International Journal of Chemistry Studies
www.chemistryjournal.in
ISSN: 2581-348X
Received: 28-10-2023, Accepted: 14-11-2023, Published: 30-11-2023
Volume 7, Issue 2, 2023, Page No. 19-22

Synthesis, crystal-structure refinement characterization and the review of the applications of the transition metal-based supramolecular materials

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Abstract
Transition metal-based supramolecular complex was synthesized via solution-mediated mechanism under solvothermal conditions by reaction of alpha-diimine ligand with platinum (II) salt, which led to the formation of a novel Pt (II) supramolecular complex. The complex was characterized using mass-spectrophotometer for the determination of the molecular weight of the complex. The powder x-ray diffraction analysis showed that the complex is pure, isolable as a bulk phase and stable to the removal of 80% DMF from the ports. While the spectroscopic characterization revealed that the complex crystalizes in triclinic space group p(-1) with cell parameters a=4.902Å, b=5.784Å, c=13.571Å, alpha=87.00Å, beta=88.16Å, gamma=89.55Å. In the zigzag platinum (II) metal chain, the alternating platinum (II) center is link by two uncoordinated carboxylic acid spacer. Thus, between the carboxylic acid group, a novel O-H----O hydrogen bonds and pairs of N-H---Cl hydrogen bonds coordination entities has been found which function as the connectors to cross-link the two-dimensional zigzag chains.

Keywords: Supramolecular complex, coordination, solvothermal, self-assembled, ligand

Introduction

The concept of supramolecular chemistry has attracted lots of attention from chemists, biologists and material scientists due to its wide diversity of structural and functional characteristics. This involves the noncovalent interactions between the host and guest molecules (Ma and Zhao, 2015) [9], which comprises of the hydrogen-bonding interaction, π-π stacking interaction, electrostatic interaction, van der waals force, hydrophobic/hydrophilic attraction for proper elucidation of the systems (Shi *et al.,* 2020) [13]. Supramolecular materials are self-assembled (Knight *et al.,* 2018) [7] and well ordered materials synthesized via noncovalent interactions of chemical moieties such as organic, inorganic, hybrid nature building blocks for the formation of multifunctional coordination frameworks (Baumer *et al.,* 2021) [2].

However, the association of ligand with a receptor is a form of self-assembly process (Dakovic *et al.,* 2018) [3]. Hence, the formation of molecular crystals, colloids, (Vilanova *et al.,* 2016) [15], lipid bilayers, phase-separated polymers as well as self-assembled monolayers (Laker *et al.,* 2017) [8].

Nevertheless, coordination bond such as hydrogen bond had been proved to be effective for the construction of highly efficient self-assembled coordination polymers (Desiraju, 2013) [4], in the presence of transition metal ions, with high charge to mass ratio as well as the availability of d-orbitals, which exhibits numerous desirable physical and physiochemical properties such as antitumor (Pashkina *et al.,* 2021) [11], antifungal, antibacterial (fathalla *et al.,* 2023) [5] as well as antiviral (Abate *et al.,* 2022) [1] agents. In other words, the potentials of metal complexes as molecular building blocks in self-assembled complexes with regard to different properties which include biomedicine, pharmaceutical, biological, industry etc are numerous and was recognised many decades ago (Baumer *et al.,* 2021) [2].

Furthermore, microporous and mesoporous materials, otherwise known as nanoporous materials, are widely used in catalysis, separation technology as well as adsorption due the fact that one main challenges to commercialize hydrogen energy is to develop appropriate onboard hydrogen storage systems, capable of charging and discharging large quantities of hydrogen with fast enough kinetics to meet commercial requirements (Xiao *et al.,* 2009) [16]. However, metal-organic framework (MOF) is a new type of inorganic and organic hydrid nanoporous particulate materials with diverse networks which enhances hydrogen storage through tuning the structure and property of MOFs (Raptopoulou, 2021) [12]. Other uses of the self-assembled coordination complexes include the impartation of specific colour to fabric. Example is the use of phthalocyanine extensively by dyes and pigment industries.

As part of the continuing investigation on supramolecular materials otherwise known as self-assembled coordination polymer, synthesis, complexation of the organic moieties with transition metal is structurally investigated and the review of the applications.

Material and Methods

All the solvents and reagents used were of analytical grade and were used as supplied unless otherwise stated. The product was characterized by spectroscopy data (FTIR, PXDP). The IR spectra were performed using attenuated total reflection fourier transform infrared spectrophotometer using KBr Pellets (Perkin-Elmer 883) in the range 4000-400cm. (Idim, 2017) [6]. A powder x-ray diffraction pattern was recorded at ambient temperature on a Burker D8 advance diffractometer. Data were collected with the aid of flat plate sample holder.

Synthesis of the Ligand

To synthesize the ligand of the self-assembled coordination complex, a methanolic solution of co-ligand, 2, 4-pentanedione (1.0ml) was added drop wise to a stirred solution of 4-aminobenzoic acid ligand (4.1g) dissolved in methanol, followed by adding 4 drops of formic acid with constant stirring magnetically for 24h and then allowed to

stand at ambient temperature during which the brown crystals formed after 4 days were filtered and dried at ambient temperature.

The Metal Complex

The supramolecular (self-assembled) material was obtained by the microwave solvothermal synthesis (MSS) technique (Idim, 2017) [6]. The reaction precursor was prepared under constant temperature of 80ºC and stirring speed by dissolving the alpha diimine ligand and the platinum (II) salt in 1.9ml of dimethylformamide and stired magnetically for homogeneity. The mixture was then sealed in a purex glass and kept at 80ºCfor 24h. The resultant products were filtered, washed and dried at ambient temperature.

Result

Complexation of the platinum (II) ion with the alpha dii okmine ligand via solution-mediated mechanism under solvothermal condition. The isolated complex was stable in air and ambient temperature and insoluble in water but soluble in common organic solvents such as methanol and chloroform. Some information such as the empirical formular, moleculer mass, colour of the isolated complex is depicted in Table 1.

Discussion

Coordination polymer with uncoordinated donor sites which can act as ligands in metal-organic frameworks (MOFs) in which different metal centres may have different structural and/or functional roles has been investigated. This polymer was synthesized via solution-mediated mechanism under microwave condition and was fully characterized by infrared spectroscopy reported (Idim, 2017) [6]. The mass spectroscopy was used to determine the molecular mass of the complex, while the powder X-ray diffraction analysis showed that the complex is pure. The crystal structure was refined by the full-matrix least-square on F^2. However, Platinum, nitrogen, oxygen and carbon atoms were placed in the ideal calculated positions and refinded using the riding model with U(eq) trace of the orthogonalized Uij tensor. The single crystal of x-ray diffraction studies of the compounds showed that the complex crystalizes in triclinic space groups (P(-1), with cell parameters a=4.902 (Tella *et al.*, 2018), b=5.784 Å, C=13.571 Å, alpha = 87.00º, beta= 88.16º, gamma=89.55º. The complete data collection is found in Table 1.

The analytical and physical data of the complex as well as the infrared vibrational frequencies of the complex had been reported (Idim, 2017) [6].

The main structural feature in the complex is a zigzag Pt (II) metal chain, in which the alternating Pt (II) center is linked by 2-uncoordinated carboxylic acid spacers. A novel O-H---O hydrogen bonds between carboxglic acid groups and pairs of N-H---Cl hydrogen bonds coordination entities has been found which acts as the connectors (Fathalla *et al.*, 2023) [5] to cross-link the two-dimensional zigzag chains. The zigzag nature of the tapes arises from the platinum coordination plane and the amine ligand being non-coplanar with the angle between the mean/planes being 107º. These are interesting pair of chains exhibited by the complex in the solid state because in supramolecular chemistry, hydrogen bonds have been broadly applied in crystal engineering molecular recognition and catalysis (Meeuwissen and Reek, 2010) [10]. Thus, the complex forms a hydrogen bonded dimer with the parameters H(4)---O(5)1.782, O(4)-H(4)---O(5)170º. The complex showed a two-dimensional coordination polymer (Cp) comprised of the repeated two trans-located coordinated amine group and one of the nitrogen ligands link the chains into a two dimensional network.

Table 1: Crystal data and structure refinement for trans-[$PLCl_2$ ($NH_2C_0H_4CO_2H)_2$]

Empirical formula	C_{14} H_{14} Cl_2 N_2 O_4Pt
Formula weight	540.26
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P – 1 v
Colour	Light brown
Unit cell dimensions	a=4.90200(10) Å α=87.0040(10)º b=5.7840(2) Å β=88.1620(10)º c=13.5710(4) Å, y=89.553(2)º
Volume	384.050(19) $Å^3$
Z	1
Density (calculated)	2.336 Mg/m^3
Absorption coefficient	9.503 mm^{-1}
F(000)	256
Crystal size	0.18 x 0.12 x 0.03 mm^3
Theta range for data collection	3.01 to 27.42º
Index ranges 17<=1<=17	-6<=h<=6, -7<=k<=7
Reflections collected	5400
Independent reflections	1748 [R(int) = 0.0765]
Completeness to theta = 27.42º	99.0%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1748/0/107
Goodness-of-fit on F^2	1.037
Final R indices [1>2sigma(1)]	R1 = 0.0584, wR2 = 0.1539
R indices (all data)	R1 = 0.0598, wR2 = 0.1594
Largest diff. peak and hole	5.413 and -4.624 e, $Å^{-3}$

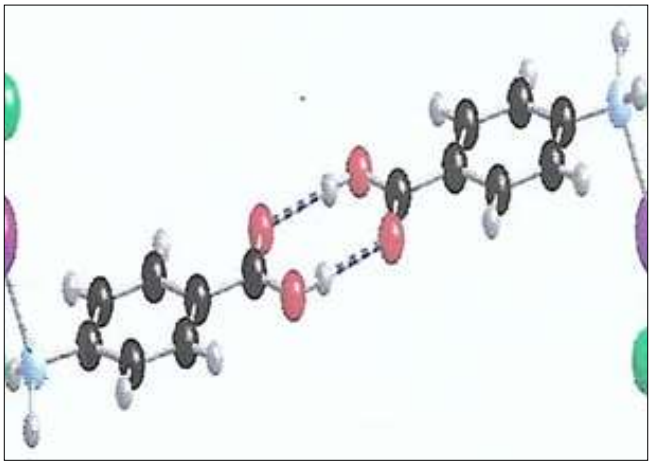

Fig 1: supramolecular structure of trans-bis (4-carboxyphenylamino) dichloroplatinum II complex

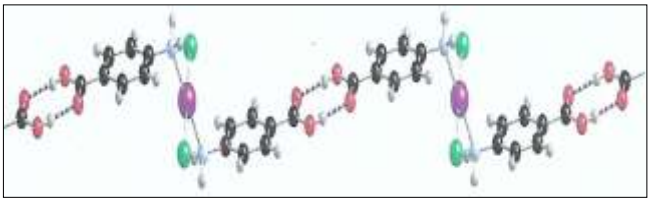

Fig 2: Zigzag hydrogen-bonded tapes in the supramolecular structure

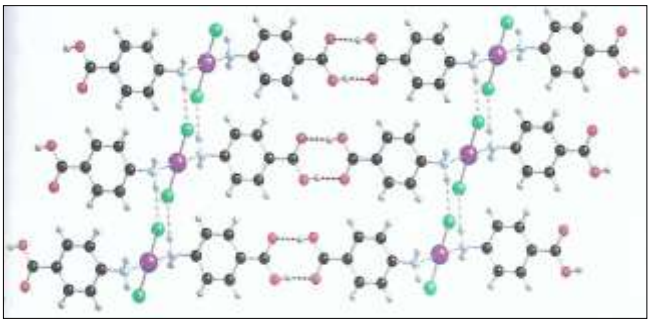

Fig 3: Connectivity of the hydrogen-bonded sheets in the syupramolecular complex

Furthermore, the powder x-ray diffraction pattern (PXRD) of the complex obtained from single-crystal diffraction indicates that the porous structure is maintained with the largest difference peak and hole of 5.413 and -4.624 eÅ^{-3} respectively which is in good agreement with that of the simulated pattern obtained from the powder x-ray diffraction. Thus, the immobilization of coordinatively unsaturated metal centres into porous frameworks is a very attractive idea because a regular arrangement of metal centres in a certain space induces regioselectivity or shape/size selectivity towards guest mdecules. Powder X-ray diffraction confirms that the solid is isolable as a bulk phase and stable to the removal of 80% DMF from the pores. This is use to investigate the structural stability because, it is an important factor in the study of the microporous functions of coordination polymers. Data were collected using a flat plate sample holder. The intensity data were collected by the continuous counting method (step 0.03^{o} and time 3.3) in the 2Ɵ range 5-50^{o}).

Conclusion

The supramolecular coordination complex formed by non-covalent interactions between two chemical moieties otherwise known as host and guest molecules have been structurally characterized. The metal-ligand stoichiometry in this complex is 1:2 associated with two uncoordinated carboxylic acid molecules. However, different metal centres exhibit numerous structural and functional roles. Thus, the carboxyphenylamino dichloro ligand acts as a bidentate coordinator. Thus, the various types of interaction signifies different degree of strength, directionality, functionality in coordination complexes. Nevertheless, in this study, the uncoordinated carboxylic acid groups can act as donor sites in metal-organic frameworks synthesis as well as hydrogen bonds which is effective for the construction of highly efficient self-assembled coordination polymer. However, the ability to tune the pore size, shape as well as high surface area and functional groups has made this material attractive for adsorption-based application and for catalysis. Therefore, this material is useful for catalysis, adsorption as well as ion-exchange studies.

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