Zn(II) complex for highly sensitive and selective detection of acetone at room temperature

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NMR: Nuclear magnetic resonance, TGA: Thermogravimetric analysis, FTIR: Fourier transform infrared, , LMCT: Ligand to metal charge transfer



Abstract

A Zn(II) perchlorate complex has been prepared and characterized by single X-ray crystallography, nuclear magnetic resonance spectroscopy, thermogravimetric analysis, infrared spectroscopy, elemental analysis, and UV-vis spectroscopy. The complex crystallizes in the monoclinic space group P21/c (Z = 4) with a pentacoordinated zinc center. Interestingly, the Zn complex was found be to a potential fluorophore that could sense acetone and other ketones with high selectivity and sensitivity.

Keywords: X-ray crystallography; H-bonding; Acetone; Fluorescence Sensing; DFT

1. Introduction

Acetone is a toxic reagents found extensively in nature and its poisoning can occur through various external mode such as inhalation, ingestion or direct body contact to living creatures because of its easy volatilization and toxicity. It is mostly harmful to the central nervous system's overall health. Similarly, the harmful chemical affects both cardiovascular and digestive health. Acetone is also highly toxic to the respiratory tract and the urinary system¹. Acetone is predicted to stay mainly in the environmental compartment to which it is released. This is true when acetone is released to water (greater than 99% is predicted to remain in water). Therefore it is of paramount importance to design a novel sensor to detect acetone at a ppm level which is of extremely beneficial not only for environment safety but also for the safety of human beings². Supramolecular interactions play a crucial role in the structure and function of many molecules. Owing to the important applications of coordination complexes, such molecules comprising supramolecular interactions have become a broad area of study ^{3,4} as it is easy to synthesize, simple process, low cast materials and easy availability and it can be used as sensors for practical applications. The coordination behavior and chemical properties of bipyridyl ligands have been widely studied owing to the electron donating capability of its N atoms, which makes it a versatile ligand. Moreover, the electron donation and coordination through N atom simulate the environment in biological systems 5-7. There are also several bipyridine compounds with interesting photophysical properties and wide applications^{8–10}. Luminescent coordination complexes display significant potential for fluorescence sensing because of their short response time, high sensitivity, ease of detection, and cost-effectiveness. These compounds can be used to detect small molecules, especially volatile organic solvent molecules and explosive materials such as trinitrotoluene and dinitrotoluene 11-18. Therefore, it is of paramount importance to shed light on the nature and dynamics of this important class of bipyridyl ligands and its substituents. Late transition metal ions (e.g., d^{10} systems) coordinated to entities capable of supramolecular interactions, such as N- or O-based ligands, can fluoresce remarkably ^{16–20}. Zn(II)-2,2'-bipyridyl (bpy) has been studied for the last few decades and has been one of the complex and exciting systems because of their crucial properties both in the solid state ^{21,22} and in solution ^{23,24}.

Most importantly, it has a π conjugated system that can be utilized for photoluminescence. It is well-known that Zn²⁺, Cd²⁺, and Ln³⁺ are usually adopted as luminescent cations, and we shall exploit these in our future work. An additional advantage of using Zn(II) d¹⁰ system in fluorescence sensing is their selectivity toward certain solvents such as acetone ¹⁷. The detection of different solvents has received great attention because of the increasing solvent toxicity and wastewater, which are relevant for environmental and industrial monitoring, human health, food safety, etc. Sun et al. have elegantly described the selective behavior of d¹⁰ systems and π conjugated ligands in their articles [14-16,19]. However, this also raises the question of whether such systems can sense different solvents or environmentally harmful explosive materials in the presence of different ligands/framework.

Considering these, we have synthesized [Zn(bipy)₂(H₂O)](ClO₄)₂ and characterized it by single Xray crystallography, NMR spectroscopy, TGA, IR spectroscopy, elemental analysis, UV-vis spectroscopy, and fluorescence spectroscopy. The results predict that the synthesized complex can be used as an acetone sensor without the requirement of any additional processes such as preactivation, heating, or pH variation. The results could be relevant not only to the Zn(II) d¹⁰ system but also to related systems involving bpy-like ligands, e.g., pyridyl–imidazole derivatives, imidazolinones, etc.

2. Material and methods

2.1 Materials

All reagents were of the highest commercial grade and were used without further purification.

2.2 Methods and instrumentation

Microanalysis (CHN) was carried out with a Carlo Erba Analyzer Model 1108. Molar conductance was measured at room temperature on a Digsun electronic conductivity bridge. FTIR spectrometer (Interspec 2020) was used for recording the IR spectra of samples in KBr pellets in the range 4000–400 cm⁻¹. Electronic spectra were recorded on UV-1700 PharmaSpec UV-vis spectrophotometer (Shimadzu). Emission spectra were recorded on a Shimadzu RF-6000 fluorescence spectrophotometer. TGA/DSC was performed on Universal V3.8 B TA SDT Q600 Build 51 thermal analyzer under a nitrogen atmosphere using alumina powder as the reference material. ¹H and ¹³C NMR spectra were recorded at 25 °C on JEOL 400 NMR spectrometer.

2.3 Crystal structure determination

Detailed crystal structure measurement, has been given in full in Supplementary material.

2.4 Synthesis

The complex ([Zn(bipy)₂(H₂O)](ClO₄)₂) was obtained by dissolving 2 mmol 2,2'-bpy (0.312 g) and 1 mmol ZnClO₄·6H₂O (0.372 g) in 30 mL ethanol. The solution was stirred at room temperature. A colorless precipitate appeared after ca. 6 h, which was re-dissolved in water/acetonitrile (20:80) mixture and kept for crystal growth. After seven days, colorless, needle-shaped crystals were obtained, which were washed with hexane and stored for further analysis. Yield, 60%; m.p., 265 °C. Anal. Calc. for C₂₀H₁₈Cl₂N₄O₉Zn (%) C, 40.39; H, 3.05; N, 9.42, Found: C, 41.48; H, 2.99; N, 9.35. Conductivity (1 x 10⁻³ M, DMSO): 210.0 Ω^{-1} cm² mol⁻¹ (1:2 electrolyte).

IR (KBr, cm⁻¹): 3481 (OH, H₂O); 3101 (CH, aromatic); 1442 (CH, aromatic); 1601, 1576, 1493 (bipyridyl N); 1100 (ClO₄); 413 (Zn-O); 415 (Zn-N). UV–vis (DMSO, nm): 209, 295.

3. Results and Discussion

3.1 Synthesis and characterization

The product ([Zn(bipy)₂(H₂O)](ClO₄)₂) was characterized using single X-ray crystallography, NMR, TGA, IR, elemental analysis, and UV-vis spectroscopy. Elemental analyses were in good agreement with the product composition (Scheme S1). Other data were also in good agreement with the colorless product obtained. The complex is stable toward air and moisture.

3.2. X-ray structure of [Zn(bipy)₂(H₂O)](ClO₄)₂

The ORTEP structure of the Zn complex is shown in Supplementary material, Fig. S1. This complex crystallizes in the monoclinic space group P21/n (Z = 4) with a pentacoordinated zinc center. The crucial parameters of the Zn complex are listed in Supplementary material, Table S1.

The Zn complex adopts a square pyramidal geometry by coordinating through the N atoms of the two bipyridyl molecules and O atom of one water molecule. Two uncoordinated perchlorate anions present in the lattice complete the charge balance and are extensively involved in hydrogen bonding. The unit cell of $[Zn(bipy)_2(H_2O)](ClO_4)_2$ (Fig. 1) shows the coordination of the four Zn(II) ions with the uncoordinated perchlorate anions.



Fig. 1. Unit cell of [Zn(bipy)₂(H₂O)](ClO₄)₂

Fig. 2 shows the space-fill model of $[Zn(bipy)_2(H_2O)](ClO_4)_2$. The Zn–N bond distances are in the range 2.061 (3)–2.104 (3) Å, while the Zn–O bond distance is 2.028 Å (Supplementary material, Table S2). All the bond angles are in the range 79.03 (13)–178.83(13) (°).



Fig. 2. Space-fill model of [Zn(bipy)2(H2O)](ClO4)2

All the bond lengths and bond angles of the synthesized complex are almost the same as that of similar coordination complexes 25 . The complex exhibits hydrogen bonding between the bonded water molecule and non-bonded perchlorate anions. The oxygen atoms (O2, O3, O4) of one of the perchlorate anions are involved in C–H……O intermolecular interactions with the H atoms of the bonded bipyridyl molecule in the range 2.525(13)–2.966(27) Å. O atoms (O7, O8, O9) of another

perchlorate anion are involved in C–H······O intermolecular interactions with the H atoms of the coordinated bipyridyl molecule in the range 2.477(11)–3.004(28) Å.

3.3 NMR spectral studies

The chemical shifts were identified by their intensity and multiplicity patterns. The total number of protons as calculated from the integration curves are in agreement with the expected molecular composition of the compound. The complexation between the metal cation and the complex would decrease the electron density at the N atoms, hence weakening the shielding effect on the neighboring protons and causing a downfield shift of the signal. The ¹H NMR spectrum of the Zn complex displays several interesting features in comparison to the free bipyridyl ligand (Supplementary material, Fig. S2). Signals in the ¹H NMR spectrum due to aromatic protons appeared in the range 7.8–8.7 ppm, while those due to coordinated water molecules appeared at 3.42 ppm. Signals at around 1.0 ppm were attributed to trace amount of ethanol. In the ¹³C NMR spectrum, signals from aromatic carbon appeared at 123–149 ppm (Supplementary material, Fig. S3).

3.4 Thermal studies

Thermogravimetric analysis of the Zn(II) complex was carried out from 25 to 800 °C to study its pyrolysis pattern. The thermogram of the complex (Supplementary material, Fig. S4) suggests that weight loss occurs in three steps over the temperature range 75–160, 210–350, 320-360, 365-600 and 610–800 °C. These were in close agreement with the proposed structure. The weight loss in the temperature range 75–160 °C confirmed the removal of traces of ethanol while that in the range 210-350 °C corresponded to the removal of coordinated water molecules ^{26,27}. This conclusion was based on the fact that the water molecules are extensively hydrogen bonded with the neighboring

perchlorate anions, and hence, required more heat compared with the lattice water molecule. The weight loss in the range 320–360 °C corresponded to the removal of both the perchlorate anion. At 365–600 °C, the compound exhibited ~41% weight loss, corresponding to the decomposition of the bipyridyl group. Finally, the plateau from 710 to 850 °C corresponded to the formation of zinc oxide as the final product.

3.5 IR spectroscopy of $[Zn(bipy)_2(H_2O)](ClO_4)_2$

The infrared spectrum of [Zn(bipy)₂(H₂O)](ClO₄)₂ (Supplementary material, Fig. S5) shows a band of the relatively weak peak at 3101 cm⁻¹ owing to aromatic CH stretching and a sharp, intense peak at 1442 cm⁻¹ owing to aromatic CH bending. Absorption bands at 1601, 1576, and 1493 cm⁻¹ are consistent with the coordination of N atom to the metal ²⁸. The corresponding peaks were observed at slightly lower frequencies in the free bipyridyl ligand. Besides, a strong OH band at 3481 cm⁻¹ was also observed for the Zn complex owing to the presence of coordinated water molecules ²⁹. The crystal structure of the complex suggests that there are no interactions between the metal center and the anions, although there is a weak hydrogen bond between one of the perchlorate oxygen atoms and the aqua-group of the cation. The T2 mode near 1100 cm⁻¹ appears as an intense band, characteristic of perchlorate anions. The several smaller bands observed between 600 and 700 cm⁻¹ are indicative of significant interactions between the perchlorate group and the cation. The splitting observed in this region may arise because of various factors, and the region is generally less informative than the lower energy region. This conclusion is borne out by the results obtained for the coordinated perchlorates.

The medium intensity bands in the region 413–415 cm⁻¹ corresponded to (Zn-O) and (Zn-N) 30 , thus providing additional evidence for the formation of the complex.

3.6. Electronic spectra of [Zn(bipy)₂(H₂O)](ClO₄)₂

The UV spectrum of the complex exhibited bands at 209 nm, which corresponded to the π - π * transitions due to the long-lived triplet excited state of the aromatic moiety. This band undergoes hypsochromic shift concerning the free bipyridyl ligands. Also, LMCT transitions for the complex was observed at around 295 nm (Supplementary material. Fig. S6). No d–d electronic transitions were observed owing to the completely filled d-orbital ³¹.

3.7 Fluorescence Sensing Property

It is reported that the d¹⁰-based ions possessing a closed-shell electronic configuration with π conjugated skeleton ligands have a trivial effect on the luminescence intensity, while other metal ions with different electronic configurations quench the luminescence, especially in solvents such as acetone ^{16–20}. To explore the potential applications of our synthesized Zn-based coordination complex in probing small organic molecules, we examined the effect of organic solvents on the fluorescence of the Zn complex.

The fluorescence of the Zn complex $(1.0 \times 10^{-5} \text{ M})$ was studied in DMSO at room temperature. The complex exhibited remarkable fluorescence, and intense emission bands were observed at λ_{em} = 330 nm (λ_{ex} = 295 nm). It has been reported that the formation of certain architectures can increase the rigidity of the aromatic backbone of the ligands and enhance the intra/intermolecular interactions among them, thus favoring energy transfer ^{18,20}. The formation of metal complexes with π -conjugated organic ligands enhances the fluorescence intensity compared with the free ligands, because the latter restricts the deformation of the ligand and induces nonradiative relaxation ³². The fluorescence sensing experiment with the synthesized Zn complex was performed in the presence of different organic solvents such as methanol, ethanol, isopropanol, isobutanol, chloroform, dichloromethane, carbon tetrachloride, benzene, toluene, ethylbenzene, acetonitrile, and acetone.



Fig. 3. Fluorescence spectra of $[Zn(bipy)_2(H_2O)](ClO_4)_2$ dissolved in DMSO (blank) and upon the addition of different organic solvents.

Fig. 3 shows that only the addition of acetone quenched the fluorescence up to 98% (decrease in emission intensity). The addition of other solvents did not exhibit any remarkable quenching.

These results indicate that the Zn complex can significantly and selectively sense acetone. Furthermore, it was found that the quenching of the fluorescence of the Zn complex upon the addition of acetone was not affected by the presence of other organic solvents (Fig. 4). It clearly confirms that the Zn complex can effectively sense acetone even if the sample is contaminated with other solvents. Besides, we did not preactivate our system by heating, pH maintenance, or any other external factor, which is in contrast to lanthanides and few other coordination complexes that require preactivation ^{33–35}.

For a detailed examination of the sensitivity of the Zn complex for sensing acetone, the quenching efficiencies of the Zn complex in DMSO with increasing amounts of acetone was investigated. Supplementary material. Fig. S7 shows that the fluorescence quenching efficiency increased sharply at low concentrations of



Fig. 4. Quenching efficiency of $[Zn(bipy)_2(H_2O)](ClO_4)_2$ upon the addition of different organic solvents except for acetone (blue) and subsequent addition of acetone (orange).

acetone. The quenching was nearly proportional to the acetone concentration, and complete quenching was observed upon the addition of 50 μ L (1.7 vol%) of acetone. This demonstrates that the Zn complex can selectively sense even minimal amounts of acetone. Thus, [Zn(bipy)₂(H₂O)](ClO₄)₂ is a potential candidate for the selective sensing of acetone.

In order to explore whether the interaction between the C=O bond of acetone and the frameworks of the Zn complex caused the fluorescence quenching of the complex, the fluorescence in various ketones was examined. Fig. 5 shows that ketones such as cyclohexanone, 4-heptanone, and 5-

nonanone exhibited the highest quenching. This suggests that the fluorescence quenching may be caused by the interaction between the C=O bond of ketone and the frameworks of Zn complex.



Fig. 5. Fluorescence intensity of $[Zn(bipy)_2(H_2O)](ClO_4)_2$ in various ketones upon excitation at 295 nm.

The observed fluorescence quenching effect may be attributed to the interactions between the Zn(II) ion framework and acetone since zinc(II) is oxophilic in nature and it might be possible that acetone may bond with Zn(II) complex through supramolecular interaction. Upon excitation, an energy transfer from the ligands to the acetone molecules occurred and resulted in fluorescence quenching. It would be very interesting to prove further regarding our theory if we get X-ray crystal structure from acetone rich solution that would show whether the ketone coordinates to Zn(II) but despite our several effort we could not get crystal of the same.

DFT Studies

To get deeper insight into the mechanism of the fluorescence-quenching behaviors of Zn(II) complex with acetone, a series of DFT calculations were carried out. Firstly, we have screen the energies of frontier molecular orbitals of all the solvents and Zn(II) complex (Fig 6).



Fig. 6. Frontier molecular orbital of various molecules used in sensing studies.

From the analysis of the HOMO and LUMO energies of solvents, it is found that the HOMO energy of acetone, benzene, toluene and ethyl benzene is greater than the HOMO energy of Zn(II) complex alone. On addition of these solvents to the Zn(II) complex may restrict the π - π * intramolecular charge transfer (responsible for the fluorescence), occurring from one bipyridyl moiety to another as the HOMO and LUMO are mainly located on both of the bipyridyl moiety of

Zn(II) complex after the formation of either ground state or excited state CT-adduct. But our observed experimental results suggested that only acetone molecule restricted intermolecular charge transfer of Zn(II) complex because quenching is observed only in the case of acetone. Surprisingly, HOMO energy of benzene, toluene and ethyl benzene is greater than acetone yet, fluorescence quenching is observed only in the presence of acetone (if HOMO energy is the only factor).



Fig. 7. Frontier molecular orbital of the aggregate of Zn(II)-complex with the various used solvents.

To find out the reason, we have optimized Zn(II) complex with each solvents used for sensing and analyzes their geometric parameters and frontier molecular orbitals (FMO) distribution (Fig. 7). The FMO analysis of adducts of Zn(II) complex with solvents suggested that HOMO and LUMO separately located on only acetone and one bipyridyl moiety of Zn(II) complex, respectively, while in all other cases mix distribution of FMOs were observed (Fig. 7, 8). Hence, in all other cases especially benzene, toluene and ethyl benzene which forms adducts of Zn(II) complex, the intermolecular π - π * charge transfer is still not affected after adduct formation.



Fig. 8. Comparative Frontier molecular orbital diagram.

Furthermore, we have also carried out the electron localization function (ELF) analysis to explore the nature of noncovalent forces which stabilizes the acetone-Zn(II) complex adduct. The ELF analysis suggested that the acetone-Zn(II) complex stabilize through the lone-pair $\cdots \pi$ interaction between the lone-pair of carbonyl group and π cloud of bipyridyl moiety of Zn(II) complex (Fig. 9) while in all other cases, distances and geometric orientation of other solvents and Zn(II) complex are not compatible to form any kind of non-covalent interactions (Supplementary material. Fig. S8).

In short, observed selective fluorescence quenching effect in presence of acetone attributed to the lone-pair $\cdots \pi$ interactions between the bipyridyl moiety of Zn(II) complex framework and carbonyl



Fig. 9. Electron localization function (ELF) map of the aggregate of Zn(II)-complex with different solvents.

group of acetone which form a stable acetone-Zn(II) adduct.

Upon excitation, electron transfer from the acetone molecule to the bipyridyl moiety of Zn (II) complex occurred due to which intermolecular π - π * charge transfer between bipyridyl moieties are broken and fluorescence quenching occurs (Fig. 10).





Fig. 10. Schematic representation of the mechanism of the fluorescence quenching.

In brief, acetone molecule distinctly reduce energy transfer to complex **1**, to produce remarkably luminescent quenching which is absent in rest of the molecules. In addition, the weak intermolecular hydrogen-bonding interactions thanks to the presence of various hydrogen bonding donors and acceptors also may exist between bipyridyl moieties which was broken resulting quenching.

4. Conclusions

A Zn perchlorate complex of 2,2'-bipyridyl, [Zn(bipy)₂(H₂O)](ClO₄)₂, has been prepared and characterized by single X-ray crystallography, NMR, TGA, IR, elemental analysis, and UV-vis spectroscopy. The complex crystallizes in the monoclinic space group P21/c (Z = 4) with a pentacoordinated zinc center. Due to the presence of intermolecular interactions in the complex, as observed in the packing diagrams, these complexes can participate in fluorescence sensing. The high quenching efficiency and excellent selectivity of the complex for acetone and other ketones make it a potential functional material for the detection of ketones, which was further proved by DFT analysis. This study provides new physical insights into the rational designing of coordination complexes-based functional materials. Future work in this direction will be crucial to elucidate the detailed roles of d¹⁰-based complexes in sensing.

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Conflicts of interest

There are no conflicts to declare

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