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Complex Formation of Adenine–Uracil Base Pair with some Transition Metal Ions

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Abstract

Mixed complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ions with 6-aminopurine (adenine, ADN) and uracil (URL) were prepared from aqueous ethanol solution at pH about 7. The new complexes have the formulae $M_2(ADNURL)(OH)_2 \cdot H_2O$ for M = Mn(II), Zn(II), Cd(II) and $M_2(ADNURL)(OH)_4 \cdot 3H_2O$ for M = Co(II), Ni(II), Cu(II). The mixed complexes were characterized by elemental, infrared, electronic, ESR spectral and magnetic measurements. ADN behaves as a bidentate ligand. The probable binding sites of ADN are N_3 and N_7 nitrogens and of URL is C_2=O. Polymeric structures have been suggested with ADN and OH as the bridging ligands.

Introduction

The participation of RNA in protein synthesis was shown several years before it was observed that DNA is the genetic material. Several bivalent metal ions are involved in the biosynthesis of nucleic acids. Copper was identified in RNA in yeast [1] and in the tobacco mosaic virus. Transition metals may aid in keeping the configuration of RNA [2] and may act as an intermediate to keep proteins bound to RNA. The site of binding may be the purine or pyrimidine bases. Different potentially reactive sites are present in both the uracil (URL) and adenine (ADN) bases. Hence, it would be interesting to observe the simultaneous reactions of ADN and URL with some transition metal ions. Accordingly the present paper deals with the synthesis of the mixed complexes of some divalent metal ions [Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II)] with ADN and URL in aqueous ethanol medium and their characterization studies are made.

Experimental

Synthetic Method

All the reagents used were analytical grade. Metal nitrates are from E. Merck, ADN and URL used were from BDH and Loba chemie respectively.

ADN and URL in a molar ratio of 1:1 were refluxed in ethanol for 6 h till all the ligands dissolved. The resultant solution was mixed with hot metal nitrate solution in equimolar ratio. The pH of the solution was adjusted to about 7 by adding sodium hydroxide (0.01 M) with continuous stirring which resulted in the formation of precipitates [Mn(II), brown; Co(II), violet; Ni(II), light green; Cu(II), bluish green; Zn(II), white; Cd(II), white]. They were filtered and washed several times with absolute ethanol and finally with ether and dried in an oven at about 50 °C.

The metal ions were determined by dissolving the complexes in very dilute acids and titrating against EDTA [3]. Carbon, hydrogen and nitrogen were analysed by a Perkin-Elmer model 240C elemental analyzer. Infrared spectra were obtained on Nujol mulls using a Perkin-Elmer model 783 spectrophotometer covering the range 4000–200 cm^{-1}. Solid state (Nujol mull) electronic spectra were obtained with a Hitachi 320 spectrophotometer in the range 200–900 nm and variable temperature magnetic susceptibility measurements were done at TIFR, Bombay. The ESR spectra of the complexes in powdered form were recorded on an X-band Varian-11 ESR spectrometer using TCNE as a (*g*) marker.

Results and Discussion

The molar ratio of the new synthesized mixed complexes was 2:1:1 M:ADN:URL where M stands for metal ion. All the complexes are coloured except those of zinc and cadmium as reported in Table 1. They are insoluble in common organic solvents as well as in water except copper(II) and nickel(II) complexes which form hydroxide in water. The complexes do not melt upto 300 °C. Three molecules of aqua ligand are coordinated to the complexes of Co(II), Ni(II) and Cu(II) ions. This is also evident with the characteristic ν(OH) absorptions at 3500–3250 cm^{-1} corresponding to coordinated water molecules [4, 5]. Tentative ν(M–O) (aqua) bands have also been assigned. Mn(II), Zn(II) and Cd(II) also form hydrous complexes.

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TABLE 1. Analytical Data and Colour of the Complexes

Complex	Colour	M (%)		C (%)		H (%)		N (%)	
		Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
$Mn_2(OH)_2(ADN)(URL)\cdot H_2O$	brown	26.86	26.67	26.40	26.43	3.18	3.15	23.96	23.94
$Co_2(OH)_4(ADN)(URL)\cdot 3H_2O$	violet	24.20	24.25	22.18	22.15	3.90	3.94	20.12	20.16
$Ni_2(OH)_4(ADN)(URL)\cdot 3H_2O$	yellowish green	24.13	24.10	22.20	22.24	3.90	3.92	20.14	20.17
$Cu_2(OH)_4(ADN)(URL)\cdot 3H_2O$	bluish green	25.61	25.65	21.76	21.73	3.83	3.85	19.75	19.72
$Zn_2(OH)_2(ADN)(URL)\cdot H_2O$	white	30.42	30.39	25.12	25.15	3.02	3.06	22.80	22.83
$Cd_2(OH)_2(ADN)(URL)\cdot H_2O$	white	42.91	42.95	20.61	20.63	2.48	2.45	18.70	18.74

Due to the insolubility of the mixed complexes studies in solution could not be performed (e.g. molar conductivities, NMR etc.). It may be inferred from the insolubility of the mixed complexes in organic solvents that they are polymeric in nature.

Infrared Spectra

The infrared spectra of ADN [6] and URL [7] are reported in the literature. Some principal IR frequencies of the above two ligands and their corresponding tentative frequencies exhibited by their mixed complexes are given in Table 2.

Various possible sites of coordination of ADN [8, 9] and URL [10, 11] with metal ions are reported in the literature. But the hydrogen bond of the A–U pair will influence the coordination of the cations. Hence, in discussing the IR spectra of the complexes, the hydrogen bonding has also been taken into consideration.

The $\nu(NH_2)$ and $\delta(NH_2)$ bands (Table 2) of ADN shift towards the lower frequency side upon complex formation. Occurrence of these frequencies shift may be due to the hydrogen bond formation of the NH_2 group with the oxygen bonded to the C_4 position of the URL which is also evidenced from the lowering in carbonyl frequency of the 4-keto group of the complexes with respect to the free URL *i.e.* $HN_6{-}H\cdots O{=}C_4$ bonding. The ν_{N_1} frequencies

TABLE 2. Some Principal Infrared Spectral Data for Adenine, Uracil and its Mixed Ligand Complexes (cm^{-1})

Band assignment	ADN	URL	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
$\nu(NH_2)$	3358s, b		3315s	3340s	3318m	3320s	3325m	3324m
$\nu(NH_2)$, $2\delta(NH_2)$	3294s							
$\nu(C_8{-}H)$, $\nu(C_2{-}H)$, $\nu(NH_2)$	3118s		3196s	3200m	3195m	3195m	3195m	3200m
$\nu(N{-}H)$		3160m						
$\nu C_2{=}O$		1712s	1656s	1660s	1660s	1660s	1658s	1656s
$\delta(NH_2)$, $\nu(C_4{=}O)$, $\nu(C{=}C)$ in phase	1675s	1675s	1642s	1643s	1634s	1645s	1642s	1640s
			1650s	1652s	1645s	1645s	1650s	1650s
$\nu(C_4{-}C_5)$, $\nu(N_3{-}C_4{-}C_5)$	1560s		1550m	1545m	1578m	1570m	1578m	1510m
$\delta(N_{(1)}{-}H)$		1510m	1512m	1510w	1515w	1507m	1510w	1510w
$\delta(C_2{-}H) + \nu(C_8{-}N_9) + \delta(C_8{-}H)$	1449s		1454s	1456s	1456s	1456s	1456s	1452s
$\delta(N_1{-}C_6N_6)$	1420s		1402s	1400m	1400m	1405s	1413m	1402m
$\delta(N_{(3)}{-}H)$		1417s	1402m	1400m	1400m	1405s	1413m	1402m
$\nu(C_5{-}N_7{-}C_8)$	1335s		1342m	1342m	1338m	1340m	1350w	1350w
$\nu(N_9{-}C_8) + \nu(N_3{-}C_2) + \delta(C{-}H)$	1309		1306m	1310m	1315m	1314m	1305w	1302s
	1300		1306m	1280m	1272m	1314m	1305w	1302m
$\delta(C_8{-}H) + \nu(N_7{-}C_8)$	1232sh		1218w	1215m	1196s			
$\nu(C_8{-}N_7) + \delta(C_6{-}N_6{-}H) + \nu(C_1{-}N_2)$	1156w		1147m	1146m	1138m	1148m	1152m	1142m
$\nu(C_2{-}N_3) + \nu(N_9{-}R)$	1126m		1147m	1116w	1116w	1118w	1115w	1110w
	1126m		1110m	1115w	1115w	1118w	1115w	1110w
$\rho(NH_2)$	1023m		1018m	1030m	1020m	1036m	1025m	1030m
$\rho(NH_2) + \nu(N_1{-}C_6)$	939s		930s, b	920w	920m	937m	935w	942m
$\delta(N_1{-}C_2{-}N_3) + \nu(C_5{-}N_7)$, $\nu(N_9{-}H)$	871m		832w	835m	828w	835w	835w	835w
$\nu(M{-}OH_2)$			377m	410w	414mb	418m	380m	345m
$\nu(M{-}O)$			273m	242s	242s	242m	275wb	275m
				239m		239s		
$\nu(M{-}N)$			278mb	259m	239s	258m	280wb	270m
			264mb	235s	222w		268w	244s

of ADN are lowered to appreciable extent (Table 2), δ_{N_3H} frequency which appears at 1417 cm^{-1} of URL is also lowered in the new complexes. These may be due to the formation of hydrogen bond between N_1 of ADN and N_3–H of URL as $N_1 \cdots H–N_3$. Again from Table 2 it is obvious that the frequencies of the ν_{N_3} and ν_{N_7} bands are lowered considerably in comparison to the ν_{N_9} band of the complexes with respect to those of ADN frequencies. On the basis of these observations it may be proposed that the two binding sites of ADN are N_3 and N_7 and not N_9.

The other cations in the respective molecules are coordinated to $C_2{=}O$ of URL supported by an appreciable lowering in the frequencies of the $C_2{=}O$ band in the complexes compared to free URL at 1712 cm^{-1}. This binding of cations to $C_2{=}O$ of URL directly enhances the proton donor ability at the N_3 atom of URL. Considering the above arguments it may be tentatively suggested that out of the metal binding sites of ADN *i.e.* N_3, N_7, N_9, C_6–NH_2 and of URL $C_4{=}O$, $C_2{=}O$, N_3H, N_1H, the sites employed for bonding with ADN are N_3 and N_7 whereas in URL, it is $C_2{=}O$. The presence of ν(M–O) [12] and ν(M–N) [8] bands in the lower frequency region suggest the coordination number six for Co(II), Ni(II) and Cu(II) while four for Mn(II), Zn(II) and Cd(II).

The bridging OH stretching vibrations appear at about 3300–3400 cm^{-1} [13] and the bridging OH bending mode appears at about 950 cm^{-1} for the metal ions suggesting an OH bridging polymeric structure of the complexes. Also, taking into consideration the insolubility of the complexes bridging structures are favoured.

ESR Spectra

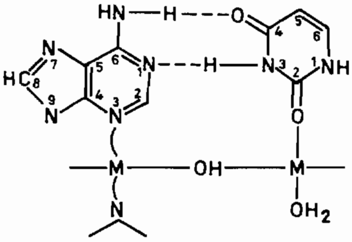
The room temperature electron spin resonance spectra of the solid samples of Mn(II)–ADN–URL, Co(II)–ADN–URL, Ni(II)–ADN–URL and Cu(II)–ADN–URL show a single signal centred at $g = 2.109$, 2.229, 2.178 and 2.167 respectively. The appearance of a narrow line for the Mn(II), Co(II) and Ni(II) complexes suggests internuclear interactions whereas a broad line is observed for the Cu(II) complex which is the result of weak internuclear interactions.

Magnetic Studies

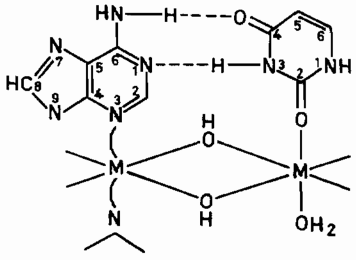
The room temperature magnetic moments of the Mn(II), Co(II), Ni(II) and Cu(II) complexes are 4.33, 3.67, 2.65 and 1.73 BM as against the spin only value of 5.92, 3.87, 2.83 and 1.73 BM, respectively, indicating a high spin nature of the Mn(II), Co(II), Ni(II) and Cu(II) complexes. The temperature dependent magnetic measurements of Mn(II)–ADN–URL, Co(II)–ADN–URL, Ni(II)–ADN–URL and Cu(II)–ADN–URL complexes are reported in Table 3. The new complexes are high spin, as expected,

TABLE 3. Variable Temperature Magnetic Studies of the Complexes

T (K)	χ_M $\times 10^6$	$\chi_{M'}$ $\times 10^6$	μ_{eff}(BM)	
			dimer	monomer
$Mn_2(OH)_2(ADN)(URL) \cdot H_2O$				
20.08	200798.32	200946.42	5.68	4.02
22.02	177429.55	177577.65	5.59	3.95
24.40	162042.7	162190.8	5.63	3.98
26.20	154060.78	154208.88	5.68	4.02
29.20	134442.54	135490.64	5.61	3.96
31.81	120594.39	120742.49	5.54	3.92
35.61	109390.85	109538.95	5.59	3.95
90.45	42746.579	42894.79	5.57	3.94
120.45	34351.131	34499.231	5.76	4.08
142.50	30340.935	30489.035	5.89	4.17
163.18	27023.147	27171.247	5.95	4.21
291.00	15963.851	16111.951	6.12	4.33
$Co_2(OH)_4(ADN)(URL) \cdot 3H_2O$				
20.00	107121.73	107345.43	4.14	2.93
23.01	93415.744	93639.444	4.15	2.93
24.70	89115.825	89339.525	4.20	2.97
26.00	82665.946	82889.646	4.15	2.94
30.00	75678.577	75902.277	4.27	3.02
32.26	71378.658	71602.358	4.29	3.04
35.35	66541.249	66764.949	4.34	3.07
42.00	55253.961	55477.661	4.32	3.05
61.00	38054.284	38277.984	4.32	3.06
86.00	29991.936	30215.636	4.56	3.22
129.00	21929.587	22153.287	4.78	3.38
291.00	11341.036	11564.736	5.19	3.67
$Ni_2(OH)_4(ADN)(URL) \cdot 3H_2O$				
21.23	49223.481	49447.181	2.90	2.05
24.13	44937.855	45161.555	2.95	2.09
26.20	42182.809	42406.509	2.98	2.11
28.17	40346.112	40569.812	3.02	2.14
30.00	38203.299	38426.999	3.04	2.16
32.40	36366.602	36590.302	3.08	2.18
35.20	34223.788	34447.488	3.11	2.20
42.80	28407.581	28631.281	3.13	2.21
84.50	17081.282	17304.982	3.42	2.42
129.50	12489.54	12713.24	3.63	2.57
169.5	10040.61	10264.31	3.73	2.64
291.0	5816.2074	6039.9074	3.75	2.65
$Cu_2(OH)_4(ADN)(URL) \cdot 3H_2O$				
20.08	18778.329	19002.029	1.75	1.24
23.72	15540.686	15764.386	1.73	1.22
29.39	13112.454	13336.154	1.77	1.25
30.52	12788.689	13012.389	1.78	1.26
34.95	11331.75	11555.45	1.79	1.27
37.18	10576.3	10800.0	1.79	1.27
40.83	9928.772	10152.472	1.82	1.29
48.85	8121.087	8344.787	1.81	1.28
68.50	6151.5215	6375.2215	1.87	1.32
126.36	4262.8967	4486.5967	2.13	1.51
163.18	3615.368	3839.068	2.24	1.58
291.00	2377.9566	2601.6566	2.46	1.73



M = Mn(II), Zn(II), Cd(II)



M = Co(II), Ni(II), Cu(II)

Scheme 1.

and the subnormal paramagnetism is due to magnetic exchange via the bridging ligands.

Electronic Spectra

In the electronic spectrum of the Mn(II) mixed complex transition bands appear at 425 and 472 nm; 340 and 364 nm suggesting the geometry of the complex to be tetrahedral [14].

The electronic spectrum of the Co(II)–ADN–URL complex shows a weak band around 820 nm (12 195 cm^{-1}) and a strong band at 520 nm (19 230 cm^{-1}) assigned to ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_2)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)(\nu_3)$ respectively [14]. The ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)(\nu_1)$ transition could not be observed as it is likely to appear beyond 1000 nm. This spectrum suggests an octahedral geometry.

The electronic spectrum of the Ni(II) complex shows two bands at 625 (16 000 cm^{-1}) and 378 (26 455 cm^{-1}) nm assigned as ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)(\nu_2)$ and ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)(\nu_3)$ transitions respectively [15]. Its ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)(\nu_1)$ transitions, however, could not be obtained as they are likely to appear beyond 900 nm. It thus favours an octahedral geometry.

The electronic spectrum of Cu(II)–ADN–URL shows a strong absorption band at 600 nm (16 666 cm^{-1}) indicating the hexacoordination of the metal ion.

On the basis of above studies, the structure of the complexes may be as in Scheme 1.

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