Self-Assembled Synthesis and Characterization of Novel [Co(1-vinylimidazole)$_6$].NO$_3$ Polymer: Highly Efficient Antimicrobial Agent

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Summary: Cobalt coordination polymer *i.e.* [Co(1-VI)$_6$]·NO$_3$ was successfully synthesized with cobalt metal and (VI = vinylimidazole) and characterized by elemental analysis, FTIR, UV/Vis spectroscopy and X-ray crystallography. The structure of the compound was determined by single X-ray crystallography at temperature 296 K with a Bruker APEX II CCD diffractometer using Mo-Kα radiations (λ = 0.71073 Å), R = 0.0642 and 0.0989. Orthorhombic unit cell parameters are a = 16.1341 (6) Å, b = 16.5179(16) Å, c = 18.2664(16) Å, V= 4868.0 (8) Å, Dx = 4, Mr = 937.91. The X-ray crystallography studies showed that the compound is polymeric in nature, in which cobalt atom coordinated with six N atoms of the 1-vinylimidazole ligands in a distorted orthorhombic geometry. As-prepared compound was screened in vitro against a variety of microorganisms, such as Gram-positive (G +ve) *Staphylococcusaureus* (*S. aureus*) and Gram-negative (G -ve) *Escherichia coli* (*E. coli*) bacterial strains, and fungal species with *Aspergillus niger* (*A. niger*) and *Rhizopus stolonifer*(*R.stolonifer*)by applying disk diffusion method. MIC (minimum inhibitory concentration) value for prepared [Co(1-VI)$_6$]·NO$_3$ compound is 125 µg.mL^{-1}a this MIC value cobalt polymer showed higher activity against *E. coli* and *S. aureus* () as compared to fungi including; *R. Stolonifer*and*A. Niger* at 125 µg.mL^{-1}).This study helps to reduce the risk of infectious diseases caused by various microorganisms.

Keywords: Cobalt; Vinylimidazole; Coordination polymer; Antimicrobial activity; Structural activity relationship.

Introduction

With so much focus on technologies like microelectronics, catalysis, magnetism and separations. The preparation and topologies of novel compounds with useful features continues to be a significant priority. [1]. As a result, coordination polymers, which have one-, two-, or three-dimensional structures are made up of a metal-ligand framework linked by hydrogen bonds, keep attracting a lot of interest. [2]. While different compounds with unique characteristics and unusual structures have been discovered, predicting structure based on simply information of the metal and ligands used is not difficult but still difficult. As a result, focusing on the characteristics that give direction to forecast the structures of coordination polymers will be an interesting goal. Cobalt metal is one of the world's most abundant elements, occurring in a different medium such as rocks, surface water, soil, air, water, plants, and animals. Cobalt is essential for all living things since it is a component of vitamin B12, which is the human body's only supplier of cobalt. 1-2 Cobalamin (vitamin B12) is a nonpolymeric biomolecules that is one of the largest and most structurally complicated yet discovered. Although studies have discussed this finding, it is widely assumed that plant species do not synthesis or use cobalamin. Cobalamin is primarily produced by bacteria [3]. Cobalamin is required for DNA synthesis, nervous system support, red blood cell creation, and infant growth and development. Corrin was employed to retain the cobalt in the cobalamin-based proteins. Another non-corrin cobalt enzyme, nitrile hydratase, is found in bacteria and has the ability to metabolize nitriles. There is evidence to support cobalt's importance in immunological mechanisms [4]. Co^{+2} has been widely studied in various applications including electrochemical, electro-catalysis, magnetism and photocatalytic materials due to its unique chemical and physical properties. Many parameters, such as reactant ratios, organic ligands, and reaction temperature, can influence the resultant topologies of the desired cobalt (II), however organic ligands governs more features in polymer of cobalt (II) [5]. Tetracoordinate square-planar ($3d^24p^2$) cobalt complexes have a reasonably strong orbital contribution (eff= 2.2-2.9 B.M.) octahedral ($3d^24p^4$) cobalt complexes have 1.7-1.9 B.M magnetic moment [6]. Imidazole complexes have a variety of topologies and are widely used in material, bioactivity, and catalysis. [7]. Imidazole and its derivatives acting as a

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ligands for transition metal ions, forming a variety of polymers. Pyridine nitrogen of the imidazole was used for the coordination with central metal atom in all known imidazole complexes rather than the pyrrole nitrogen. Hexa-coordinated nitrate and perchlorate complexes of cobalt (II) are pink or chocolate red in color, whereas tetra-coordinated complexes are always purple or violet in color. [8]. Polar imidazole ring has two nitrogens separated by methylene, with the imino nitrogen acting as an acceptor and the amino hydrogen acting as a donor [9]. Because of its capacity to make hydrogen bonds with medicine, proteins, and also used as a bio-agent. As oxygen transport membranes, polyimidazoles are utilized. [10]. Furthermore, altering the functional groups in imidazole ring it creates chemical and physical changes in polymers. Biocompatibile imidazole rings are used in biomimetic applications [9, 11].

The aim of present study is, to prepared polymer of cobalt metal and 1-vinylimidazole ligand *i.e.* $[Co(1\text{-}VI)_6]\cdot NO_3$. The X-ray crystallography studies clearly show that the compound is polymeric in nature, in which cobalt atom coordinated with six N atoms of the 1-vinylimidazole ligands in a distorted orthorhombic geometry. Furthermore, antimicrobial activity of as-prepared compound was studied.

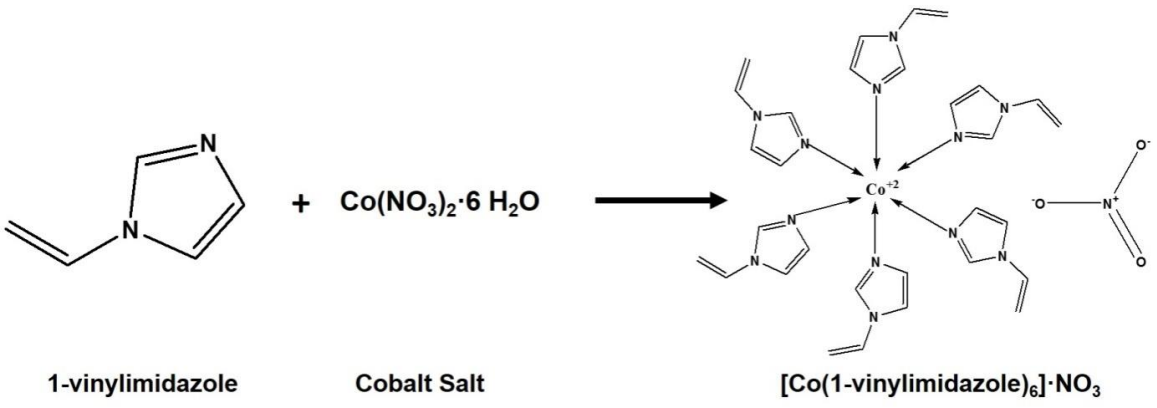
Experimental

Materials and methods

The reagents and material used is of analytical grade. Cobalt nitrate hexahydrate, 1-vinylimidazole E. Merck, Darmstadt (Germany). Methanol (Sigma-Aldrich). A Nicolet 5700 FT-IR was used to measure the infrared spectra (4000–500 cm^{-1}). The electronic spectra of the complex and ligand (200-800 nm) were examined using a UV/Vis spectrophotometer LIBRA S-22. The melting point was calculated without correction using a Yanaco melting point equipment. The Elemental Thermo-scientific analyzer was used to perform the CHNS analysis. Structural Relationship Analysis Study gives information about electron-donating and withdrawing group effect on the aromatic ring. Single Crystal X-ray Diffraction (SXRD) APEX II CCD Bruker diffractometer radiation of Mo*Kα* was used [10].The topology refined with Least-squares matrix using SHELX-97, the direct method was not used to solve the structure. Hydrogen atoms inferred from neighbouring sites. Bruker program was used to resolve the peak intensities and Bragg's angle.

Synthesis of $[Co(1\text{-}VI)_6]\cdot NO_3$

$[Co(1\text{-}VI)_6]\cdot NO_3$ polymer was formed in methanol from $Co(NO_3)_2.6H_2O$ and imidazole in a two-neckedround bottom flask. When the solution is mixed, it turns red; then mixture placed three to four days at normal temperature, red colour crystals formed. Recrystallization of the solid yielded red crystals of the chemical appropriate for single X-ray crystal structure study. (Scheme- 1). The obtained crystals are stable. Yield= 75%; Colour:Red; Anal. calcd. for $C_{40}H_{50}CoN_{18}O_6$: C, 51.22; H, 5.33; N, 26.89, O,10.24%. Found: C, 49.02; H, 4.93; N, 25.18%. UV/Vis (CH_3OH, λ_{max}, nm, (ε)): 200-250 (π-π*); FT-IR (KBr, ν, cm^{-1}): 1000-1100 (C-H bending vibration), 1200-1600 (C=C) (C=N), (bending of vinyl imidazole), 3200 (C-H) (medium sharp peak of vinyl stretching).



Scheme-1: ThePlausible mechanism for Co (1-vinylimidazole)$_6$].NO_3.

Assessment of antimicrobial activity

The antimicrobial activity of novel synthesized $[Co(1\text{-}VI)_6]\cdot NO_3$ compound was tested against four microbial strains; 2 bacteria (*i.e.S. aureus* and *E. coli*) and 2 fungi (*i.e.R. stolonifer*and *A. niger*) using the disc diffusion method [12]. Although assist of the ATCC (American Type Culture Collection), and antimicrobial activity of all four microbes. Muller Hinton Agar (MHA) and Sabour Dextrose Agar (SDA) were used for the growth of bacteria and fungi species respectively [13]. Concentrations of 1000, 500, 250, and 125 $\mu g.mL^{-1}$ were primed in 100% dimethylsufoxide (DMSO) to confirm the antibacterial and antifungal activity of prepared $[Co(1\text{-}VI)_6]\cdot NO_3$ compound, whilst DMSO was taken as the negative control [14]. The microbial (i.e., bacterial and fungal) suspensions were regulated to 10^6 $CFU.mL^{-1}$ and stretch on different solid Petri plates with diverse sterile swabs dampened with the bacterial and fungal suspension. Afterward, a immersed What man No. 1 (6 mm) filter paper by means of 12 µL of $[Co(1\text{-}VI)_6]\cdot NO_3$ compound (dilute with DMSO) was located on the top of the microbial Petri plates. After that bacterial and fungal plates were placed separately into two different temperature varied incubators at 30 °C and 38°C for 24 hours respectively. After completion of incubation duration, the antibacterial and antifungal activity of $[Co(1\text{-}VI)_6]\cdot NO_3$ compound was recorded next to each microbes by calculate the diameter of inhibition in millimeter (mm) throughout the discs and planned values of MIC [15]. These assays were carried out in thrice and results are articulated as mean ± SD (standard deviation).

Results and Discussions

Crystal structure

The ORTEP plot of $[Co(1\text{-}VI)_6]\cdot NO_3$ is shown in Fig. 1 octahedral distortion was confirmed. Dimeric interaction *via* H (18)·H(4) and H(24)·N(8) was found in Fig. 2. Several non-bonding interactions have also revealed one-dimensional chain structure indicating that the vinylimidazole rings form a supramolecular assembly. The bond length of $[Co(1\text{-}VI)_6]\cdot NO_3$Co1—N5 2.160, Co1—N1 2.162, Co1—N3 2.181 is different when compared with the literature Co1—N5 2.136, Co1—N1 2.192, Co1—N3 2.207.13 We have found that in both the compounds equatorial bond is longer than the axial. Crystal data of the structure refinement was given in Table-1.

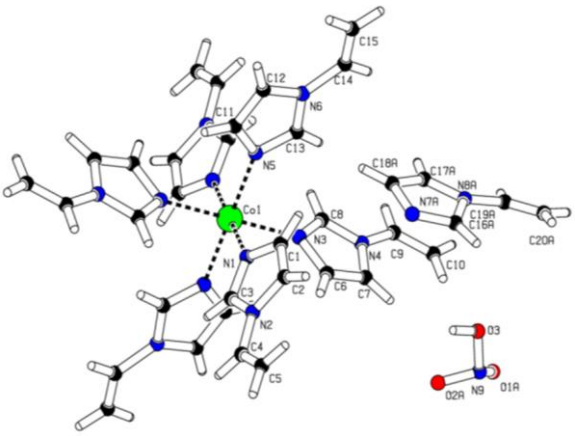


Fig. 1: The molecular structure of $[Co(1\text{-}VI)_6]\cdot NO_3$, anisotropic displacement of ORTEP is drawn at the 50% probability level.

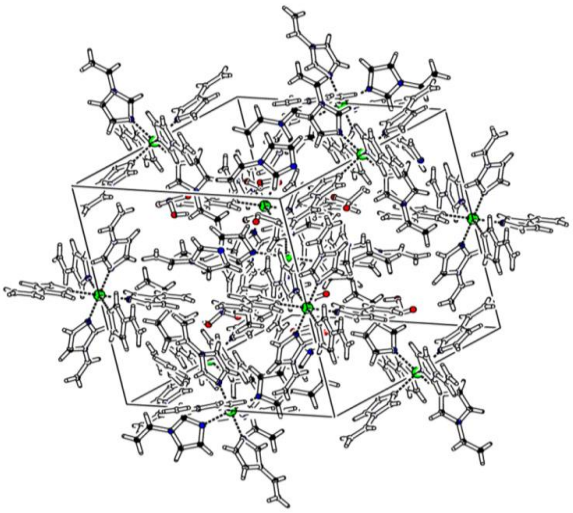


Fig. 2: The molecular packing diagram of $[Co(1\text{-}VI)_6]\cdot NO_3$. Supramolecular one dimensional pattern of compound 1 through multiple C–H·π interactions.

Characterizations

The self-assembled approach was used to make $[Co(1\text{-}VI)_6]\cdot NO_3$ The production of the polymer $[Co(1\text{-}VI)_6]$. NO_3 was confirmed by FT-IR. C-H bending observed at 1000 cm^{-1} in the FT-IR spectra (Fig. 3), and other medium peaks emerged below this range. Between 1200 and 1600 cm^{-1}, C-N bending was observed. At 3200 cm^{-1}, the medium sharp peak of C-H stretching was discovered. In addition, UV/Vis and elemental studies further verified the presence of $[Co(1\text{-}VI)_6]\cdot NO_3$ (Fig. 4). UV-visible study shows that [Co (1-VI)$_6$]. NO_3 polymer exhibited π-π^* transition in the range of 200-250 nm. Elemental analysis studies show that confirmation of C, 49.02%; H, 4.93%; N, 25.18% in prepared compound.

Table-1: Crystal data and details of the structure refinement for $[Co(1\text{-}VI)_6]\cdot NO_3$.

Parameters	Compound
Empirical formula	$C_{40}H_{50}CoN_{18}O_6$
Formula weight	937.91
Temperature (K)	296
Crystal system	Orthorhombic
Space group	*Pica*
a, (Å)	16.1341(16)
b, (Å)	16.5179(16)
c, (Å)	18.2664(16)
Volume (Å^3)	4868.0 (8)
Z	4
ρ_{calc} (g/cm^3)	1.280
μ (mm^{-1})	0.42
F(000)	1964.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection (°)	6.758 to 53.706
Index ranges	$-19 \le h \le 20, -21 \le k \le 15, -18 \le l \le 23$
Reflections measured	27856
Independent reflections	5351 [R_{int} = 0.058, R_{sigma} = 0.642]
Data/restraints/parameters	5351/16/310
Goodness-of-fit on F^2	1.098
Final R indexes [I≥2σ (I)]	R_1 = 0.0680, wR_2 = 0.2458

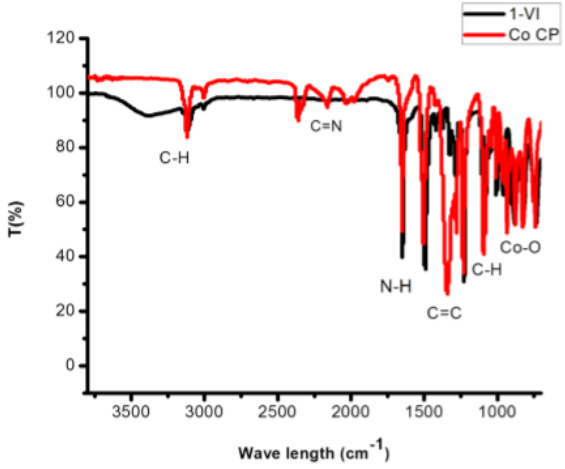


Fig. 3: FTIR Spectra of $[Co\ (1\text{-}VI)_6]\cdot NO_3$cobalt coordination polymer.

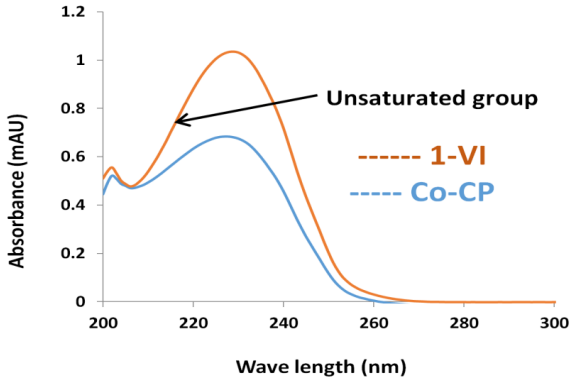


Fig. 4: UV/Vis of$[Co\ (1\text{-}VI)_6]\cdot NO_3$ coordination polymer.

Antimicrobial activity

The antimicrobial data in Table-2 explainsthat $[Co(1\text{-}VI)_6]\cdot NO_3$ compound had variable antimicrobial (antibacterial and antifungal) activity against all the four strains (2 bacteria and 2 fungi). The synthesized $[Co(1\text{-}VI)_6]\cdot NO_3$ compound revealed a maximum zone of diameter 14, 9, 5, and 2 mm respectively at the concentrations 1000, 500, 250, and 125 μg.mL^{-1} beside *E. coli*, similarly against *S. aureus* $[Co(1\text{-}VI)_6]\cdot NO_3$ compound exhibits the 11, 6, 4 and 2 mm in diameter at concentrations 1000, 500, 250 and 125 μg.mL^{-1}. Likewise antifungal activity against *R. Stolonifer* $[Co(1\text{-}VI)_6]\cdot NO_3$had the zone of inhibition 6 and 2 mm, correspondingly at 1000 and 500 μg.mL^{-1} concentrations. Similarly, against *A. Niger;*$[Co(1\text{-}VI)_6]\cdot NO_3$ has exhibited zone 8 and3 mm in diameter at 1000 and 500 μg.mL^{-1}, respectively; whilst no any zone appeared at 250 and 125 μg.mL^{-1} concentrations.

The antimicrobial activity of $[Co(1\text{-}VI)_6]\cdot NO_3$was determined against four microbes and activity was calculated in four different criterion. Such as, zones from 10–14 mm in diameter was considered very high activity, zones from 5–10 mm considered high activity, zones from 2–5 mm exhibited relatively high activity, and likewise, less than 2 mm demonstrate no activity.

At 1000, 500, 250 and 125 μg.mL^{-1} of $[Co(1\text{-}VI)_6]\cdot NO_3$ compoundshows very high activity, high activity and relatively high activity next to *E. coli* and *S. aureus*; whilst against *R. Stolonifer*and*A. Niger* at 1000, 500. 250 and 125 μg.mL^{-1} of $[Co(1\text{-}VI)_6]\cdot NO_3$ compound shows high, relatively high and no activity, which illustrate that prepared $[Co(1\text{-}VI)_6]\cdot NO_3$ compound is good antimicrobial agent against *E. coli* and *S. aureus* as compare to fungi including *R. Stolonifer* and *A. Niger* as shown in Table-2.

MIC was the minimum concentration at which bacterial growth inhibited completely [16].In vitro various concentrations of $[Co(1\text{-}VI)_6]\cdot NO_3$ compound like; 1000, 500, 250, and 125 μg.mL^{-1} were prepared and used against four microbes. However, it is noteworthy that $[Co(1\text{-}VI)_6]\cdot NO_3$ compound shows higher activity next to *E. coli* and *S. aureus* (MIC at 125 μg.mL^{-1}) as compared to *R. Stolonifer* and *A. Niger* (MIC at 500 μg.mL^{-1}), whereas DMSO (control) showed no any activity against all four different strains. Thus in Table-2 results show that $[Co(1\text{-}VI)_6]\cdot NO_3$ compoundis more competent to lessen the colonies of bacteria including *E. coli* and *S. aureus* as compare to fungi including *R. Stolonifer* and *A. Niger* [17]. The present study revealed as-prepared compound is capable tokill bacteria and restrains in peptidoglycan synthesis [18].

Table-2: Zones of inhibition (mm in diameter) for antimicrobial activities of prepared $[Co(1\text{-}VI)_6]\cdot NO_3$ compound.

Concentration (µg/mL)	Zones of inhibition in mm ± SD			
	Bacteria (MIC 125 µg.mL^{-1})		Fungi (MIC 500 µg.mL^{-1})	
	E. coli	*S. aureus*	*R. Stolonifer*	*A. Niger*
1000	14± 0.04	11 ± 0.03	6 ± 0.02	8 ± 0.03
500	9 ± 0.02	6 ± 0.03	2 ± 0.00	3 ± 0.01
250	5 ± 0.01	4 ± 0.02	-	-
125	2 ± 0.00	2 ± 0.01	-	-
Control (DMSO)	-	-	-	-

Structureactivity relationship (SAR)

The benzene rings with electron releasing groups had better antibacterial action than their precursors, according to this study. As a result, aryl/vinyl groups donate electrons, and the aromatic ring is activated by their resonance action. [19]. Pyrole modified with an electron-donating substituent in the third position has a good antibacterial activity. Compounds with an electron-donating group have high activity, while unsubstituted derivatives have moderate activity, according to SAR. [20].The lipophilic character of metal is increased by the lipid layer of the cell membrane [21].Electron-releasing groups in the ring gives a positive effect on the activity.

Conclusion

In this study, a novel self-assemble approach was used to make $[Co\ (1\text{-}VI)_6]\cdot NO_3$ polymer and characterized by UV/Vis, IR, CHNS, and single-crystal X-ray analysis. Due to the presence of imidazole ligands, crystal packing studies revealed that the polymer contains many nonbonding interactions. Antimicrobial activity of metal ions is increased when it is coordinated with ligands. Coordination reduces the polarity of the metal atom. As a result, this research could be useful in the future for controlling illnesses caused by various microbes.

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