Synthesis, Characterization and Crystal Structure Determination of a New Indium (III) Complex: [In(5,5'-DiMeBiPy)Cl₃(DMSO)].2(DMSO)

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http://dx.doi.org/10.13005/ojc/300154

(Received: December 05, 2013; Accepted: January 07, 2014)

ABSTRACT

[In(5,5'-DiMeBiPy)Cl₃(DMSO)].2(DMSO) complex (5,5'-DiMeBiPy is 5,5'-Dimethyl-2,2'-bipyridine) was prepared from reaction of InCl₃·4H₂O with 5,5'-DiMeBiPy in 1.1 molar ratio in DMSO. This compound has been characterized by IR, ¹H NMR, UV-Vis spectroscopy as well as X-ray crystallography. This compound crystallizes in the space group P₁ of the triclinic system. The unit cell dimensions is: a = 8.6695(8) Å, b = 12.8456(14) Å, c = 13.0877(12) Å, α = 78.258(8)°, β = 85.270(8)°, γ = 74.932(8)°. According to X-ray structure determination, there are one molecules of the complex and two DMSO solvent molecules in the asymmetric unit. In this complex the geometry at the indium (III) center is octahedral, formed by two nitrogen atom of 5,5'-DiMeBiPy ligand, three chloride ions and one DMSO molecule in trans position to chloride ion.

Key words: Indium (III), 5,5'-Dimethyl-2,2'-bipyridine, DMSO, Crystal structure.

INTRODUCTION

Metal complexes containing 2,2'-bipyridine and phenanthroline ligands have gained importance due of their versatile roles as molecular scaffolding for supramolecular assemblies, and due to their applications in catalysis, electrochemistry biochemistry and ring-opening metathesis polymerization and biochemistry¹⁻⁹.

On the other hand, the chemistry of indium compounds is of interest owing to their important application in catalysts, electronics and optics¹⁰⁻¹⁴. Several In(III) complexes, which have the formula [In(N-N)Cl₃(Solv)], (Solv = DMSO, DMF, H₂O, MeOH and EtOH), are known, such as [In(BiPy)Cl₃(H₂O)], [In(BiPy)Cl₃(EtOH)], and [In(BiPy)Cl₃(MeOH)]. However, [In(Phen)Cl₃(DMSO)], [In(4,4'-DiMeBiPy)Cl₃(DMSO)], [In(Phen)Cl₃(H₂O)], [In(Phen)Cl₃(EtOH)], [In(5,5'-DiMeBiPy)Cl₃(MeOH)] and [In(4,4'-DiTertBuBiPy)Cl₃(MeOH)], CH₃OH, are known, where BiPy is 2,2'-bipyridine, Phen is 1,10-phenanthroline, 4,4'-DiMeBiPy is 4,4'-dimethyl-2,2'-bipyridine, 5,5'-DiMeBiPy is 5,5'-dimethyl-2,2'-bipyridine and 4,4'-DiTertBuBiPy is 4,4'-diteriarybuthyl-2,2'-bipyridine).

We recently reported the coordination chemistry of In(III) with some substituted bipyridine ligands such as [In(4,4'-DiMeBiPy)Cl₃(MeOH)].

CH₃OH, [In(5,5'-DiMeBiPy) Cl₃(DMF)], H₂O, and [In(6-MeBiPy)Cl₃(DMSO)], (where 6-MeBiPy is 6-methyl-2,2'-bipyridine). Herein the synthesis, characterization and crystal structure of a new indium(III) complex containing 5,5'-Dimethyl-2,2'-bipyridine ligand by the formula of [In(5,5'-DiMeBiPy) Cl₃(DMSO)].2(DMSO) have been reported.

EXPERIMENTAL

Materials and instruments
All chemicals were purchased from Merck and Aldrich. Infrared spectra (4000-250 cm⁻¹) of solid samples were taken as 1% dispersion in KBr pellets using a Shimadzu-470 spectrometer. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AC-300 MHz spectrometer operating in the quarter mode.

Synthesis of [In(5,5'-DiMeBiPy)Cl₃(DMSO)].2(DMSO)
5,5'-Dimethyl-2,2'-bipyridine (0.20g, 1.10 mmol) in methanol (5 ml) was added to a solution of InCl₃.4H₂O (0.32g, 1.10 mmol) in methanol (5 ml) and the resulting colorless solution was stirred for 30 min at 40°C. The suitable crystals for the X-ray diffraction experiment were obtained by methanol diffusion to a colorless solution in DMSO. Suitable crystals were isolated after one week (yield 0.54 g, 76.7%). IR (CsI, cm⁻¹): 3105m, 2993m, 2918, 1588m, 1514m, 1478s, 1396m, 1330s, 1313m, 1256m, 1141m, 1050s, 986m, 944s, 868m, 840s, 715m, 645w, 525m, 425m, 394m, 343m, 310m, 275m. ¹H NMR (DMSO-d₆, ppm): 2.63 (s, 3 H), 8.40 (d, 1 H), 8.83 (d, 1 H) and 9.28 (s, 1 H). ¹³C NMR (DMSO-d₆, ppm): 19.3 (s), 126.1 (s), 141.3 (s), 144.9 (s), 147.6 (s) and 152.6 (s). UV-Vis: λmax (DMSO, nm), 295.

RESULTS AND DISCUSSION

Synthesis
Compound [In(5,5'-DiMeBiPy)Cl₃(DMSO)].2(DMSO) was obtained from reaction of one equivalent of InCl₃.4H₂O with one equivalent of 5,5'-Dimethyl-2,2'-bipyridine in dimethylsulfoxide at room temperature, in 63% yield, Eq. (1):

Table 1: Crystallographic and structure refinements data of [In(5,5'-DiMeBiPy)Cl₃(DMSO)].2(DMSO)

| Complex | Formula | Weight | Temperature /K | Wavelength /Å | Crystal system | Space Group | Crystal size /mm³ | a /Å | b /Å | c /Å | Volume / Å³ | Z | Density (calc.) /g cm⁻³ | θ ranges for data collection | F(000) | Absorption coefficient | Index ranges | Data collected | Unique data (Rint) | Parameters, restrain | Final R₁, wR₁ a (Obs. data) | Final R₁, wR₁ a (All data) | Goodness of fit on F² (S) | Largest diff peak and hole /e Å⁻³ |
|---------|---------|--------|----------------|---------------|----------------|-------------|----------------|------|------|------|-------------|-----|----------------------|--------------------------|--------|---------------------|----------------|----------------|------------------|-----------------|----------------|-------------------|
| C₁₈H₃₀Cl₃InN₂O₃S₃ | 639.82 | 298(2) | 0.71073 | Triclinic | P | 0.50×0.40×0.35 | 8.6695(8) | 12.8456(14) | 13.0877(12) | 1377.3(2) | 2 | 0.1543 | 2.43-26.00 | 648 | 1.397 | -10 ≤ h ≤ 10 | 10935 | 5378, 0.0963 | 272, 0 | 0.0581, 0.1513 | 0.0663, 0.1566 | 1.057 | 1.479, -1.548 |

Crystal structure determination and refinement
The X-ray diffraction measurements were made on a Bruker SMART 1000 CCD area detector diffractometer at 298 K (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å). The structure was solved by SHELX-97 and SHELXTL and absorption correction was done using the SADABS and APEX2 programs. Data collection, cell refinement and data reduction were done by APEX2, SAINT, SHELXTL, PLATON and MERCURY.
The suitable crystal for X-ray diffraction experiment was obtained by slow evaporation of DMSO in room temperature after three weeks. Synthesized complex was thoroughly characterized by elemental analysis, IR and $^1$H-NMR spectroscopy. Elemental analysis data (C, H, N) support the general composition of the complex and the structures have been established by single-crystal X-ray diffraction study.

The labeled diagram of $[\text{In(5,5'-DiMeBiPy)}\text{Cl}_3(\text{DMSO})]_2(\text{DMSO})$. Thermal ellipsoids are at 50% probability level.
NMR, IR and UV-vis investigation

Compound \([\text{In}(5,5'\text{-DiMeBiPy})\text{Cl}_3\text{(DMSO)}].2\text{(DMSO)}\) is stable in air and can be used directly for routine analyses. The vibrational band present at 3105 cm\(^{-1}\) is assigned to \(v(C-H)\) cycle and two vibrational bands present at 2993 and 2918 cm\(^{-1}\) are assigned to \(v(C-H\text{Me})\). The several bands in the range 1588-1313 cm\(^{-1}\) are assigned to \(v(C=N)\) and \(v(C=C)\) vibrations. Medium to strong vibration bands in the range 986-525 cm\(^{-1}\) are assigned to deformation vibrations \(\delta(C=C=N)\) and \(\delta(C=C=C)\) in the pyridine rings. In addition, two strong signals at 1050 and 944 cm\(^{-1}\) has been assigned to \(v(S=O)\) for free and coordinated DMSO, respectively. Far infrared spectra for title complex were recorded between 425 and 264 cm\(^{-1}\). In-O stretching vibration is seen at 425 cm\(^{-1}\). The In-N stretching vibration is seen at 394 and 343 cm\(^{-1}\) and In-Cl stretching vibration is seen at 310 and 275 cm\(^{-1}\).

The UV-Vis spectrum of the DMSO solution of 1 have band at 295 nm which can be assigned to \(\pi\rightarrow\pi^*\) transition. NMR spectroscopy studies were conducted to characterize the chemical structure of title complex. A comparison between \(^1\)H and \(^{13}\)CNMR spectra of title complex and 5,5'-dmbpy ligand, clearly indicated the coordination of ligand to In(III). It can be deduced from NMR data that in the solution, the 5,5'-dmbpy ligand have a symmetrical environment. As expected, the \(^1\)H NMR spectrum exhibited a singlet at 2.63 ppm for methyl, a doublet at 8.40 ppm, a doublet at 8.83 ppm and a singlet at 9.28 for the aromatic rings. The \(^{13}\)C NMR spectrum showed a singlet at 19.3 ppm, for CH\(_3\) groups and five singlets at 126.1 to 152.6 ppm for the aromatic rings.

Description of the molecular structure of \([\text{In}(5,5'\text{-DiMeBiPy})\text{Cl}_3\text{(DMSO)}].2\text{(DMSO)}\)

The colorless prismatic crystals of \([\text{In}(5,5'\text{-DiMeBiPy})\text{Cl}_3\text{(DMSO)}].2\text{(DMSO)}\) were grown by slow evaporation of DMSO solution during three weeks. Table 1 shows details of collected data and refinement of the X-ray crystal structure determination for this compound. Selected bond lengths and bond angles are presented in Table 2. The crystal structure of this complex consists of 3 chloride ion, one chelating 5,5'-Dimethyl-2,2'-bipyridine and one DMSO. Two DMSO molecules are in the unit cell as solvent. ORTEP view with numbering scheme and packing diagram is shown in Figure 1. The complex have distorted octahedral geometry. In this complex indium has pseudo-octahedral coordination with fac-arrangement of chlorine atoms. In-Cl bond lengths differ strongly around indium center. The bond lengths In1-Cl3 (chlorine atom is trans to oxygen) is longer than distances In1-Cl1 and In1-Cl2 [C1 and C12 atoms are trans to nitrogen atoms].

As it is shown in Figure 2, the 5,5'-Dimethyl-2,2'-bipyridine ligands form \(\pi\) bonding stacks in which each bipy ligand lies between two bipy ligands of adjacent indium complexes. The centroid to centroid...
distance between adjacent aromatic rings are 3.605 and 3.937 Å. Weak C-H...Cl and C-H...O hydrogen bonds are linked adjacent molecules in another direction to generate a 3D packing, Table 3.

ACKNOWLEDGMENTS

We would like to thank the Islamic Azad University, Omidieh Branch for financial support.

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