Selective detections of nitroaromatic explosives by monomeric and polymeric Bi(III) complexes

Ozge Gungor, Muhammet Kose *

Chemistry Department, Kahramanmaras Sutcu Imam University, 46100, Kahramanmaras, Turkey

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ABSTRACT

In this work, two new Bi(III) complexes $[Bi(L^1)(NO_3)]_n$ and $[Bi(L^2)(NO_3)_3]$ were synthesized and their structures were characterized by the spectroscopic and analytical methods The structure of complex $[Bi(L^1)(NO_3)]_n$ was determined by single crystal X-ray diffraction study. X-ray diffraction data showed that the complex crystalizes as a coordination polymer. In the structure each ligand uses a N_3O_2 donor set to bind Bi(III) metal center and two pyrdine nitrogen atoms to bind another two Bi(III) ions. The Bi(III) ion sits in the cavity of the N_3O_2 donor set of a ligand forming a pentagonal plane. Two pyridine nitrogen atoms (N1 and N7) of two separate ligands are located at the axial positions of a Bi(III) ion resulting in a 3D metal-organic framework. The fluorimetric detections of nitroaromatic compounds [nitro benzen (NB), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP) and 2,4,6-trinitrphenol (2,4,6-TNP)] by the Bi(III) complexes was investigated. Complex $[Bi(L^1)(NO_3)]_n$ exhibit good sensitivity for NB and 2,4,6-TNP with K_{sv} values of 2.96×10^6 and 1.87×10^6 M^{-1}, respectively.

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1. Introduction

Recently, rapid and selective detection of nitro explosives have received considerable attention due to their importance in security and environmental issues [1–3]. Trinitrotoluene(TNT), trinitrophenol also known as picric acid (TNP), p-nitroaniline (PNA), 4-nitrophenol (4-DNP), 2,4-dinitrophenol (DNP) and nitrobenzene (NB) are among nitroaromatic explosives [4]. Environmental contamination of nitroaromatic compounds (NACs) may arise from weaponry manufacture, storage, disposal, and leakage from undischarged field mines [5]. Ingestion of NACs can be hazardous to living beings and may cause several health problems including liver damage and dermatitis [6–8]. Sniffer dogs and sophisticated instruments are widely used to detect nitroaromatic explosives [9]. Sniffer dogs are regarded as the best field methods for the detection of nitroaromatic explosives, however the explosive detection by sniffer dogs have drawbacks such as the high cost of expensive training and regular re-training maintaining. Moreover, dogs proper care are need and are easily fatigued [10]. Several instrumental techniques including gas chromatography, energy dispersive X-ray diffraction, mass spectrometry, ion mobility spectrometry, electrochemical fluorescence, nuclear quadrupole resonance, electron capture detection, capillary electrophoresis and surface enhanced raman spectroscopy have been developed to detect nitroaromatic compounds with high sensitivity [11–15]. The instruments and techniques have also suffered from high cost and not easy applied in site field. Fluorescent chemosensors are another alternative to detect NACs in solid state as well as in solution media [16–18]. Nitroaromatic compounds have been reported to show quenching effect in the emission band of fluorescent materials. Polymers/monomers with delocalized π-electrons have shown to serve as fluorescent sensors for detection of NACs [19–21]. Organic compounds with pyrene, napthalene or the other polyaromatic groups have been studied as fluorimetic detections of NACs [22–24]. In our previous study, pamoic acid esters were tested as fluorescent probes for NACs and showed some promising results [25]. Metal-organic frameworks (MOFs) have been widely used as fluorescent probes for the selective and sensitive sensing of NACs with low detections limits [26–32].

In continuance of our interest in the design of new fluorescent probes for NACs, two new Bi(III) complexes $[Bi(L^1)(NO_3)]_n$ and $[Bi(L^2)(NO_3)_3]$ of pentadentate ligands (H_2L^1 and L^2) were prepared and their structures were characterized by the analytical and spectroscopic methods. The solid state structure of the new polymeric complex $[Bi(L^1)(NO_3)]_n$ was studied by single crystal X-ray diffraction study. Absorption and emission behaviours of the complexes were investigated in solution. Chemosensor properties of the complexes for the detection of nitro aromatic compounds [nitro benzen

* Corresponding author.
E-mail address: muhammetkose@ksu.edu.tr (M. Kose).

(NB), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP) and trinitrophenol (TNP)] were investigated by the fluorimetric method and results were compared with literature values.

2. Experimental

2.1. General

All chemicals and solvents were purchased from commercial suppliers (Aldrich or Merck) and used as received. The precursor 2,6-diformylpyridine was synthesized from 2,6-pyridinedimethanol using manganese dioxide as an oxidising agent [33]. The purity of the 2,6-diformylpyridine was followed by TLC and no further characterization was carried out. Infrared spectra were obtained (4000–450 cm^{-1}) on a Perkin Elmer Spectrophotometre 100 FT-IR. The absorption spectra were measured in the 200–800 nm range on a Perkin Elmer Lambda 45 spectrophotometer. The single-photon fluorescence spectra of the synthesized compounds were obtained on a Perkin Elmer LS55 luminescence spectrometer. All samples were prepared in spectrophotometric grade solvents and analysed in a 1 cm optical path quartz cuvette.

2.2. Synthesis of the ligands (H_2L1 and $L2$)

The ligands were prepared according to the our previous reports [34,35]. To a refluxing solution of 2,6-Diformylpyridine (0.54 g, 4.00 mmol) in MeOH (70 mL), pyridine-4-carbohydrazide (1.097 g, 8 mmol) or 4-aminoantipyrine (1.626 g, 8 mmol) was added and the reaction mixtures were refluxed for 4 h. The precipitations formed upon cooling to the room temperature, precipitations were filtered and dried under vacuum.

H_2L^1: Color: White, Yield: 85%. **Elemental analysis**: Calc. For $C_{19}H_{15}N_7O_2$ (F.W.:373.37): C, 61.12; H, 4.05; N, 26.26. Found: C, 60.95; H, 3.47; N, 25.35%. ^{1}H NMR (DMSO-$d6$); 11.95 (s, 2H, NH), 8.61(s, 2H, CH=N), 7.95 (t, 1H, CH pyridine), 7.89 (d, 2H, CH pyridine), 7.81 (d, 4H, CH aromatic), 6.98 (d, 4H, CH aromatic). **IR (ATR, cm^{-1}):** 3400–3100 (broad), 2891, 1662, 1603.

L^2: Color: Yellow, Yield: 89%. **Elemental analysis**: Calc. For $C_{19}H_{27}N_7O_2$ (F.W.:505.57): C, 68.28; H, 5.38; N, 19.39. Found: C, 67.90; H, 5.18; N, 19.12%. ^{1}H NMR (DMSO-$d6$); 9.15 (s, 2H, CH=N), 7.93 (d, 2H, CH pyridine), 7.80 (t, 1H, CH pyridine), 7.49 (t, 4H, CH phenyl), 7.39 (d, 4H, CH phenyl), 7.29 (t, 2H, CH phenyl), 2.45 (s, 6H, C—CH$_3$), 3.13 (s, 6H, N—CH$_3$). **IR (ATR, cm^{-1}):** 2923, 2853, 1645, 1592.

2.3. Synthesis of the complexes $[Bi(L^1)(NO_3)]_n$ and $[Bi(L^2)(NO_3)_3]$

The ligands (0.373 g, 1 mmol for H_2L^1 and 0.506 g, 1 mmol for L^2) were refluxed in MeOH (50 mL). To the refluxing solutions, Bi(NO$_3$)$_3$·5H$_2$O (0.395 g, 1 mmol) was added and the colour of the mixtures turned to orange-yellow with clear solutions. The reaction mixtures were further refluxed for 6 h. The volume of the solutions were reduced to 15 mL on a rotary evaporator. The orange-yellow precipitates were filtered and dried in air.

$[Bi(L^1)(NO_3)]_n$: Color: Orange-Yellow, Yield: 68%. **Elemental analysis**: Calc. For $C_{19}H_{13}N_7O_2Bi(NO_3)\cdot5H_2O$ (F.W.:732.41) for monomeric unit: C, 31.16; H, 3.17; N, 15.30. Found: C, 30.45; H, 2.95; N, 15.10%. **IR (ATR, cm^{-1}):** 3300–3100 (broad), 2915, 1664, 1636, 1543, 1469, 1406, 1357, 1280, 1143, 1014, 934, 842, 819, 745, 722, 678, 542, 518, 442.

$[Bi(L^2)(NO_3)_3]$: Color: Orange-Yellow, Yield: 71%. **Elemental analysis**: Calc. For $C_{29}H_{27}N_7O_2Bi(NO_3)_3$ (F.W.:900.57): C, 38.68; H, 3.02; N, 15.55. Found: C, 38.18; H, 2.82; N, 15.04%. **IR (ATR, cm^{-1}):** 3015, 2920, 1650, 1615, 1577, 1460, 1343, 1267, 1171, 1015, 930, 805, 743, 693, 621, 585, 451.

Table 1
Crystallographic data and structure refinement for $[Bi(L^1)(NO_3)]_n$.

Identification code	$[Bi(L^1)(NO_3)]_n$
Empirical formula	$C_{19}H_{13}BiN_8O_5$
Formula weight	642.35
Crystal color	Yellow-Orange
Crystal system	Orthorhombic
Space group	$Pbca$
Unit cell a (Å)	30.984(5)
b (Å)	16.102(5)
c (Å)	12.006(5)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å3)	5990(3)
Z	8
Abs. coeff. (mm^{-1})	5.923
Refl. collected	115281
Completeness to θ = 25.242°	99.8%
Ind. Refl. [R$_{int}$]	7461 [0.0736]
R1, wR2 [I > 2σ (I)]	0.0507, 0.0895
R1, wR2 (all data)	0.0705, 0.00973
CCDC number	1813388

2.4. X-ray structure solution and refinement

X-ray diffraction data for complex $[Bi(L^1)(NO_3)_3]_n$ were collected at ambient temperature 293(2) K) on a Bruker D8 QUEST diffractometer using Mo-$K\alpha$ radiation (λ = 0.71073 Å). Data reduction was performed using Bruker SAINT [36]. SHELXS97 was used to solve and SHELXL2014/6 to refine the structures [37]. The structure was solved by direct method and refined on F^2 using all the reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters. The hydrogen atoms bonded to carbon and oxygen atoms were inserted at calculated positions using a riding model and refined with temperature factors riding on the carrying atoms. The crystallographic data and details of the structure solutions and refinements are given in Table 1. Bond lengths and angles for $[Bi(L^1)(NO_3)]_n$ are given in the Supplementray File.

3. Results and discussion

In this work, two new Bi(III) complexes $[Bi(L^1)(NO_3)]_n$ and $[Bi(L^2)(NO_3)_3]$ were synthesized and characterised by spectroscopic methods. The molecular structure of complex $[Bi(L^1)(NO_3)]_n$ was determined by single crystal X-ray diffraction study. Single crystals of $[Bi(L^2)(NO_3)_3]$ were not able to grow from several organic solvents, therefore, no definite structure was obtained for this complex. In the synthesis, the ligands H_2L^1 and L^2 were prepared from the reaction of 2,6-diformylpyridine with pyridine-4-carbohydrazide or 4-aminoantipyrine according to our previous methods [34,35]. The ligand H_2L^1 has two azomethine groups and two pyridine-4-carbohydrazide units on each side of the central pyridine ring. The ligand H_2L^1 can fold a metal ion with N$_3$O$_2$ to form pentagonal plane. The two pyridine end units were chosen intentionally to extend the pentagonal plane to form 3D metal organic frame work (MOF). The ligand L^2 has also two azomethine groups and 4-aminoantipyrine units on each side of the central pyridine ring. The ligand L^2 can also provide a pentagonal platform for Bi(III) with N$_3$O$_2$ type donor atoms, yet cannot extend its structure into coordination polymer. The ligands H_2L^1 and L^2 were then reacted with Bi(NO$_3$)$_3$·5H$_2$O to give the polymeric $[Bi(L^1)(NO_3)]_n$ and monomeric $[Bi(L^2)(NO_3)_3]$ complexes with high yield and purity. The proposed structures of the complexes are shown in Fig. 1. The microanalysis data (CHN) are in well agreement with calculated values. The orange-yellow colored complexes $[Bi(L^1)(NO_3)]_n$ and $[Bi(L^2)(NO_3)_3]$ are stable at room temperature in the solid state without decomposition. The com-