An Infrared and Raman Spectroscopic Study of Pyrazinecadmium (II) Tetracyanometalate (II) Benzene (1/1) Clathrates: Cd(C₄H₄N₂)Cd(CN)₄·C₆H₆ and Cd(C₄H₄N₂)Hg(CN)₄·C₆H₆

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Abstract. Two new benzene clathrates of the form Cd(Pyrazine)M(CN)₄·C₆H₆, where M = Cd or Hg, have been prepared and their infrared and Raman spectra are reported.

Key words. Hofmann-Td-type benzene clathrate, Cd-pyrazine complex, benzene inclusion compound, IR and Raman spectra.

1. Introduction

It has been shown that the host frameworks of the Hofmann-Td-type clathrates appear to be excellent reservoirs for thermally unstable radicals such as the cyclohexadienyl, C₆H₇, radical [1, 2]. These compounds are formulated as Cd(II)₄L₂M(II)(CN)₄·nG, where L₂ is a bidentate ligand or a pair of unidentate ligand molecules, M is Cd or Hg and n is the number of G (guest) molecules depending on the bulkiness of the ligands. The host framework is formed from endless chains of —Cd—L₂—Cd— extending along the a and b axes alternately and the tetrahedral M(CN)₄ ions arranged between the consecutive crossing —Cd—L₂—Cd— chains with the N-ends bound to the Cd atoms [3–6]. This structure provides two kinds of cavities, α and β, for the guest molecules. The α cavity is a rectangular box similar to those in Hofmann-type hosts, while the β cavity is a twisted biprism, as has been demonstrated in previous papers [3–6]. The clathrate compounds possessing the Td-type of host lattice reported to date have been formed with the following ligands: ammonia, ethylenediamine, trimethylenediamine and propylenediamine [5, 7].

In our previous work we have reported the vibrational spectroscopic results of M'(pyz)Ni(CN)₄·nC₆H₆ clathrates (where M' = Ni or Cd, pyz = pyrazine, n = 0–0.5) [8], which are obtained by replacing the two NH₃ molecules between adjacent square planar tetracyanonickelate sheets in the Hofmann type clathrates, M'(NH₃)₂Ni(CN)₄·2C₆H₆, by a bidentate pyrazine ligand, in which the sheets are

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spread out in the form of a three-dimensional host structure. Now we have prepared pyrazinecadmium (II) tetracyanometalate (II) benzene (1/1), Cd(pyz) M(CN)₄ C₆H₆ (M = Cd or Hg, abbreviated to Cd-M-pyz-B), for the first time, using tetrahedral Cd(CN)₄ or Hg(CN)₄ ions instead of square planar Ni(CN)₄, with the aim of giving further examples of Td-type clathrates. In this study the IR and Raman spectroscopic results of Cd-Cd-pyz-B and Cd-Hg-pyz-B are reported.

2. Experimental

2.1. PREPARATIONS

All chemicals used were reagent grade (Merck) and used without further purifica-

2.1.1. Cd-Cd-pyz-B

The colourless crystals were prepared by a diffusion method in a U-tube as follows: a mixture of benzene and chloroform (1:20 v/v) was put into a U-tube to a depth of about two thirds of its height. One limb of the U-tube was filled with a solution of Cd(CN)₂ (2 mmol) in water (10 mL) saturated in benzene. The other limb was filled with a solution of pyrazine (1 mmol) in benzene (10 mL). The whole system of three phases was allowed to stand at room temperature for three weeks. Needle-like colourless crystals grown at the interface between the aqueous and organic phases were removed and washed on a sintered glass filter with a benzene solution of water and kept in a desiccator containing molecular sieve and a saturated benzene atmosphere.

2.1.2. Cd-Hg-pyz-B

The preparation of this clathrate was similar to the previous one using a solution of Cd(CN)₂ (1 mmol) and Hg(CN)₂ (1 mmol) in place of Cd(CN)₂ (2 mmol).

2.1.3. Analytical Results

The freshly prepared samples were analysed for metal content by an X-ray fluorescence method on a GE SPG-7 XRF spectrometer, with the results as follows (%): Calculated for Cd(C₄H₄N₂)Cd(CN)₄ C₆H₆: Cd, 46.16. Found: Cd, 46.20. Calculated for Cd(C₄H₄N₂)Hg(CN)₄ C₆H₆: Cd, 19.54; Hg, 34.88. Found: Cd, 19.60; Hg, 34.90.

2.2. SPECTRA

Infrared spectra of the compounds were recorded between 4000 and 300 cm⁻¹ on Perkin Elmer 1330 and Nicolet MX-IE spectrometers which were calibrated using polystyrene and CO₂ bands. The samples were prepared as mulls in nujol and hexachlorobutadiene between CsI plates.

The Raman spectra of the samples were excited using the 488.0 nm line of an Ar ion laser and recorded on a Cary 81 spectrometer with a slit width of 3.2 cm⁻¹ by use of a spinning cell.