

A Novel Phenyl Hydrazinium Pyridine-3-carboxylate Ligand: Synthesis, Characterization and Structural Determination

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Abstract

A novel precursor ligand for the synthesis of several complexes of transition and inner transition elements namely phenyl hydrazinium pyridine-3-carboxylate has been synthesized in aqueous medium and characterized by elemental analyses, infrared spectra, thermal analyses and X-ray single crystal techniques. The crystal of the ligand belongs to the monoclinic crystal packing system with P21/c space group. The crystal data are: $a=9.2840(2)$ Å, $b=6.16300(10)$ Å, $c=20.7010(5)$ Å, $\alpha=90^\circ$, $\beta=90.5160(10)^\circ$ and $\gamma=90^\circ$, $V=1184.41(4)$ Å³. The final R indices R1 and wR2 are 0.0328 and 0.0863 for reflection 2085 with $[I > 2\sigma(I)]$. The volume and calculated density of the crystal are $1184.41(4)$ Å³ and 1.297 mg/m³.

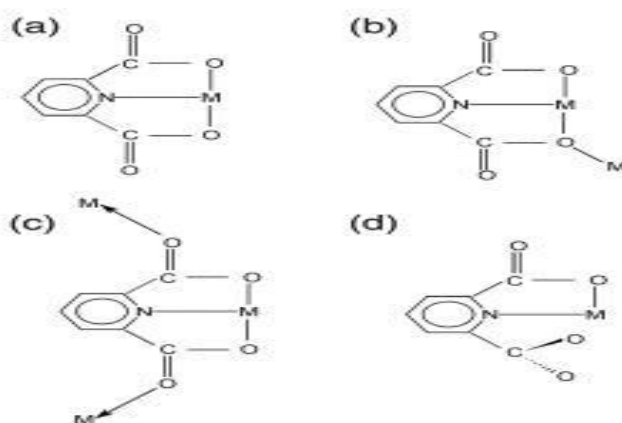
Keywords : Phenyl hydrazine, Pyridine-3-carboxylic acid, Monoclinic system, Thermal analysis.

1. Introduction

For the construction of coordination polymers with metals, the selection of organic ligands is very important. One of the appropriate organic ligands for the network geometries of the coordination polymers is the series of multidentate ligands containing oxygen and nitrogen atoms to have a great possibility for the design of multifunctional chemical architectures[1]. Lanthanide complexes with organic ligands with conjugate groups have been widely studied because of the characteristic luminescent properties. Luminescent metal complexes with nitrogen containing ligands have been reported in the investigation of their interesting photophysical properties and various coordination modes[2]. However, the studies on the lanthanide complexes are more difficult than those of transition metal complexes because of high coordination

number of lanthanide ions. Pyridine carboxylates have been extensively used to prepare and design lanthanide complexes because nitrogen and oxygen atoms, which have high affinity to lanthanide ions, could be coordinated to and transfer energy to lanthanide ions[3].

Picolinic and dipicolinic acids are the versatile ligands with N,O-chelator and has diverse coordination modes[4-8]. It has many important biological functions in the body metabolism such as enzyme inhibitor[9], plant preservative[10] and food sanitizer[11]. During the past few years, these properties have attracted the interest of scientists not only in the field of coordination chemistry but also in both inorganic and bioinorganic chemistry[12-13]. Picolinates and dipicolinates commonly coordinate to transition metals by either carboxylate bridges between metal centers, to form polymeric or dimeric complexes[14-15] or bidentate (O, N, O') chelation to one metal ion[16-17] as shown in the figures (a) to (d).



Recent investigations on hydrazinium[18-20] and phenyl hydrazinium[21] complexes of lanthanide carboxylates are limited to ethylenediaminetetraacetic acid. Dipicolinic acid with O,N,O chelating mode also capable of coordination with transition metal ions and lanthanide(III) ion has not been studied in detail. Nevertheless, recently two transition metal complexes of picolinic acid with phenyl hydrazinium cation has been reported[22,23] and due to the steric effect, phenyl hydrazinium ion may prefer to stay outside the sphere. As the complexes of phenylhydrazinium picolinates are scarce in the literature, it is considered much interesting to prepare a ligand of phenyl hydrazinium with pyridine-3-carboxylic acid and thereby facilitating various routes for the synthesis of several complexes of transition and inner transition metals and hence the present investigation.

2. Materials and Methods

The chemicals used were of AnalaR or equivalent grade. Phenyl hydrazine and pyridine-3-carboxylic acid were used as received from Sigma Aldrich. The ligand is prepared and analyses were carried out using fresh doubly distilled water and the solvents were distilled before use. The C,H and N analyses were carried out using a

Perkin-Elmer model 1240 CHN analyzer. The infrared spectra of the solid samples in the range 400-4000 cm^{-1} were recorded on a Thermo NICOLET AVATAR 330 FT-IR spectrophotometer using KBr pellets. The TG-DTA curves were recorded on a SWI TG/DTA 6200 thermal analyzer using about 5 mg of the samples with the heating rate of 10°C per min and platinum cups as sample holders. X-ray powder diffraction patterns were recorded on a Druker D8-Focus diffractometer with a scan speed 5 sec/step using Cu-K α radiation ($\lambda=1.540598 \text{ \AA}$) and scintillation counter as a detector.

2.1 Synthesis of Phenyl hydrazinium Pyridine-3-carboxylate ligand

To an aqueous solution (40 mL) of pyridine-3-carboxylic acid (3.69 g, 0.03 mols), phenylhydrazine (6.48 g, 0.06 mols) in 10mL water was added slowly with constant stirring. The resulting solution was concentrated to one-third of its original volume and allowed to cool at room temperature. After 24 h to 48 h, the crystals formed were removed, washed several times with ice cold distilled water and dried in air.

2.2 X-ray structure determination

The X-ray intensity data were collected on a Enras 7-Nonius CAD-4 diffractometer system with graphite monochromated Mo-K α radiation ($\lambda=0.71073 \text{ \AA}$). The structure was solved by direct methods using SIR92 program and completed using Fourier techniques and refined by applying full matrix least square techniques. Refinement was carried out using SHELXL-97 program[24,25]. Most of the hydrogen atoms could be located in difference Fourier map. Their positions were constrained at chemically idealized positions wherever geometry permitted. These hydrogen atoms were given riding model refinement. Other hydrogen atoms were isotropically refined.

3. Results and Discussion

Phenyl hydrazinium salt of pyridine-3-carboxylate is prepared by the aqueous reactions between pyridine-3-carboxylic acid and phenyl hydrazine. The crystals obtained are stable in air and soluble in water. The compositions of the complexes were determined by micro analyses.

3.1 Infrared Spectra

The bands observed in the region 3200-3500 cm^{-1} which are attributed to the presence of N-H stretching of phenyl hydrazinium cation. The N-N stretching of phenyl hydrazinium moiety is appeared at 960-980 cm^{-1} . The ν_{asy} and ν_{sym} stretchings of carboxylate group is observed in the region 1600-1650 cm^{-1} and 1350-1400 cm^{-1} . The difference between the ν_{asy} and ν_{sym} stretchings of carboxylate group indicates the ionic nature of the carboxylic group.

3.2 Thermal Analyses

The simultaneous TG-DTA of the ligand in air was recorded to understand the degradation patterns. The ligand undergoes continuous decomposition in the temperature range 90° C to 270° C resulting in the complete decomposition of the ligand. Two species with 92.8% and 67.5% mass seem to be prominent from TG curve

which could be attributed due to the loss of NH_3^+ and NHNH_3^+ , CO_2 moieties respectively. However, as the ligand contain carbon, hydrogen oxygen and nitrogen, no residue would be left out as they would go out as gases such as CO_2 , N_2 , NH_3 and water vapour.

3.3 Crystal and Molecular Structure of Phenyl Hydrazinium Pyridine-3-Carboxylate ligand

Crystal structure is monoclinic system with P21/c space group. The unit cell of phenyl hydrazinium pyridine-3-carboxylate ligand has four units of phenyl hydrazine and four units of pyridine-3-carboxylic acid molecules which are mainly associated through intermolecular hydrogen bonds that play a vital role in stabilizing the crystal structure. It is quite understandable that the intermolecular hydrogen bonding is due to the oxygen atom of the carboxylic group and the nitrogen of phenyl hydrazinium cation. The net structure is formed through the hydrogen bonds and static interactions.

The crystal data are given in Table.1. The ORTEP and crystal packing diagrams are shown in Figs. 1 and 2 respectively.

Table 1: Crystal data and structure refinement for phenyl hydrazinium pyridine-3-carboxylate ligand

Identification code	Shelxl
Empirical formula	C12 H13 N3 O2
Formula weight	231.25
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/c
Unit cell dimensions	a=9.2840(2) Å alpha=90 deg. b=6.16300(10) Å beta=90.5160(10) deg. c=20.7010(5) Å gamma=90 deg.
Volume	1184.41(4) Å ³
Z, Calculated density	4, 1.297 Mg/m ³
Absorption coefficient	0.091 mm ⁻¹
F(000)	488
Crystal size	0.20 x 0.20 x 0.20 mm
Theta range for data collection	2.19 to 24.99 deg.
Limiting indices	-11<=h<=11, -7<=k<=6, -24<=l<=24
Reflections collected / unique	10292 / 2085 [R(int)=0.0252]
Completeness to theta	=24.99 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9890 and 0.9438
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2085 / 4 / 170
Goodness-of-fit on F ²	1.045
Final R indices [I>2sigma(I)]	R1=0.0328, wR2=0.0863

R indices (all data)	R1=0.0412, wR2=0.0940
Largest diff. peak and hole	0.142 and -0.193 e.Å ⁻³

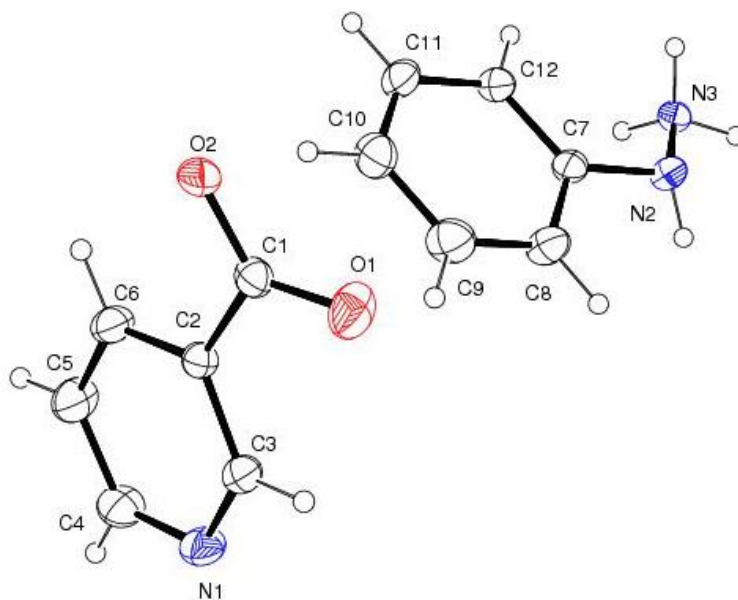


Fig. 1: ORTEP diagram of phenyl hydrazinium pyridine-3-carboxylate ligand

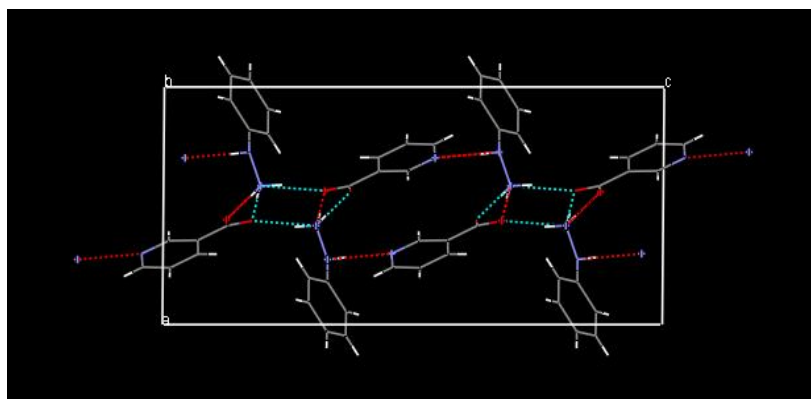


Fig. 2: Packing diagram of phenyl hydrazinium pyridine-3-carboxylate ligand

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5. Supplementary Material

Crystallographic data for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre (Deposition number: CCDC-886714). The details regarding atomic coordinates, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and torsion angles of the ligand can be obtained from the authors on request.

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