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Synthesis and characterization structural of alkali cations (Li^+, Na^+, K^+, Rb^+, Cs^+) carboxylate-dithiocarbamate complexes of L-Proline

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ABSTRACT

The alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) carboxylate-dithiocarbamate complexes of *L*-proline have been prepared from the reaction of *L*-proline with carbon disulfide in the presence of two equivalents of the corresponding alkali metal hydroxide. The resulting compounds have been characterized by FAB^+ mass spectrometry, IR spectroscopy, NMR (^1H, ^{13}C) spectroscopy. The X-ray single crystal crystallography analysis of the complexes of K^+, Rb^+ and Cs^+ complexes showed that the coordination modes of dithiocarbamate and carboxylate groups to the alkali metal is modulated by the resonance effect, the ionic radius of the sulfur and oxygen atoms as well as the size, charge-density, and Lewis-acidity of the metal ions. In this way in the solid state polymeric structures in 2D for K^+ and Rb^+ complexes, and 3D in the case of Cs^+ are generated. The distances C···M, M···S1 and M···S2 suggest the existence of cation···π and van der Waals interactions that can be described as a η^3 coordination mode of the *dtc* group to the alkali metal ions.

1. Introduction

Non-covalent interactions with alkali metal ions are of importance for the biological function of specific enzymes and the selectivity of Na^+, K^+ and Ca^{2+} ion channels [1–6]. The alkali metals cations are able to form complexes with proteins, and in the biological systems they are involved in electrolyte balances, osmotic systems and on channels [7–9]. In addition metal cation-amino acid interactions are key components of the secondary structure and biological function of proteins, enzymes and macromolecular complexes [10]. The α-amino acids are utilized by the living cells as building blocks for peptides and proteins synthesis, and are thus fundamental to all life forms [11]. Proline belongs to the essential group of amino acids, and within them, is the only one with a secondary α-amino group, which can explain its basic character. Interactions of proline with alkali metals have been measured in gas phase by using electrospray ionization (ESI) [12].

A wider variety of coordination modes to main group metals cations are displayed by carboxylate-dithiocarbamate compounds, which are often synthesized by the reaction of amino acids with carbon disulphide in basic media [13–24]. Perhaps some of the most exciting applications of the above mentioned ligands are in the field of stabilization of metal nanoparticles and indeed, the syntheses of spherical and monodispersed gold nanoparticles (AuNPs) and the use of all of the 20 naturally occurring α-amino acids have been reported [25]. The carboxylate-dithiocarbamate derivative of proline has also been used in synthesis of organotin(IV) complexes and as chelating agent for Cu^{2+}, Pb^{2+}, Cd^{2+} ions [26,27]. Studies in the self-assembly of macrocycles, cavitands, and capsules of the dithiocarbamate-carboxylates derivatives from amino acids have also been reported [28]. To our knowledge, to date the L-prolinedithiocarbamic acid dipotassium salt [KS_2CNProK] is the only known alkali metal complex of the dithiocarbamate of proline, however its structure is not known.

The dithiocarbamates from α-amino acids with several metal

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