Development of Exchange Biased {3d-4d/5d} Assemblies: A rational Route Towards High T_b Nanomagnets

Final Technical Report

Of CSIR HRDG funded EMR Project

Scheme No. 01(2789)/14/EMR-II

Submitted By

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Department of Chemical Sciences
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FORM-F

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Human Resource Development Group
(Extra Mural Research Division)
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

PROFORMA FOR PREPARING FINAL TECHNICAL REPORT
(Five copies of the report must be submitted immediately after completion of the research scheme)

1. Title of the scheme

Development of Exchange Biased {3d-4d/5d} Assemblies: A rational Route Towards High T_b Nanomagnets	Scheme No.: 01(2789)/14/EMR-II Date of Commencement : 01/10/2014 Date of termination : 30/09/2017

2. Name and address of Principal Investigator

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3. Name of Sponsoring laboratory of CSIR (If applicable): NOT APPLICABLE

4. Total grant sanctioned and expenditure during the entire tenure

	Amount Sanctioned	Expenditure
Staff	12,12,000	3,20,871
Contingency	4,50,000	4,57,652
Equipment	NIL	NIL
Overhead	31,382	24,979
Total	16,62,000	8,03,502

5. Equipment(s) purchased out of CSIR grant: NIL

6. Research fellows associated with scheme

Name& Designation	Date of Joining	Date of leaving
Ms. Mamon Dey	19/01/2015	15/12/2016

7. Name(s) of the fellow(s) who received Ph.D. by working in the scheme, along with the Title(s) of thesis:

Ms. Mamon Dey for the thesis entitled "Investigation of single ion magnetic anisotropy of seven coordinated complexes of Mn(II), Co(II) & Ni(II) and their application in building heterometallic assemblies.

8. List of research papers published/communicated, based on the research work done under the scheme (Name(s) of author(s), Title, Journal, Volume number, Year and Pages should be given for each paper published and a copy of each of them should be enclosed; reprints/copies of papers appearing after submission of FTR should also be sent to CSIR):

[a] Surprises from and old reaction: a new 1-D heterometallic tris(pyridine-2-aldoximato)nickel(II)-sodium complex, Mamon Dey, Anuran Goswami and Nayanmoni Gogoi, *Transition Metal Chemistry*, **2016**, *41*, 509-516.

[b] Enhanced Catalytic Activity and Near Room Temperature Gas Sensing Properties of SnO_2 Nanoclusters@Mesoporous Sn(IV) Organophosphonate Composite. Borah, S.; Bhattacharyya, B.; Deka, J.; Borah, A.; Devi, A.; Deka, D.; Mishra, S.; Raidongia, K.; Gogoi, N. *Dalton Transactions* **2017**, *46*, 8664-8672.

[c] Cyano bridged heterometallic Mn (II)-Fe (III) aggregates: synthesis, structure and magnetic properties. Dey, M.; Sarma, B.; Gogoi, N. *Inorganica Chimica Acta* **2018**, *469*, 20-24.

[d] Pd nanoparticles dispersed on ZrIV organophosphonate: A robust and reusable catalyst for Suzuki-Miyaura cross coupling reactions. Borah, S,; Mishra, S.; Cardenas, L.; Gogoi, N. *European Journal of Inorganic Chemistry*, DOI: 10.1002/ejic.201701313.

9. Details of new apparatus or equipment designed or constructed during the investigation: NIL

10. The likely impact of the completed work on the scientific/technological potential in the country (this may be attached as Enclosure-I): Enclosed

11. Is the research work done of some industrial or agricultural importance and whether patent(s) should be taken? ~~Yes/~~No; if yes, what action has been/should be taken:

12. How has the research work complemented the work of CSIR Laboratory that sponsored your scheme? NOT APPLICABLE

13.Detailed account of the work carried out in terms of the objective(s) of the project and how for they have been achieved; results and discussion should be presented in the manner of a scientific paper/project report in about 5000 words; and this should be submitted as Enclosure-II to this report. Enclosed.

14. An abstract of research achievements in about 200-500 words, suitable for publication. Several linear trinuclear 3d complexes, $[M_3(dpa)_4X_2]$ ($M = Co^{2+}$, Ni^{2+} etc.; dpa = dipyridyl amine; X = Cl, Br) have been prepared. Analytical, spectroscopic and structural characterization of these precursor complexes have been carried out to unambiguously establish their purity. Reactions leading to the formation of exchange bias species were carried out by using the linear trinuclear 3d complexes as building blocks and cyanometallates as linkers. Several heterometallic cyano bridged species have been prepared and analytical, spectroscopic and structural characterizations have been carried out. Low temperature magnetic studies was performed on one of the cyanobridged 3d-4d assembiles and strong exchange interaction was observed. Further, by interlinking another linear trinuclear fragment $[Ni_2Na(pao)_6]$, a new one dimensional system, $\{[Ni_2Na_3(pao)_6(H_2O)_2](C_5H_5N)_2(H_2O)_2\}_n$ has been developed. Analytical, spectroscopic and structural characterization has been carried out to establish the identity of this 1D complex.

15. Mention here whether or not the unspent grant has been refunded to CSIR: Unspent grant is NIL.

Date: 21/03/2018

Signature of PI

Enclosure -I

Likely impact of the completed work on the scientific/technological potential in the country:

Increase in the blocking temperature of single molecule magnets, even by a few Kelvin's can tremendously contribute to the development of much denser electronic storage media. The results obtained and experience gained from this project is expected to facilitate development of magnetic materials for application in information storage, sensor etc. Several cyano bridged 3d-4d/5d assemblies are synthesized during the course of this project by interlinking linear trinuclear 3d building blocks by 4d/5d cyanometallates briding ligands. Magnetic studies on one of the 3d-5d aggregate clearly revealed the presence of strong exchange interaction between the spin carriers and quick magnetization was observed at low temperature on application of small external magnetic field. Presence of strong exchange bias can be primarily attributed to the observed magnetic feature. We anticipate that further exploration of the magnetic properties using ac magnetization measurements along with structural correlation will allow one to design better single molecule magnets by using the present principle as guideline. Thus, the present project has paved way for development of magnetic materials which will eventually find application in information storage, sensor devices etc.

Enclosure-II

PROJECT COMPLETION REPORT

1. Project Title: **Development of Exchange Biased {3d-4d/5d} Assemblies: A Rational Route Towards High T_b Nanomagnets**	Sanction No. **01(2789)/14/EMR-II**

2. PI (Name & Address): Dr. NAYANMONI GOGOI
Department of Chemical Sciences
Tezpur University
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Email: ngogoi@tezu.ernet.in

3. Co-PI (Name & Address): Not Applicable

4. Broad area of Research: Chemical Sciences

4.1 Sub Area: Inorganic Chemistry

5. Approved Objectives of the Proposal:

(i) Synthesis of the linear trinuclear building block, [$M_3(dpa)_4X_2$] [dpa: dipyridylamine; X = halide or pseudhalide] and 4d/5d cyanometallate bridging ligands using established procedures.

(ii) Synthesis of novel {3d-4d/5d} aggregates via interlinking the linear trinuclear [$M_3(dpa)_4X_2$] building blocks through suitable 4d/5d cyanometallate bridging metallo-ligands.

(iii) Structural and magnetic characterization of these {3d-4d/5d} aggregates.

(iv) Simulation of magnetic data to retrieve key parameters and carry out magneto-structural correlation.

6. Date of Start: 01 October 2014

7. Date of completion: 30 September 2017

8. Methodology: The methodology to be adopted for the execution of this project can be broadly divided into three well defined and complementary tasks (I)-(III):

I. Synthesis of linear trinuclear 3d building blocks, [$M_3(dpa)_4X_2$] (M = Co^{2+}, Ni^{2+} etc.; dpa = dipyridyl amine; X = Cl, Br) and 4d/5d cyanometallates e.g. $K_3[W(CN)_8]$ by using established synthetic routes.

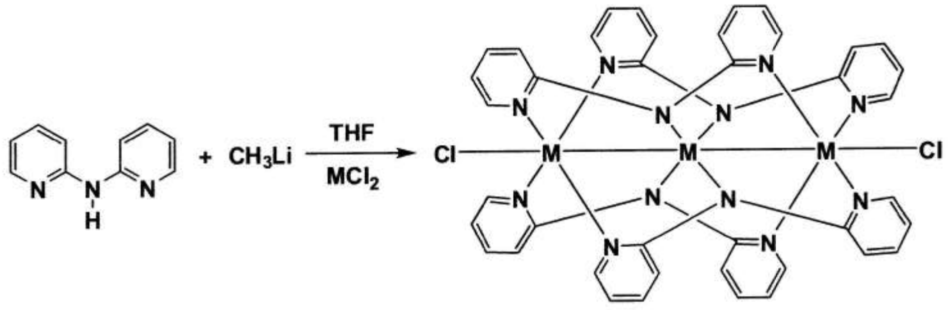
II. Subsequently, {3d-4d/5d} aggregates shall be prepared by bridging magnetically anisotropic linear trinuclear 3d building blocks $[M_3(dpa)_4X_2]$ (M = Co^{2+}, Ni^{2+} etc.; dpa = dipyridyl amine; X = Cl, Br) with cyanometallates linkers.

III. Structural and magnetic characterization of the ferrimagnetic systems: Conventional physical characterizations- IR, elemental analysis and Single crystal X-ray diffraction measurements shall be performed in order to elucidate the solid state structure of the resulting hetero-nuclear assemblies.

9. Salient Research Achievements:

9.1 Summary of achievements: The following important milestones have been achieved:

A. Several already reported linear trinuclear complexes, $[M_3(dpa)_4Cl_2]$ (M = Co^{2+}, Ni^{2+}) have been prepared by using tridentate ligands and single crystal X-ray analysis was carried out to establish their molecular structures.



M = Co^{II}, Ni^{II}

B. Reactions of the linear trinuclear complexes, $[M_3(dpa)_4Cl_2]$ (M = Co^{2+}, Ni^{2+}) with cyanometallates were investigated. Several heteronuclear species have been isolated and their analytical, spectroscopic and structural characterization were performed. However, due to the inability to isolate X-ray quality single crystals, structural characterization using single crystal X-ray diffraction technique could not be performed. Magnetic properties of a cyano bridged heteronuclear species, $[\{Ni_3(dpa)_4\}\{W(CN)_8\}]^-$ was investigated and it shows quick magnetic ordering on application of external magnetic field.

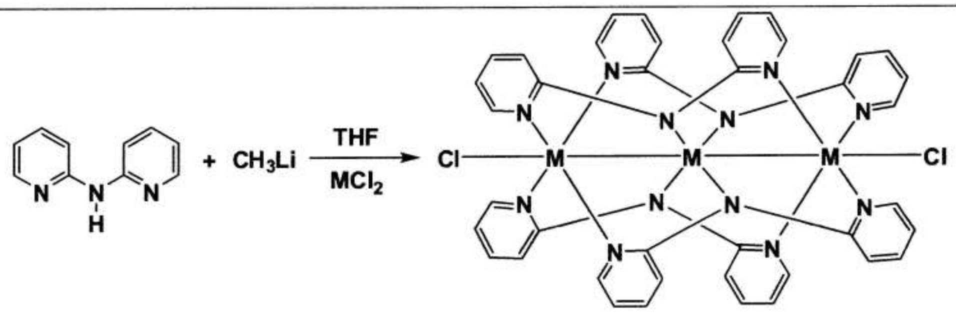
C. Reaction of several other linear trinuclear complexes *viz.* $[Mn_3(OAc)_6L_2]$ [L = 2,2'-bipyridine or phenanthroline] with different cyanometallates have been investigated and two new cyano bridged [Mn-Fe] species have been isolated.

D. New heteronuclear one dimensional species, $\{[Ni_2Na_3(pao)_6(H_2O)_2](C_5H_5N)_2(H_2O)_2\}_n$ [pao = pyridine-2-aldoxime] containing linear trinuclear structural motif, $[Ni_2Na(pao)_6]$ bridged by another metalloligand has been synthesized and structurally characterized.

9.2 Detailed description of research work carried out during the project:

This research proposal aimed to build {3d-4d/5d} aggregates by strategically incorporating the key parameters governing the energy barrier for magnetization reversal viz. high spin magnetic units, stronger exchange interaction between the magnetic units, uniaxial anisotropy and exchange anisotropy. The 3d building blocks are chosen carefully to provide high spin and uniaxial magnetic anisotropy while the 4d/5d cyanometallate linkers shall enhance the spin exchange interaction. The chosen linear trinuclear 3d complex, $[M_3(dpa)_4X_2]$ (M = Co^{2+}, Ni^{2+};X = Cl, Br) can provide high ground state spin and uniaxial anisotropy due to its linear structure and thereby constitute a potential 3d building block.[10] Additionally, within the trinuclear 3d building block, $[M_3(dpa)_4X_2]$ strong antiferromagnetic interactions (-100 cm^{-1}) is present between the metal ions and this will eventually assist in inducing strong exchange anisotropy in the proposed {3d-4d/5d} assemblies.[11] The labile terminal halides in $[M_3(dpa)_4X_2]$ can be easily replaced by other bridging ligands and thus facilitate the assembling of hetero-metallic extended structures.[12] Even though the trinuclear $[M_3(dpa)_4X_2]$ provides an excellent opportunity to produce designed polymeric structures with versatile magnetic character, the possibility to use these units as building blocks for molecular magnetic materials have been largely overlooked so far.

During initial stages of the project two linear trinuclear 3d precursor complexes $[M_3(dpa)_4Cl_2]$ (M = Co^{2+} (**1**) & Ni^{2+}(**2**)) were prepared from commercially available starting materials (Scheme 1). Both the compounds were characterized by using analytical and spectroscopic techniques and the data obtained in all the cases are consistent with the desired composition. However, the yield of the precursor complexes were found to be very poor and therefore it restricted the number of reactions investigated during the later stages of the project.



M = Co^{II}, Ni^{II}

Scheme 1: Preparation of linear trinuclear precursor complexes $[M_3(dpa)_4Cl_2]$ (M $=Co^{2+}$ (**1**) & Ni^{2+}(**2**))

Apart from the above, two more related linear trinuclear complexes, $[Ni_3(dpa)_4(CH_3CN)_2](BPh_4)_2$ (**3**) and $[Ni_3(dpa)_4(N_3)_2]$ (**4**) were prepared and characterized. Single crystal X-ray diffraction studies were performed on two derivatives of the linear trinuclear precursor complexes. In both the cases, the four tridentate dpa ligands bridge the three nickel centers in a strictly linear arrangement (Figure 1). The central Ni(II) ion has a square planer geometry and the associated Ni-N_{amido} bond distances measure 1.884-1.887 Å as compared to terminal Ni-$N_{pyridine}$ bond distances which measure 2.035-2.084 Å. The two terminal Ni(II) ions have square pyramidal coordination environment as four of the equatorial coordination sites are occupied by pyridinic N atom while the axial coordination sites are occupied by either acetonitrile or azido ligand in case of **3** and **4** respectively.

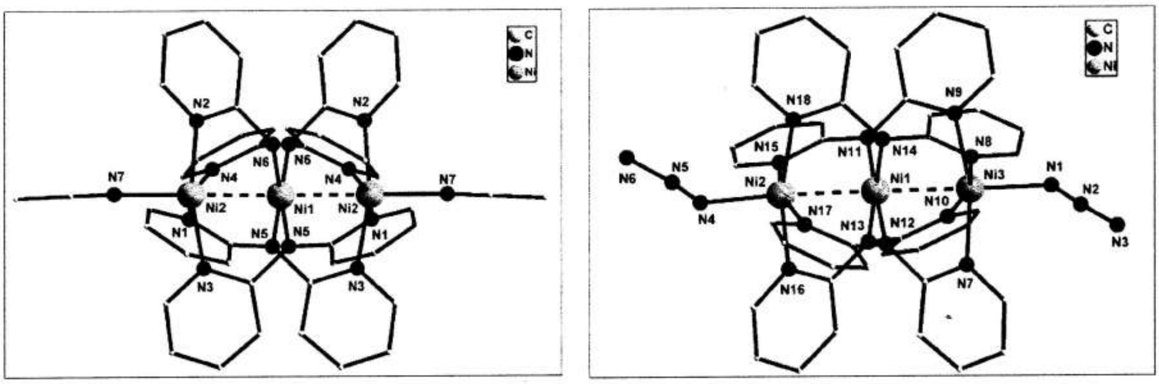
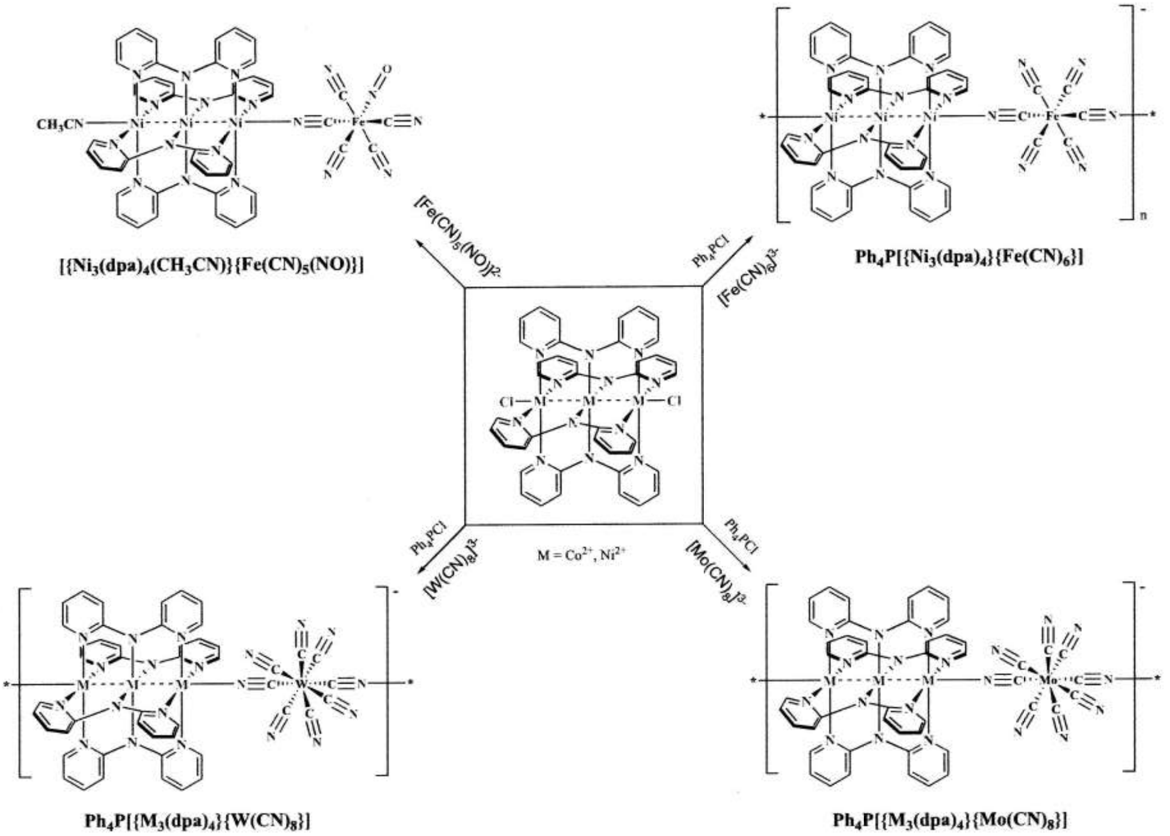


Figure 1: Molecule structures of $[Ni_3(dpa)_4(CH_3CN)_2](BPh_4)_2$ (**3**) and $[Ni_3(dpa)_4(N_3)_2]$ (**4**). The BPh_4 anion in **3** and hydrogen atoms in both **2** and **3** are omitted for clarity.

After the successful synthesis of the linear trinuclear precursor complexes, albeit in very poor yield, we investigated the reaction of these complexes with cyanometallate based linkers. It was anticipated that cyanometallate linkers will replace the labile terminal ligands in **1-4** and thus result in heterometallic assemblies with interesting magnetic features. Several new heteronuclear polymeric species have been prepared by bridging linear trinuclear 3d building block, $[M_3(dpa)_4Cl_2]$ ($M = Co^{2+}, Ni^{2+}$) with cyanometallates e.g. $Na_2[Fe(CN)_5(NO)]$, $K_3[Fe(CN)_6]$, $Bu_4N[M(CN)_8]$ [M = Mo(V) and W(V)] (Scheme 2). In all cases, the self-assembly between the trinuclear 3d building block $[M_3(dpa)_4Cl_2]$ ($M = Co^{2+}, Ni^{2+}$) with cyanometallates are found to be extremely facile and lead to the isolation of cyano bridged polymeric species (Scheme 1).



Scheme 1: Synthesis of cyano bridged heterometallic species.

Elemental analysis and ICP-AES studies were performed on all the heterometallic aggregates and the results obtained satisfactorily conform to the given formulations. Spectroscopic investigations of the resulting complexes have unequivocally established presence of a linkage between cyanometallate unit with the trinuclear building block through cyanide bridge. IR spectra of all the cyano bridged compounds show distinct peak at ~2100 cm^{-1} which is characteristic of C≡N stretching vibration of cyano group (Figure 2). Moreover, all peaks characteristic of the trinuclear building blocks are also observed in the IR spectrum of the heterometallic complexes.

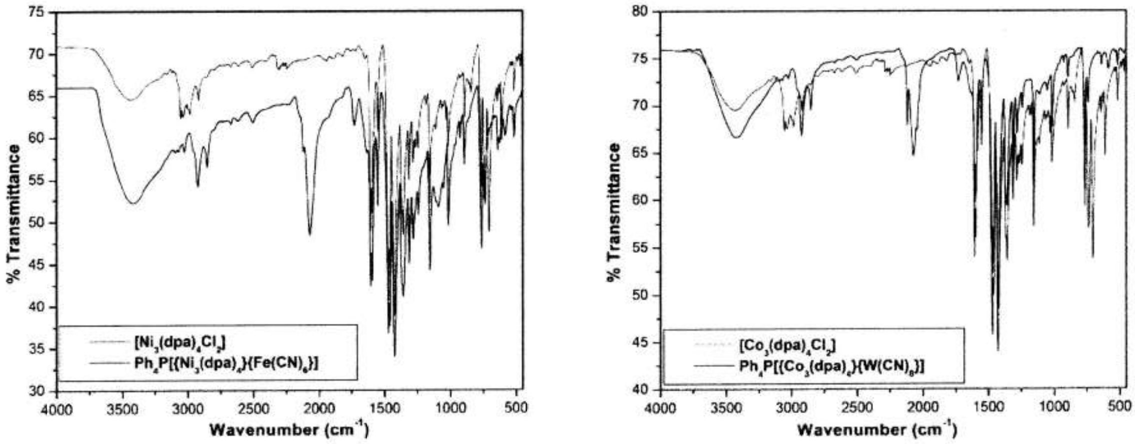


Figure 2: IR spectra of the precursor complexes and resulting cyano bridged heterometallic aggregates as KBr disc.

However, due to the facile nature of the reactions, very small and poor quality crystals are obtained for the cyano bridged heterometallic complexes and this impeded their accurate structural analysis by single crystal X-ray diffraction technique. Powder X-ray diffraction patterns of the polymeric aggregates showed weakly intense peaks (Figure 3). Nevertheless, structural analysis of the powder X-ray diffraction patterns by indexing of peaks resulted the lattice parameters and all the reasonably intense peaks could be indexed to specific crystal planes. Attempts are currently underway to produce good quality single crystals of the heterometallic assemblages by slow diffusion of the reactants.

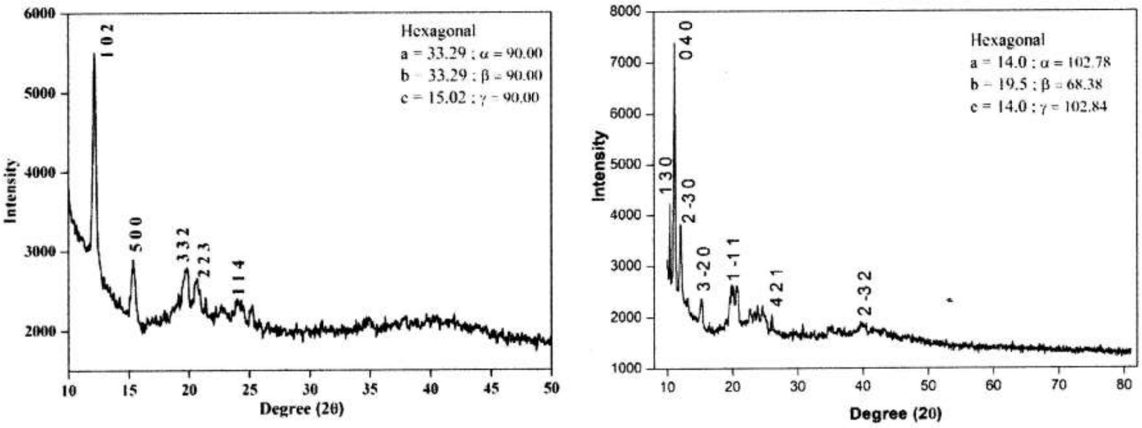


Figure 3: Powder X-ray diffraction pattern of $Ph_4P[\{Ni_3(dpa)_4\}\{Fe(CN)_6\}]$ (left) & $Ph_4P[\{Co_3(dpa)_4\}\{W(CN)_8\}]$ (right).

Magnetic properties of the cyano bridged {3d-5d} aggregate, $Ph_4P[\{Co_3(dpa)_4\}\{W(CN)_8\}]$ was initially investigated under a static magnetic field of 1000 Oe between temperature range 2-300 K (Figure 4). The X_MT value at 300 K was found to be 0.84 cm^3Kmol^{-1} which is slightly higher than the expected value of 0.75 cm^3Kmol^{-1} calculated for two magnetically isolated S=1/2 centers with g = 2.0. The higher value of X_MT than the calculated X_MT can be attributed to g values larger than 2.0 due to the presence of magnetic anisotropy in Co^{2+}. Moreover, on decreasing the temperature below 300 K, the X_MT value remain static upto 30 K. However, on cooling below 30K, X_MT increases abruptly to reach a maximum of 22.4 cm^3Kmol^{-1} at 11 K. This abrupt increase in X_MT can be attributed to intra-chain magnetic ordering facilitated by ferromagnetic interaction between the Co(II) and W(V) centers. Further, magnetization studies performed at 2K reveal that small external field can trigger magnetic ordering as magnetization increases abruptly to reach saturation magnetization value. Moreover, the saturation magnetization value of 1.94 Nβ is close to the expected saturation magnetization value for a S=1 ground spin state.

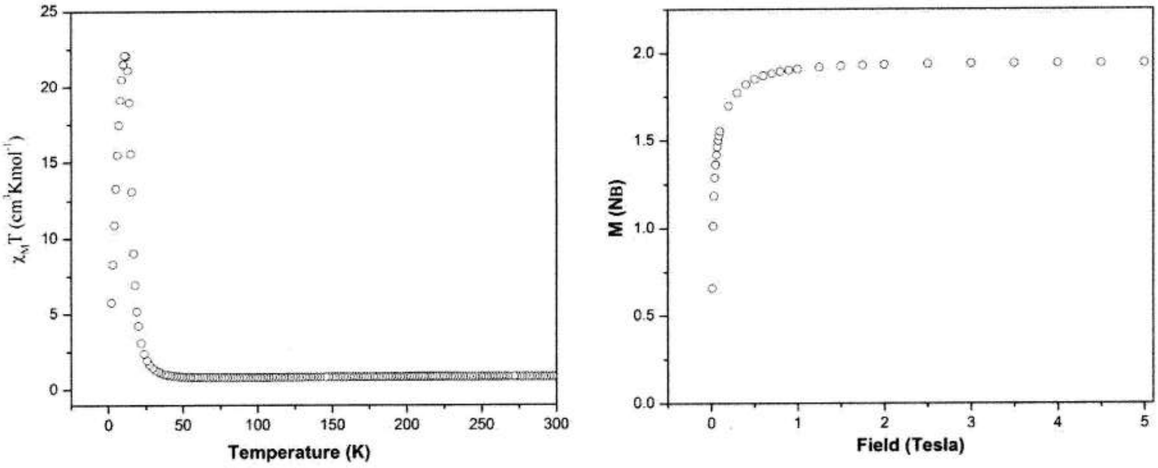


Figure 4: X_MT vs T plot (left) and M vs H plot (right) of $Ph_4P[\{Co_3(dpa)_4\}\{W(CN)_8\}]$.

In addition to $[M_3(dpa)_4Cl_2]$, self-assembly reactions of cyanometallate linkers with another class of linear trinuclear 3d complex, $[Mn_3(OAc)_6L_2]$ [L = 2,2'-bipyridine or phenanthroline] (Chart 1) were also investigated. Reactions of $[Mn_3(OAc)_6L_2]$ with $K_3[Fe(CN)_6]$ are found to be highly facile and immediately resulted in brown precipitates. Small needle shaped crystals of brown color could be obtained by slow diffusion of the reactants in a test tube. Analytical and spectroscopic analysis of the crystalline products obtained by self-assembly of $[Mn_3(OAc)_6L_2]$ with $Na_3[Fe(CN)_6]$ clearly reveal the formation of cyano-bridged polymeric species where the trinuclear precursors are retained.

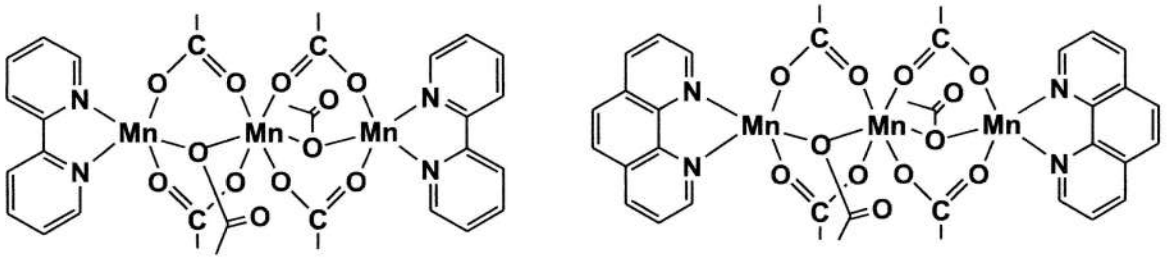


Chart 1: Structure of trinuclear acetate bridged M(II) complexes, $[Mn_3(OAc)_6L_2]$.

IR spectra of the resulting cyano bridged heterometallic aggregates clearly reveal the presence of cyano linkage as intense peaks were observed near 2100 cm^{-1} in case of both the heterometallic aggretates (Figure 5). The bands at 2066 and 2146 cm^{-1} clearly proves the presence of cyanide ions in bridging and terminal positions, respectively. The shift of ν(C≡N) to higher wave number (2146 cm^{-1}) compared with that of $K_3[Fe(CN)_6]$ (2119 cm^{-1}) suggests a lowered symmetry about the $[Fe(CN)_6]^{3-}$ entity and the formation of CN^- bridges. Further, all peaks associated with the trinuclear precursor complexes were also observed in the IR spectrum of the cyano bridged heterometallic aggregates and this clearly establish the structural integrity of the trinuclear units present in the precursor complexes within the heterometallic aggregates. The strong peak at 1344 cm^{-1} is due to C–N stretching vibration. The band at 1615 cm^{-1} is due to C=O stretching vibration, confirming presence of acetate group. The peak for C=N is merged with that for C=O at 1615 cm^{-1}. The medium intensity band at 598 cm^{-1} can be attributed to ν(Fe-C) stretching vibration. The peak at 421 cm^{-1} is responsible for Mn–N stretching vibration and around 455 cm^{-1} is characteristic for Mn–O stretching vibration. Thus, formation of cyano bridged heterometallic aggregates by interlinking of the trinuclear building blocks $[Mn_3(OAc)_6L_2]$ is established. However, elemental analysis and ICP-AES analysis of the heterometallic aggregates did not conform with the expected formulations and this can be attributed to the presence of large amount of solvent molecules within the crystal lattice. Thermogravimetric analysis of the heterometallic aggregates show ~16% weight loss below 100 °C and the presence of large number of solvent molecules within the crystal lattice is established.

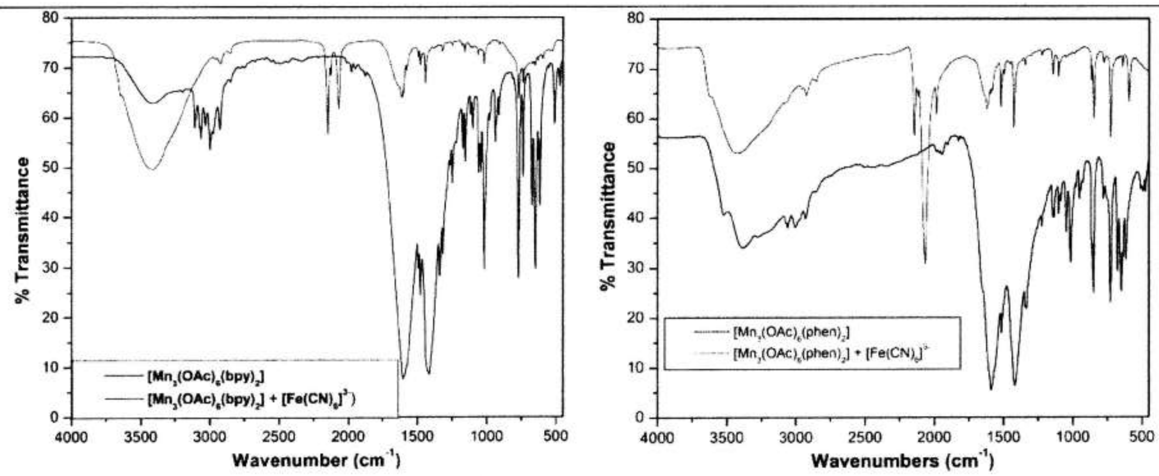


Figure 5: IR spectra of the precursor complexes, $[Mn_3(OAc)_6L_2]$ and their cyano bridged heterometallic aggregates as KBr disc.

Although single crystalline products were obtained in both the cases, the qualities of single crystals are not suitable enough for single crystal X-ray diffraction studies. Therefore, powder X-ray diffraction analysis was performed on the heterometallic aggregates prepared from $[Mn_3(OAc)_6L_2]$. Attempts were made to index the peaks observed in powder X-ray diffraction pattern of the heterometallic aggregates (Figure 6). However, in both the cases we failed to obtain a correct unit cell dimensions.

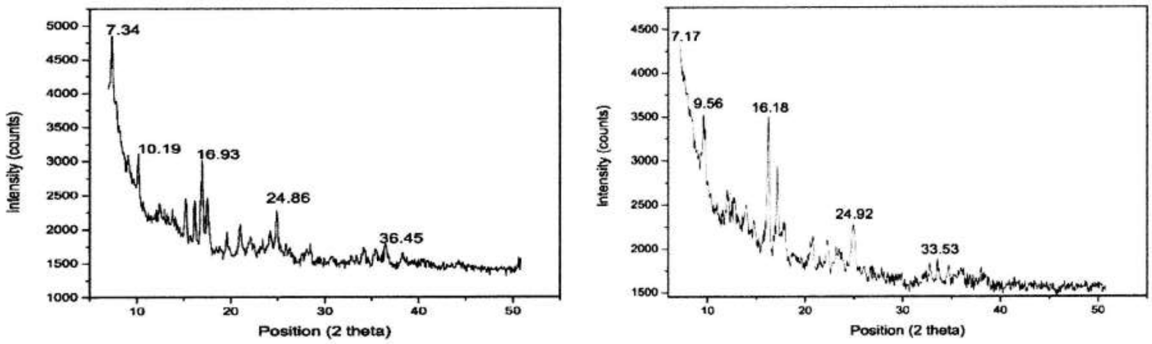


Figure 6: Powder X-ray diffraction patterns of cyano bridged heterometallic species formed by $[Mn_3(OAc)_6L_2]$.

The final goal of the project was to develop heterometallic assemblies by interlinking of linear trinuclear building blocks. One of the most versatile bridging metalloligand that was employed for interlinking trinuclear 3d building blocks was $[Ni(pao)_2(py)_2]$ (pao = pyridine-2-aldoxime). During the synthesis of the bridging metalloligand, $[Ni(pao)_2(py)_2]$ by an established procedure, we serendipitously encountered formation of a hitherto unknown 1-D polymeric heterometallic structure. The new 1D polymeric heterometallic complex, $\{[Ni_2Na_3(pao)_6(H_2O)_2](C_5H_5N)_2(H_2O)_2\}_n$ features linear trinuclear $[Ni_2Na(pao)_6]$ fragments bridged together by $Na(H_2O)_2$ linkers as shown in Figure 7. The bridging pentadentate coordination mode of tris(pyridine-2-aldoximato)nickel(II) group in this complex is unique and has not been observed earlier.

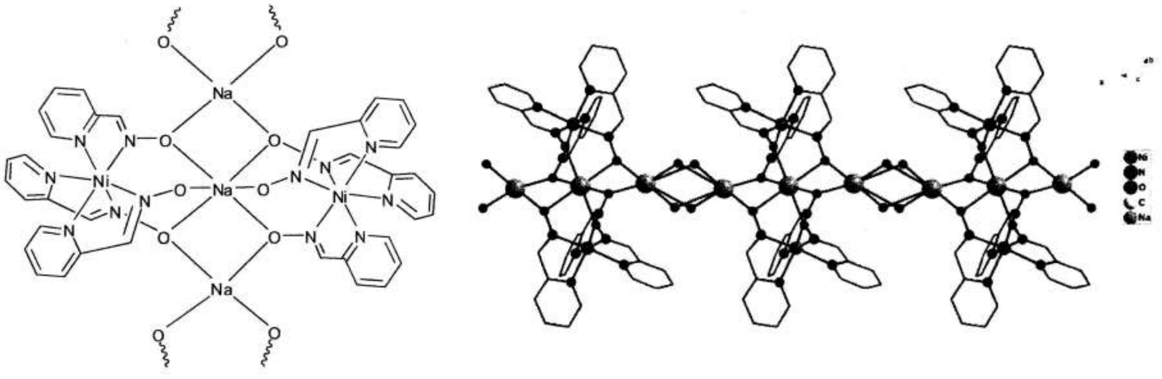


Figure 7: Schematic diagram of the new 1D complex and its crystal structure.

Thus, in conclusion, the reaction of several trinuclear linear 3d complexes with different 3d/4d/5d cyanometallate based linkers have been investigated. Facile reaction of the linear trinuclear complexes with all the cyanometallate based linkers have been observed. Analytical and spectroscopic investigations clearly established the formation of cyano bridged heterometallic aggregates in all the cases, while the linear trinuclear units remained intact within the heterometallic aggregates. However, the facile nature of the reactions prevented isolating x-ray quality single crystals of the heterometallic aggregated and this impeded accurate structure determination. Neverthless, basic structural data e.g. unit cell parameters was obtained in case of a couple of cyano bridged heterometallic aggregates by indexing of powder X-ray diffraction patter. Moreover, extensive low temperature magnetization measurement was performed for one of the cyano bridged heterometallic aggregates, $Ph_4P[\{Co_3(dpa)_4\}\{W(CN)_8\}]$. The magnetization measurement established the presence of strong magnetic correlation between the spin carriers and this lead to observation of easy magnetization. Dynamic susceptibility studies and accurate structural data will eventually allow us to rationalize the observed magnetic features of the heterometallic aggregate. The inability to grow x-ray quality single crystals of the resulting heterometallic aggregates turned out to be the biggest obstacle in performing their magneto-structural correlation. Efforts to grow good quality single crystals of the above heterometallic aggregates are currently undergoing in our laboratory.

Enclosure-II

10. List of Publications from this Project (including title, author(s), journals & year (s)

(A) Papers published only in cited Jornals (SCI):

1. Surprises from an old reaction: a new 1-D heterometallic tris(pyridine-2-aldoximato)nickel(II)-sodium complex, Mamon Dey, Anuran Goswami and Nayanmoni Gogoi, *Transition Metal Chemistry*, **2016**, *41*, 509-516.
2. Enhanced Catalytic Activity and Near Room Temperature Gas Sensing Properties of SnO_2 Nanoclusters@Mesoporous Sn(IV) Organophosphonate Composite. Borah, S.; Bhattacharyya, B.; Deka, J.; Borah, A.; Devi, A.; Deka, D.; Mishra, S.; Raidongia, K.; Gogoi, N. *Dalton Transactions* **2017**, *46*, 8664-8672.
3. Cyano bridged heterometallic Mn (II)-Fe (III) aggregates: synthesis, structure and magnetic properties. Dey, M.; Sarma, B.; Gogoi, N. *Inorganica Chimica Acta* **2018**, *469*, 20-24.
4. Pd nanoparticles dispersed on ZrIV organophosphonate: A robust and reusable catalyst for Suzuki-Miyaura cross coupling reactions. Borah, S,; Mishra, S.; Cardenas, L.; Gogoi, N. *European Journal of Inorganic Chemistry*, 2018, .

(B) Papers published only in Conference Proceedings, Popular Journals etc.

Nil

11. Patents filed/to be filed: Nil

FORM-L
UTILISATION CERTIFICATE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Human Resource Development Group
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

CSIR-HRDG Scheme No. **01(2789)/14/EMR-II**

S.No.	Particulars	Letter No. /Bank Transaction ID Nos. & Date	Amount
1	Grants received from CSIR during the year	**Letter No. 01(2789)/14/EMR-II dated 25th April 2017** **Transaction ID: SYNB0009100*P17110838435364 Dated 8th November 2017**	**35,863**
2	Unspent balance of previous year		**51,769**
3	Interest earned/accrued on CSIR grant		**NIL**
		Total	**87,632**

1. Certified that out of Rs. **35,863/-** (Rupees Thirty Five Thousands Eight Hundrend and Sixty Three Only) of grant-in-aid released by Extramural Research (EMR) Division of HRDG (CSIR) vide letter No./Bank Transaction ID Nos. **SYNB0009100*P17110838435364** dated **08/11/2017** as given in the margin during the year 2017 and Rs. **NIL** earned/accrued as interest from bank on grants released by CSIR and Rs. **51,769/-** (Fifty One Thousand Seven Hundred and Sixty Nine Only) on account of unspent balance of the previous year, a sum of Rs. **87,632/-** (Eighty Seven Thousands Six Hundred and Thirty Two Only) has been utilized for the purpose for which it was sanctioned and that the balance of Rs. NIL remaining unutilized at the end of the year has been surrendered to EMR, HRDG (CSIR) (vide letter No. **NOT APPLICABLE**, DD/Cheque No. **NOT APPLICABLE** dated **NOT APPLICABLE**)/ ~~will be adjusted towards the grant-in-aid payable during the next year~~.

2. Certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned have been duly fulfilled/are being fulfilled and that I have exercised the following checks to see that the

Finance Officer
Tezpur University

money was actually utilized for the purpose for which it was sanctioned. The detail expenditure incurred during the year is shown in the enclosed "Statement of Accounts (Receipt & Payment)".

(Kinds of checks exercised)

1. Vouchers and Statement of Accounts
2. Grant-in-Aid
3. Expenditure Register
4. Bank statements for accrual interest

27/2/18

Signature of Authorised Officer
with Date& Seal
Finance Officer
Tezpur University

Countersigned by Registrar/Dean/Director
Of the institute with Date & Seal
Registrar
Tezpur University

The Utilization certificate and statement should be signed by Head of the Finance & Accounts and countersigned by Registrar/Dean/Director of the University/Institute.

Consolidated Statement of Accounts

(From 01/10/2014 till 30/09/ 2017)

Scheme Number : **01(2789)/14/EMR-II**

Title of the Research Scheme : **Development of Exchange Biased {3d-4d/5d} Assemblies: A Rational Route Towards High T_b Nanomagnets.**

Name of the Principal Investigator : Dr. NAYANMONI GOGOI, Assistant Professor, Department of Chemical Sciences, Tezpur University, Napaam-784028, Assam

Date of Commencement : 01/10/2014 Date of Termination: 30/09/2017

		Receipts (Particulars of grants received)						Payments (Particulars of grants spent)						
Period (ending 31 March)	Transaction ID., date & Amount	Stipend	Contingency	Overhead	Equipment Grant	Bank Interest	Total	Stipend	Contingency	Overhead	Equipment Grant	HRA + MA	Total	Balance
01/10/14 – 31/3/15	**P14 092346 635679 Dated 23/08/14 For ₹ 2,07,000**	**1,32,000**	**75,000**	**NIL**	**NIL**	**NIL**	**2,07,000**	**33,871**	**74,996**	**NIL**	**NIL**	**NIL**	**1,08,867**	**98,133**
01/04/15 - 31/03/16	**P1509016079 5711 Dated 01/08/15 For ₹ 2,25,314**	**69,871**	**1,50,000**	**5,443**	**NIL**	**NIL**	**2,25,314**	**1,68,000**	**1,49,825**	**5,360**	**NIL**	**NIL**	**3,23,185**	**262**
01/04/16 - 31/03/17	**P1608181191 6438 Dated 09/08/16 for ₹ 3,33,897**	**1,68,000**	**1,49,821**	**16,076**	**NIL**	**1,428**	**3,35,325**	**1,19,000**	**1,54,770**	**10,048**	**NIL**	**NIL**	**2,83,818**	**51,769**
01/04/17 - 30/09/17	**P1711083843 5364 Dated 08/11/17 for ₹ 35,863**	**NIL**	**26,000**	**9,863**	**NIL**	**NIL**	**35,863**	**NIL**	**78,061**	**9,571**	**NIL**	**NIL**	**87,632**	**NIL**
Total		**3,69,871**	**4,00,821**	**31,382**	**NIL**	**1428**	**8,03,502**	**3,20,871**	**4,57,652**	**24,979**	**NIL**	**NIL**	**8,03,502**	**NIL**

Signature of Registrar with Stamp

Registrar
Tezpur University

27/2/18

Signature of Finance Officer with Stamp

Finance Officer
Tezpur University

12/02/2018

Signature of PI with Stamp

Department of Chemical Sciences
Tezpur University
Tezpur - 784028