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Adenosine-5′-monophosphate Complexes of Pt(II) and Mg(II) Metal Ions. Synthesis, FT–IR Spectra and Structural Studies

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Several complexes of Pt(II) and Mg(II) metal ions with adenosine-5′-monophosphate have been isolated. The complexes are of the formulae cis *and* trans-*$[Pt(L)_2(NH_3)_2]Cl_2\cdot xH_2O$, $Pt(L)_nCl_2\cdot xH_2O$ and Mg-(L′)·xH_2O, where n = 1, 2, 3, x = 5, 6–10 and L = disodium salt of adenosine-5′-monophosphate (5′-$AMPNa_2$) and L′ = adenosine-5′-monophosphate dianion (AMP^{2-}).*

Due to the distinct spectral similarities with the structurally known N_7-bonded Ni(5′-AMP)·$6H_2O$, the mononucleotide binds to Pt(II) and Mg(II) ions through the N_7-atom of the purine ring system.

No direct metal–phosphate interaction was observed for the platinum(II) complexes synthesized here. The Mg–AMP compounds showed direct Mg–phosphate interaction if prepared at acidic pH and no direct Mg–phosphate bonding was observed when prepared at neutral or slightly basic pH values.

Introduction

In our previous report [1], we demonstrated how guanosine-5′-monophosphate (5′-GMP) is bonded to Mg(II) and Pt(II) metal cations through the N_7-atom of the guanine base. Evidence for this came through comparison of the spectroscopic properties of a series of structurally known N_7-bonded metal–GMP complexes with those of the corresponding Pt(II) and Mg(II) complexes. In the present work, several complexes of 5′-AMP with Mg(II) and Pt(II) metal ions which have not been reported before have been synthesized and characterized by elemental analysis, molar conductivity and FT-IR spectroscopy. The structurally known [2] Ni(5′-AMP)·$6H_2O$ compound was prepared and its FT-IR spectrum was recorded in order to detect any characteristic features of each structure which could be compared with those from the spectra of Mg(II) and Pt(II) complexes and to establish a correlation between spectral change and the N_7-coordination sites used by 5′-AMP.

Experimental

Materials

All the chemicals were reagent grade and used without any further purification. K_2PtCl_4 was purchased from Johnson Matthey and Mallorty Ltd., and was converted to *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ according to routine methods [3]. 5′-AMP acid and sodium salt forms were purchased from Sigma Chemical Company.

Synthesis of Pt(II) Complexes

The Pt(II) complexes of 5′-AMP were prepared by the addition of a stoichiometric amount of K_2PtCl_4 or *cis*- and *trans*-$Pt(NH_3)_2Cl_2$ to the solution of the nucleotide in 200 ml of water, in the presence of the appropriate amount of NaCl at room temperature and at pH = 7. The solutions were kept in the dark for one week and then the amount of water was reduced to 40 ml under low pressure at 50 °C. A mixture of ethanol–ether (50 ml) was then used to bring down the precipitate (yellowish) which was redissolved in a small amount of water and reprecipitated by the addition of ethanol–ether, then dried in a desiccator over $CaCl_2$ and analyzed to have the empirical formula of $Pt(L)_nCl_2\cdot xH_2O$, where n = 1, 2, 3 and x = 6. The complexes are soluble in H_2O and acidic solutions only and not in the common organic solvents. Their colour varies from yellow for the 1:1 to white for the 3:1 complexes. They show high values for molar conductivity, and this is mainly due to the presence of Na^+ ions [4] associated to the 5′-AMP Na_2 molecule. In these Pt(II)–AMP complexes the Pt(II) ion does not replace the sodium ions from 5′-$AMPNa_2$. The analysis and millimolar conductances are shown in Table I. The structurally known Ni(AMP)·$6H_2O$

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TABLE I. Analytical Data and Millimolar Conductances of Pt(II) and Mg(II) AMP Complexes.[a]

Compounds		M^{2+}	C	H	N	Cl	Colour	Conductivity (Ω^{-1} cm^2 mol^{-1})	pH
1. $K[PtLCl_3]C_2H_5OH$[b]	Found.	24.77	18.30	2.50	8.90	13.53	yellow	200	7
	Calc.	25.04	18.50	2.44	9.00	13.68			
2. $PtL_2Cl_2{\cdot}6H_2O$		16.85	20.03	3.79	11.21	5.85	pale yellow	250	7
		16.83	20.72	3.28	12.10	6.13			
3. $[PtL_3Cl]Cl{\cdot}6H_2O$		11.15	21.92	4.25	12.28	4.20	white	300	7
		12.58	22.22	3.25	13.54	4.58			
4. *cis*-$[PtL_2(NH_3)_2]Cl_2{\cdot}6H_2O$		16.45	18.93	3.78	13.42	5.95	white	250	7
		16.35	20.13	3.69	14.10	5.96			
5. *trans*-$[PtL_2(NH_3)_2]Cl_2{\cdot}6H_2O$		16.30	19.23	3.89	13.68	5.95	white	220	7
		16.35	20.13	3.69	14.10	5.96			
6. $MgL'{\cdot}10H_2O$		4.10	21.69	4.76	11.51	–	white	160	7
		4.44	21.77	5.98	12.70	–			
7. $MgL'{\cdot}5H_2O$		5.10	25.83	4.95	13.84	–	white	120	4
		5.31	26.03	4.98	15.18	–			

[a] L is 5′-$AMPNa_2$ in all the Pt(II) complexes and L′ is AMP^{2-} in the Mg(II) compounds. [b] The amount of K^+ calculated is 5.00 and found 4.70.

complex was prepared by routine methods [2] and was analyzed for metal.

Preparation of Mg(II) Complexes

The magnesium(II) complexes were synthesized at two different pH ranges, namely 6–4 and 7–9. The nucleotide, 5′-$AMPNa_2$ (1 mmol), was dissolved in 30 ml of H_2O and added to the solution of 1 mmol of $MgCl_2{\cdot}6H_2O$ in 20 ml of solution. The pH value was adjusted as mentioned above with 0.1 *N* HNO_3 or 0.1 *N* NaOH, then it was heated at 60 °C for 30 minutes to redissolve the formed insoluble precipitate. After cooling down to room temperature, a white precipitate appeared. This was filtered off and washed with cold water and air dried. The Mg(II) complex synthesized from acidic media is not soluble in H_2O and can be recrystallized from acidic solution, whereas the Mg(II) compound obtained from neutral or basic pH is very soluble in hot water and crystallizes from aqueous solution. The complexes show a conductivity value of 120–160 Ω^{-1} cm^2 mol^{-1}, corresponding to 2:2 electrolytes [4] (the Mg(II) ion replaces the Na^+ ions in 5′-$AMPNa_2$). The analytical data and millimolar conductances are given in Table I.

Physical Measurements

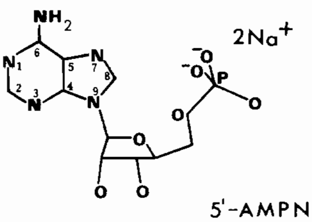
The FT-IR spectra were recorded on a DIGILAB FTS-15/C Fourier Transform Michelson Infrared Interferometer, equipped with a high-sensitivity Hg-CdTe detector and a KBr beam splitter with a spectral resolution of 2 to 4 cm^{-1} and KBr pellets. Conductance measurements were carried out on a E365B METROHM conductoscope.

Elemental Analysis

The Pt(II) content was analyzed by atomic absorption and the Mg(II) content determined complexometrically. C, H and N were analyzed at Schwarzkopf Microanalytical Laboratory (US). The halide was determined as silver halide.

Results and Discussion

X-ray analysis shows [2] that the Ni(II) ion is bonded to the N_7-atom of the adenine ring, as well as to five water molecules in the $Ni(AMP)6H_2O$ compound (two of these water molecules are strongly hydrogen-bonded to the phosphate group). The FT-IR spectrum of this compound is recorded and compared with those of the corresponding Mg(II) and Pt(II) complexes, studied here. The results are discussed in two regions, namely 4000–2700 cm^{-1} and 1700–400 cm^{-1}. It should be noted that our discussion is largely based on the assignments made by Lord and Thomas [5], Novak [6]. Chinsky [7] and the normal mode calculations by Tsuboi *et al.* [8–11], and is in good agreement with the observations of these authors. The structure of 5′-$AMPNa_2$ with the numbering of the atoms is illustrated below:



5′-$AMPNa_2$

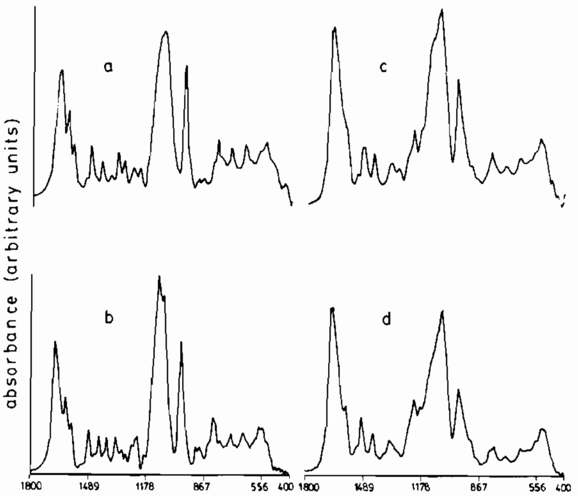


Fig. 1. FT-IR spectra of 5'-AMPNa$_2$ and its metal complexes in the region 1800–400 cm^{-1} for a, 5'-AMPNa$_2$; b, Ni(AMP)6H$_2$O; c, Pt(AMP)$_2$Cl$_2$·6H$_2$O and d, [Pt(AMP)$_3$]Cl·6H$_2$O.

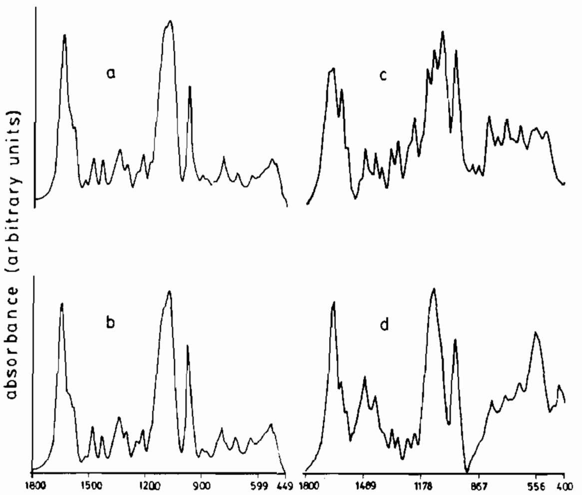


Fig. 2. FT-IR spectra of 5'-AMP–metal complexes in the region 1800–400 cm^{-1} for a, *trans*-[Pt(AMP)$_2$(NH$_3$)$_2$]Cl$_2$·6H$_2$O; b, *cis*-[Pt(AMP)$_2$(NH$_3$)$_2$]Cl$_2$·6H$_2$O; c, Mg(AMP)·5H$_2$O (pH = 4) and d, Mg(AMP)·10H$_2$O (pH = 7).

4000–1700 cm^{-1}

In this region, due to the presence of strong intramolecular hydrogen-bonding in both the free 5'-AMP acid [12] and its metal compound [2], it is very difficult to draw any conclusions on coordination sites used by the free base on complexation. The asymmetric and symmetric stretching vibrations of the hydrogen-bonded NH$_2$, NH, OH as well as the aromatic C$_2$–H, C$_8$–H and the sugar exocyclic stretching frequencies appear in the spectra of the free ligand and show no considerable alteration in the spectra of 5'-AMP metal complexes. The small shifts of the bands observed in this region of the spectra are mainly due to rearrangement of the strong hydrogen-bonding network of the free base upon complexation. The possible assignments of the bands related to this region of the spectra are given in Table II.

1700–400 cm^{-1}

The free 5'-AMP shows a broad and strong absorption band at 1655 cm^{-1} and two other bands with medium intensities at 1606 and 1576 cm^{-1}, which are mainly assigned to the bending (scissoring) mode of NH$_2$ and the stretching vibrations of C$_5$–C$_6$ and C$_4$–C$_5$ frequencies, respectively [8–11] and are strongly coupled. These absorption bands appeared at 1665, 1605 and 1579 cm^{-1} in the spectrum of the structurally known N$_7$-bonded Ni(AMP)·6H$_2$O. The small shifts of the bending mode of NH$_2$ at 1655 to 1665 cm^{-1}, together with the NH$_2$ stretching vibration at 3400 cm^{-1} to a lower frequency, are due to replacement of the intramolecular hydrogen-bonding of the NH$_2$ group in the crystal structure of 5'-AMP acid [12] (the NH$_2$ group is hydrogen-bonded to the phosphate group and a water molecule), by the stronger hydrogen bonding of the NH$_2$ group to a coordinated water molecule in Ni(AMP)·6H$_2$O [2]. These changes are not due to any kind of metal–NH$_2$ interaction, where metalation or deprotonation of the NH$_2$ group causes alteration or disappearance of the absorption frequencies of this group [13, 14].

It has been suggested that N$_1$-coordination causes a split of the absorption band at 1598 cm^{-1} to a doublet at about 1618 cm^{-1} and at 1604 cm^{-1} in the spectra of 9-Me-adenine mercury complexes [13]. Such a split does not occur here in the spectra of N$_7$-bonded Ni(AMP)·6H$_2$O and our Pt(II) and Mg(II) complexes (Figs. 1 and 2). The band at 1576 cm^{-1}, in the spectra of the free base, shifted to a higher frequency in the spectra of Ni(II), Pt(II) and Mg(II) complexes. This small shift is due to the inductive effect of the metal ion electrophile bonded to the N$_7$-coordination site, which causes less electron delocalization, and finally less contribution to the skeletal vibration of the ring system. Similar shifts were observed in the IR spectra of N$_7$-bonded 9-Me-adenine mercury complexes [13].

The two absorption bands at 1506(w) and at 1479 cm^{-1} (m) in the spectra of 5'-AMP were mainly assigned to the purine ring vibrational frequencies [8, 10]. The former shifted to about 1510–25 cm^{-1} and the latter showed splitting and considerable intensity changes in the spectra of Ni(II), Pt(II) and Mg(II)-AMP complexes (Table II). Since these absorption bands contain C$_8$–H bending and N$_7$–C$_8$ stretching frequencies [8, 10], this indicates that the N$_7$-position of the adenine ring is also the possible

TABLE II. FTIR Absorption Bands (cm^{-1}) of Free 5'-AMP and Metal Complexes with Possible Assignments.

$5'AMPNa_2$	$Ni(AMP)6H_2O$	$KPt(AMP)Cl_3$	$Pt(AMP)_2Cl_2 \cdot 6H_2O$	*cis*-$Pt(NH_3)_2$-$(AMP)_2Cl_2 \cdot 6H_2O$	*trans*-$Pt(NH_3)_2$-$(AMP)_2Cl_2 \cdot 6H_2O$	MgAMP10H2O	$MgAMP5H_2O$	Possible Assignments
3543m	3520m	3540m	3530m	3520m	3530m	3530m	3520m	νNH_2 asymmetric [5, 9]
3471m	3446m	3460m	3450m	3440m	3455m	3450m	3440m	
–	3427m	3420w	3430m	3410w	3415m	3430w	3400m	νNH_2 symmetric [5, 9]
3379s	3387s	3380s	3370m	3365m	3370s	3385s	3380s	
3354s	3355s	3350s	3360m	3350s	3360s	3340s	3350s	νOH bonded [5, 9]
3331s	3331sh	3330s	3340s	3330s	3335m	3330m	3330m	
–	3320m	3315m	3320w	3325m	3320m	3325m	3330m	
3271s	3288m	3280s	3275m	3265m	3260m	3275m	3275m	νNH_2 and $2x\delta(NH_2)$ [6]
3234s	3255m	3250m	3240m	3245s	3235m	3250s	3250m	
–	3223m	3225w	3215m	3220m	3215w	3220w	3220w	
3190s	3190s	3180m	3175m	3185m	3170m	3190s	3180w	νC_8-H [8–10]
3167vs	3157m	3165s	3155s	3160s	3155s	3160m	3150m	
3111s	3134m	3125m	3120m	3130s	3125m	3120s	3130m	νC_2-H [8–10]
–	3100w	–	–	–	–	–	–	
3068m	3070w	3080m	3070m	3065m	3077m	3075m	3080m	νNH [8–10]
–	3030vw	–	–	–	–	–	–	
2970w	2960m	2960w	2970m	2950m	2965m	2950w	2975m	νCH_2 asymmetric [5, 9]
2929m	–	2925w	2930m	2920m	2930m	2939m	2940m	
2881m	2880w	2880m	2870m	2875m	2870m	2870m	2860w	$\nu(CH_2)$ symmetric [5, 9]
2850vw	–	–	–	–	–	–	–	$\nu(CH)$ [5, 9]
2800vw	2800vw	2800w	2790w	2790w	2800m	2800vw	2780w	
2744w	2760vw	2760w	2755w	2740w	2760w	2750w	2750w	
1655vs	1665vs	1660vs	1660bs	1658bs	1660	1670sh	1660sh	δNH_2 [8–10]
–	–	–	–	–	–	1660vs	–	
1606s	1605s	1605sh	1600sh	1601sh	1600sh	1606s	1600sh	νC_5-C_6, δNH_2 [8–10]
1576s	1579m	1584m	1583m	1585m	1580sh	1579m	1573w	νC_4-C_5, $\nu N_3-C_4-C_5$ [8–10]
1506w	1510w	1510w	1525w	1525w	1515m	1510w	1510sh	νC_8-N_7, δC_8-H [10]
–	1478s	1497s	1492s	1496s	1490s	1479s	1481vs	δC_8-N_7, νC_8-N_9, δC_8-H, δC_2-H [8, 10]
1479s	–	–	–	–	–	–	–	
–	1451w	1460vw	1485sh	1458w	1460w	1465w	–	
1425sh	–	1437m	1433s	1430w	1430w	1425vw	1426w	δCH_2, δCH [22]
1421m	1424m	–	1420vw	1415w	1410w	1420w	–	$\nu N_1-C_6-N_6$ [8]
1398w	1397w	–	–	–	–	1400sh	–	
1375m	1375w	1370sh	1370vw	1375sh	1380w	1390m	1380sh	νPyrimidine ring [6]
1334m	1335m	1343m	1343m	1340m	1345m	1338m	1339m	νC_8-N_9, νC_2-N_3, νC_5-N_7, [7, 8]
–	1300w	1304sh	1300m	1300sh	1310sh	1300m	1304m	δC_8-H, νN_7-C_8 [7, 8]
1303m	–	–	–	–	–	–	–	
–	1280m	1260sh	1250sh	1290w	1290w	1270w	–	
1245m	1248sh	1248sh	1245sh	1246sh	1250sh	1248m	1252m	$\nu N_7-C_8-N_9$, νC_2-H, δN_1-C_8 [7, 8]

	1229sh	–	–	1240sh	1245sh	1220sh	–	$\nu N_7-C_8, \delta C_8-H$ [8–10]
1215m								
	1219m	1213s	1215s	1215s	1213s	1215m	1213m	
1175sh	1180m	1180m	1180sh	1181sh	1180sh	1184sh	1180sh	$\nu C_8-N_7, \delta C_6-NH$ [8–10]
1110sh	1111vs	1110sh	1107sh	1110sh	1112sh	–	1148s	$\nu C-O$ [9]
1092bs	1072s	1074bs	1084bs	1085bs	1080bs	1111bs	1111s	νPO_3^{2-} deg. [9, 20]
							1088s	
976vs	980s	974s	974s	974vs	975vs	996s	999vs	νPO_3^{2-} sym. [9, 20]
900w	903m	900sh	904m	900m	905m	901w	900m	νribose-phosphate [23]
869w	881m	870w	890w	880w	875m	868w	870m	
815sh	835m	810w	810sh	815sh	810sh	816s	815sh	
797m	806s	783m	793m	793s	791s	795sh	797s	$\nu P-O$ [9, 20]
777sh	771sh	–	–	–	–	768m	–	νribose–phosphate [23]
728s	710m	720w	719m	719m	718m	717s	721m	breathing-mode [8]
684vw	686w	–	687vw	–	–	687w	–	imidazol ring def. [18]
646sh	650sh	640m	640m	644m	646m	640s	647m	$\delta NH, \delta C_6-NH_2$
616w	636m	609vw	–	611vw	610w	–	–	
570w	594w	594w	590w	592	585w	577sh	580w	PO_3^{2-} deg. def. [9, 20]
530s	555m	555sh	550m	557sh	550m	555m	555s	δNH, ribose def. [5, 23]
540w	553m	522s	525m	532s	530m	–	540sh	
480w	480w	513vw	510w	475sh	480sh	503m	470w	νPO_3^{2-} asym. def. [9, 20]
420m	420w	430vw	420vw	430w	420w	426vw	430m	skeletal def. [11]

s, strong; m, medium; b, broad; sh, shoulder; w, weak; v, very; ν, stretching, δ, bending.

coordination site for Pt(II) and Mg(II)–AMP complexes. Similar shifts have been observed [15, 16] in the vibrational spectra of the divalent metal complexes of the N_7-bonded ATP (adenosine-5′-triphosphate) and the 9-Me-adenine platinum(II) complexes.

Four absorption bands at 1303(m), 1245(m), 1215(m) and 1175 cm^{-1} (sh) in the spectrum of the free base were assigned mainly to N_7–C_8, N_7–C_8–N_9 stretching and C_8–H bending frequencies [8–11]. The 1303 and 1215 cm^{-1} absorption bands each appeared as a doublet at 1300–1280 cm^{-1}, 1229–1215 cm^{-1} and the other two absorptions appeared with medium intensities at higher frequencies in the spectra of Ni(AMP)·6H_2O. Since these absorption bands are related to the vibrational frequencies involving the imidazole ring, it seems that the N_7-metalation of 5′-AMP changes the electron distribution of the ring system, where the vibration is mostly localized, and therefore causes the purine ring distortion. It has been found [17] that the $C{=}N^+$ groups have in general higher frequencies than the parent C=N groups, therefore protonation [18] or metalation [19] could bring an increase in the infrared absorption band of the C=N stretching frequency of the imidazole ring in the Ni(II)–AMP compound. Similar behaviour was observed in the spectra of all Pt(II) and Mg(II) complexes synthesized here.

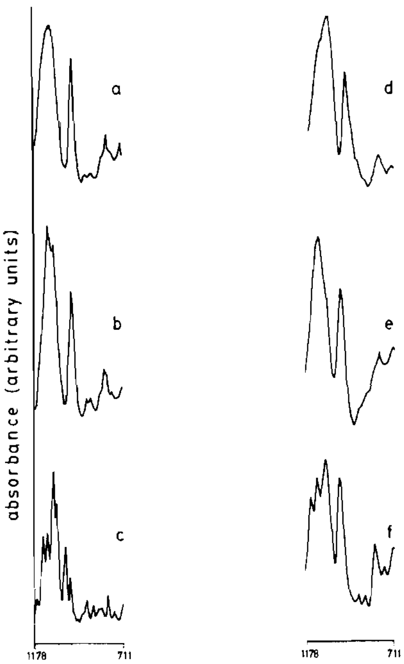


Fig. 3. FT-IR spectra of 5′-AMPNa$_2$ and its metal complexes in the region 1178–711 for a, 5′-AMPNa$_2$; b, Ni(AMP)·6H_2O; c, Cu(AMP)·3H_2O; d, *cis*-[Pt(AMP)$_2$(NH$_3$)$_2$]Cl$_2$·6H_2O; e, Mg(AMP)·10H_2O (pH 7) and f, Mg(AMP)·5H_2O (pH = 4).

5′-AMP Phosphate Vibrational Frequencies

Previously, we reported [1] the OPO$_3^{2-}$ vibrations of mononucleotides. The absorption bands due to the phosphate group of 5′-AMP occur at 1092 cm^{-1} (broad, strong band related to the PO$_3^{2-}$ degenerate vibration), 976 cm^{-1} (strong, sharp band assigned to the PO$_3^{2-}$ symmetric vibration) and 797 cm^{-1} (medium intensity related to the P–O stretching vibration). The other two absorptions at 530 and 420 cm^{-1} belong to the PO$_3^{2-}$ degenerate and asymmetric deformation frequencies [9, 20].

The Ni(II) ion is indirectly bonded to the phosphate group, through two hydrogen-bonded water molecules in Ni(AMP)·6H_2O. This indirect coordination of the phosphate group causes a small shift in the vibrational frequencies at 1092 and 976 cm^{-1} ($\Delta\nu$ = ±20 cm^{-1}), but does not cause any splitting of these absorption bands. The absorption bands at 797, 530 and 420 cm^{-1} do not show any considerable perturbation upon phosphate hydrogen-bonding (Fig. 3).

The Cu(II) ion is directly bonded to the PO$_3^{2-}$ in Cu$_3$(GMP)$_3$·8H_2O [21] and Cu(IMP)·nH_2O [22]. This direct coordination causes considerable shifting and splitting of the phosphate absorption bands at 1092, 976 and near 800 cm^{-1}, whereas indirect bonding of the phosphate group *via* hydrogen-bonded water molecules does not alter the position of the said absorption bands in the analogous Ni(II), Co(II) and Mn(II) complexes [1].

The IR spectrum of CuAMP·3H_2O synthesized here shows that the phosphate group is directly bonded to the Cu(II) ion (the crystal structure of this compound is not yet known). The spectrum of this compound is substantially different from that of the corresponding Ni(II) complex in the region 1100–900 cm^{-1} (Fig. 3). There is a splitting of the bands at 1092, 976 and 797 cm^{-1}, which is indicative of a direct phosphate–copper coordination.

The IR spectra of Mg(AMP)·5H_2O synthesized at pH 4 showed marked similarities with the bands at 1092, 976 and 797 cm^{-1} (Fig. 3), whereas the spectra of Pt(II) and Mg(II) complexes obtained from neutral solutions bear similarities with the Ni(AMP)·6H_2O compound containing indirect metal–OPO$_3$ bonding *via* a hydrogen-bonded water molecule (Fig. 3).

Sugar Vibrational Frequencies

The sugar vibrational frequencies of 5′-AMP appeared as strong, broad absorption bands at 3400–2700 cm^{-1} (Table II), and as sharp absorption bands in the region 1400–400 cm^{-1} [5, 9]. Most of these absorption bands are obscured by the strong broad bands of the phosphate group and the base residue, so that pure assignments of the sugar ring vibrations are difficult to make. The two weak absorption bands at 900–800 cm^{-1}, in the spectra of 5'-AMP, are assigned to the sugar–phosphate vibrational frequencies [23]. These absorption bands are sensitive to metal complexation and this is mainly due to the conformational changes around the phosphate–ribose bond upon direct or indirect phosphate coordination [24].

A band with medium intensity at 728 cm^{-1} in the spectra of the free base assignable to the breathing mode of the aromatic ring system [8] shifted to a lower frequency in the spectra of all N_7-bonded AMP metal complexes. The out-of-plane deformation modes of NH_2 and NH [8, 8–11] at 700–500 cm^{-1} in the spectra of the free base appeared in the same position with no considerable modification in the spectra of the 5'-AMP metal complexes.

The metal–nitrogen and Pt–halide stretching vibrations of 5'-AMP complexes studied here occurred in the lower region (400–200 cm^{-1}) of the spectra and will be reported elsewhere.

Conclusion

Using the spectroscopic and structural properties of the crystallographically known Ni(AMP)·$6H_2O$ compound compared to those of the Mg(II) and Pt(II) complexes studied here, the following remarks can be made. The atomic motions of the purine and pyrimidine ring vibrations in the 5'-AMP molecule are strongly coupled, and therefore the vibrations are mixed, so that an individual assignment for each absorption band is difficult to make. Metalation of the free base residue also modifies the electronic distribution within the ring system and gives more information for the study of the vibrational frequencies.

Metal N_7-binding of the adenine ring in the structurally known Ni(AMP)·$6H_2O$ and the corresponding Pt(II) and Mg(II) complexes have common spectral changes, which are summarized below:

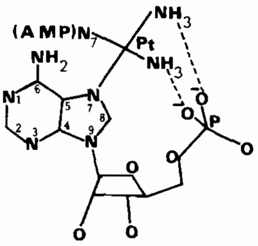
(a) Similar spectral changes were observed in the region 1700–1570 cm^{-1} (related to the NH_2 bending and the skeletal vibrational frequencies) with those in Ni(AMP)·$6H_2O$;

(b) Modification of the absorption bands at 1506 and 1479 cm^{-1} (assigned to the C_8–H bending and the N_7–C_8 stretching vibration);

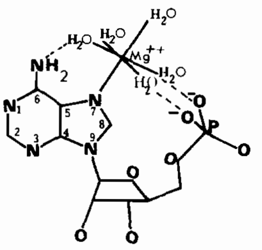
(c) Splitting and shifting of the absorption bands at 1303, 1245, 1215 and 1175 cm^{-1} (attributed to the C_8–H bending, N_7–C_8 and N_9–C_8 stretching frequencies) and

(d) The shift of the band at 728 cm^{-1} in the spectrum of the free base related to the breathing mode of the ring system to a lower frequency at about 710–720 cm^{-1} in the spectra of the metal complexes. The characteristic features of phosphate bonding are: (a) a splitting and shifting of the absorption bands at 1092 and 976 cm^{-1} which is indicative of direct metal–phosphate coordination and (b) the shifting of the said absorption frequencies with no splitting which is an indication of indirect phosphate metal interaction, through hydrogen-bonded water molecules.

It is worth noting that the reaction between Pt(II) and 5'-AMP produces N_7-bonded metal complexes with no direct Pt–OPO_3^{2-} interaction. The indirect Pt–phosphate bonding occurs through hydrogen-bonded and coordinated NH_3 molecules (Scheme A). Furthermore, the Mg(II) complexes synthesized in acidic solution show direct Mg–phosphate interaction as well as N_7-bonding, whereas for the Mg(II) complexes obtained in neutral media indirect metal–phosphate interaction takes place *via* a coordinated water molecule (Scheme B).



A



B

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