The Hexakis(N,N'-dimethylurea)cobalt(II) Cation: A Flexible Building Block for the Construction of Hydrogen Bonded Networks

Giannis S. Papaefstathiou[a], Robby Keuleers[b], Constantinos J. Milios[a], Catherine P. Raptopoulou[c], Aris Terzis[c], Herman O. Desseyn[b], and Spyros P. Perlepes[a]

[a] Department of Chemistry, University of Patras, 26504 Patras, Greece
[b] Laboratorium Anorganische Scheikunde, Rijksuniversitair Centrum Antwerpen, Groenenborgerlaan 171, 2020 Antwerpen, Belgium
[c] Institute of Materials Science, NCSR "Demokritos", 15310 Aghia Paraskevi Attikis, Greece

Reprint requests to Prof. H. O. Desseyn, Fax: +32(0) 3 2180233
or to Prof. S. P. Perlepes, e-mail: perlepes@patreas.upatras.gr

Z. Naturforsch. **58b,** 74–84 (2003); received September 9, 2002

The ligand N,N'-dimethylurea (DMU) is used to propagate the octahedral coordination geometry of $[Co(DMU)_6]^{2+}$ into 1D and 2D assemblies *via* a combination of coordinative bonds and interionic hydrogen-bonding. Compounds $[Co(DMU)_6](ClO_4)_2$ (**1**), $[Co(DMU)_6](BF_4)_2$ (**2**) and $[Co(DMU)_6](NO_3)_2$ (**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 $[Co(DMU)_6]^{2+}$ cations and ClO_4^-, BF_4^- or NO_3^- counterions. The great stability of the $[Co(DMU)_6]^{2+}$ cation in the solid state is attributed to a *pseudo*chelate effect which arises from the existence of strong intracationic N-H···O(DMU) hydrogen bonds. The $[Co(DMU)_6]^{2+}$ 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(ClO_4^-, NO_3^-) or N-H···F(BF_4^-) and weak C-H···F(BF_4^-) or C-H···O(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