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Synthesis and structural characterization of potassium coordination polymers based on a copper-bis(dithiolato) complex: Role of coordinating solvents and counter cation

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We have synthesized two new potassium metal coordination polymers $\{[K(CH_3COCH_3)_3][Cu(btdt)_2]\}_n$ (**1**) and $\{[K(CH_3CN)_2][Cu(btdt)_2]\}_n$ (**2**) of diverse dimensionality based on a copper coordination complex $[Cu^{III}(btdt)_2]^{1-}$ ($\{btdt\}^{2-}$ = 2,1,3-benzenethiadiazole-5,6-dithiolate). Recrystallization of the dark brown solid, obtained from the reaction mixture of H_2btdt, KOH and $CuCl_2·2H_2O$ in MeOH, from the coordinating solvents acetone and acetonitrile results in the formation of 3-D and 2-D extended networks in compounds (**1**) and (**2**) respectively. The crystal structures of (**1**) and (**2**) have been discussed in comparison with those of recently reported sodium coordination polymers $\{[Na(CH_3OH)_4][Au(btdt)_2]\}_n$ (**3**), $[Na(DMF)_2][Au(btdt)_2]\}_n$ (**4**) and $\{[Na(CH_3CN)_2][Au(btdt)_2]\}_n$ (**5**). Compounds (**1**) and (**2**) have additionally been characterized by routine spectroscopy including elemental analyses.

Keywords: Coordination Chemistry, Coordination polymers, Metal-organic frameworks, Crystal structures, Counter cation, Coordinating solvents, Potassium, Copper

The design and synthesis of coordination polymers or metal-organic frameworks (MOFs), that involve careful selection of organic ligands with suitable functional groups and metal ions, have substantial interests for producing solid-functional materials.[1-7] These materials have applications in the areas of gas storage and non-linear optical, conducting and magnetic materials.[8-12] In this context, square-planar metal-dithiolene complexes have drawn considerable attention, because these coordination complexes have been used as building blocks for the construction of polymeric compounds, that have been used as conducting, magnetic and non-linear optical materials.[13-20] The coordination polymers are generally described in terms of structural diversity and diverse dimensionality, that are, in turn, greatly affected/ controlled by the choice of the ligands,[21-23] metal/ ligand ratios,[24-25] solvents[26-29] and counterions.[30] Among these factors, influence of solvents and counter ions are particularly interesting because simply the variations in solvents and counter ions in a particular synthesis results in a wide range of self-assembled structures.[26-30] However, influence of coordinating solvents and counterions on the coordination networks, based on a square-planar metal bis(dithiolene) complex, has not been explored. Also, potassium based coordination polymers associated with dithiolene complexes are very few in the literature.[31]

Recently, we have reported a systematic study of the solvent effects on the formation of crystalline coordination networks of diverse dimensionalities (from 1D to 3D) by employing different coordinating solvents such as MeOH, DMF and CH_3CN through their coordination to the sodium cation.[32] We also have demonstrated that the geometry of the central carbon of the crystallizing coordinating solvents plays an important role in directing the dimensionality of coordination polymers.[32] In the present study, in order to investigate the effect of counter cation, we have synthesized two new coordination polymers $\{[K(CH_3COCH_3)_3][Cu(btdt)_2]\}_n$ (**1**) and $\{[K(CH_3CN)_2][Cu(btdt)_2]\}_n$ (**2**) using potassium ion (K^+) as a counter cation. These compounds have been characterized unambiguously by single crystal X-ray crystallography, their spectral characterizations (IR, NMR and UV-vis) and elemental analyses.