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An Unusual Reaction of Adenine and Adenosine on Montmorillonite

A New Way of Prebiotic Synthesis of Some Purine Nucleosides?

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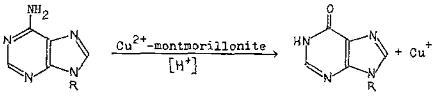
Nucleosides are one of the classes of compounds which are fundamental to life on Earth. One of the most important results of prebiotic synthesis is the formation of adenine from HCN. Adenine can be formally regarded as a pentamer of HCN. It is tempting to consider clays as possible chemical microreactors in prebiotic syntheses. The working hypothesis is that montmorillonites could have served as supports and as catalysts for the emergence of the first biomolecules. The adsorption of biomolecules is a key step in these reactions, but there are so far no reports of direct observation of a conversion of nucleosides during their adsorption on montmorillonite. Here, a conversion of adenine and adenosine into hypoxanthine and inosine catalyzed by Cu^{2+}-montmorillonite at room temperature is described.

Native montmorillonite (Jelšový Potok) as well as other metal-doped montmorillonites were obtained from H. Slosiariková. Montmorillonite (1 g) was dispersed in 300 ml of water. To this suspension was added 50 ml of water containing 1 mmol of biomolecule(s) and 1 ml of conc. HCl under vigorous stirring at room temperature. After adsorption the product was isolated by filtration, washed with H_2O, dried under an infra-lamp and pulverized to give a montmorillonite-biomolecule(s) complex. Among the ions of Mg, Ca, Mn, Co, Zn, Fe, and Cu, only copper was found to be active under these conditions.

The Cu^{2+}-montmorillonite has been found to have catalytic activity for conversion of adenosine to inosine and adenine to hypoxanthine:



R = H, adenine or hypoxanthine
R = D-ribose, adenosine or inosine

Hypoxanthine and inosine gave spectroscopic data in accord with their authentic standards and the catalog spectra [1]. Figure 1 shows the KBr infrared spectra in the region of 1800 – 1300 cm^{-1} of the Cu^{2+}-montmorillonite and its complexes with studied biomolecules. From comparison with the catalog spectra and the spectra of the authentic standards, the bands at 1695 and 1700 cm^{-1} were assigned to the $C_6{=}O$ stretching vibrations of inosine (Fig. 1b) and hypoxanthine (Fig. 1c, d), while the band at 1670 cm^{-1} was attributed to C_6-NH_2 bending bond of adenosine and adenine. On attaching the nucleoside or nucleobase to the montmorillonite, the intensities of surface OH groups (δOH = 1625 cm^{-1}) decreased. Simultaneously, the band at 1670 cm^{-1} completely vanished after 24 h adsorption and new peaks at 1695 or 1700 cm^{-1} developed. This behavior is entirely different from usual Cu^{2+}-nucleoside chemistry in which the adenosine and adenine act as a monodentate ligand and no oxidation occurs in the pH range of 0 – 14.

This unusual behavior is also supported by EPR experiments (Fig. 2). In the first derivative EPR spectrum of the Cu^{2+}-montmorillonite (Fig. 2A, *a*), four hyperfine lines were resolved on the low-field side while on the high-field side a single strong band results. The spectroscopic splitting factors calculated from the spectrum are $g_\parallel$ = 2.365 and $g_\perp$ = 2.088 with a hyperfine constant $A_\parallel$ of −0.0153 cm^{-1}. EPR spectra in Fig. 2B are closely similar. Differences between these data and the *g* factors measured for solutions of Cu^{2+} complexes [2,3] are attributed to

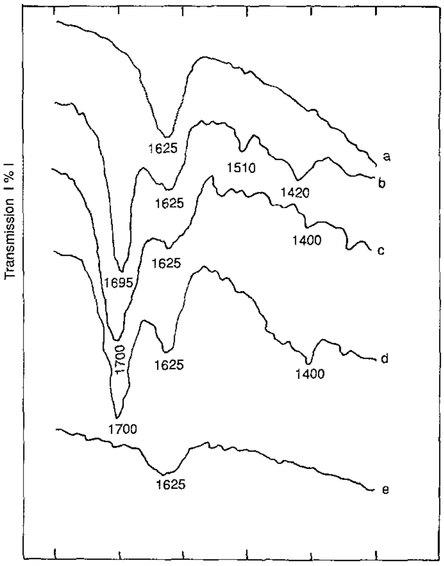


Fig. 1. Infrared spectra for (*a*) Cu^{2+}-montmorillonite and its complexes with (*b*) adenosine, (*c*) hypoxanthine, (*d*) adenine, and (*e*) D-ribose after 24 h adsorption

the environmental effect of the silicate lattice. For solution of corresponding Cu^{2+} complexes both the g factors and $A_{\|}$ values are typical of tetragonal Cu^{2+} complexes with weak axial perturbation [2,3]. It was found [4] that the exchangeable Cu^{2+} ion in montmorillonite is coordinated by four H_2O molecules in a plane parallel to the three layers and by two oxygen atoms belonging to upper and lower tetrahedron chains. Thus, the coordinated copper polyhedron present in the interlayer region is a deformed tetrahedral pyramid in shape. This fact is also supported by the quotient $f = g_{\|}/A_{\|}$ [5] which may be a convenient empirical index of tetrahedral distortion [3,5]. In the case of complexes, spectra of which are depicted in Fig. 2, this quotient ranges from 151 to 162 cm^{-1}. Examples of what are deduced to be rather more flattened tetrahedra are provided by the coordination sphere of Cu^{2+}.

This distorted tetrahedral coordination may be a main reason for unusual oxidative conversion of adenosine to inosine. For usual solution Cu^{2+}-nucleoside chemistry, in the case of adenosine the metal-binding site is N_7 and in each instance the exocyclic NH_2 on the adenine framework is involved in an interligand hydrogen bond with an acceptor group on another ligand in the coordination sphere, i.e., chelation is indirect [6]. These tetragonal D_{4h} Cu^{2+} complexes are relatively stable while for distorted tetrahedral Cu^{2+} complexes the tendency to reduce Cu^{2+} → Cu^{+} is more pronounced. From Fig. 2B it is obvious that no conversion occurs during the adsorption of hypoxanthine and D-ribose.

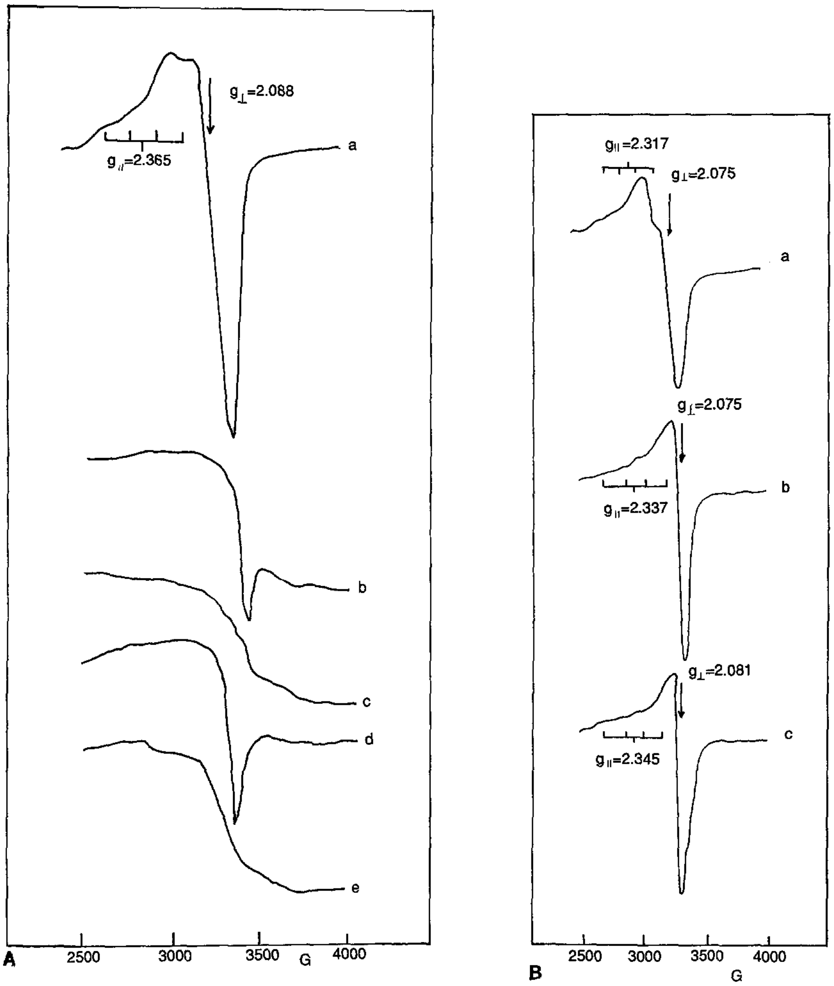


Fig. 2. EPR spectra A) of (*a*) Cu^{2+}-montmorillonite and its complexes with (*b*) adenine after 1 h and (*c*) 24 h adsorption, (*d*) adenosine and (*e*) adenosine and GlyGly after 1 h adsorption at room temperature, B) of (*a*) hypoxanthine, (*b*) D-ribose after 24 h adsorption, and (*c*) GlyGly after 1 h adsorption on Cu^{2+}-montmorillonite at room temperature

One of the most significant results with all investigated complexes is that peptides or amino acids are effective activators in the Cu^{2+}-montmorillonite-catalyzed conversion of purine compounds. When a simple binary Cu^{2+}-adenosine complex is formed, the oxidative deamination of adenosine to inosine is completed after 24 h, whereas formation of mixed-ligand complexes between peptide or amino acid, adenosine or adenine, and Cu^{2+} dramatically accelerate this conversion which is completed after 1 h adsorption (Fig. 2A, *e*).

Yields presented here lead to new aspects for possible prebiotic nucleobase syntheses based on Cu^{2+}-montmorillonite which could have served as a prototypical enzyme "purine deaminase".

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