Investigation of the Vibrational Spectra of Some Partially Deuterated $Cd(NH_3)_2Cl_2$, $Hg(NH_3)_2Cl_2$, $Pd(NH_3)_4Cl_2$ Complexes

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Due to the exchange of hydrogen by deuterium in ammonia, four types of isotopic species (NH_3, NH_2D, NHD_2, ND_3) are present in the structure of the investigated complexes. Since chemical isolation of the mixed isotopic parent is not possible, it is expected that in the IR spectra of partially deuterated analogues, bands would appear due to vibrations of all isotopic species. In order to obtain information on the bands due to vibrations of different types of isotopomeres of coordinated ammonia, the FT-IR spectra of a series partially deuterated $Cd(NH_3)_2Cl_2$, $Hg(NH_3)_2Cl_2$ and $Pd(NH_3)_4Cl_2$ complexes, were recorded and studied. The spectra were recorded in the region between 400 and 4000 cm^{-1}, at room temperature and at liquid nitrogen boiling temperature. The corresponding bands due to vibration of all isotopic species of coordinated ammonia were studied. The bends originating from the deformation NH_2D and NHD_2 vibrations appear in the region bellow 1600 cm^{-1} and the shifting towards lower frequencies varies with the different types of isotopomeres.

Along with the experimental studies, quantum chemical studies of several model systems mimicking the title complexes were also carried out. The B3LYP and mPW1PW91 density functional levels of theory were employed, with the 6-31++G(*d*,*p*) basic sets on all atoms except metal-atom, for which various effective core potentials were used. Theoretical studies included full geometry optimizations of the mentioned species, followed by subsequent harmonic vibrational analyses of all possible isotopomers. The shifting of the band due to different types of $(NH,D)_3$ groups towards low frequencies is in good agreement with the theoretical predictions, but it is different for different types of isotopic species.