PH Controlled the Supramolecular Assemblies of Two Guanosine Monophosphate Cadmium Metal Coordination Complexes: Structure and Chirality

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Abstract

In biological systems Chirality is important property from small molecules to macromolecules. The construction of homochiral coordination supramolecules in crystal and helical delivers the connection of molecular and macromolecular chirality. Complexity and properties in the presence of cadmium ion and bpe auxiliary ligand for bio-molecular guanosine-5- monophosphate disodium salt (GMP) was studied. The two Complexes **1** and **2** have been investigated the impact of auxiliary ligand bpe, hydroxy group on the sugar motif and pH for coordination of GMP ligands. The interaction of mixed ligands for growth and advancement of chiral complexes was controlled by the alteration of pH values for coordination of guanosine-5-monophosphate nucleotide with cadmium Cd (II) metal. The chirality of complexes **1** and **2** was studied with solid circular dichroism (CD) spectroscopy, including supramolecular chirality and extended auxiliary ligand (EAC) combining with the crystal structure analysis. The various hydrogen bonding and auxiliary ligand are the special means of transporting chirality from isolated molecules to dynamic supramolecular three-dimensional designs of GMP nucleotide crystals. The research results will be benefit to the controlling supramolecular assembly with well-defined structure and properties.

Introduction

Chirality is popular in biological processes, varying from small molecules such as amino acids, nitrogenous bases and sugars to macroscopic structures like single-stranded RNA, dual-helical DNA, and α -helical protein. In addition to helping the body to preserve its biological functions, broad bio components are often built to establish modern applications such as Biocomputing, bio catalysis, biomedicine, and material science.^[1–6] It is difficult that bio-macromolecules crystallize, chiral coordination polymers occur as crystalline materials with specified structures, and chirality is normally expressed exclusively at a molecular level.^[7] In non-biological environments, supramolecular coordinate complexes relate to an array of metal-organic compounds consisting of metal ions as nodes and tiny organic ligands as bonds in one, two, and tridimensionality structures. These products typically have corrected structures to be engineered and developed by careful selection of metal ions and ligands.^[8–9] Coordination complexes for metal-nucleotides are essential both in chemistry as well as in biology.

See polymers are desirable templates for the mediation of the synthesis of supramolecular coordination complexes.^[10–11] Adenosine, cytidine, guanosine, thymidine, uridine phosphate are the five main nucleotide complexes in living cells, which provide distinct types of metal attachment with specific nucleotides. N7 and O motif donors strongly coordinate with metal ions for the purine basis of nucleotides.^[12–13] The definition refers to the axial chirality, which defines a chiral conformation of the coordinating polymer formed from bridge ligands in organic chemical engineering. Because of chiral induction, GMP wraps the metal-ligand axis. A variety of bipyridyl bridge ligands have been used in previous research to effectively tune the chiral and structural function of the complexes.^[14–15] Nucleotide coordination capability shifts in the order below: GMP > IMP > AMP > UMP > TMP>CMP^[16] Different factors, including solvents, pH, metal ions, may affect the synthesis of nucleic acid materials.^[17–18]

Nucleic acids materials are ideal for a number of fields, e.g., diagnosis,^[19–20] therapeutics,^[21–22] biosensing,^[23–26] nutritional and environmental toxins,^[27–29] medicinal research, information technology,^[30] luminescence,^[31] adaptive incorporation,^[32] etc., due to their strong targeting performance. In chirality analysis, solid-state CD spectroscopy, in conjunction with single-crystal structure determination, is an essential method to explain the structure of coordination supramolecule.^[33] In biomedical, luminescent, and the production of antibodies, nuclear coordination polymer materials have been used alongside; this analysis also uses artificial data storage devices.^[34] Coordinating substances vary from coordination chemistry in general from crystal architecture and engineering. The frequency of the interactions gives the metal-organic compounds a degree of structural modularity. The structural characteristics of the compounds are governed by their properties as an effective, multidimensional centre and by the metal ions participating.^[35–36]

The pH plays vital role for coordination of metal with different ligands. The nitrogen containing ligand with cadmium metal coordination occurs at slightly basic pH. The phosphate group coordinated with metals in acidic environment.^[37, 38–41] While nitrogen points in GMP nucleotide coordinated with metal in slightly basic conditions.^[36, 42, 43, 44, 45, 46] From above studies it is found that GMP coordination complexes with cadmium metal in crystalline state can be constructed by tuning the pH. The previous studies of nucleotide coordination supramolecular complexes different factors, synthesis methods were studied. On the basis of these studies, we expand the synthesis of coordination complexes from GMP nucleotide with cadmium metal and bpe auxiliary ligand by varying the pH.

In this work, the two coordinate complexes **[Cd(GMP)(bpe)(H₂O)₃]·7H₂O** (pH=6) and **[Cd(GMP)(H₂O)₅]·3H₂O** (pH=8) were synthesized using Guanosine-5'-monophosphate (GMP), 1,2-di(4-pyridyl) ethylene (bpe) with transition metal cadmium at different pH values. The comprehensive discussion of the relationship between the crystal structure and chirality of complexes 1 and 2 are presented in this work, especially the comparison of their pH controlling in the supramolecular assembly. The strategy for design is focused on N-donor 1,2-Di(4-pyridyl) ethylene(bpe) as the bridging ligand for (i) tuning the GMP bases in complexes **1** and **2** of supramolecular compounds (ii) to tune noncovalent interactions, (iii) The effect of GMP with respect to pH in the organization of a targeted molecule and chiral supramolecular construction. The study explaining the different binding sites of GMP to Cadmium metal with respect to pH. N6 binding position of guanine base in GMP favours to form the Cadmium coordination complex at high pH value. Oxygen of Phosphate group in GMP, bpe ligand favours the coordination with cadmium metal at low pH value.

Materials And Methods

All chemicals have been withdrawn from the industry for synthesis. Without further treatment, these analytic grade chemicals were used for the synthesis of complex 1. Atmospheric reactions were both conducted. In the 4000-400 cm⁻¹ area, FTIR spectra have been reported with KBr pellets on the Nicolet-360 FTIR spectrometer. Sample Powder x-ray diffraction (PXRD) experiments were performed using Japanese

graphite monochromatized Mo K α radiation ($\lambda=0.71073 \text{ \AA}$) Ringku D/max gA x-ray diffractometer. CD measuring on the JASCO J-810 spectropolarimeter was achieved at 25°C under steady nitrogen flow. The ratio of crystalline and KBr powder to solid-state CDs measuring GMP ligand and complex 1 was 1:200, while literature pushing the mixture into the plate^[35].

Synthesis Complex 1:

The crystalline coordination compound (Complex 1) of GMP having Cd(II) transition metal ion and bpe was synthesized. In 10-ml water the nucleotide GMP (16mg, 0.04mmol), Cd(NO₃)₂.2H₂O, (12mg, 0,04mmol) were dissolved and stirred in the air for 30 minutes. The reaction mixture has been complemented by the solution bpe (7 mg, 0,04 mmol) in ethanol (5 mL). The pH was adjusted by using carboxylic acid and NH₄OH. The resulting mixture with pH=6 was stirred and filtered. After two weeks of evaporation at room temperature, colorless crystals ideal for X-ray diffraction has been collected. The yield of crystalline materials depends on the weight of GMP, are 69 percent.

Synthesis Complex 2:

To synthesize the complex 2 (GMP-Cd), 16mg (0.04mmol) of Na₂GMP was dissolved in 5ml of distilled water and the metal salt Cd(NO₃)₂.2H₂O (12mg, 0.04 mmol) was dissolved in 5ml of water. The reaction mixture was supplemented by the solution bpe (7 mg, 0,04 mmol) in ethanol (5 mL). These three solutions were mixed and stirred for 25 minutes, during the stirring an opaque precipitate were formed which were dissolved by adding small amount of carboxylic acid to make the solution clear. After that the pH of solution was adjusted at pH=8.0 by adding NH₄OH solution and stirred for 30 minutes. The mixture of reacting species was heated at 60°C for 24 hours then filtered and left for two weeks. The clear colourless crystals were obtained suitable for single crystal X-ray diffraction analysis. The percentage yield of complex is 71% by weight of GMP for reaction.

Refinement Details of The Crystal Structure for Complexes 1-2:

The X-ray single crystal data collection for complexes 1-2 were conducted on a Bruker SMART CCD diffractometer with graphite monochromated radiation of Mo K α ($\mu = 0.71073 \text{ \AA}$). The crystalline framework was solved by direct approaches and refined by utilizing the Olex2, SHELXL. Anisotropically, non-hydrogen atoms have been refined. Hydrogens were handled with the default parameters OLEX2. Table 1 includes criteria of crystal structure determination and refinement. Geometric measurements were carried out on the hydrogen atoms connected to carbon, Nitrogen, and oxygen, and their locations and thermal parameters were calculated during structural refinement. In their geometrically generated places, hydrogen atoms belong to the water molecules. Table1, S2-S6 offers a summary of additional crystallographic details for the Structural analysis of complex 1 and Complex2 and lists chosen bond lengths and angles with their standard deviations for complexes 1-2.

Results And Discussion

Considering all data gathered and study findings available, we agreed to investigate using GMP-Cd-bpe, a precursor complex by varying the pH, to construct supramolecular species with noncovalent interactions (Hydrogen bonding and π - π interactions) as nucleotides may coordinate closely with the number of metal ions. Nucleotide fragments, metal ions and mixed N-donor ligands play an important function in supramolecule for structural chirality. The role of hydroxyl groups and pH in the assembly of GMP-Cd-bpe, and GMP-Cd chiral supramolecular complexes has also been addressed in pentose sugar, N-donor bridging ligand bpe, and noncovalent interactions. The ligands of guanosine (GMP, dGMP, GDP etc.) are coordinated with metal ions in acidic and neutral pH varying from 4-9.^[36, 38]

The complexes 1 and 2 both are composed of Cd(II) metal ions and nucleotide ligand expect for supplementary N-donor ligands in complex 1. In complex 1, the metal ions combine to bpe to create a similar independent unit with two neighbouring bpe ligands while in complex 2 each Cd (II) is coordinated with one nucleotide ligand through nitrogen N6 of guanine base ring and five water molecules through oxygen atoms due to the variation in pH=6-8 shown in **figure 1(a-b)**. Complex 1 single crystals (GMP-Cd-bpe) have been synthesized at pH= 6; GMP demonstrates the greater potential for coordination through oxygen of phosphate in the crystalline state with Cd(II) ions, for supramolecular chiral complex. Cadmium metal, three water molecules and two bpe ligands organize the complex 1. Nucleotide GMP provides better stability in organized complexes with slightly acidic to neutral and slight basic pH values. The pH is a very significant and effective approach for regulating supramolecular structure forming in complex 1. The slight acidic pH=6 favours the coordination of GMP, bpe with Cadmium metal in complex 1. The relationship between pyridine rings of the bpe and GMP intrachain and interchain π - π stacking has tuned the orientation for GMP (**figure 2, S2**). The space group of complex 1 is *P1*, suggesting the chirality of the crystalline complex 1. A Cd(II) ion coordinated with one GMP ligand, two bpe ligands and three coordinated water molecules to form the molecular structure of complex 1. (**Fig. 1, Tables S1 and S2**). In complex 2, Cd (II) is coordinated with one GMP through N6 of Guanine Base and five water molecules at pH 8. The synthesis of complexes 1-2 suggested that the GMP ligand can coordinate through oxygen of phosphate group at slight acidic pH=6 in complex 1 and in complex 2 GMP is coordinated with Cadmium at slight basic pH=8 through N6 of guanine base of GMP. The basic pH favours the metal coordination of GMP through Nitrogen of guanine base while Acidic pH favours the Coordination of GMP through Oxygen of phosphate group. The purine AMP ligand coordinated with copper metal through oxygen of phosphate group at pH 3.65-5.82.^[37] While in this work we synthesize the two GMP coordination supramolecular complexes at pH 6 and 8 for complex 1 and complex 2 respectively.

It must be mentioned that the same structure of complex 2 has been reported in 1976 by Katsuyuki Aoki and was measured by Cu $K\alpha$ radiation (0.15406 nm).^[47] Compare to the structure reported before, diffraction data of complex 2 were collected by Mo $K\alpha$ radiation (0.071073 nm), and more independent reflections were observed in experiment, which mean the locations of the non-hydrogen atoms and hydrogen atoms can be determined more accurately. Additionally, all the hydrogen atoms of GMP and solvent molecules have been added and refined in complex 2, which is helpful to study the structure of complex 2 and the chirality of the supramolecular helical chains formed by hydrogen bonding.

The chirality of the GMP ligand persisted based on the octahedral geometry of the Cd(II) centre in molecules 1-2 and molecular chirality. In complex 1, the nucleotide ratio with bpe is 1:2, rendering GMP ligand wide freedom, especially for the phosphate group metal coordination. It contributes to several H-bonding structures in molecular crystal structure packaging from the perspective of supramolecular chemistry. The molecules are connected to form a 1D chain by strong intermolecular forces H-bonds among, O6 – H6C ...N2, O6 – H6D...O3, O7-H7A...O10, O12- H12A...O13, and N7 – H7 ... O12 in complex 1(Figure 3, Table S6) and in complex 2 the H-bonds are O4-H4A...O17¹, O7-H7A...O15², O10-H10A...O12³, O10-H10B...O1, O12-H12...O11⁵ which stabilize the structure of supramolecular design and these intermolecular interactions are responsible for construction of these complexes (**figure 2 a-b**).

The chain and the 3D structure arose primarily from the versatility of the sugar motif, organization of phosphates and water molecules which coordinated with metal and form Hydrogen bonding to pack the neighbouring chains. The twisting angles between sugar motif and guanine base are 67.939(155)° in Complex **1**, and 79.506(377)° in complex **2** (**figure S1 c-d**). These angles are responsible for orientation of ligands around the Cd (II) in both complexes and for the construction of such supramolecular coordination complexes. In complex 1 hydroxyl of sugar motif creates hydrogen bonding with water molecules coordinated with Cd (II) metal this hydrogen bonding connects two parallel layers of coordination polymers. These 1D chains are then installed in H-binding to create the 3D supramolecular chiral architectures in the presence of solvent water molecules. The 1D chain composed of half the bpe and half the GMP chain shown in (**figure 2a-b, S2 a-d**). The molecules are unequivocally intertwined through H-bonding to expand the structure of the 2D supramolecule. In addition, these 2D sheets are wrapped based on packaging and H-bonding. The 3D topology of complex 1 with one node and intermolecular interactions as a connection is the network that clearly shows the link between complex molecules packaging in the crystal lattice (**figure 2a-b**). Chiral dichroism (CD) experiments have verified both the ligand chirality and complex 1 (**Fig. 6**).

Table 1: Structural Refinement and Crystalline Data for Complexes 1 & 2.

Complexes	Complex 1 (GMP-Cd-bpe)	Complex 2 (GMP-Cd)
Empirical formula	C ₂₂ H ₃₈ CdN ₇ O ₂₁ P	C ₁₀ H ₂₈ CdN ₅ O ₁₆ P
Formula weight	879.96	617.74
Temperature/K	296.15	296.15
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1	<i>C</i> 2
<i>a</i> /Å	7.045(3)	27.891(4)
<i>b</i> /Å	10.127(4)	11.3556(17)
<i>c</i> /Å	13.508(5)	6.7542(10)
<i>α</i> /°	109.007(11)	90
<i>β</i> /°	90.834(14)	92.737(4)
<i>γ</i> /°	91.751(16)	90
Volume/Å ³	910.4(6)	2136.8(5)
<i>Z</i>	1	4
ρ_{calc} /g/cm ³	1.605	1.920
μ /mm ⁻¹	0.734	1.187
<i>F</i> (000)	450.0	1256.0
Crystal size/mm ³	0.25 × 0.23 × 0.2	0.25 × 0.21 × 0.18
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.19 to 62.898	3.874 to 62.886
Index ranges	-9 ≤ <i>h</i> ≤ 10, -13 ≤ <i>k</i> ≤ 14, -19 ≤ <i>l</i> ≤ 15	-38 ≤ <i>h</i> ≤ 39, -15 ≤ <i>k</i> ≤ 15, -9 ≤ <i>l</i> ≤ 9
Reflections collected	8160	13772
Independent reflections	7218 [<i>R</i> _{int} = 0.0440, <i>R</i> _{sigma} = 0.1559]	6186 [<i>R</i> _{int} = 0.0447, <i>R</i> _{sigma} = 0.0576]
Data/restraints/parameters	7218/45/489	6186/2/317
Goodness-of-fit on <i>F</i> ²	0.956	1.075
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0593, <i>wR</i> ₂ = 0.1209	<i>R</i> ₁ = 0.0408, <i>wR</i> ₂ = 0.0947

Final R indexes [all data]	$R_1 = 0.1006$, $wR_2 = 0.1475$	$R_1 = 0.0440$, $wR_2 = 0.0962$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	1.19/-1.93	2.00/-1.05
Flack parameter	-0.01(3)	0.067(15)

In complex 1, each cadmium is coordinated with three oxygen atoms of three water molecules, two nitrogen atoms of two neighbouring bpe molecules and one GMP by the phosphate group's oxygen. The organized distances are $\text{\AA}$ (Figure S1 f), Cd1-N4 = 2.3121(93) $\text{\AA}$, Cd1-O7 = 2.2987(96) $\text{\AA}$, Cd1-O4 = 2.3551(88) $\text{\AA}$, Cd1-O3 = 2.3021 $\text{\AA}$, Cd1-O1 = 2.2308(89) $\text{\AA}$ and Cd1-N3 = 2.3640(89) $\text{\AA}$ in Complex 1. In Complex 1, the distances between coordinated Guanine base ring and 1,2-Di(4-pyridyl) ethylene (bpe) rings are 3.4559 (196) $\text{\AA}$. O1-P1 = 1.5205(92) $\text{\AA}$, O9-P1 = 1.5902(74) $\text{\AA}$, O13-P1 = 1.4964(108) $\text{\AA}$ and O10-P1 = 1.5001(77) $\text{\AA}$ as shown in **Table S1, figure S5**, are the bond lengths of phosphate and oxygen in the phosphate group. In complex 2, each cadmium is coordinated with five oxygen atoms of five water molecules, one nitrogen atoms N6 of guanine base. The organized distances are $\text{\AA}$ (Figure S1 f), Cd1-O4 = 2.304(4) $\text{\AA}$, Cd1-O7 = 2.304(4) $\text{\AA}$, Cd1-O10 = 2.273(4) $\text{\AA}$, Cd1-O13 = 2.368(5) $\text{\AA}$, Cd1-O14 = 2.253(5) $\text{\AA}$ and Cd1-N6 = 2.294(5) $\text{\AA}$ in Complex 2. In Complex 2, the distances between P-O in coordinated Guanosine monophosphate are P1-O3 = 1.519(4) $\text{\AA}$, P1-O5 = 1.617(4) $\text{\AA}$, P1-O17 = 1.521(4) $\text{\AA}$ and P1-O15 = 1.515(4) $\text{\AA}$ as shown in **Table S2, figure S6** are the bond lengths of phosphate and oxygen in the phosphate group.

A crucial consideration for the construction of noncovalent interactions, i.e. π - π interactions and hydrogen bonding in relation with GMP and bpe, is the molecular length orientation of the ligand bpe and pH value. The orientation of the base ring, sugar ring and solvent molecules stabilize the structure and create the noncovalent interactions among the layers and within the layer of complex 1. Nucleotide linking displays a peculiar activity to create π - π connections and lateral interactions at slight acidic pH in complex 1 and slight basic pH in complex 2. The continuous Hydrogen bonding and π - π interactions (3.388 $\text{\AA}$), (3.482 $\text{\AA}$) are about to transfer the chirality in supramolecular structure in complex 2. These 2D layers packed in such a way to form 3D structure and shows that network of complex with single node demonstrating crystal lattice packing of compound (**figure 3, S4**). Hydrogen bonding among the nitrogenous base of Guanine, metal coordinated water molecules and π - π interactions orient the complex molecule in such a way to form butterfly like structure as shown in **figure 3 (a-d)**. This is one of the best example, to representing the chiral GMP ligand develop the Chiral Coordination supramolecules which are biomimetic materials. The chiral biomimetic materials could be used in fields of fluorescent materials, bioimaging and drug delivery etc.

In purine (Adenosine and Guanosine) nucleotides, the oxygen of Phosphate group, hydroxyl of sugar motif, Nitrogen atoms of nucleobases are capable binding spots for transition metals like (Cd, Cu, Ag, Ni, Mn, Co etc.).^[36, 44]

The pH sensitivity of nucleotides plays vital role for coordination abilities of nucleotides, stability of supramolecular complexes.^[37-46, 48] The metal recognition through N-binding sites of monophosphate nucleotide shows different binding sites due to endocyclic nitrogen. The Nitrogen N6 is favourably coordinated with metals (Mn, Cd, Pt, Ni) at basic pH = 8-9.^[37, 38, 43, 41, 44, 46] 2D layers are produced in complexes by the bridging ligand bpe and solvent molecules through comprehensive π - π interactions and hydrogen bonding in 3D supramolecular frameworks. These interactions occur between the phosphate oxygen atom, organized solvent molecules, purine base (guanine) and ribose sugar hydroxy (**figure 2, S3**). These intermolecular interactions transform 2D chirality into 3D supramolecular architecture. The crucial factor for building noncovalent interactions, i.e. π - π interactions and hydrogen bonding between purine base ring, hydroxyl groups of sugar motif, phosphate group of GMP in both complexes 1-2 and the length as well as orientation of bridging ligand in complex 2 by tuning the pH=6-8.

The orientation of the base ring, sugar ring and solvent molecules stabilizes the arrangement and induces noncovalent interactions between layers of complexes 1-2. The mixture of nucleotide demonstrates a peculiar activity in constructing π - π interactions and side-chain interactions. Nucleotide GMP is twisted in **complex 1** along the bpe axis. We have proposed the perception of organic chemistry as axial chirality into a coordination polymer which creatively enhances extending axial chirality (EAC) based on controllable pH conditions.

Now the **complex 2** offer great examples for understanding the EAC. In **complex 2**, the chiral character of GMP makes bpe a chiral environment and locks up the axial chirality through the coordination link to the infinite chain. The Supramolecular Chirality is based on the GMP orientation and the direction of the sugar motif of GMP, and structure and binding ability of phosphate group.

CD Spectra:

Spectroscopy of Circular Dichroism (CD). Supramolecular chirality and the EAC were present in complex 1 and 2 according to the structural analysis. The solid-state CD spectrum was recorded to identify the new chirality and EAC of GMP in complexes 1-2. All samples were phased pure and tested with a single crystal by measuring X-ray powder diffraction (XRPD). For GMP, the CD spectrum of the solid samples had two typical large peaks centred near 220 and 280 nm. Specifically, for the intermolecular π - π^* and n - π^* transitions, the stronger and broader negative envelope is about 260nm for complex 1 and 280 nm for complex 2 were observed. The positive absorption of about 220 nm in GMP is related to the intermolecular π - π^* interaction of nucleotide bases, which shows that GMP is ribonucleotide. There was a net positive absorption of 330 nm in complex 1 compared to the ligand. This positive peak also indicating the presence of auxiliary ligand in complex 1 which shows π - π interactions with nucleotide bases. Because coordinating Cd(II) with GMP prevents ligand mutarotation, ligands are kept in their complexes. Compared to GMP, the solid-CD (**Fig. 6**) for complex 1-2 was significantly similar. A positive and new peak of 330 nm indicated a further chiral source due to the supramolecular chiral structure of complex 1.^[9-10] The complex 1 and GMP CD spectra can be attributed to the EAC of bpe, and complex

2 also shows the extended chirality which is due to π - π^* transitions between bpe and purine of GMP and GMP structural research can be confirmed.

This work has confirmed the experimental findings that GMP chirality can be well-preserved when coordinated into Cd(II). The chirality of this centrally complex molecule can be transmitted by hydrogen bonding and π - π interactions to its supramolecule architecture. Spectroscopy of solid-state circular dichroism has been performed for the GMP complexes and proposes an effective method for study of delivering chirality. It offers a new way of delivering chiral from nucleotide-metallic complex molecules to its supramolecular architecture, which is important to understand life's origin. Preparation of appropriate nucleotide-metal complexes in future.

Conclusion

In conclusion, the construction of GMP-Cd-bpe (1) induced by cadmium and bpe auxiliary ligand at pH 6. The difference in N-donor auxiliary ligand (bpe) and pH corresponds to various protonation degree of GMP, which leads to the different combination modes of metal ions with GMP. At the suitable pH 6, the protonation of phosphate groups creates the electrostatic interaction of cadmium ions with the phosphate of GMP and becomes the dominant force, inducing the formation of GMP-Cd-bpe (1) complex and further the supramolecular structure. While, At pH=8 the GMP base is coordinated with Cd(II) in complex 2. The both GMP complexes (1-2) consists of the three-dimensional network formed by a one-dimensional structure. The formation of the GMP coordination complex with cadmium metal can prepare chiral GMP supramolecular complexes only by tuning the competition between the electrostatic interaction and π - π interaction via N-donor Auxiliary ligand bpe and pH. In this work we find that the Slightly acidic pH=6 favours the coordination of GMP nucleotide with Cd(II) metal through oxygen of phosphate group and basic pH=8 favours the coordination of GMP with Cd(II) through the nitrogen of guanine base in complex 2. The present work is hoping to provide useful strategies for constructing GMP, based chiral supramolecular assemblies with different metals and suitable auxiliary ligands. Which can be used for bioimaging, drug delivery, energy materials, fluorescence materials, data storage devices, molecular recognition, understanding of biological diseases, metal adsorbing materials from industrial wastes.

Declarations

Author contribution

Muhammad Javed Iqbal is First author and major contributor of this work. All authors are contributed in work and writing of this manuscript.

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Data availability

Supplementary Information (SI) available: Structural information, I.R. Spectra, UV-Vis Spectra, PXRD and figures of crystals are available. Data can be obtained from the corresponding authors through e-mail.

Code availability

The CCDC numbers of crystals : 2101635 and 2101641.

Conflict of interest

The authors declare no competing interests.

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Figures

Figure 1

Coordination Environment of Cadmium (II) in (a) Complex 1 (GMP-Cd-bpe), Cd (II) is coordinated with two bpe, one nucleotide GMP ligands and three water molecules (b) Complex 2 (GMP-Cd), Cd (II) is coordinated with one nucleotide GMP ligands and five water molecules.

Figure 2

Hydrogen bonding among the 1D layers into 3D of supramolecular complex (a) View a (b) motif of supramolecule showing hydrogen bonding among different point in complex 1 (Yellow Hydrogen bonds).

Figure 3

The Chiral metal coordinated molecular structure showing orientations of Nucleotide Guanine bases in complex 2 (a-b) a-view of Complex 2, like a top view of butterfly (c-d) structure showing side view of butterfly in c-view of complex 2. The chiral Molecules generate chiral materials which shows similarities in structure to living things.

Figure 4

The Chiral metal coordinated molecular porous structure showing hydrogen bonding, (a) Columnar view with orientations of Nucleotide Guanine bases and auxiliary ligand in complex 1 (b) structure showing helical structure of phosphate groups through solvent molecules in complex 2.

Figure 5

Showing the coordination of metal with GMP and bpe ligands to form the supramolecular structure of complex 1.

Figure 6

The solid-state CD spectra of the GMP ligand and its complexes 1 and 2 (KCl : [sample] = 200 : 1).

Supplementary Files

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- [Scheme1.png](#)
- [Complex1.cif](#)
- [Complex2.cif](#)
- [SupportingInformation.docx](#)