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The transition metal-based coordination complex: Synthesis, spectroscopic characterization and the review of the applications

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Abstract

A well-ordered transition metal-based coordination complex was synthesized through wet synthetic technique called solvothermal technique. The complex was characterized based on the fourier transform infrared spectrophotometer, powder x-ray diffractometer. The light brown crystalline complex with the molecular mass of 540.26 showed different functional groups with their vibrational band characteristics including the symmetric and asymmetric stretching vibrations of the carboxylate group (COO) at the region of 1521 and 1596 cm^{-1} respectively. The symmetric vibration of C-N, C-OH, C=O, OH occurred in the regions 1309, 1284, 1659, 3229-2671cm^{-1} respectively. The presence of many hydrogen bond interactions between cationic, anionic moieties in the lattice are for structure stabilization for the optimization of the potential applications. The uncoordinated carboxylic acid groups and other functional groups incorporated into the coordination complex with divers interactions of atoms and their chelation mode, account for their stable and unique architecture that necessitate the use of coordination complexes in different field of science and technology.

Keywords: Transition metal, coordination complex, synthesis, functional group, asymmetric and symmetric vibrations

Introduction

Transition metal-based coordination complexes have attracted significant attention as a result of their numerous physical and chemical properties, including the functional groups, chelation mode, bond lengths and angles, large surface area, porosity etc. These, among others are the properties that account for their shape, size, geometries and their excellent stability needed for optimal performances in numerous processes including the electrochemical, thermal, photochemical (Baruah 2022) [1], pharmaceutical (Negrescu *et al*., 2022) [12]. Processes as well as environmental applications such as gas capturing and storage (Tiwari *et al*., 2022) [16], wastewater treatment and management (Jain *et al*., 2022) [6]. Furthermore, the porous crystalline coordination materials known as the metal organic framework materials consisting of metal ions/cluster, the secondary building units (SBUs) coordinated to the organic ligand by coordinative bonds to form one-, two- or three- dimensional structures with different functional groups have wide potential applications (Liu *et al*., 2023) [11]. However, the coordination potential of the amide functional group of the materials exhibited a higher Lithium ion (Li^+) storage performance (Wang *et al*., 2018) [17]. The N-donor ligand-base one-dimensional coordination complex which are classify based on the N-donor functional groups exhibits unique architecture due to the presence of hydrogen bond, carbonyl, hydroxyl, amino as well as carboxyl functional groups (Zhao *et al*., 2022) [19] for divers applications. Other potential properties are the diversity in metal, eco-friendly (Ren *et al*., 2022) [15] as well as energy sustainability from alternate fuel source which makes the potential applications of the coordination complexes possible, since the emission of carbondioxide (greenhouse gas) is a threat to human life, hence, use for gas capturing (Eriksson *et al*., 2021) [20] and storage (Qazvini *et al*., 2021) [13].

The application of coordination complex are also considered based on pharmaceutics (Kundu *et al*., 2023) [10]. Thus, they are potential drug delivery vehicles as a result of their substantial drug absorption capacity and slow released processes which protect and convey sensitive drug components to expected locations (Kundu *et al*., 2023) [10]. However, exploiting the presence of functional groups of coordination complexes has expand their applications in diverse fields, hence, they are also suitable for catalysis (Zhao *et al*., 2022) [19]. Functional groups changed the selectivity of a carbon-bydrogen activation reaction (Chris 2022) [12].

Studies demonstrated that the coordination complex of a homologous series, P-terphenyl-4, 4-dicarboxylic acid having hydroxyl side groups, ranging from 0 to 4 as functional groups have been synthesized (Kim *et al*., 2011) [7] for the post synthetic modifications of higher-dimensional frameworks including IRMOF-16, HCC-1 with accessible specific number of hydroxyl functional groups (Kim *et al*., 2012) [8] for activation processes (Kim *et al*., 2013) [9]. Functional groups also improved the efficiency in the removal of particulate matters from air (Yoo and Jhung 2019) [18].

Nevertheless, the use of solvothermal technique in the synthesis of coordination complex has been found to be one of the efficient techniques (Raptopoulou, 2021) [14]. Thus, as a continuation of research study on the coordination complexes, synthesis, infrared characterization is carried out on a two-dimensional transition metal-based coordination complex with a numbers of functional groups that promote the use of this material for the synthesis of higher ordered dimensional network structures. Nevertheless, the strength of the metal-coordination complex is dependent on the type of functional groups that the metal-based coordination complex possesses. (Eriksson *et al*., 2021) [20]. In order words, depending on the type of functional groups presence in the coordination sphere, the coordination capacity, as well as mode of chelation to the cation will vary (Eriksson *et al*., 2021) [20]. Thus, for material to be adaptable in diverse areas of applications, proper insight into the physical and chemical properties, through adequate understanding of its structure become necessary (Idim 2017) [5].

Materials and Methods

All chemical reagent and solvents used were of analytical grade. The infrared spectra of the ligand and metal complex were recorded on KBr pellets (Perkin-Elmer 883) in the range 4000 - 400 cm^{-1} on fourier transform infrared spectrophotometer. Powder x-ray diffraction pattern was recorded at ambient temperature on a Bruker D8 Advance diffractometer.

Synthesis of the ligand

For the synthesis of ligand, 4 drops of formic acid was added to a mixture of 2, 4-pentanedione (1.0 ml) and 4-aminobenzoic acid (4.1 g) with constant stirring magnetically for 24 h and kept at ambient temperature. The brown crystals formed were filtered and dried at ambient temperature.

Synthesis of the metal Coordination complex

The Coordination complex was synthesized via wet synthetic technique known as solvothermal technique (Idim 2017) [5]. The salt of platinum (II) ion and the alpha diamine ligand were dissolved in 1.9 ml of dimethyl formamide and stir magnetically for proper mixing. Thereafter, the mixture was placed in a pyrex glass and store at 80^{o}C for 24 h. The products formed were dried at ambient temperature after proper filtering and washing.

Result

The selected bond lengths of the coordination complex are shown in table 1, while table 2 showed the selected bond angles. Table 3 showed the various functional groups of the coordination complex. The complex was analyzed in the ratio of 1:2 stoichiometry of ML_2. The isolated solid crystalline product was non-hygroscopic, stable in air and ambient temperature and insoluble in water but soluble in common organic solvents such as methanol.

Discussion

Structure evaluation of coordination complex with respect to their bond lengths, bond angles as well as their functional groups cannot be overemphasized due to their inherent potential characteristics. However, the selected bond lengths and angles are shown in table 1 and 2 respectively. The selected spectral bands and their assignments are presented in table 3 and in figure 2. Thus, the IR spectra of the complex indicates that the ligand behaves as a tetradentate ligands because the metal coordinates through two chlorine atoms and two amine donor sites and form coordinates bonds With the central metal atom.

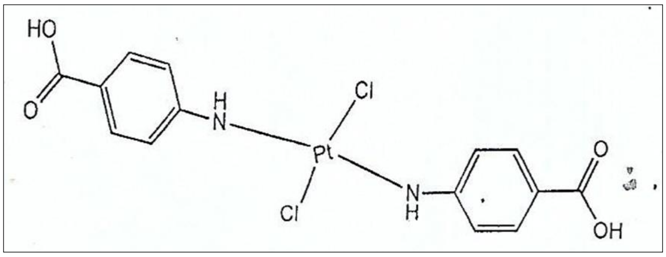

Fig 1: The structure of trans-bis (4-carboxyphenylamino) dichloroplatinum II complex

Table 1: Selected bond lengths [Å] after interaction of the metal and the ligand coordinatively.

Coordination molecules	Bond Lengths (Å)
$Pt_{(1)}-N_{(3)}\#_1$	$2.065_{(10)}$
$Pt_{(1)}-N_{(3)}$	$2.065_{(10)}$
$Pt_{(1)}-Cl_{(1)}$	$2.293_{(3)}$
$Pt_{(1)}-Cl_{(1)}\#_1$	$2.293_{(2)}$
$N_{(3)}-C_{(9)}$	$1.430_{(14)}$
$O_{(4)}-C_{(10)}$	$1.277_{(15)}$
$O_{(5)}-C_{(10)}$	$1.262_{(15)}$
$C_{(6)}-C_{(7)}$	$1.385_{(17)}$
$C(6)-C_{(12)}$	$1.395_{(17)}$
$C_{(7)}-C_{(9)}$	$1.387_{(15)}$
$C_{(8)}-C_{(11)}$	$1.384_{(16)}$
$C_{(8)}-C_{(9)}$	$1.395_{(16)}$
$C_{(10)}-C_{(12)}$	$1.489_{(15)}$

Table 2: Selected bond angles (^{o} C) of the Coordination complex

$N_{(3)}\#_1-Pt_{(1)}-Cl_{(1)}\#_1$	$87.3_{(3)}$
$N_{(3)}-Pt_{(1)}-C_{l(1)}\#_1$	$92.7_{(3)}$
$Cl_{(1)}-Pt_{(1)}-C_{l(1)}\#_1$	180.0
$C_{(9)}-N_{(3)}-Pt_{(1)}$	$115.4_{(7)}$
$C_{(7)}-C_{(6)}-C_{(12)}$	$120.4_{(11)}$
$C_{(6)}-C_{(7)}-C_{(9)}$	$119.7_{(11)}$
$C_{(11)}-C_{(8)}-C_{(9)}$	$119.5_{(10)}$
$C_{(7)}-C_{(9)}-C_{(8)}$	$120.8_{(10)}$
$C_{(7)}-C_{(9)}-N_{(3)}$	$120.7_{(10)}$
$C_{(8)}-C_{(9)}-N_{(3)}$	$118.5_{(10)}$
$O_{(5)}-C_{(10)}-O_{(4)}$	$124.4_{(10)}$
$O_{(5)}-C_{(10)}-C_{(12)}$	$118.0_{(10)}$
$O_{(4)}-C_{(10)}-C_{(12)}$	$117.6_{(10)}$
$C_{(8)}-C_{(11)}-C_{(12)}$	$120.1_{(10)}$
$C_{(6)}-C_{(12)}-C_{(11)}$	$119.4_{(10)}$
$C_{(6)}-C_{(12)}-C_{(10)}$	$121.9_{(10)}$
$C_{(11)}-C_{(12)}-C_{(10)}$	$118.7_{(10)}$

Table 3: Infrared vibrational frequencies of the ligand and the coordination complex

Ligand	complex	Band assignment
3461 $_{(M)}$	3458 $_{(M)}$	Amine bands, NH_2 (asymmetric vibration)
3364 $_{(S)}$	3361 $_{(S)}$	Amine bands, NH_2 (symmetric vibration)
3090 - 225	3229 - 2671	OH (stretch)
1686 Vs- 618 $_{(M)}$	1659 $_{(S)}$	C=O (stretch)
_	1596 $_{(S)}$	COO (asymmetric vibration)
_	1596 $_{(S)}$	COO (asymmetric vibration)
1351 $_{(S)}$	1309 $_{(S)}$	C - N (symmetric vibration)
1296 $_{(Vs)}$	1284 $_{(Vs)}$	C - OH (symmetric vibration)
1079 $_{(W)}$	1171-1023 $_{(W)}$	NH_2

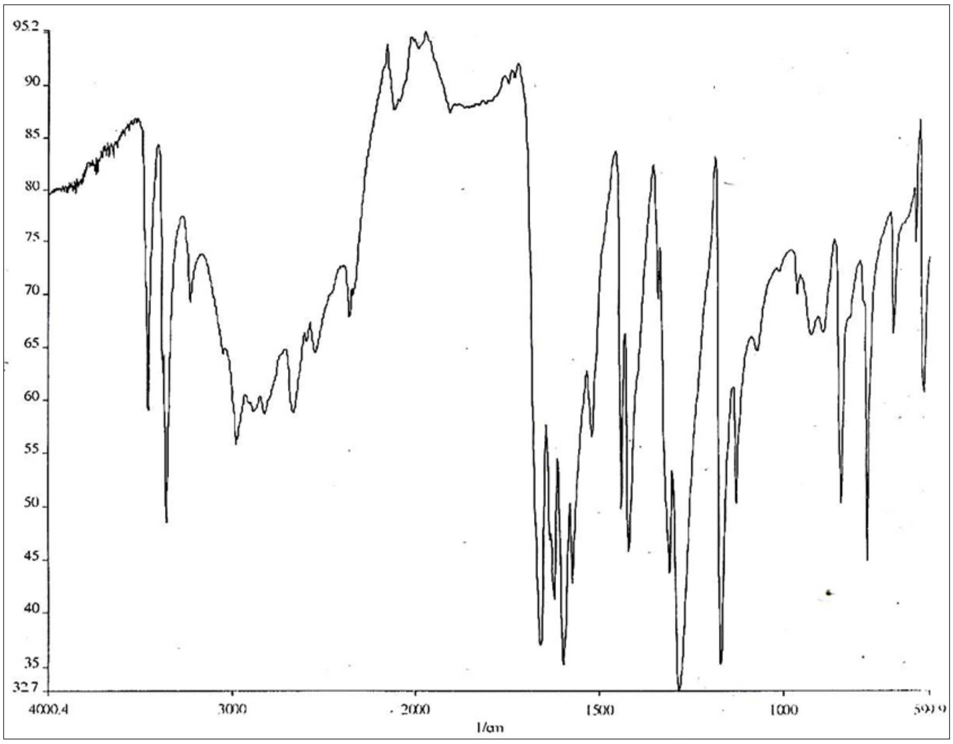

Fig 2: Infrared spectrum of the complex

The ligand as well as the complex shows strong bands at 3364 and 3361 cm^{-1} respectively due to the symmetric stretching vibrations of the amino groups. The presence of strong band in the region 1351 and 1309 cm^{-1} in the spectra of the ligand and the complex assigned to C-N group symmetric vibrations. Very strong band at the region 1296 and 1284 are due to the presence of C-OH group symmetric vibration modes of both the ligand and the coordination complex respectively. The coordination complex walso shows strong new bands at the region 1596 and 1521 associated with the asymmetric and symmetric vibrations of COO groups respectively which were not observed in the ligand. The band at the region 3090 and 3229 were assigned to the stretching vibrations of OH group of the ligand and the complex respectively, in which that of the complex was shifted to lower region 2671 cm^{-1}. IR spectrum of the ligand has shows broad band at 1079, while that of the complex shows at 1171 cm^{-1} which were assigned to NH_2 groups. However, bonding of the ligand to the metal ions under investigation occur via coordinate covalent interaction with Nitrogen of the carboxyphenyl groups. The bond angles [^{o}C] around the metal ion and donors are at the range 87.3(3)-179.99(1)^{o}. The selected bond lengths around the metal atom (M) and the Nitrogen was 2.065Å, while that of the carbon-carbon are in the range 1.384-1.409Å. The oxygen - carbon bond length ranges between 1.262 - 1.277Å

Conclusion

A novel transition metal-based coordination complex synthesized via the reaction precursors, 2, 4-pentanedione and 4-aminobenzoic acid shows good complexing structure as a result of incorporating the different functional groups into the coordination sphere. Hence, enhances their potential applications in different field of science and technology. However, in this study, a novel coordination complex with different functional groups such as the carbonyl, amine, carboxylic acid groups with uncoordinated donor sites which can act as a chelating agent in the synthesis of higher dimensioned coordination networks has been synthesized. Thus, the ability to incorporate diverse functional groups, tuning of the pore size and shape has necessitate the use of coordination complexes for gas capturing, storage as well as catalysts. Thus, this material can be utilized in studying their potentials regarding the catalysis, wastewater treatment as well as gas adsorption.

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