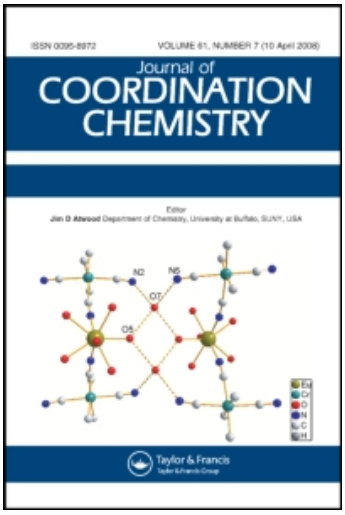

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# NOTE: INFRARED SPECTROSCOPIC STUDIES OF Cu(II) COMPLEXES OF PURINE AND PYRIMIDINE BASES IN $D_2O$ SOLUTION

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# NOTE:

# INFRARED SPECTROSCOPIC STUDIES OF Cu(II) COMPLEXES OF PURINE AND PYRIMIDINE BASES IN $D_2O$ SOLUTION

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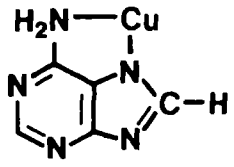
Studies of metal complexes of purine and pyrimidine bases and their derivatives have received considerable attention recently.[1-15] The present investigation aims to elucidate the proton ionization sites and metal ion binding sites in these ligands in aqueous solution from IR spectroscopic study of these systems in $D_2O$. The method employed consisted of the IR study of the ligands in pure $D_2O$ solution in the absence and presence of metal ion at a definite pD value. An Elico pH meter with a mini combination glass and calomel electrode was used to measure the pH of the solution. A Beckman model IR-12 spectrophotometer using a KRS-5 cell with a teflon spacing of 0.1 mm was used for all IR measurements.

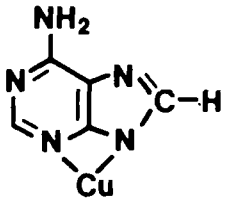
*Purines and their 1:1 Cu(II) Complexes.*

*Adenine:* IR spectra of adenine sulfate in $D_2O$ solution at different pD values (pD = 2, 4 and 10) show three prominent absorption bands at about 1470 $cm^{-1}$, 1670 $cm^{-1}$ and 3450 $cm^{-1}$ (Table I). The first two bands correspond to coupled C=C and C=N vibrations and the last one to N-H stretching vibrations. At pD = 10 the band at 1670 $cm^{-1}$ was shifted to about 1620 $cm^{-1}$ indicating that at higher pD values (pD = 9.5) the C=C or C=N double bond character of the purine system is partially lost in the monoionic species of adenine. The first and second deprotonation from adenine is from the $N_1H^+$ and $N_9$ groups, respectively. Regarding the mode of binding of Cu(II) to adenine, two chelate structures could be considered as shown in Scheme 1, a conclusion well supported by other studies.[10-12, 16-19]

Scheme 1




I




II

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In the IR spectra of the 1:1 Cu(II)-adenine complex in $D_2O$ at pD = 4, the absorption bands at 1470 $cm^{-1}$ and 3450 $cm^{-1}$ of adenine are shifted to lower frequencies by about 50 $cm^{-1}$ due to metal chelation (Table I). This equally favours both the above structures *I* and *II* for the Cu(II)-adenine chelate in solution, since in both the structures chelation would affect C=N, C=C and N-H stretching vibrations. However structure *I* is preferred over *II* since a strainless five membered chelate ring is formed in the former case (log K of Cu-adenine = 8.0[1]). A linear correlation between the basicity of various substituted purines and the corresponding stability of their 1:1 metal complexes[3] indirectly favours similar chelate structures for the metal complexes of all substituted purines.

*2, 6-Diaminopurine:* IR spectra of 2, 6-diaminopurine in $D_2O$ at different pD values (pD = 2, 4 and 10) show absorption bands at around 1470 $cm^{-1}$ and 3450 $cm^{-1}$, corresponding to the C=N and N-H stretching vibrations, and these were unchanged at all the pD values studied (Table I). The proton ionization sites in 2, 6-diaminopurine are considered to be the same as in adenine. However the presence of an extra amino group at position two[2] of the pyrimidine ring increases the overall basicity of 2, 6-diaminopurine.

In the presence of Cu(II) at pD = 4, both the above IR bands of 2, 6-diaminopurine were shifted to lower frequencies indicating that binding of Cu(II) involves both C=N and N-H groups (Table I). Three possible structures could be predicted for the Cu(II)-2, 6-diaminopurine chelate as shown in Scheme 2. IR spectra cannot clearly distinguish between the above structures. However, based on the higher stability of a 5-membered ring, structure *III* may be preferred for the Cu(II)-2, 6-diaminopurine chelate in solution. This conclusion is also supported by an earlier study.[1,2]

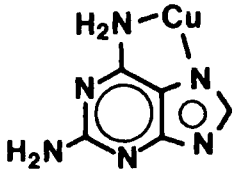
TABLE I

Infrared spectroscopic data for nucleic acid bases and their 1:1 complexes with Cu(II) in pure deuterium oxide solution ($D_2O$). $\mu$ = 0.2 M, concentration = $3 \times 10^{-3}$ to $5 \times 10^{-2}$ M

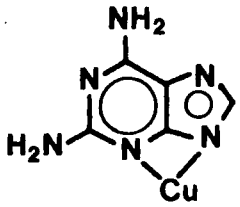
| Compound | IR bands[a] ($cm^{-1}$) | Assignment |
|---|---|---|
| adenine | 1470 s, 1670 m | coupled vibration of C=C and C=N |
| | 3450 s | N-H stretch |
| Cu(II)-adenine (pD = 4) | 1420 s | C=N |
| | 3400 s | N-H stretch |
| 2, 6-diaminopurine | 1470 s | C=N |
| | 3450 s | N-H stretch |
| Cu(II)-2, 6-diaminopurine (pD = 4) | 1420 s | C=N |
| | 3410 s | N-H stretch |
| uracil and thymine | 1470 s | C=N |
| | 1620 m | C=C |
| | 1645 s | C=O |
| | 3450 s | N-H stretch |
| Cu(II)-uracil and thymine (pD = 5.5) | 1470 s | C=N |
| | 1620 m | C=C |
| | 1645 s | C=O |
| | 3420 s | N-H stretch |
| cytosine | 1470 s | C=N |
| | 1670 s | C=O |
| | 3450 s | N-H stretch |
| Cu(II)-cytosine (pD = 4) | 1470 s | C=N |
| | 1670 s | C=O |
| | 3420 s | N-H stretch |

[a] s = strong, m = moderate

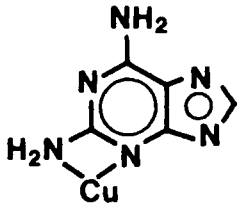
Scheme 2



III



IV



V

*Pyrimidines and their 1:1 Cu(II) Complexes*

*Uracil and Thymine:* IR spectra of uracil and thymine in $D_2O$ at various pD values (pD = 3, 7, 5 and 11) show absorption bands around 1470 $cm^{-1}$, 1620 $cm^{-1}$, 1645 $cm^{-1}$ and 3450 $cm^{-1}$ throughout (Table I). The first three bands correspond to coupled vibrations of C=N, C=C and C=O groups and the last one to N-H stretching vibrations. At pD = 11, the band at 1470 $cm^{-1}$ was unchanged in uracil but all other bands were shifted to lower frequency by about 40 $cm^{-1}$. This clearly indicates that the *keto*-character of both uracil and thymine is retained even at high pD values. The first deprotonation from neutral uracil and thymine is from the $N_3H$ group and the second ionization from the $N_1H$ group (pD > 12).

In the IR spectra of uracil and thymine in the presence of Cu(II) at pD = 5.5 only the band at 3450 $cm^{-1}$ shifted to a lower frequency (by about 30 $cm^{-1}$). Hence it is evident that the *keto*-group in both uracil and thymine is not involved in complexation with Cu(II) and the most probable site for Cu(II) coordination in these ligands is $N_3H$ group.[20]

*Cytosine:* IR spectra of cytosine in $D_2O$ at different pD values (pD = 2, 4 and 10) indicate absorption bands at about 1470 $cm^{-1}$, 1670 $cm^{-1}$ and 3450 $cm^{-1}$ corresponding to C=N, C=O and N-H stretching vibrations (Table I). At higher pD values (pD > 10) the C=O band at 1670 $cm^{-1}$ almost vanishes indicating the disappearance of the *keto*-character of cytosine. The first deprotonation from protonated cytosine is from the $N_3H^+$ group (a fact well supported by other investigators[17-19,21-24]) and the second ionization from neutral cytosine is from the $N_1H$ group.[25,28,29] The IR spectrum of cytosine in the presence of Cu(II) at pD = 4 showed only the band at 3450 $cm^{-1}$ shifted (to about 3420 $cm^{-1}$). Hence the C=O group of cytosine is not involved in complexation with Cu(II). Further, the involvement of the $C_4NH_2$ group in the binding of Cu(II) to cytosine is not probable as established by earlier workers.[20,29]

Hence from our present investigation we conclude that the $N_3H$ group of cytosine is the binding site of choice for Cu(II) in aqueous solution. This conclusion is well substantiated by previous investigations,[30] and cytosine thus acts essentially as a monodentate. An assumption is made in this study that the 1:1 mixture of Cu(II) and all the ligands investigated at pD = 4 contain fully complexed metal as was found in a preliminary equilibrium study. In general, the interaction of metal ions with pyrimidine bases is considerably weaker as compared with that of purines in aqueous solution. Strong evidence is obtained from the stability of the $Cu(II)^{1-3}$ complexes of these ligands. This is expected because in the case of purines metal chelation involving 4 or 5 membered ring systems is preferred, whereas pyrimidines mostly act as monodentates, the metal binding being effectively confined to the $N_3$ group.

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