cis-isomer = 7.9, trans-isomer = 7.2, whereas for free inosine it is 9.0. The difference in acidity of isomers and in the stability of the Pt–Cl bond may be accounted for by the higher trans-effect of NH_3 compared with inosine.

Solutions of isomeric aquocomplexes [Pt(NH₃)₂- $[InoH_2O]^{2+}$ have been obtained by the action of AgNO₃ on isomeric triamines. The curves of potentiometric titration with an alkali of isomeric aquoions practically coincide and correspond to titration of the mixture of a strong acid (the first portion of the curve) and coordinated water (the second portion). The titration curve of the synthesized complex $[Pt(NH_3)_2Ino](NO_3)_2$ obtained in solid state by the action of inosine on the solution of cis-[Pt(NH₃)₂(H₂O)₂](NO₃)₂ is of the same type. Since the acidic properties of isomeric aquocomplexes and [Pt(NH₃)₂Ino](NO₃)₂ are similar it may be concluded that in the aqueous solutions of these compounds there are no complexes with inosine bidentate coordinated through N(7), O(6) atoms. At the first portion of the curve the strong acid is titrated, it being formed in solution due to partial polymerization of complexes according to the type:

$$-Pt - N(7) O(6) - Pt - N(7) O(6) - NH_3 NH_3 NH_3 NH_3 NH_3 NH_3 NH_3$$

1 B. Rosenberg, Biochim., 60, 859 (1978).

- 2 N. Hadjiliadis and T. Theophanides, *Inorg. Chim. Acta, 16*, 77 (1976).
- 3 P. C. Kong and T. Theophanides, *Inorg. Chem.*, 13, 1167 (1974).
- 4 G. V. Fazarkley and K. K. Koch, *Inorg. Chim. Acta*, 36, 13 (1979).
- 5 A. I. Stetsenko, E. S. Dmitrieva and K. I. Yakovlev, J. Clin. Hematol. Oncol., 7, 522 (1977).

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The Interplay of Hydrogen Bonding and Metal-Nucleic Acid Interactions

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Since hydrogen bonding plays a crucial role in the structure and function of nucleic acids and metal ions are involved in many biological processes involving nucleic acids, it is of interest to look at the interplay of these two features. The crystal structures of several metal complexes of nucleic acid components have been reported in the literature [1, 2] and they demonstrate such an interplay. This article briefly reviews this aspect. Metal ions can interact directly with the phosphate back bone (M-O-P-) and also through

water bridged interactions $(M-O-H\cdots O-P-)$; both types have been realised in the crystal structures of

nucleotides [2]. The interligand hydrogen bond is a common

feature in the metal complexes of purines [1, 2].

$N(6)-H\cdots X-M-N(7)$	in adenine X = H-bond
$N(6)-H\cdots X-M-N(1)$	acceptor
$\begin{array}{c} O(6) \cdots HX - M - N(7) \\ O(6) \cdots HX - M - N(1) \end{array}$	in guanine X = H-bond donor N(1) = deprotonated

The ability of $Rh_2(CH_3COO)_4$, an antitumor agent, to interact specifically with adenine and not with guanine has been attributed to its indirect chelation with the former but not with the latter [3]. A similar interligand hydrogen bond has been implicated in the mode of action of *cis*-Pt(amine)₂ [2]. A coordinated H_2O molecule can function as a H-bond acceptor and/or donor and consequently can participate in the complexes of guanine as well as adenine.

When M binds to N(7) of A, W.C. sites are available for base pairing and A:A pairing involving W.C. sites has been observed in some metal complexes [4]. In the crystal structure of $[(Pt(NH_3)_2(9-EtG)(1-MeC)]^{2+}[(Pt(NH_3)_2(9-EtG-H)(1-MeC)]^+(ClO_4)_3, coordination of Pt to N(7) (a non W.C. site) has changed the pK of the base from 9.8 to 8.2 facilitating deprotonation at N(1); the (G-G)⁻ pair exists in the crystal lattice rather than the (G-C) pair [5] (9-EtG-H = the deprotonated base).$

In certain metal complexes, protons are transferred to other sites on the bases by incoming metal ions [6] suggesting that the metal ion can alter the relative stability of different tautomers. Metal induced activation or deactivation of C-H protons in purines has been reported [7, 9]; this suggests that metal ions can also influence C-H···X types of interactions [8] commonly observed in the crystal structures of nucleobases. Metal ion-nucleic acid interaction vis-a-vis hydrogen bonding is emerging as a fascinating structural feature [7].

"I believe that as the methods of structural chemistry are further applied to physiological problems it will be found that the significance of the hydrogen bond for physiology is greater than that of any other single structural feature." Linus Pauling [10].

- 1 D. J. Hodgson, Prog. Inorg. Chem., 23, 211 (1977).
- 2 R. W. Gellert and R. Bau, in 'Metal Ions in Biological Systems', H. Sigel (Ed.), Marcel Dekker, New York, 1979, Vol. 8, pp. 1-55.
- 3 N. Farrell, J. Inorg. Biochem., 14, 261 (1981).

- 4 E. Sletten and B. Thorstensen, Acta Crystallogr., B30, 2438 (1974); E. Sletten and M. Ruud, *ibid.*, B31, 982 (1975).
- 5 R. Faggiani, C. J. L. Lock and B. Lippert, J. Am. Chem. Soc., 102, 5418 (1980).
- 6 C. Gagnon, J. Hubert, R. Rivest and A. L. Beauchamp, Inorg. Chem., 16, 2469 (1977).
- 7 B. Lippert, J. Amer. Chem. Soc., 103, 5691 (1981).
 8 R. Taylor and O. Kennard, J. Am. Chem. Soc., 104, 5063 (1982).
- 9 J. R. Jones and S. E. Taylor, Chem. Soc. Rev., 3, 329 (1981).
- 10 L. Pauling, 'The Nature of the Chemical Bond', 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p. 450.