The ligand N,N'-dimethylurea (DMU) is used to propagate the octahedral coordination geometry of \([\text{Co(DMU)}_6]^{2+}\) into 1D and 2D assemblies via a combination of coordinative bonds and interionic hydrogen-bonding. Compounds \([\text{Co(DMU)}_6](\text{ClO}_4)_2\) (1), \([\text{Co(DMU)}_6](\text{BF}_4)_2\) (2) and \([\text{Co(DMU)}_6](\text{NO}_3)_2\) (3) have been prepared from the reactions of DMU and the appropriate hydrated cobalt(II) salts in EtOH, MeCN or Me_2CO (only for 1) in the presence of 2,2-dimethoxypropane. Crystal structure determinations demonstrate the existence of \([\text{Co(DMU)}_6]^{2+}\) cations and \(\text{ClO}_4^-, \text{BF}_4^-, \text{NO}_3^-\) counterions. The great stability of the \([\text{Co(DMU)}_6]^{2+}\) cation in the solid state is attributed to a pseudochelate effect which arises from the existence of strong intracationic N-H⋯O(DMU) hydrogen bonds. The \([\text{Co(DMU)}_6]^{2+}\) cations and counterions self-assemble to form a hydrogen-bonded 1D architecture in 1, and different 2D hydrogen-bonded networks in 2 and 3. The precise nature of the resulting supramolecular structure is influenced by the nature of the counterion. Two main motifs of intermolecular (interionic) hydrogen bonds have been observed: N-H⋯O(\(\text{ClO}_4^-, \text{NO}_3^-\)) or N-H⋯F(\(\text{BF}_4^-\)) and weak C-H⋯O(\(\text{NO}_3^-\)) hydrogen bonds. The complexes were also characterized by vibrational spectroscopy (IR, far-IR, low-frequency Raman). The spectroscopic data are discussed in terms of the nature of bonding and the known structures.

**Key words:** Cobalt(II)/N,N'-Dimethylurea Complexes, Hydrogen-Bonded Coordination Complexes, Vibrational Spectroscopy