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## Adenine Ribbon with Watson–Crick and Hoogsteen Motifs as the “Double-Sided Adhesive Tape” in the Supramolecular Structure of Adenine and Metal Carboxylate

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Hydrogen-bonding and stacking interactions are essential in determining the equilibrium conformations in biological macromolecules.<sup>1</sup> In coordination chemistry this type of interaction can lead to supramolecular formation, especially in mixed ligand complexes.<sup>2</sup> The study of supramolecular systems emerging above the traditional frontiers of science, is important in chemistry, biology, and medicinal and material sciences, and enables the development of the new areas of experimental and theoretical works.<sup>3</sup>

Adenine and its derivatives form a large family of biological compounds offering a variety of hydrogen-bonding functional groups.<sup>4</sup> The two most often occurring types of hydrogen bonding involving adenine are: Watson–Crick interaction, observed in DNA,<sup>5</sup> and Hoogsteen bonding, dominating in the complexes of adenine with Rebek imides.<sup>6</sup>

There is an extremely large number of reports devoted to both the theoretical and experimental studies of adenine; therefore, we will mention here only several recently published reports on diverse investigations concerning this compound.<sup>7</sup>

We have obtained by self-assembly the cocrystals of  $[M(\text{quin-2-c})_2(\text{H}_2\text{O})_2] \cdot 2\text{Ade}$  (where quin-2-c = quionline-2-carboxylate ion,  $M = \text{Mn}^{2+}$ (**1**),  $\text{Fe}^{2+}$ (**2**), and  $\text{Co}^{2+}$ (**3**)), in which the extensive systems of hydrogen bonds and  $\pi$ - $\pi$  interactions result in supramolecular structure. The striking feature of the structure of **1** is the fact that the adenine molecules form simultaneously the Watson–Crick and Hoogsteen types of hydrogen bonding in the crystal. It should be stressed that both the quionline-2-carboxylate ion and adenine molecule are planar and permit the  $\pi$ -stacking interactions.

The crystal of **1** is built of the complex molecules  $[\text{Mn}(\text{quin-2-c})_2(\text{H}_2\text{O})_2]$  (**4**) and ribbons of adenine (**5**).<sup>8</sup> Figure 1 shows the molecular structure of **1**, whereas Figure 2 illustrates the fragment of adenine ribbon. The molecular motif **4** has been already reported as an independent structure (**6**).<sup>9</sup> The geometries of **4** and **6** are in good agreement; the minor differences concern the coordination sphere and the hydrogen bond parameters. The Mn(II) ion in **4** and **6** is coordinated by four oxygen and two nitrogen atoms in pseudooctahedral geometry. In **4** and **6** the manganese ions together with water molecules are located within the thick, parallel layers and are connected by strong hydrogen bonds.<sup>10</sup> The distances between manganese ions in the layers are very similar in **4** and in **6** and are close to 7 Å.

The adenine ribbons found in the crystal of **1** are formed of hydrogen-bonded nucleobase molecules in AA2<sup>2</sup> configuration.<sup>4</sup> Both Watson–Crick and Hoogsteen faces<sup>4</sup> of adenine are involved in the hydrogen-bonding system within the ribbon. It should be emphasized that the ribbon or layer arrangements of nucleobase pairs are common;<sup>4</sup> however, the ribbons consisting solely of

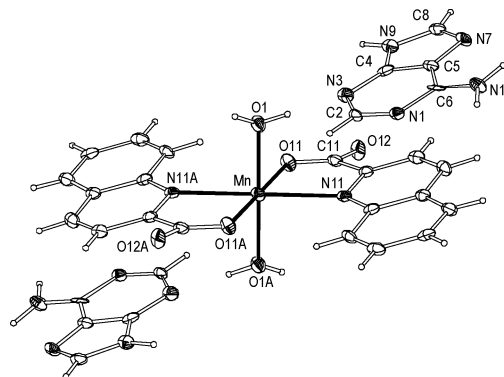


Figure 1. Molecular diagram of **1**.

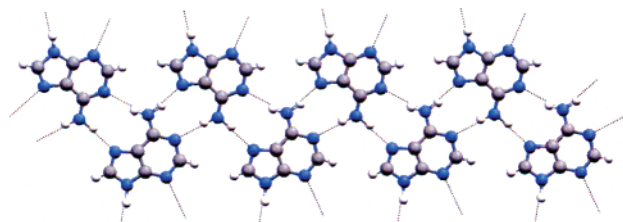


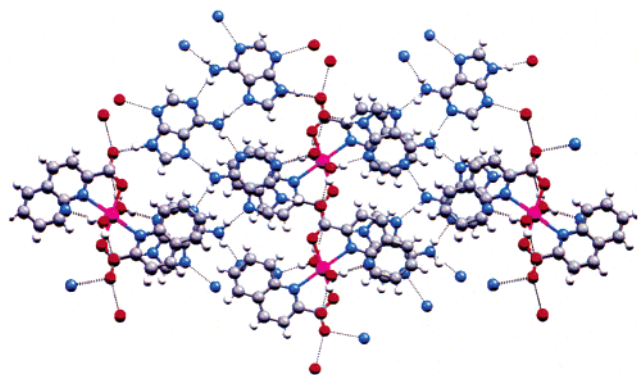
Figure 2. Adenine ribbon, view along the *a* axis.

adenine molecules have not yet been observed. A similar pattern of ribbon structure has been found in the crystal of 9-methyladenine.<sup>11</sup> The same spatial arrangement of the adenine molecules was also used as the model for adenine bilayers deposited on graphite surfaces, studied by scanning tunneling microscopy,<sup>12</sup> and for adenine aggregates formed on Cu, examined by the RAIRS method.<sup>13</sup>

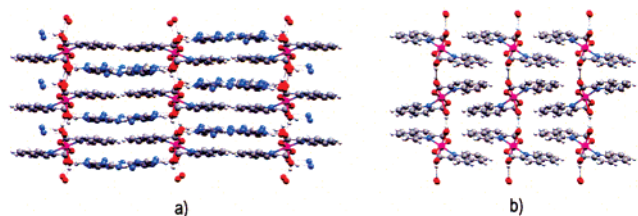
The Watson–Crick distance in **5** equals 2.985(6) Å and is in the normal range,<sup>4</sup> whereas the Hoogsteen contact in **5** is slightly longer than typical, and equals 3.061(5) Å.

The layers containing manganese and the ribbons of adenine are connected together by strong hydrogen bonds, Figure 3. Each adenine molecule acts as a donor (N9H9) and as an acceptor (N3) in the interaction with the atoms from the coordination sphere of manganese.<sup>10</sup> The ribbons **5** are perpendicular to manganese layers. It is also interesting to note the weak intramolecular C–H···O interactions in **4**, which stabilize the equatorial plane comprising 15 atoms.<sup>10</sup>

The second type of noncovalent forces stabilizing the crystal **1** are the face-to-face  $\pi$ - $\pi$  interactions between the planar heterocycles of adenine and quionline-2-carboxylate. The stacks formed along the *a* axis by the alternately packed **5** and quionline rings fill the space between the manganese layers, creating the wide organic layers. The area of interaction is very large, and the shortest



**Figure 3.** Adenine ribbon connected with **4** and overlapping of quinoline and adenine rings in stacks.



**Figure 4.** Packing of the crystals of **1** (a) and of **6** (b).

contacts are lower than 3.32 Å. It should be noted that a face-to-face alignment of the rings is very rare.<sup>14,15</sup>

The wide organic layer can be described as an infinite wall built of bricks (the quinoline rings) tightly joined by the “double-sided adhesive tapes” (adenine ribbons). Very close packing in the crystal of **1** is reflected by the relatively high density of **1** (1.625 g/cm<sup>3</sup>) vs that of **6** (1.527 g/cm<sup>3</sup>).

The organization of the crystals of **1** and **6** is very similar, Figure 4 a and b. The structure **6** can be regarded as the host which after filling by the guest **5** changes only in one dimension and in which the distance between layers containing manganese doubles.

In the IR spectrum of **1**, in the region 3000–1600 cm<sup>-1</sup> there are two very broad bands. The first band, located between 3000 and 2500 cm<sup>-1</sup> is very strong, whereas the second band centered at 1900 cm<sup>-1</sup> has the medium intensity. These bands can be assigned to the stretching vibrations of the hydrogen-bonded N–H and O–H groups. It should be noted that in the IR spectrum of adenine several strong, well-resolved bands are observed in the frequency region 3200–2500 cm<sup>-1</sup>, and no absorption is found near 1900 cm<sup>-1</sup>. The occurrence of a broad complicated bands below 3000 cm<sup>-1</sup> is characteristic for the systems containing conjugated hydrogen bonds and indicates a large proton polarizability.<sup>16,17</sup> Hydrogen-bonded chains show particularly large proton polarizabilities due to the collective proton motion and may allow for the directed long-range transport of protons.<sup>18</sup>

In conclusion, the supramolecular structure of **1** has been created by three types of molecular recognition: (a) between adenine molecules, (b) between molecules of **4**, and (c) between ribbons **5** and layers consisting of **4**. The first interaction, between the base molecules results in the double-faced hydrogen-bonding recognition

unit and leads to the ribbon form, **5**. Molecules of **4** collected within the parallel layers are joined by hydrogen bonds. Finally, the multiple stacking interactions between heterocycles are accompanied by the third group of hydrogen bonds, which complete the very effective set of weak interactions and build the closely packed structure. Efforts to study the presented compounds by experimental and theoretical methods are being undertaken.

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**Supporting Information Available:** Synthetic procedures and spectroscopic and analytical data as well as hydrogen-bonding parameters; X-ray crystallographic file for **1** in CIF format. This material is available free of charge via Internet at <http://pubs.acs.org>.

## References

- (1) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1211–1250.
- (2) Lehn, J.-M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 89–112.
- (3) Holliday, B. J.; Mirkin, Ch. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2023–2043.
- (4) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1994.
- (5) Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 737–738.
- (6) Castellano, R. K.; Gramlich, V.; Diederich, F. *Chem. Eur. J.* **2002**, *8*, 118–129.
- (7) (a) Watanabe, S.; Yoshimi, Y.; Ikekita, M. *J. Neurosci. Res.* **2003**, 754–759. (b) Honma, Y. *Drug Dev. Res.* **2003**, *59*, 14–22. (c) Ichimura, T.; Hayazawa, N.; Hashimoto, M.; Inouye, Y.; Kawata, S. *J. Raman Spectrosc.* **2003**, *34*, 651–654. (d) Kejnovská, I.; Kypr, J.; Vorlíková, M. *Electroanalysis* **2003**, *15*, 584–592. (e) Rowan, S. J.; Suwanmala, P.; Sivakova, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3589–3596. (f) Plützer, Chr.; Hünig, I.; Kleinermans, K. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1158–1163. (g) El Amri, Ch.; Baron, M.-H.; Maurel, M.-Ch. *Spectrochim. Acta A* **2003**, *59*, 2645–2654. (h) Srivatsan, S. G.; Parvez, M.; Verma, S. *J. Inorg. Biochem.* **2003**, *97*, 340–349.
- (8) Crystal data for **1**: monoclinic,  $P2_1/n$ ,  $a = 7.161(2)$  Å,  $b = 28.055(6)$  Å,  $c = 7.651(2)$  Å,  $\beta = 110.3(1)^\circ$ ,  $T = 100(1)$  K,  $V = 1441.6(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $\mu = 0.529$  mm<sup>-1</sup>. scan type  $\omega$ -2 $\theta$ , 1853 measured, 1767 independent [ $R_{int} = 0.0355$ ], 1320 observed [ $I > 2\sigma(I)$ ], 243 parameters;  $R1 = 0.0454$ ,  $wR2 = 0.1310$ . Preliminary examination and intensities data collections were carried out on a KUMA KM4  $\kappa$ -axis diffractometer with graphite-monochromated Mo K $\alpha$  and with scintillation. Data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELXTL-NT v5.1 software. Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode. Other hydrogen atoms were located in a difference map and refined free. All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC-236871s contain the supplementary crystallographic data for this paper. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. [Fax: +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk].
- (9) Okabe, N.; Koizumi, M. *Acta Crystallogr.* **1997**, *C53*, 852–854.
- (10) See the Supporting Information for hydrogen-bonding data.
- (11) McMullan, R. K.; Benci, P.; Craven, B. M. *Acta Crystallogr.* **1980**, *B36*, 1424–1430.
- (12) Reiter, M. M.; Jamitzky, F.; Trixler, F.; Heckl, W. M. *Phys. Status Solidi A* **2001**, *187*, 171–176.
- (13) McNutt, Haq, S.; Raval, R. *Surf. Sci.* **2003**, *1531*, 131–144.
- (14) Janiak, Ch. *J. Chem. Soc., Dalton Trans.* **2000**, 3885–3896.
- (15) Faraoni, R.; Castellano, R. K.; Gramlich, V.; Diederich, F. *Chem. Commun.* **2004**, 370–371.
- (16) Zundel, G.; Eckert, M. *J. Mol. Struct.* **1989**, *200*, 73–92.
- (17) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.
- (18) Kumara Swamy, K. C.; Kumaraswamy, S.; Kommana, P. *J. Am. Chem. Soc.* **2001**, *123*, 12642–12649.

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