemicals for industrial processes and subsequently facilitating the advancement of science in different fields. Oxidation process plays a crucial role in organic reaction for the synthesis of several valuable organic compounds in the fields of pharmaceuticals, agrochemicals, etc. [10–12]. Although in chemical industries mainly molecular oxygen is

used as a primary oxidant, [13–17] direct oxidation of small organic molecules by molecular oxygen is still difficult because of its spin restriction that reduces its reactivity severely with ending up of poor yield [18–21]. In this connection phenoxazinone synthase (PHS) needs special mention for its biological importance, which is a penta copper oxidase that efficiently activates molecular dioxygen at ambient condition to catalyze the oxidative coupling of two molecules of a substituted o-aminophenol to the phenoxazinone chromophore in the final step for the biosynthesis of actinomycin D [22,23]. Actinomycin D is an aromatic heterocyclic natural product which is clinically used for treatment of choriocarcinoma, wilms tumors, rhabdomyosarcoma, and Kaposi's sarcoma [24]. So, it is important to develop metal complexes which can efficiently mimic PHS by oxidizing o-aminophenol to 2-aminophenoxazin-3-one chromophore [25].

On the other hand, Schiff base ligands are classical chelating ligands which are vigorously used to understand molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, etc. [26,27]. Their ease of synthesis and reactivity with almost all metal ions present in the periodic table make them suitable synthons for the development of coordination chemistry. Literature has witnessed rich coordination chemistry involving H_2L (Scheme 1) ligand with reports of numerous

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2019 Sl. No. 20 Gokul Saha

A REVISIT TO THE RELATION BETWEEN IRREGULARITY INDEX AND SCALING INDEX IN A STATIONARY SELF-SIMILAR SIGNAL OBEYING FRACTIONAL GAUSSIAN NOISE

GOKUL SAHA[1], KAUSIK RAKSHIT[2],
KOUSHIK GHOSH[3] AND KRIPASINDHU CHAUDHURI[4]

Abstract. For a stationary self-similar signal obeying fractional Gaussian noise there is a conventional linear relation between the irregularity index and Hurst exponent. The Hurst exponent is coined as the scaling index and the irregularity index indicates the irregularity for a self-affine signal. The commonly used range of irregularity index with the boundary conditions are found as consistent for different stationary self-similar signals obeying fractional Gaussian noise but the familiar linear relation between these two indices does not seem to be consistent in all such cases. To get rid of this problem instead of taking a linear relation we contend to take a cubic relationship between these two indices together with the same boundary relationships. The present consideration possibly construes the matter towards a persuading inference.

I. Introduction. A stationary signal is one whose primary statistical attributes like mean, variance, autocorrelation etc. remain more or less unaltered at different phases of time or space. On the contrary for a non-stationary signal these statistical properties show prominent changes at different segments of time or space.

A signal $x(\xi)$, where ξ is either time or space variable, is said to obey a fractional Gaussian noise (Mandelbrot and van Ness, 1968) if

(a) $x(\xi)$ is stationary

(b) The transition of $x(\xi)$ to $x(\xi + \xi')$ for an increment $n(\xi, \xi') = x(\xi + \xi') - x(\xi)$ is $n(0, 1)$ for every ξ'.
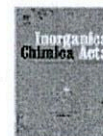
2019 Sl. No. 21 Goutam Mahata

Research paper

A simple triazole-linked bispyrenyl-based xylofuranose derivative for selective and sensitive fluorometric detection of Cu^{2+}

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Ananta Kumar Atta [a] 🔏 ✉

Abstract

Triazole-linked xylofuranose derivatives having one pyrene or two pyrene moieties were synthesized and their fluorescence properties towards various cations and anions were investigated. Only, bis-triazoles appended bispyrenyl-based sugar derivative 1 exhibited selective and sensitive fluorescence quenching effect in the presence of Cu^{2+} ions over a wide range of cations and anions in acetonitrile. The ON-OFF type fluorescence response of 1 was explained by the conformational changes from strong excimer emission of pyrene to weak pyrene monomer emission due to an interaction between Cu^{2+} and inward-facing triazole groups. The limit of detection (LOD) of sensor 1 for Cu^{2+} was found to be 0.15 μM, which is well accepted as per WHO's guidelines.

2019   Sl. No. 22 Newtan Biswas

Sustainable Development and Hierarchy of Needs in Global and Indian Context

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Abstract

The widely accepted and quoted definition of Sustainable Development reads as, "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs." (Report of the World Commission on Environment and Development: Our Common Future). Here the most important concept, according to the present researcher is 'meet the need'.

The 'need' of human beings is very interisting as well as peculiar.

Abraham Maslow nicely tried to depict this amazing 'need' of human beings. He first introduced the concept of a hierarchy of needs in his 1943 paper "A Theory of Human Motivation". It is basically a motivational theory, comprising a five-tier model of human needs, often depicted as hierarchical levels within a pyramid.

The needs, from the bottom of the hierarchy upwards, are: physiological, safety, love and belonging, esteem and self-actualization.

As per the theory the needs lower down in the hierarchy must be satisfied before individuals can attend to needs higher up.

Now the questions are, to what extent human beings are satisfied in terms of their physiological need, safety need, love and belonging need, esteem need and self-actualization need?

Is it possible to fulfill all the needs as said by Maslow in his hierarchy of needs?

Even, if the 'needs' are not fulfilled, then how can we achieve Sustainable Development? Its all about amazingly misterious human mind.

In this article an attempt has been made to find out those answers, because if the 'need' of the present does not 'meet', as per Maslow's theory then the concept of Sustainable Development will remain confined only within books and seminers. We need to think criticall and seriously to achieve Sustainable Development.

Key Words: Sustainable Development, Meets, Need, Future Generations, Hierarchy of Needs.

2019 Sl. No. 23 Newtan Biswas

Professionalism of Teacher Educators Regarding Obligation Towards Student
Teachers, Through the Eyes of Student Teachers in Selected Districts of West Bengal

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Abstract

In this 2019, we lost many things as Indians. Rapidly we are loosing our tradition, our cultural heritage and above all our identity. In doing so, we are accepting the western lifestyle. With the influence of ever-deepening globalization and development of information and technology and the role playing by media, our identity is re-shaping and giving us a new cultural identity. We need to save our own uniqueness- our identity.

The entire world agrees with the view to impart professionalism among teachers. The process has started earlier.

Teacher educators are also a part of teaching community. Their role is no less important. It is they who make teachers. They also must behave in a professional way. Now it is the time to evaluate them from the professional point of view. The learners are considered as an important part of teaching-learning system, so, while evaluating the professionalism of teacher educators, the researcher tries to evaluate the professionalism of the teacher educators, through the eyes of the teacher-student, who are pursuing or have completed B.Ed from the institute recognized by NCTE in West Bengal. The teacher educators must be responsible towards the teacher-student, society and their profession, as that the future teacher can shape a better society. So, the dream of a good society remains in the hand of teacher educators.

In this research paper an attempt has been made to evaluate the Professionalism of teacher educators regarding their obligation towards the student teachers, through the eyes of student teachers in West Bengal.

Key Words: *Professionalism, Teacher Educators, Student Teachers, West Bengal.*

Introduction:

Change is an inevitable part of human life as well as society as a whole. If this change comes gradually, step-by-step then it becomes spice of life, if not, the individual or society may

A NEW PROPOSAL ON THE RELATION BETWEEN IRREGULARITY INDEX AND SCALING INDEX IN A NON-STATIONARY SELF-AFFINE SIGNAL OBEYING FRACTIONAL BROWNIAN MOTION

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AND KRIPASINDHU CHAUDHURY[4]

Abstract. For a signal the power spectral density $p(F)$ usually follows a power law given by $p(F) \propto \frac{1}{F^\alpha}$ (F being the frequency). This power law index α is known as irregularity index. This relation was first observed by Johnson (1925). Since then this power law relation has been experienced in different contexts of Physics, Biology, Technology, Economics, Psychology, Language and Music. For a non-stationary self-affine signal obeying fractional Brownian motion a linear relation between the irregularity index α and Hurst exponent H was proposed as $\alpha = 1 + 2H$ (Higuchi, 1990). This Hurst exponent is coined as the scaling index for a self-affine signal (Hurst, 1951). We have $0 < H < 1$ (Hurst, 1951) and eventually this gives $1 < \alpha < 3$ obeying the boundary principles as $H = 0$ when $\alpha = 1$ and $H = 1$ when $\alpha = 3$. Although the present range of α with these boundary conditions are found to be consistent for different non-stationary self-affine signals obeying fractional Brownian motion but this linear relation between α and H does not seem to be agreeable in all such cases. To resolve this issue instead of taking a linear relation we argue to take a cubic relationship between these two indices together with these boundary relationships. The present consideration possibly interprets the matter towards a convincing conclusion.

1. Introduction. A stationary signal is one whose primary statistical features like mean, variance, autocorrelation etc. remain more or less unchanged at different phases of time or space. On the contrary for a non-stationary signal these statistical properties show conspicuous changes at different phases of time or space. Non-stationarity is often revealed as time variability or space variability like periodicity, monotonic behaviour, step resembling trends, random walking etc.

A signal $x(\xi)$, where ξ is either time or space variable, is said to obey a fractional Brownian motion (Mandelbrot and van Ness, 1968) if

Revisiting Motherhood: A Psycho-social Probe Exploring the Changing Trends in the Attitudes and Perspectives of Educated Women

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Mothers, motherhood and mothering long have been the subject of academic research, public discussion and debate. The changing times, the revolution and evolution of the woman's role in society have produced subsequent modifications in the normative prescriptions and expectations in the perception of motherhood. This study used a cross-sectional qualitative research method used on adult mothers to investigate their experiences of motherhood, to hear what they had to say about their attitudes, values, concerns and needs. It also aimed to gather expectational data on motherhood from female college students to investigate the perceptions and opinions regarding their own future mothering role. Data was collected through 40 individual interviews involving a semi-structured set of open-ended questions raised by three experts. Analysis of the interviews was conducted using a qualitative content analysis approach. Also, the perception of 70 female college students ranging from 18 – 24 years about their own future mothering role was taken. Results showed significant differences in a considerable portion of the study between the group of mothers interviewed and the college students. Also important attitudinal differences between the two groups are revealed. Additionally, in conjunction with prior research, mothers have shown variations in their perception of motherhood with varying age of their motherhood experience.

Keywords: Motherhood, perception, conflict and role.

The recent times have witnessed dramatic transitions in the woman's role in the human society. The massive rise in the level of education a woman receives nowadays, together with the other simultaneous improvements in the woman's current socio-politico-economical position, particularly in the urbanized set-up, have introduced powerful role-revisions for the woman. Therefore, consequent modifications in the normative social time-table and prescriptions for the woman have begun to demand increasing research attention.

A crucial normative socio-cultural expectation from the woman is the attainment of motherhood, and the dedicated nurturance of her offspring(s). However, the gradual shifts in the familial role of the woman has also created scope for newer perspectives and attitudes to emerge in her about the predominant expectations in the society. Moreover, it would be justified to assume that the expansions in the role of the woman outside the immediate boundaries of the home, would create obvious hindrances in her duties of child-rearing and caring for the family as a whole. Such increasing complexities and challenges of functioning are of high likelihood to alter perceptions, and attitudes of the early adult women who have to opt for motherhood in the near future as well as bring about changes in the experience of mothers (both early adults and middle adults).

Major theories on mother-child relationships and the role of the mother by Psychoanalysts and other theorists (Freud, Klein, Winnicot, Bowlby and others) have been very popular. Motherhood is an essential part of many women's lives, particularly in societies where traditional gender roles persist (Watts et al 2015). Mothering is a primary identity for adult women, and women's gender identity is reinforced by mothering (McMahon, 1995). Marriage and childbearing almost often define a woman's position within the family and her community (Benza and Liamputtong, 2015).

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Revisiting the non-resonant Higgs pair production at the HL-LHC

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ABSTRACT: We study the prospects of observing the non-resonant di-Higgs pair production in the Standard Model (SM) at the high luminosity run of the 14 TeV LHC (HL-LHC) upon combining multiple final states chosen on the basis of their yield and cleanliness. In particular, we consider the $b\bar{b}\gamma\gamma$, $b\bar{b}\tau^+\tau^-$, $b\bar{b}WW^*$, $WW^*\gamma\gamma$ and $4W$ channels mostly focusing on final states with photons and/or leptons and study 11 final states. We employ multivariate analysis to optimise the discrimination between signal and backgrounds and find it performing better than simple cut-based analyses. The various differential distributions for the Higgs pair production have non-trivial dependencies on the Higgs self-coupling (λ_{hhh}). We thus explore the implications of varying λ_{hhh} for the most sensitive search channel for the double Higgs production, viz., $b\bar{b}\gamma\gamma$. The number of signal events originating from SM di-Higgs production in each final state is small and for this reason measurement of differential distributions may not be possible. In order to extract the Higgs quartic coupling, we have to rely on the total number of events in each final state and these channels can be contaminated by various new physics scenarios. Furthermore, we consider various physics beyond the standard model scenarios to quantify the effects of contamination while trying to measure the SM di-Higgs signals in detail. In particular, we study generic resonant heavy Higgs decays to a pair of SM-like Higgs bosons or to a pair of top quarks, heavy pseudoscalar decaying to an SM-like Higgs and a Z-boson, charged Higgs production in association with a top and a bottom quark and also various well-motivated

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Probing the type-II seesaw mechanism through the production of Higgs bosons at a lepton collider

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We investigate the production and decays of doubly-charged Higgs bosons for the Type-II seesaw mechanism at an e^+e^- collider with two center of mass energies, $\sqrt{s} = 380$ GeV and 3 TeV, and analyze the fully hadronic final states in detail. Lower mass ranges can be probed during the 380 GeV run of the collider, while high mass ranges, which are beyond the 13 TeV Large Hadron Collider discovery reach, can be probed with $\sqrt{s} = 3$ TeV. For such a heavy Higgs boson, the final decay products are collimated, resulting in fat jets. We perform a substructure analysis to reduce the background and find that a doubly-charged Higgs boson in the mass range 800–1120 GeV can be discovered during the 3 TeV run, with integrated luminosity $\mathcal{L} \sim 95$ fb^{-1} of data. For 380 GeV center of mass energy, we find that for the doubly-charged Higgs boson in the range 160–172 GeV, a 5σ significance can be achieved with only integrated luminosity $\mathcal{L} \sim 24$ fb^{-1}. Therefore, a light Higgs boson can be discovered immediately during the run of a future e^+e^- collider.

I. INTRODUCTION

With the discovery of the Higgs boson at the Large Hadron Collider (LHC), we start to develop an understanding of how the standard model (SM) fermion and gauge boson masses are generated in terms of the Brout-Englert-Higgs (BEH) mechanism. However, one of the main puzzles that still remains unclear is the origin of light neutrino masses and mixings. The same BEH mechanism can, in principle be employed to generate Dirac mass of SM neutrinos by extending the SM to include right-handed neutrinos. However, the required large hierarchy of the Yukawa couplings raises uncomfortable questions. A completely different ansatz is that neutrinos are their own antiparticles and hence, their masses have a different origin than the other SM fermions. A tiny eV Majorana neutrino mass can be generated by the seesaw mechanism, where light neutrinos acquire their masses from a lepton

number violating (LNV) $d = 5$ operator $LLHH/\Lambda$ [1,2]. Such operator is not forbidden as the lepton number is only a classical symmetry of the SM, violated by quantum effects.

There are three proposed categories, commonly known as, Type-I, -II, and -III seesaw mechanisms in which the SM is extended by a $SU(2)_L$ singlet fermion [3–9], $SU(2)_L$ triplet scalar boson [10–13], and $SU(2)_L$ triplet fermion [14], respectively. In particular, the second possibility, i.e., where a triplet scalar field with the hypercharge $Y = +2$ is added to the SM, is the simplest model with an extended Higgs sector. The neutral component of the triplet acquires a vacuum expectation value (vev) v_Δ, and generates neutrino masses through the Yukawa interactions. Perhaps, the most appealing feature of this model is its minimality. The same Yukawa interaction between the lepton doublet and the triplet scalar field generates Majorana masses for the neutrinos, and also dictates the phenomenology of the charged Higgs bosons.

A number of detailed studies have already been performed for the Hadron colliders like, Tevatron [15] and LHC [15–29] to search for the triplet Higgs scenario. One attractive feature of this model is the presence of the doubly-charged Higgs boson, and its distinguishing decay modes. Depending on the triplet vev, the doubly-charged Higgs boson can decay into same-sign dilepton, same-sign gauge bosons, or even via a cascade decay [16–18].

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2018 Sl. No. 28 Saurabh Niyogi

Probing nonstandard neutrino interactions at the LHC Run II

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ABSTRACT

Searching for non-standard neutrino interactions, as a means for discovering physics beyond the Standard Model, has been one of the key goals of dedicated neutrino experiments, current and future. This has received recent fillip in the wake of reported anomalies in leptonic B-decays. We demonstrate here that much of the parameter space accessible to such dedicated neutrino experiments is already ruled out by the RUN II data of the Large Hadron Collider experiment.

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1. Introduction

Precision measurements of the neutrino mixing parameters, made over the past few decades has significantly shortened the list of unanswered questions in the standard scenario to just the issues of the neutrino mass hierarchy i.e., sign(Δm_{31}^2), the CP phase and the correct octant for the mixing angle θ_{23}. While the simplest way to generate neutrino masses is to add right handed neutrino fields to the Standard Model (SM) particle content, it is hard to explain the extreme smallness of the said masses. Several scenarios going beyond the SM have been proposed to this end, often tying up with other unanswered questions such as (electroweak) leptogenesis [1,2], neutrino magnetic moments [3–6], and even dark energy [7,8] (by invoking neutrino condensates). An agnostic alternative is to add dimension-five terms consistent with the symmetries and particle content of the SM, which naturally leads to desired tiny Majorana masses for the left-handed neutrinos. Irrespective of the approach, once new physics is invoked to explain the non-zero neutrino masses, it is unnatural to exclude the possibility of non-standard interactions (NSI) as well. Indeed, NSI has been studied in the context of atmospheric neutrinos [9–14], CPT violation [15,16], violation of the equivalence principle [13], large extra dimension models [17], sterile neutrinos [18–20] and collider experiments [21–24].

While no incontrovertible evidence for such NSI exists, certain anomalies in leptonic B-decays [25–30], together, strongly indicate a new physics scale of a few TeVs [31]. Not only is the existence of analogous neutrino-NSI conceivable, there exist theoretically well-motivated scenarios wherein NSI would manifest primarily in the neutrino sector (e.g., those referred to earlier). Consequently, the search of NSI constitutes a major stated goal of neutrino experiments. We demonstrate, in this letter, that much of the parameter space that such a future dedicated neutrino experiment would be sensitive to, can already be ruled out by an analysis of the LHC data.

At sufficiently low energies, a wide class of new physics scenarios can be parametrized, in a model independent way, through the use of effective four-fermion interaction terms.[1] The investigation of these assumes further importance as the aforementioned anomalies in B-decays are quite well-explained on the introduction of such terms [31]. While these, in general, would incorporate both charged-current (CC) and neutral-current (NC) interactions, we shall confine ourselves largely to the latter (coming back to the former only later). The dimension-6 neutrino-quark interactions can, then, be expressed, in terms of the chirality projection operators P_X ($X = L, R$), as

$$\mathcal{L}_4 = -2\sqrt{2}\, G_F \, \epsilon_{\alpha\beta}^{qX} \left(\bar{u}\gamma_\mu P_X q \right)\left(\bar{\nu}_\alpha \gamma^\mu P_L \nu_\beta \right) + H.c. \qquad (1)$$

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[1] The obvious caveat is the situation where the NSI is occasioned by a light (well below the weak scale) mediator [32–34]. Not only do such models need ultrasmall fermionic couplings, the model-dependence is extreme and no unified treatment is possible. Hence we shall eschew a discussion of the same.

2018 Sl. No. 29 Saurabh Niyogi

Discovery prospects of a light Higgs boson at the LHC in type-I 2HDM

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We present a comprehensive analysis of observing a light Higgs boson in the mass range 70–110 GeV at the 13/14 TeV LHC, in the context of the type-I two-Higgs-doublet model. The decay of the light Higgs to a pair of bottom quarks is dominant in most parts of the parameter space, except in the fermiophobic limit. Here its decay to bosons (mainly a pair of photons) becomes important. We perform an extensive collider analysis for the $b\bar{b}$ and $\gamma\gamma$ final states. The light scalar is tagged in the highly boosted regimes for the $b\bar{b}$ mode to reduce the enormous QCD background. This decay can be observed with a few thousand fb^{-1} of integrated luminosity at the LHC. Near the fermiophobic limit, the decay of the light Higgs to a pair of photons can even be probed with a few hundred fb^{-1} of integrated luminosity at the LHC.

I. INTRODUCTION

The recently discovered scalar particle at the LHC [1,2] closely resembles the Higgs boson conjectured in the Standard Model (SM), as its measured couplings with the gauge bosons and fermions are in reasonable agreement with the SM predictions [3]. However, the current measurements [3] still do not rule out the possibility of the observed particle belonging to an enlarged scalar sector of a beyond-the-SM scenario. Usually the additional scalars are considered to be heavy, and in some cases they are even decoupled from the low-energy effective theory. However, there may exist scenarios where some of the new physics particles are lighter than the observed Higgs. We explore this possibility in the context of the two-Higgs-doublet model (2HDM) at the 13/14 TeV LHC.

The 2HDM is one of the simplest extensions of the SM with an additional scalar doublet charged under $SU(2)$. The generic structure of the 2HDM induces large flavor-changing neutral currents (FCNCs) at the tree level and consequently faces severe constraints from the experimental data. These FCNCs can be suppressed by imposing a discrete Z_2 symmetry. This classifies 2HDM into four categories: type I, type II, flipped, and lepton specific [4].

Any 2HDM model comprises of eight real scalar degrees of freedom. In the process of the spontaneous breaking of $SU(2)_L \times U(1)_Y$ symmetry, three of these eight fields generate masses for $W^\pm$ and Z bosons, leaving behind five physical scalars, namely, a light CP-even Higgs (h), a heavy CP-even Higgs (H), a pseudoscalar (A), and charged Higgs bosons ($H^\pm$).

The Higgs boson discovered at the LHC, being CP-even [5,6], can be identified with any one of the CP-even scalars of the 2HDM. We are interested in the scenarios where the observed Higgs corresponds to the heavier CP-even scalar and h is lighter than 125 GeV. The phenomenology of such a light Higgs has been thoroughly studied for all types of 2HDM. However, the constraints from vacuum stability, perturbativity, unitarity, electroweak precision measurements, flavor observables, and LHC Higgs searches are weakest for the type-I 2HDM [7–16]. We therefore focus on the type-I 2HDM for our analysis and study the discovery prospects of the light Higgs at the future runs of the LHC.[1] We choose the mass range 70–110 GeV to avoid decay of the observed 125 GeV Higgs to a pair of on-shell light Higgses, i.e., $H \to hh$. As a result, the bounds coming from the total decay width measurement of the observed scalar [31], the measurement of Higgs signal rate [3], and direct decay of the observed Higgs to a pair of light Higgses, i.e., $H \to hh$ [32] are irrelevant in our case.

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[1]The phenomenology of such a light CP-even scalar has also been studied in the context of various supersymmetric models; see Refs. [17–20] and references therein. Also see Refs. [21–30] for analyses where the lighter CP-even Higgs boson was identified with the observed scalar and the remaining scalars (H, $H^\pm$ and A) were assumed to be heavy.

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Saurabh Niyogi

Constraining compressed versions of MUED and MSSM using soft tracks at the LHC

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ABSTRACT: A compressed spectrum is an anticipated hideout for many beyond standard model scenarios. Such a spectrum naturally arises in the minimal universal extra dimension framework and also in supersymmetric scenarios. Low p_T leptons and jets are characteristic features of such situations. Hence, a monojet with $\not{E}_T$ has been the conventional signal at the Large Hadron Collider (LHC). However, we stress that inclusion of p_T-binned track observables from such soft objects provide very efficient discrimination of new physics signals against various SM backgrounds. We consider two benchmark points each for minimal universal extra dimension (MUED) and minimal supersymmetric standard model (MSSM) scenarios. We perform a detailed cut-based and multivariate analysis (MVA) to show that the new physics parameter space can be probed in the ongoing run of LHC at 13 TeV center-of-mass energy with an integrated luminosity ~ 20-$50\,fb^{-1}$. When studied in conjunction with the dark matter relic density constraint assuming standard cosmology, we find that compressed MUED (with $\Delta R = 2$) can be already excluded from the existing data. Also, MVA turns out to be a better technique than regular cut-based analysis since tracks provide uncorrelated observables which would extract more information from an event.

KEYWORDS: Phenomenology of Large extra dimensions, Supersymmetry Phenomenology

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Jayjyanti Ray

Dynamical behaviour of an exploited fish species obeying modified logistic growth function with taxation as a control instrument

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Abstract

In this paper we discuss and analyse a mathematical model to study the dynamical behaviour of an exploited fish species which obeys the *modified logistic growth function* [1]. Fishing is permitted after imposing tax per unit harvested biomass by the Government or private agencies in order to control over exploitation. The steady states of the dynamical system are determined. The local stability for the non-trivial steady states is discussed. The global stability of the non-trivial interior equilibrium is also studied. It is also examined whether the system possesses any limit cycle. All the results are illustrated with the help of four numerical examples.

Keywords: modified logistic growth function, steady states, variational matrix, local stability, limit cycle, global stability.

1. INTRODUCTION:

Fish is a major renewable resource for the human community. However, some of the fish species are likely to become extinct due to excessive harvesting. So the Government or the private agencies have to monitor and regulate the over exploitation of the species. Various techniques in regulating fisheries have been discussed by