Research article
International Journal of Heterocyclic Chemistry, Vol. 8, No. 3, pp. 26-32 (Summer 2018)
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http://ijhc.iauahvaz.ac.ir

Consideration of C-H…O interaction in the heterocyclic organic-inorganic hybrid material: tri-prolinium12-phosphomolibdate heteropolyoxometalate

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Abstract – Crystallographic data analyses indicate that three types of prolinium cations, along with two types of hydrogen bonding, produce and stabilize the helical structure of triprolinium 12-phosphomolybdate. There are similarities between this organic-inorganic compound and peptides/proteins. The stronger "conventional" hydrogen bonds and the less common C-H…O attractions play critical roles in generating and stabilizing the DNA-like network.

Keywords: Proline, Hydrogen Bonding, Polyoxometallates, Molybdenum, Hybrid, Keggin, Protein, Peptide.

INTRODUCTION

Organic-inorganic compounds have generated much interest in the field of synthetically specialized materials. They exhibit remarkable characteristics in their electrical, magnetic and optical properties [1-4].

It is generally known that organic molecules, such as amino acids, have been extensively used as charge-compensating cations in the synthesis of polyoxometalate-based hybrids. A large number of such hybrids have been prepared during recent years [5-7]. The results obtained from crystallographic data of these compounds show that the final products become highly stable due to extensive hydrogen bonding between polyoxometalates (POMs for short) and amino acids. Recently, we have synthesized a new amino acid-POM hybrid, $(C_5H_{10}NO_2)_3PMo_{12}O_{40}.4.5H_2O$,

that contains a combination of electrostatic forces and hydrogen bonding, rendering it stable in the solid and solution states [3]. Proline (Pro for short) is the only amino acid with an aliphatic ring that comprises both the "main" and the "side-chain" in proteins. Pro is also unique because, once it forms a peptide bond, it no longer possesses a covalently bonded hydrogen. Consequently, it is not expected to occur in an α-helix or in a β-strand of proteins [8]. Nevertheless, Pro is found in the middle of α-helices. This has been explained by the existence of a non-conventional C–H· · ·O hydrogen bond involving the ring C–H groups. It is interesting that the above mentioned characteristic, normally found in naturally occurring systems, has been observed in an "artificial" (synthesized) compound [9].

The aim of this paper is an investigation of Pro's non-covalent interactions in the DNA-like organic-inorganic compound and its comparison with the proteins/ peptides containing Pro in natural systems.

RESULT AND DISCUSSION

We know that POMs in general, and the Keggin type PMO used in this research, are polyanions with their negative charge randomly distributed around the "cage" of the cluster. This random distribution of the negative charge limits our ability to predict the topography attainable upon electrostatic interaction between POMs and the three Pro cations. We are investigating the functional conformation of prolines in the title compound and have labeled three "types" of Pro as A, B and C structures, shown in Fig.1. We can see that C and B- Pros are directly connected to each other by weak hydrogen bonding [$O_{(1C)}$ · · ·$O_{(1B)}$ 2.919 Å] and do not have any interactions with the A- Pro. Furthermore, the $O_{(2S)}$ of water molecules bridges them by strong hydrogen bonding (Fig. 2). An interesting feature is the similarity of this crystal structure with that of proteins and peptides. The triple attachment of Pros with each other in the overall network occurs (we neglect the POMs here) by C-H· · ·O bonds. The importance of C-H…O interactions, as a stabilizing feature in crystals, was recognized almost four decades ago [10]. The existence of C-H…O hydrogen bonds in collagen was considered in early structural studies [11] with firm experimental evidence appearing much later [12]. Several recent studies have emphasized the role of weak C-H…O interactions in organic and biological molecules [13-17]. We also observe that, along the z-axis of Fig. 3, this C-H· · ·O interactions cause Pros to take up spatial lattice positions similar to DNA (zigzag chains). It is generally achieved (see Fig. 4) by strands of Pros

having no direct interaction with each other. They are "bridged" by oxygen atoms that are not part of the Pro molecules.

In proteins, there are many C-H…O interactions of $^{\alpha}$C-H and $^{\gamma}$C-H that play an important role in the formation of the protein structures. The Pros in the title compound have several interactions that may be categorized according to the distances of the proline carbon and the nearest "hydrogen bonded" oxygen of the neighboring species (Table1). These data indicate that the B-Pro, in our organic-inorganic compound, acts in the same way as does proline in proteins. In both cases proline is engaged in "hydrogen bonding" interaction with $^{\alpha}$C-H and $^{\gamma}$C-H. This evidence may be attributed to the interaction of NH_2^+ and one of the terminal oxygens (O_t) of the POM, rendering carbon-bonded hydrogens somewhat acidic. Also, it is clear that in A and C-Pros $^{\alpha}$C-H and $^{\gamma}$C-H show stronger hydrogen bonding interaction as compared with the other carbon atoms. Furthermore, our results indicate that A and C-Pro have C-H· ·O interaction with the POM present in the unit cell. As demonstrated by Fig.5, these interactions occur between the $^{\alpha}$C-H of the A-Pro and the O_c of the POM, as well as between the $^{\delta}$C-H of the C-Pro and the O_b & O_t of the POM. However, the B-Pro is different because of the strong interaction between NH_2^+ and O_t of the POM. Fig.6 illustrates the over-all configuration down the C- axis.

The alternating positions of the B-Pros, on the two sides of the symmetry plane, play an essential role in the stability of the crystal structure (Fig. 7). There is some degree of noncovalent overlap between neighboring POMs (with a distance of 2.814 Å between their terminal oxygens) which might be partly brought about by the protonated amine group of the B-Pro (Fig. 8). This type of spacing is not observed between two pure POM acids. Therefor, one might conclude that amino acids in general and proline in particular, may have a stabilizing effect on the lattice.

CONCLUSION

The results of our research on $(C_5H_{10}NO_2)_3PMo_{12}O_{40}.4.5H_2O$, along with careful structural data analysis, lead us to the conclusion that the presence of Pro plays an important role in generating and stabilizing the over-all helical network.

The importance of C–H…O interactions in molecular recognition, in particular the binding of Pro-containing proteins/peptides to other protein molecules, and the similarity of our DNA-like hybrid compound to protein strands, render these studies important. It could potentially lead to

pathways for selective syntheses of bio-inorganic compounds and a clearer understanding of their crystal growth.

Enantiomeric purity and, hence, retention of optical activity in the Pro-POM compound is probably due to the presence of the proline ring. Our more recent research (yet to be published) indicates that Leucine-POM network contains both enantiomers in a racemic mixture.

Acknowledgment

We thank Prof. K. Travis Holman for providing X-ray Data [3].

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Table1. Average distance (Å) and number of C-H…O interactions for each proline and C-H bond

Interactions	C^{α}-H…O	C^{β}-H…O	C^{γ}-H…O	C^{δ}-H…O
Pro-A	2.502/2	2.696/2	2.558/2	0
Pro-B	2.692/3	0	2.704/3	2.719/2
Pro-C	2.635/2	2.703/1	2.526/3	2.686/1

Figures

Fig. 1

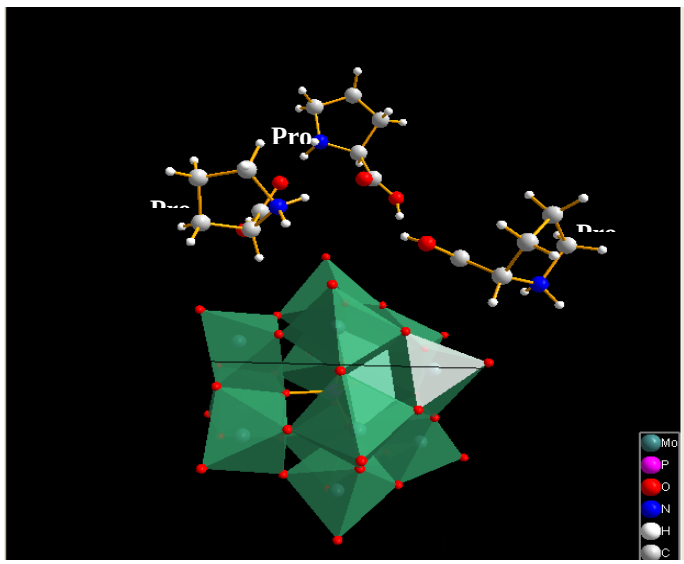

Fig. 2

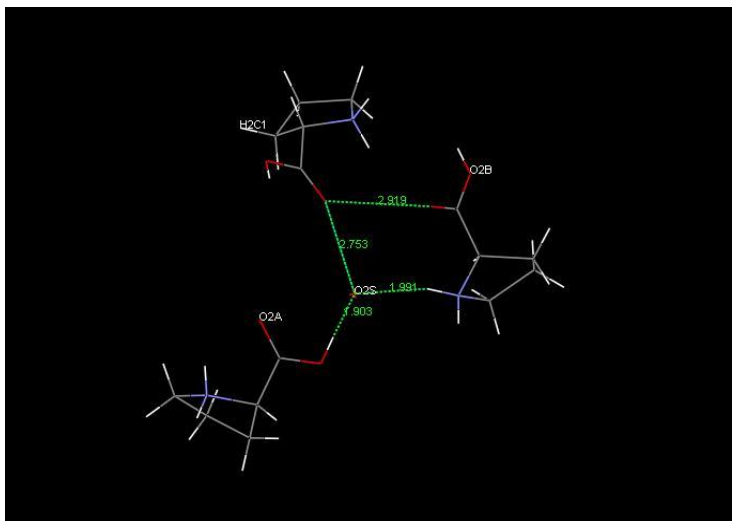

Fig. 3

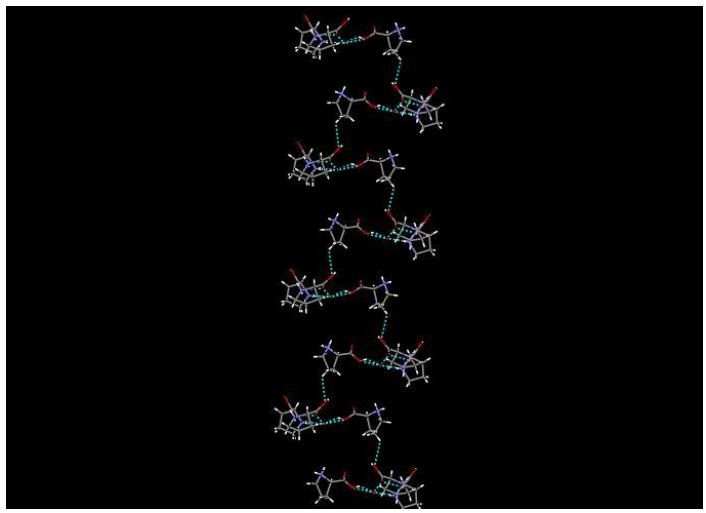

Fig. 4

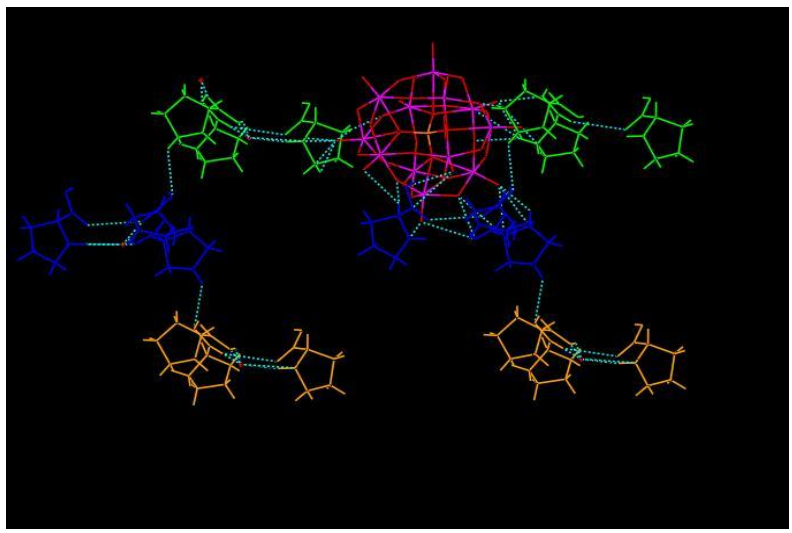

Fig. 5

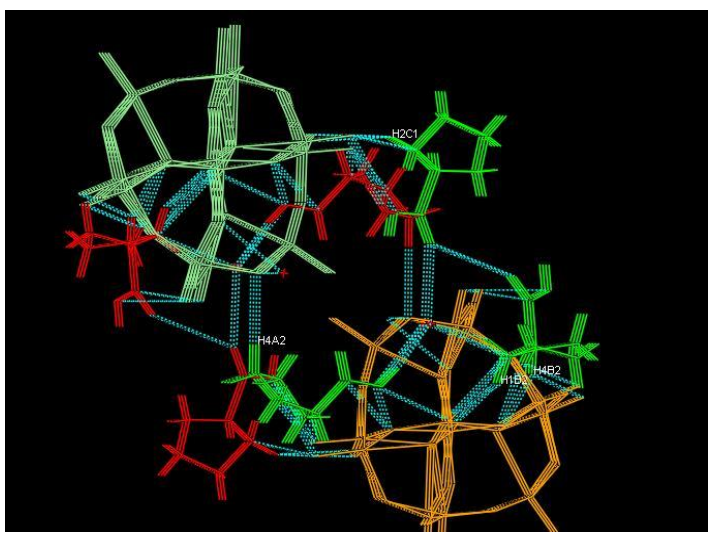

Fig. 6

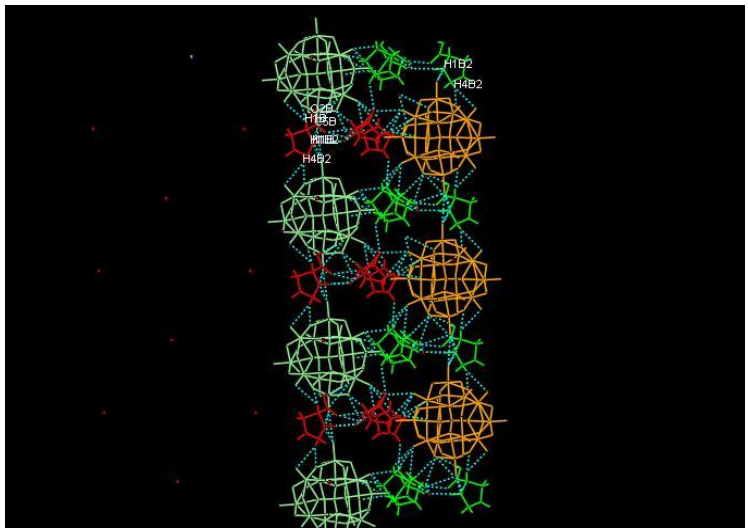

Fig. 7

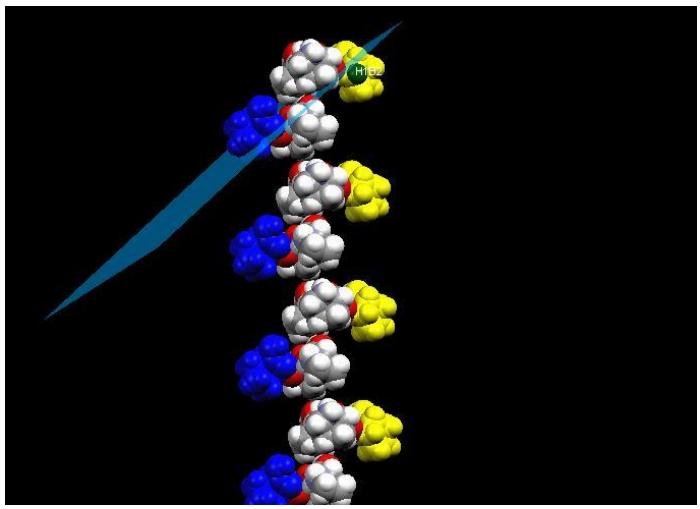

Fig. 8