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Synthetic aspects, crystal structure and antibacterial activity of two new Schiff base cobalt(III) complexes

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ABSTRACT

Two new Schiff base complexes of cobalt(III) viz. $[Co(L)(L^1)(NCS)]ClO_4$ (**1**) and $[Co(L^2)(N_3)]_2{\cdot}4H_2O$ (**2**), where L = propane-1,2-diamine, L^1 = 2-[*N*-(2-aminopropyl)ethanimidoyl]phenolate and L^2 = 2,2′-[propane-1,2-diylbis(nitriloeth-1-yl-1-ylidene)]diphenolate ion, have been prepared and characterized. The syntheses have been achieved by reacting cobalt perchlorate either with the diamine (L) and 2-hydroxyacetophenone together or with their Schiff base H_2L^2 in presence of the respective pseudohalide. The same synthetic system has yielded two complexes of different nuclearity in presence of two different pseudohalides i.e. the mononuclear **1** with thiocyanate and the binuclear **2** with azide ion. The tridentate (L^1) and tetradentate (L^2) Schiff base anions were formed in situ to bind the Co(III) ion in case of the template syntheses. The complexes have been characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction studies. Structural studies reveal that the central Co(III) ions in both the complexes **1** and **2** adopt distorted octahedral geometry and weak intermolecular H-bonding or $\pi\ldots\pi$ interactions are operative to bind the complex units in the solid state. The antibacterial activity of the complexes and related compounds has been tested against some Gram(+) and Gram(−) bacteria.

1. Introduction

Schiff bases have long been used as organic chelating ligands in the synthesis of transition metal complexes due to their greater ease of preparation and structural varieties. In recent years, there has been enhanced interest in the synthesis and characterization of such complexes due to their important catalytic, magnetic and biological properties. Schiff base complexes of cobalt in different oxidation states including +3 are very important in these respects [1–6]. Although numerous organic chelating ligands have been extensively used to synthesize cobalt complexes, reports of synthesis of complexes of cobalt(III) using the tetradentate Schiff base derived from propane-1,2-diamine and 2-hydroxyacetophenone or by in situ preparation of this type of Schiff base are lacking. Until now, a limited number of transition metal complexes containing the above type of Schiff bases along with a pseudohalide in the coordination sphere have been reported [7–11]. In the area of bioinorganic chemistry, few Schiff base complexes of cobalt(III) are known to exhibit higher antiviral and antimicrobial activities than similar other complexes of first series transition metals [12]. But, the investigation of biological properties of the above Schiff base or its complexes of Co(III) has not received adequate attention.

In the present work, we describe the synthesis of two new complexes of cobalt(III) by using a tetradentate Schiff base, H_2L^2 or by using the respective diamine and carbonyl compound to form Schiff bases in situ to bind the Co(III) ion. Both the complexes have been characterized by microanalytical, spectroscopic and single crystal X-ray diffraction studies. The same synthetic system has given rise to different types of Co(III) complexes in presence of two different pseudohalides viz. a mononuclear mixed ligand electrolytic complex, $[Co(L)(L^1)(NCS)]ClO_4$ (**1**) in presence of thiocyanate and a binuclear phenoxo-bridged non-electrolytic complex, $[Co(L^2)(N_3)]_2{\cdot}4H_2O$ (**2**) in presence of azide ion. Structural studies indicate that the central Co(III) ion adopts distorted octahedral geometry in both of **1** and **2** and the complex units are linked by weak intermolecular H-bonding or $\pi\ldots\pi$ interactions in the solid state. The complexes and the constituent Schiff base or all related compounds have also been tested *in vitro* to assess their antibacterial activities against some common reference bacteria and the results were compared with similar doses of a commercial antibiotics viz. Gattifloxacin.

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2. Experimental

2.1. Physical measurements

Elemental analyses for carbon, hydrogen and nitrogen were carried out using a Perkin-Elmer 2400-II elemental analyzer. The infrared spectra were recorded on a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer with KBr discs (4000–400 cm^{-1}). Room temperature solid phase magnetic susceptibilities were measured at 298 K with a PAR 155 vibrating sample magnetometer with $Hg[Co(NCS)_4]$ as the calibrant. Molar conductances of the complexes in dry methanol were measured using a direct reading conductivity meter of Systronics (Type 304).

2.2. Materials

Commercially available reagent grade propane-1,2-diamine, 2-hydroxyacetophenone, cobalt(II) perchlorate hexahydrate, ammonium thiocyanate and sodium azide were used without further purification. All other chemicals and solvents were of analytical grade. The tetradentate Schiff base ligand (H_2L^2) was obtained by the condensation of propane-1,2-diamine (L) and 2-hydroxyacetophenone (HAP) using similar methods as described earlier [13].

Caution! Although no problems were encountered in the present work, compounds containing perchlorate and azide are potentially explosive. Therefore, only a small amount of the materials should be used at a time and handled with proper care.

2.3. Synthesis of the complexes

2.3.1. Synthesis of $[Co(L)(L^1)(NCS)]ClO_4$ (**1**)

A methanolic solution (10 mL) of cobalt(II) perchlorate hexahydrate (0.18 g, 0.5 mmol) was added to a mixture of propane-1,2-diamine (0.04 g, 0.5 mmol) and 2-hydroxyacetophenone (0.14 g, 1.0 mmol) in methanol with constant stirring and the total volume was made up to 40 mL by adding the same solvent. To the resulting brown solution, a methanolic solution (5 mL) of NH_4SCN (0.04 g, 0.5 mmol) was added dropwise. Stirring was continued for further half an hour and the solution was left for slow evaporation at room temperature. After a week, dark brown crystals of compound **1** appeared. The crystals were collected by filtration, washed with methanol and finally dried. The same compound was also obtained by slow mixing of cobalt(II) perchlorate hexahydrate, the Schiff base ligand (H_2L^2) and NH_4SCN (all in methanolic solutions) in the molar ratio of 1:1:1 with constant stirring and then following the same procedure as above to obtain the pure crystals. Yield: 0.15–0.17 g, 64–72%. *Anal.* Calc. for $C_{15}H_{23}ClCoN_5O_5S$: C, 37.55; H, 4.83; N, 14.60. Found: C, 37.46; H, 4.72; N,14.52%. FTIR (KBr, cm^{-1}): 2939(s), 2846(s), 2124(s), 1595(s), 1540(m), 1460(s), 1400(m), 1341(m), 1235(w), 1103(s), 765(m), 625(m). Λ_M (MeOH, Ω^{-1} cm^2 mol^{-1}): 120. Diamagnetic.

2.3.2. Synthesis of $[Co(L^2)(N_3)]_2 \cdot 4H_2O$ (**2**)

The same two synthetic routes described above (Section 2.3.1) were followed in the preparation of **2** also, except that an aqueous solution of NaN_3 (0.03 g, 0.5 mmol) was used instead of NH_4SCN. Brown crystals of **2** appeared after 8–10 days in these cases. Yield: 0.13–0.15 g, 59–68%. *Anal.* Calc. for $C_{38}H_{48}Co_2N_{10}O_8$: C, 51.24; H, 5.43; N, 15.73. Found: C, 51.13; H, 5.36; N, 15.61%. FTIR (KBr, cm^{-1}): 3400(s), 2985(m), 2935(m), 2056(s), 1615(s), 1595(s), 1540(m), 1315(m), 1233(w), 1137(m), 865(w), 759(s), 667(w). Λ_M (MeOH, Ω^{-1} cm^2 mol^{-1}): 6. Diamagnetic.

2.4. Crystal structure determination and refinement

For X-ray diffraction studies, suitable single crystals of **1** and **2** with dimensions of 0.06 × 0.04 × 0.04 and 0.12 × 0.08 × 0.08 mm^3, respectively were mounted on a Nonius Kappa and a Bruker-Nonius ApexII diffractometer, both equipped with CCD area detector and graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The reflection data were collected and processed using the Bruker-Nonius program suites COLLECT, DENZO-SMN and related analysis software [14–16]. The structures were solved by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-square refinements on F^2, using the program SHELX [17]. All non-hydrogen atoms have been refined with anisotropic displacement parameters. The hydrogen atoms were partially located from the difference Fourier maps, partially placed geometrically and refined keeping restrains (riding mode). Crystallographic data and refinement details for the compounds are summarized in Table 1.

2.5. Antibacterial activity – materials and methods

Complexes **1**, **2** and a reference commercial antibiotic viz. Gatifloxacin (purchased in powder form from Span Diagnostic Limited, Surat, India) were tested *in vitro* to assess their growth inhibitory activity against two Gram positive bacteria, viz. *Staphylococcus aureus* MTCC 2940 and *Bacillus subtilis* MTCC 441 and two Gram negative bacteria viz. *Pseudomonas aeruginosa* MTCC 2453 and *Escherichia coli* MTCC 739 by Kirby Bauer method with necessary modifications [18]. The antibacterial activities of propane-1,2-diamine, 2-hydroxyacetophenone and the derived Schiff base H_2L^2 were also evaluated during the same experiment. The bacterial strains grown on nutrient agar at 37 °C for 18 h were suspended in a saline solution (0.85% NaCl) and adjusted to a turbidity of 0.5 MacFarland standards (10^8 CFU mL^{-1}). The suspension was used to inoculate sterile Petri plates of 9.0 cm diameter in which the test organisms were grown. After solidification, a hole of diameter of 0.6 cm was pierced by a sterile cork borer. All the compounds and the antibiotic were dissolved in dimethylsulfoxide (DMSO) to prepare five different concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 mg mL^{-1}) for evaluation of dose response. The discs were placed on the holes of previously seeded plates and incubated at 303 K for *B. subtilis* and at 310 K for all other bacteria. Antibacterial activities of the compounds were evaluated by measuring the inhibition zone diameters (IZD). Each of the above experiments was repeated thrice along with a control set using DMSO and the mean value was taken for comparison.

3. Results and discussion

3.1. Synthesis

In the first attempt, the one-pot reaction of cobalt(II) perchlorate, propane-1,2-diamine, 2-hydroxyacetophenone and ammonium thiocyanate in the molar ratio of 1:1:2:1 in methanol yielded **1**, a mixed ligand mononuclear cobalt(III) complex. During its synthesis, a new tridentate Schiff base, HL^1 was formed in situ in which only one of the amine group of the diamine was involved. In an aim to get another complex containing the corresponding tetradentate Schiff base H_2L^2, we performed the same reaction using pre-condensed H_2L^2 instead of its constituents. But, we obtained the same complex **1** in the second attempt also. It is interesting to note that the tetradentate Schiff base H_2L^2 has undergone dissociation to form the tridentate one in the reaction medium. However, it is difficult to account for the higher stability gained by such a mononuclear Co(III) system in **1**. In contrast, no such ligand dissociation occurs in presence of azide ion and a binuclear phenoxo-bridged complex **2** was invariably formed unlike **1** in both the two syntheses. The complexes were prepared using cobalt(II) perchlorate as the starting material but in all the synthetic routes Co^{II}