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Synthesis and spectral characterization of alkaline earth metal complexes: Crystal structure of a Ca(II) hippuric acid complex

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ABSTRACT

Alkaline earth metal (Mg, Ca, Sr and Ba) complexes of hippuric acid (hipH) have been synthesized and characterized by elemental analyses and IR spectroscopy. One of the complexes, $[Ca(hip)_2(H_2O)_2]\cdot H_2O$, was characterized by single crystal X-ray diffraction studies. The polymeric structure is based on a dimeric unit and each calcium is coordinated to four hippurate anions and two coordinated water molecules. The hippurate anion functions as a bidentate ligand through the oxygen atoms of the carboxylate groups, one of which is bridging, forming a two dimensional coordination polymer. The water coordination is further confirmed by thermal analysis. The non-linear optical activity of the complexes was also measured.

1. Introduction

As compared to the reports of *d* block transition metal polymers, alkaline earth polymeric complexes are less common. There have been a few studies in recent years on the coordination chemistry of these metals in both aqueous media and non-aqueous media [1–5]. Magnesium and calcium are essential elements and it has been suggested that these elements were in fact involved with some of the earliest forms of life because of their important role in DNA and protein synthesis [6]. Barium and strontium metals have been known as antagonists for potassium and calcium, respectively [7].

Carboxylate containing ligands have attracted attention because of the diversity of the binding modes of the carboxylate group. Hippuric acid (hipH), N-benzoylglycine, (Fig. 1) is one of the important amino acids because it is synthesized in the liver as a metabolite of benzoic acid urinary excretion [8,9]. Moster et al. reported that the excretion of between 0.7 and 1.0 g of hippuric acid was suggestive of impaired liver function [10]. Hippuric acid was also identified as a constituent of the non-protein nitrogen fraction of milk [11]. Many natural amino acids, including benzoylglycine, individually exhibit non-linear optical properties because they have a donor NH_2 and acceptor COOH, and intermolecular charge transfer is also possible [12].

Hippuric acid is a monocarboxylic acid with three types of donor sites, the nitrogen and oxygen atoms of the amide group and the oxygen atoms of the carboxylic acid group. The literature reveals that hippuric acid is potentially capable of forming coordinate bonds with many metal ions through the carboxylic oxygen as a monodentate or a bidentate ligand [13–18]. The NH of the ligand coordinates to the central metal in some complexes [19,20]. The X-ray crystal structure of a Ba(II) complex of hippuric acid, $[Ba_2(C_9H_8NO_3)_4(H_2O)_3]$, indicated that the hippurate anion is coordinated to Ba(II) as a bidentate ligand via the two oxygen atoms of the carboxylic acid group after being deprotonated [21].

In this paper we report the synthesis and spectral studies of Mg, Ca, Sr and Ba complexes of hippuric acid, along with the crystal structure of the compound $[Ca(hip)_2(H_2O)_2]\cdot H_2O$.

2. Experimental

2.1. Materials

Hippuric acid (CDH), magnesium chloride, calcium chloride, strontium chloride and barium chloride (CDH) were of AR grade and were used without further purification. The solvents used were methanol, ammonium hydroxide and water.

2.2. Synthesis of the complexes

The complexes **1–4** have been synthesized starting from the respective metal chloride essentially by following a similar synthetic procedure. MCl_2 (5 mmol) and hippuric acid (10 mmol, 0.3 g) were dissolved in a water (15 ml) and methanol (30 ml) mixture, and the resulting solution was warmed to 50 °C for one hour.

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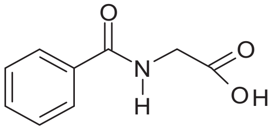

Fig. 1. Hippuric acid.

Aqueous NH_3 (25%) was added dropwise to this solution to obtain a pH of 9–10, and the resulting mixture was heated to 80 °C. The resulting turbid reaction mixture was filtered and allowed to stand at room temperature. After five or six days, the crystals obtained were separated and washed with methanol.

2.3. Physical measurements

Elemental analysis of the complexes was carried out on a Vario EL III CHNS analyzer; the IR spectra were recorded on a Thermo Nicolet Avtar 310 DTGS spectrometer (4000–400 cm^{-1}) in KBr pellets. The SHG efficiency of hippuric acid and the complexes was measured with respect to KDP by the powder technique developed by Kurtz and Perry [22] using a Quanta Ray Spectra Physics Model: Prolab 170 Nd: YAG 10 ns laser with a first harmonic output of 1064 nm at a pulse repetition rate of 10 Hz. The homogenous powder was tightly packed in a microcapillary tube and mounted in the path of the laser beam of pulse energy 6.85 mJ, obtained by the split beam technique. The thermogravimetric analysis (TG/DTG) was carried out in air with a heating rate of 10 °C/min, using a Perkin Elmer Diamond TG/DTA analyzer.

2.4. X-ray crystallography

Single crystals of the compound $[Ca(hip)_2(H_2O)_2]\cdot H_2O$ suitable for X-ray diffraction studies were grown from a solution of hippuric acid and calcium chloride in 25% ammonia solution by slow evaporation in air. A single crystal of dimensions 0.30 × 0.20 × 0.20 mm was selected and mounted on a Bruker axs Kappa apex 2 CCD diffractometer, equipped with a graphite crystal incident beam monochromator and a fine focus sealed tube Mo Kα ($\lambda = 0.71073$) X-ray source. The Smart [23] program was used for collecting frames of data, indexing the reflections and determination of lattice parameters, the Sadabs [24] program was used for absorption correction and the Shelxl [25] program for space group. The structure was solved by the direct method and refined by the full-matrix least-squares method on F^2, with all non-hydrogen atoms refined with anisotropic thermal parameters. All hydrogen atoms attached to carbon and nitrogen atoms were geometrically fixed at calculated positions and refined using the riding model, and the coordinated water hydrogen atoms were refined from Fourier maps. The lattice water O9 is disordered over two sites, with relative occupancies of 0.53 and 0.47 for the A and B components, respectively. Lattice water hydrogens could not be located in the difference Fourier map, probably due to the large thermal motion of the water molecule. The molecular graphics tools used were Platon [26] and Diamond Version 3.1f [27].

3. Results and discussion

The complexes $[Mg(hip)_2(H_2O)_2]\cdot(H_2O)_2$, $[Ca(hip)_2(H_2O)_2]\cdot H_2O$, $[Sr(hip)_2(H_2O)_2]\cdot H_2O$ and $[Ba(hip)_2(H_2O)_2]$, **1**–**4**, respectively, are formed by the reaction of hippuric acid with $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ by slow evaporation in air. The colors, elemental analyses and stoichiometries of the hippuric acid complexes are presented in Table 1. The complexes are readily soluble in water. All the complexes are found to be non-electrolytes. In all the complexes, hippuric acid deprotonates and coordinates to the metal ion as a bidentate ligand, as proven by the IR spectral data.

Table 1
Color, elemental analyses and stoichiometries of the hippuric acid complexes.

Compound	Color	Found (calculated) (%)		
		C	N	H
$[Mg(hip)_2(H_2O)_2]\cdot(H_2O)_2$ (**1**)	colorless	48.19 (47.73)	6.58 (6.19)	5.19 (5.30)
$[Ca(hip)_2(H_2O)_2]\cdot H_2O$ (**2**)	colorless	47.47 (47.96)	6.18 (6.2)	5.51 (4.88)
$[Sr(hip)_2(H_2O)_2]\cdot H_2O$ (**3**)	colorless	43.19 (43.38)	5.50 (5.56)	4.6 (4.42)
$[Ba(hip)_2(H_2O)_2]$ (**4**)	colorless	41.23 (40.78)	4.63 (3.77)	5.72 (5.28)

3.1. Infrared spectral studies

The tentative assignment for selected vibrational bands of the free ligand and their complexes, which are useful for determining the mode of coordination of the ligand, are given in Table 2.

A sharp band at 1744 cm^{-1} in hippuric acid can be attributed to the characteristic >C=O of the carboxylic acid group. Several bands in the region 2750–2478 cm^{-1} are characteristic peaks of OH of the COOH group [15]. These bands disappear in the complexes, indicating the coordination of the carboxylate group to the metal ion, by the deprotonation of carboxylic acid group. It is further supported by the appearance of two new bands at 1524 and 1429 cm^{-1} in complex **1**, assignable to ν_{as} and ν_s of COO^-. These bands are observed at 1533 and 1408 cm^{-1} in complex **2**, 1532 and 1404 cm^{-1} in complex **3** and 1524 and 1430 cm^{-1} in complex **4** [28].

The band at 3342 cm^{-1} due to ν_{NH} of hippuric acid appears at 3367, 3373, 3379 and 3399 cm^{-1} in complexes **1**–**4**, respectively. The shift in frequency is attributed to the weaker hydrogen bonding interactions in the complexes than in the ligand. The ν(M–O) band is observed at 557, 589, 590 and 586 cm^{-1} in the complexes **1**–**4**, respectively.

3.2. Crystal structure of the compound $[Ca(hip)_2(H_2O)_2]\cdot H_2O$ (2)

The molecular structure of the compound **2**, along with atom numbering scheme, is given in Fig. 2. The crystal data and structure refinement parameters are given in Table 3 and the selected bond lengths and bond angles of the molecule are summarized in Table 4. Compound **2** crystallizes in the monoclinic space group $P2_1/c$. The unit cell contains four molecules. The hippurate ion acts as a bidentate ligand.

The molecular structure of $[Ca(hip)_2(H_2O)_2]\cdot H_2O$, obtained from the single crystal X-ray diffraction studies, showed that the Ca(II) centre is octacoordinated with a distorted dodecahedral geometry. The bond parameter value shows that the geometry around Ca(II) is distorted significantly from a perfect dodecahedron [29]. Here two hippuric acid molecules deprotonate and coordinate to the Ca(II) centre as bidentate carboxylate groups. The fifth and sixth coordination positions are occupied by bridging oxygen atoms of hippurate ligands and the other coordination positions are satisfied by water molecules. The Ca(II) centre is coordinated to eight oxygen atoms O8b and O5a from two different hippurate ligands of adjacent complex units, O5, O8, O2 and O4 from two hippurate ligands and O6 and O7 from coordinated water molecules (Fig. 3). It results in the formation of an eight membered ring between adjacent calcium atoms. The Ca1 and Ca2 polyhedra are edge shared through O5 and O8b on one side and O5a, O8 on the other side, which creates two dimensional infinite polymeric chains, as schematized in Fig. 4. The Ca1–Ca2 non-bonding distance of 3.977 Å is close to those reported for binuclear complexes with a