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Synthesis, Structure and a Fourier Transform Infrared Study of Pt(II), Cu(II), and Mg(II) Complexes with Xanthosine-5′-Monophosphate

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The reaction of xanthosine-5′-monophosphate disodium salt (5′-XMPNa$_2$) with Pt(II), Cu(II) and Mg(II) ions produced compounds of the type cis- *and* trans-*Pt(NH$_3$)$_2$(XMPNa$_2$)$_n$Cl$_2$·xH$_2$O, where n = 1 or 2; Pt(XMPNa$_2$)$_n$Cl$_2$·xH$_2$O, where n = 1–4, x = 1,4 & 6; Cu(XMP)·6H$_2$O and Mg(XMP)·xH$_2$O, where x = 9 or 4. In the complexes synthesized here at neutral pH values, the nucleotide binds through the N$_7$-atom of the purine ring system, whereas for Cu(II) and Mg(II) compounds obtained at pH = 4 a direct metal–phosphate interaction as well as N$_7$-bonding is proposed.*

Introduction

In the last few decades, the coordination chemistry of metal ions with purine and pyrimidine base constituents of the DNA molecule and some of their derivatives has been the subject of many studies [1, 2]. Since the discovery of the antitumor activity of *cis*-Pt(NH$_3$)$_2$Cl$_2$ and other related platinum compounds [3], a great deal of work has been done in order to understand the mechanism of action of the platinum drug which is believed to attack the DNA molecule [4]. Most recent publications [1, 5] concerning the interaction of platinum with purine and pyrimidine base derivatives describe the guanosine-monophosphate (GMP), adenosine-monophosphate (AMP), cytidine-monophosphate (CMP), uridine-monophosphate (UMP) and inosine-monophosphate (IMP) molecules which are the major constituents of DNA and RNA. However, there is evidence that certain 'minor bases' like xanthosine which is a minor component of RNA are found in nucleic acids [6].

Xanthosine-5′-monophosphate is similar to xanthosine except that it has the ribose linked through Cl′ to the N$_9$-atom and through C4′ to an exocyclic phosphate group. It can be viewed as a precursor [7] of 5′-GMP formed by oxidation followed by transfer of the amide nitrogen of glutamine to the C2′ position as in the reaction shown below: (Scheme 1)

It has been reported that 5′-XMP is an inhibitor of 5′-GMP reductase [8] and 5′-IMP dehydrogenase [9]. Though 5′-XMP is not properly a base of DNA or RNA, it is involved in many reactions occurring in the body and is sometimes converted to other purine bases *via* the IMP molecule in certain organisms [10].

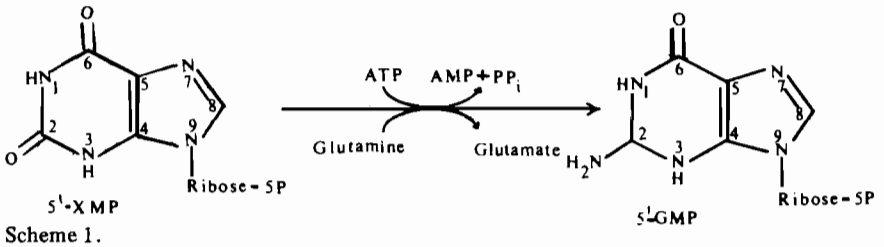
In this report we wish to describe the isolation and characterization of several Pt(II), Cu(II) and Mg(II) complexes of XMP by elemental analyses, molar conductivity and FT-IR spectroscopy. Furthermore, a correlation between the spectral changes and the coordination sites used by the XMP molecule with possible assignment of the infrared vibrational frequencies is reported.

Experimental

5′-XMPNa$_2$ was purchased from Sigma Chemical Company. K$_2$PtCl$_4$ was a loan from the Johnson Matthey Research Centre. It was converted to *cis*- and *trans*-Pt(NH$_3$)$_2$Cl$_2$ by published methods [11, 12] and it was then purified as reported [13]. All other chemicals were reagent grade and were used as supplied.

Preparation of the Platinum Compounds

The Pt(II)–nucleotide compounds were prepared by the addition of stoichiometric amounts of *cis*-



5′-XMP 5′-GMP

Scheme 1.

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TABLE I. Elemental Analysis of Pt(II), Cu(II) and Mg(II) Complexes of $XMPNa_2$.

Compound		$\%M^{2+}$	%C	%H	%N	pH
$K[Pt(XMPNa_2)Cl_3]\cdot 6H_2O$	Found	23.11	14.10	2.49	6.31	
	Calcd	22.76	14.02	2.68	6.53	
$[Pt(XMPNa_2)_2Cl_2]\cdot 6H_2O$		15.65	19.56	3.40	8.55	7
		16.39	20.76	2.86	9.41	
$[Pt(XMPNa_2)_3Cl]Cl\cdot 6H_2O$		12.38	21.41	3.49	9.91	7
		12.20	22.52	2.81	10.51	
$[Pt(XMPNa_2)_4]Cl_2\cdot 6H_2O$		9.20	23.67	3.43	10.36	7
		9.72	23.93	2.80	11.16	
cis-$[Pt(NH_3)_2(XMPNa_2)Cl]Cl\cdot H_2O$		25.96	16.73	2.94	11.87	7
		26.85	16.52	2.61	11.57	
cis-$[Pt(NH_3)_2(XMPNa_2)_2]Cl_2\cdot 4H_2O$		15.80	19.49	3.78	11.84	7
		16.41	20.20	3.03	11.78	
trans-$[Pt(NH_3)_2(XMPNa_2)Cl]Cl\cdot H_2O$		25.95	15.90	3.69	12.19	7
		26.85	16.52	2.61	11.57	
trans-$[Pt(NH_3)_2(XMPNa_2)_2]Cl_2\cdot 4H_2O$		15.75	19.30	3.60	11.25	7
		16.41	20.30	3.03	11.78	
$Cu(XMP)\cdot 6H_2O$		11.55	22.28	3.99	10.55	4
		11.90	22.48	4.30	10.49	
$Mg(XMP)\cdot 9H_2O$		4.51	22.92	4.93	9.26	7
		4.44	21.85	5.28	10.20	
$Mg(XMP)\cdot 4H_2O$		5.10	26.56	4.04	12.09	4
		5.32	26.17	4.14	12.21	

and *trans*-$Pt(NH_3)_2Cl_2$ or K_2PtCl_4 to a solution of 5'-$XMPNa_2$ in 50 ml of water at pH = 7. The solutions were kept in the dark for one week and then the volume of water was reduced to 5–10 ml under low pressure at 50 °C. A mixture of ethanol–ether was then used to precipitate the compound. This was washed with the same mixture and finally with ether. The compounds obtained were dried over $CaCl_2$ and analysed to show a composition of $Pt(XMPNa_2)_nCl_2\cdot 6H_2O$, where n = 1–4 and 6 and *cis*- or *trans*-$Pt(NH_3)(XMPNa_2)_nCl_2\cdot xH_2O$, where n = 1 or 2 and, x = 1 or 4. The complexes are soluble in water and in acidic solutions, but not in common organic solvents. They show high values of molar conductivity (500–60 Ω^{-1} cm^2 mol^{-1}) mainly due to the presence of the Na^+ ions [14], associated with the phosphate group of 5'-$XMPNa_2$, and this prevents us from drawing a conclusion on the ionic nature of these complexes. The analytical data are given in Table I.

Preparation of Cu(II) and Mg(II) Compounds

The copper(II)–XMP compound was synthesized by mixing a 1 mmol solution of $Cu(NO_3)_2\cdot 3H_2O$ with a 1 mmol solution of 5'-$XMPNa_2$ in 10 ml of water and adjusting the pH to 4 with 1 *N* HNO_3 solution. The compound was readily precipitated as a green powder and was filtered, washed with water and dried over $CaCl_2$. It was recrystallized from a solution of 1 *N* $HClO_4$ at pH = 4. The compound is soluble in acidic solutions but not in common organic solvents.

The magnesium compounds were synthesized by the addition of 1 mmol $MgCl_2\cdot 6H_2O$ to a solution of mononucleotide 1 mmol in 10 ml water at pH = 7. The ethanolic solution was used to precipitate the compound, then it was washed with alcohol and dried over $CaCl_2$. The compound analysed as $Mg(XMP)\cdot 9H_2O$ (Table I) is soluble in water. At pH = 4 the formation of $Mg(XMP)\cdot 4H_2O$ was realised (Table I) which is soluble only in acidic solutions. These two compounds show different infrared spectra particularly in the phosphate region (see Discussion).

Fourier Transform Infrared (FT-IR) Spectra

The FT-IR spectra were recorded on a DIGILAB FTS-15C/D Fourier Transform Infrared Interferometer equipped with a wide range HgCdTe detector (Infrared Associates, New Brunswick, N.J.), a KBr beamsplitter and a Globar source. The spectra were recorded as KBr pellets.

Conductance Measurements

The molar conductivity of the metal–XMP complexes was measured on a Konductoscope, E365B Metrohm.

Elemental Analysis

The Pt(II) content was determined by atomic absorption and the C, H, and N were analysed by Schwarzkopf Microanalytical Laboratory (U.S.A.).

TABLE II. FT-IR Absorption Bands (cm^{-1}) of 5'-$XMPNa_2$ and Its Metal Complexes.[a]

5'-$XMPNa_2$	$K[Pt(XMPNa_2)Cl_3]\cdot 6H_2O$	$[Pt(XMPNa_2)Cl]Cl\cdot 6H_2O$	$[Pt(XMPNa_2)_4]Cl_2\cdot 6H_2O$	$[cis\text{-}Pt(NH_3)_2(XMPNa_2)Cl]Cl\cdot H_2O$	$[trans\text{-}Pt(NH_3)_2(XMPNa_2)Cl]Cl\cdot H_2O$	$Cu(XMP)\cdot 6H_2O$	$Mg(XMP)\cdot 9H_2O$	Possible assignments [15–17, 19, 21, 22, 26]
1680bs	1670bs	1677bs	1679bs	1679bs	1672vs	1668bs	1663bs	$\nu C_6{=}O_6 + \nu C_6{=}C_5$
1668bs	–	–	–	–	–	–	–	$\nu C_2{=}O_2 + \nu C_4{=}C_5$
1612s	1623s	1619s	1619s	1619sh	1613s	–	1604s	δNH + imidazole ring
1573	1583s	1583vs	1583vs	1582s	1583vs	1581vs	1579s	ring skeletal vibrations
1529m	1537s	1530m	1536m	1540m	1539m	1539m	1535m	
1477m	1489m	1488m	1490m	1488s	1487m	1483m	1480m	$\nu N_7{-}C_8 + \delta C_8{-}H$
1489s	–	1377m	1377s	–	1370m	1370w	1373m	
1319w	1325w	1321w	1324m	1342m	1333m	1323m	1315w	$\nu N_7{-}C_8 + \nu N_7{-}C_5$
1290w	1294w	1300w	1301m	1295m	–	–	–	$+ \nu C_8{-}N_9 + \nu N_9{-}$
1205m	1213sh	1204sh	1215sh	1208s	1206m	1207m	1205m	sugar $+ \sigma C_8{-}H$
1171sh	1182s	1177s	1178s	1182s	1177s	1175sh	1169sh	
1109vs	1112sh	1106sh	1110sh	1110sh	1107sh	1110sh	1109s	νC–O (sugar)
1090bs	1074vs	1077s	1079s	1079s	1089bs	1085bs	–	νPO_3^{2-} deg.
	1063vs	1064bs	1063bs	1063bs	–	–		
976s	976s	976s	976s	975m	975s	989s	989vs	νPO_3^{2-} symmetric
911w	924m	923w	922w	923w	–	–	–	
870w	–	–	–	–	–	–	874w	ν ribose–phosphate
802m	807m	804m	804m	804m	801m	806m	804s	
783m	873m	782m	783m	781m	777m	783s	787s	νP–O
717m	727w	721m	721m	723m	723m	725w	716w	ring breathing mode
638w	633w	636w	637w	635w	630vw	630w	638w	NH out-of-plane def.
592sh	603w	604w	602w	602w	600w	598m	598m	PO_3^{2-} symmetric def.
513m	513w	529m	530m	510m	510vw	523w	523w	Skeletal def.
492sh	490sh	485sh	490w	485w	–	490w	490w	

[a]s = strong, b = broad, m = medium, w = weak, v = very, ν = stretching, δ = bending.

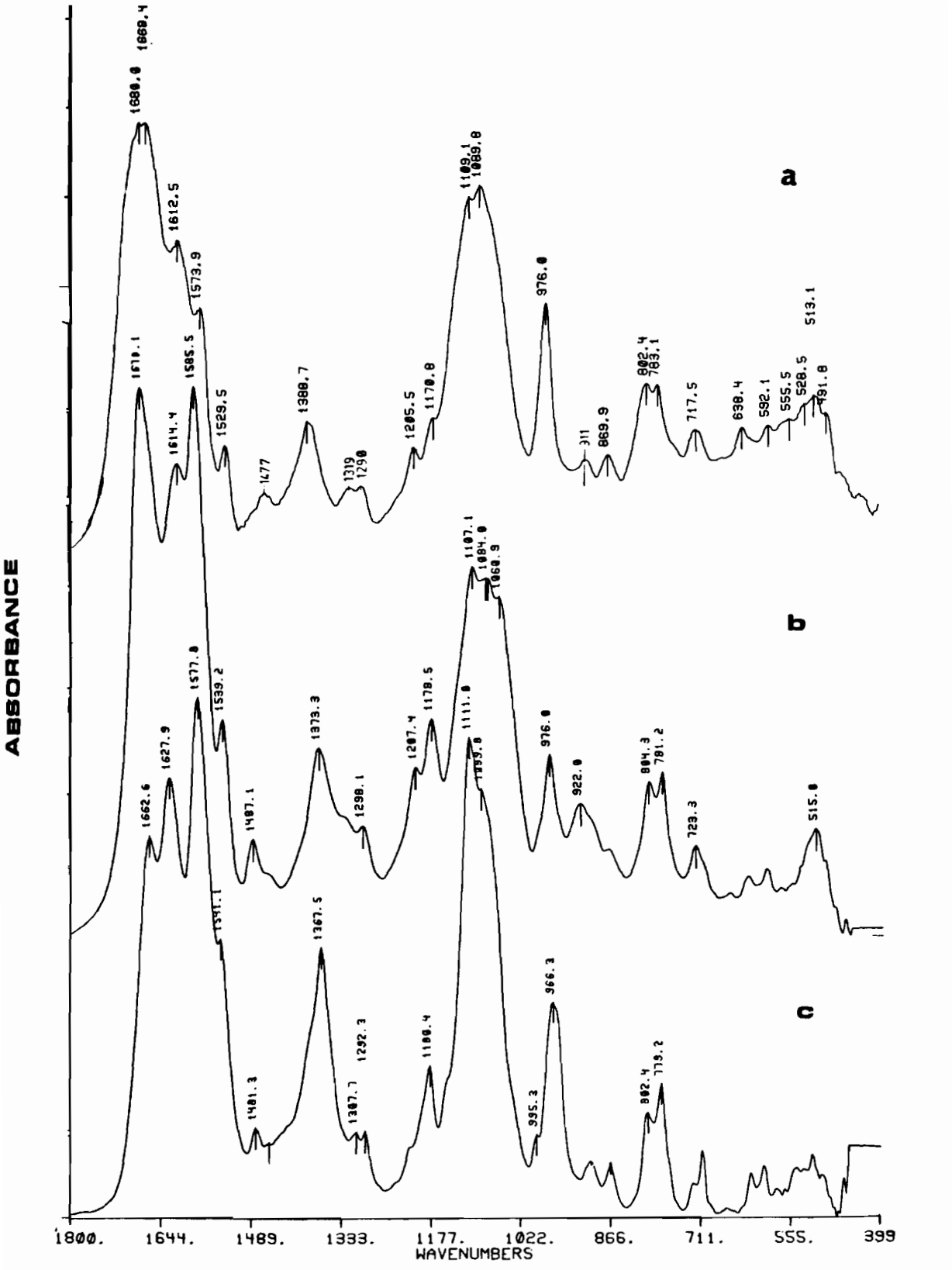


Fig. 1 (a)–(c). *(For caption see facing page).*

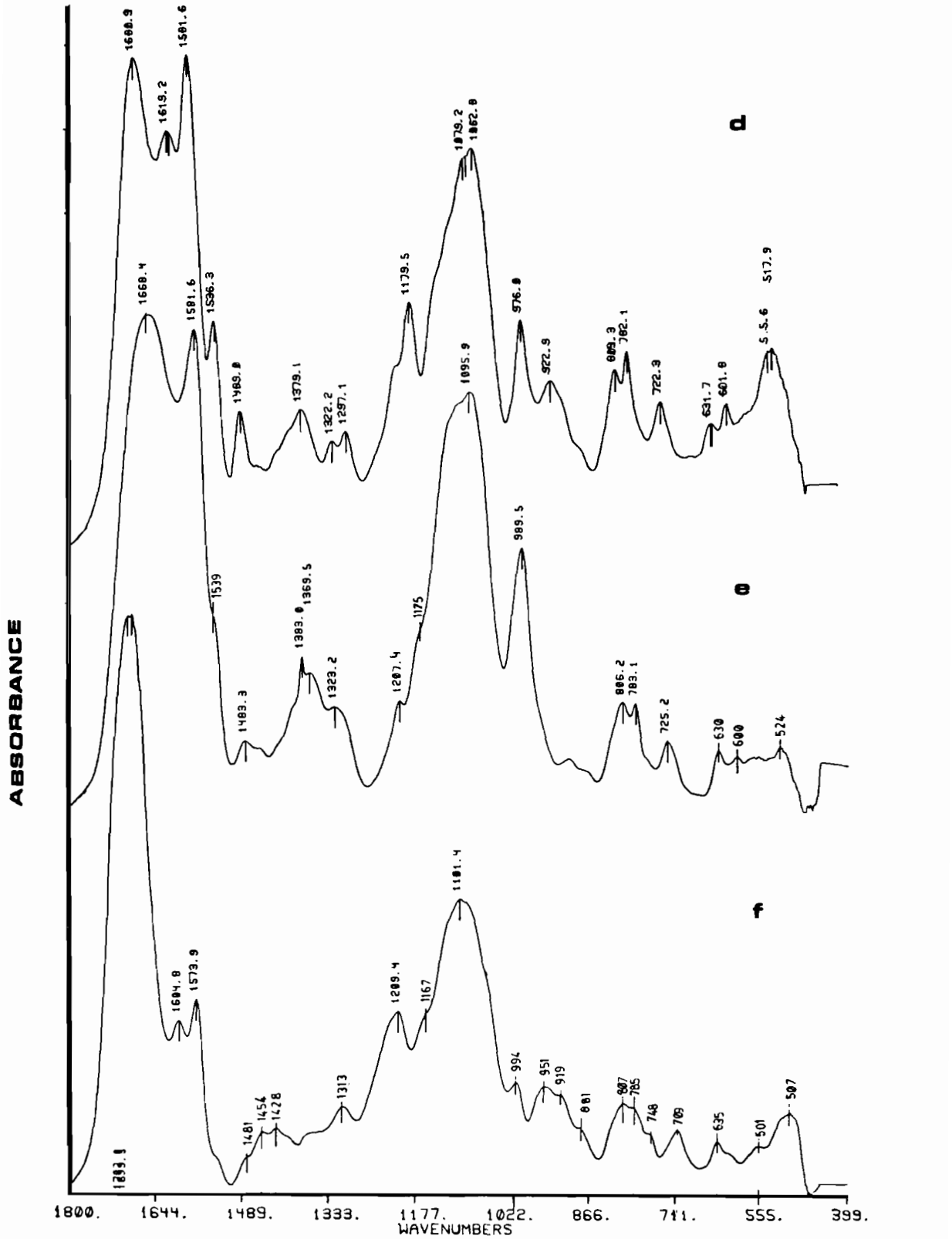


Fig. 1. FT-IR spectra of 5'-XMPNa$_2$ and its metal complexes in the region 1800–400 cm^{-1} for a, 5'-XMPNa$_2$; b, *cis*-[Pt(NH$_3$)$_2$-(5'-XMPNa$_2$)$_2$]Cl$_2$·4H$_2$O; c, *trans*-[Pt(NH$_3$)$_2$(5'-XMPNa$_2$)$_2$]Cl$_2$·4xH$_2$O; d, Pt(5'-XMPNa$_2$)$_2$Cl$_2$·6H$_2$O; e, Cu(5'-XMP)·6H$_2$O and f, Mg(5'-XMP)·4H$_2$O.

Results and Discussion

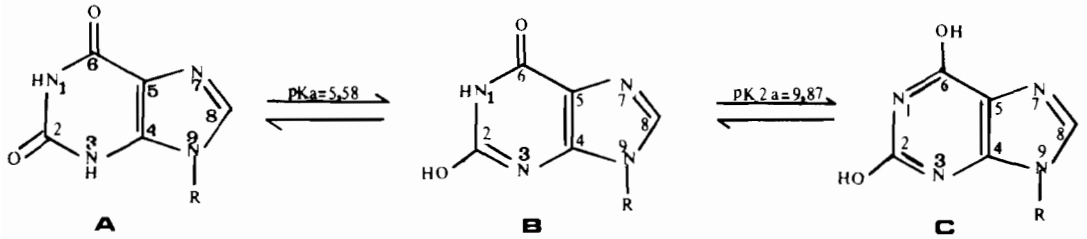
The FT-IR spectra of the free 5′-XMPNa$_2$ and its Pt(II), Cu(II) and Mg(II) complexes were recorded in the region 4000–400 cm^{-1} and the results are discussed in two different regions, namely 4000–2700 cm^{-1} and 1800–400 cm^{-1}.

4000–2700 cm^{-1}

In this region of the spectra, the symmetric and asymmetric stretching vibrations of the N–H, O–H, C–H and CH_2 groups of the free nucleotide are observed [15, 16] and exhibited no major changes upon metallation. There is evidence of strong hydrogen bonding in this region and it is very difficult to draw a definite conclusion on the nature of the coordination compounds formed.

1800–400 cm^{-1}

The 5′-XMPNa$_2$ molecule contains several donor atoms which are possible targets of metal–ligand bonding, for example, the N_7- atom of the purine ring, the N_1-, N_3-, O_6 and the O_2 of the pyrimidine ring as well as the sugar and phosphate oxygen atoms. Under neutral conditions the N_7-atom of the imidazol ring seems to be the more basic donor [17], while the rest of the donor atoms participate in metal–ligand bonding only under basic conditions. The N_3-atom is not involved in metal interaction due to the steric hindrance of the sugar moiety which can rotate around the Cl′–N9 bond. Neutral xanthosine also undergoes keto–enol–imine tautomeric conversion according to the following equation [18]:



The FT-IR spectrum of the free nucleotide showed considerable changes on complex formation. The main features of the spectra relevant to this discussion with possible assignments are shown in Fig. 1 and Table II. The two strong and broad absorption bands at 1680 and 1668 cm^{-1} in the spectrum of the free base related to the C_6=O and C_2=O stretching frequencies [17, 19], respectively, showed major changes in the spectra of the metal complexes (Fig. 1 and Table II). The absorption at 1680 cm^{-1} (C_6=O stretching) showed intensity changes and shifting ($\Delta\nu$ up to 20 cm^{-1}) in the spectra of the Pt(II), Cu(II) and Mg(II) complexes, whereas the absorption band at 1668 cm^{-1} (C_2=O stretching) was not observed in the spectra of the metal complexes (Table II). The shift of the C_6=O stretching vibration ($\Delta\nu_{max}$ = 8 cm^{-1}) in the spectra of the platinum complexes is mainly due to a rearrangement of the hydrogen bonding of the carbonyl group and it is not due to a direct Pt–carbonyl interaction since recent structural analysis of several Pt–xanthine derivative complexes showed [20] that the coordination takes place only through the N_7-atom of the purine ring system. The shift ($\Delta\nu$ = ±20 cm^{-1}) and intensity changes of the C_6=O stretching vibration in the spectra of Cu(II) and Mg(II) complexes could be attributed to an indirect metal–carbonyl interaction *via* a coordinated water molecule. Similar spectral changes occurred for the carbonyl stretching vibration in the spectra of a series of metal–GMP complexes [21] upon indirect metal–carbonyl bonding. The disappearance of the C_2=O absorption band in the spectra of all the metal–XMP complexes studied here is most probably due to the tautomeric conversion of the C_2=O group into the C–O–H group upon nucleobase metallation. Since the pK_{a1} = 5.58 (see Scheme II) and the reactions have taken place at neutral pH values, such tautomeric conversion should be feasible.

An absorption band with medium intensity at 1612 cm^{-1} in the free base spectrum is assigned [17] mainly to the N_1–H bending vibration. Although the N_3–H bending could not be identified with certainty, it could be coupled strongly with the N_1–H bending mode and would be expected to induce keto–enol tautomerism at C_2=O [18]. The N_1–H bending vibration of the free nucleotide at 1612 cm^{-1} exhibited a small shift towards higher frequencies in the spectra of all metal complexes, except in the spectra of the Cu(II) compound which is obscured by the broad and strong vibration of the C_6=O stretching vibration (Fig. 1 and Table II). The considerable shift of the N–H stretching at about 3400 cm^{-1} and that of the bending vibration at 1612 cm^{-1} upon base metallation is indicative of the non-participation of the N_1–H group in metal–ligand bonding.

Deprotonation and metallation of the N_1–H group changes considerably these absorption frequencies [17]. It should be noted that deuteration of the free 5′-XMPNa$_2$ showed shifting of both

bands at 3400 cm^{-1} (N–H stretching), at 1612 cm^{-1} (N–H in plane-bending) and at 635 cm^{-1} (N–H out-of-plane bending) to lower frequencies. Two other absorption bands with medium intensities at 1573 and 1529 cm^{-1} in the free ligand spectra assignable to the ring skeletal vibrations [17, 19], gained intensity and shifted towards higher frequencies upon ligand metallation (Fig. 1 and Table II). The changes observed for the skeletal vibrations are due to the N_7-electrophile bond which perturbs the electron distribution within the ring system and alters the ring vibrational frequencies [21]. An absorption band at 1477 cm^{-1} in the free nucleobase spectra appeared at a higher frequency in the spectra of metal complexes (Table II). Since this absorption band involves mainly the N_7–C_8 stretching and the C_8–H bending vibrations [22], the shift of this band towards higher frequencies is consistent with protonation [24] or metallation [25] of the azomethine group (C=N) which increases the C=N stretching frequency. The absorption bands near 1389, 1319, 1290, 1205 and 1170 cm^{-1} in the spectrum of the free base showed considerable intensity changes and shifting upon complex formation (Table II). Hence, these absorption bands are tentatively assigned to the purine ring vibrations involving the N_7–C_8, N_7–C_5, C_8–N_9 and N_9–sugar stretching and C_8–H bending vibrations [16, 21]. It seems that N_7-metallation perturbs the electronic distribution of the purine ring system, where the vibrations are mostly localized, and causes an imidazole ring distortion [21]. An absorption band with medium intensity at 717 cm^{-1} in the free base spectrum, which is related to the ring breathing mode [16, 21] shifted towards a higher frequency upon N_7-metallation (except in Mg(II) compounds in which it is shifted to a lower frequency due to the strong Mg–phosphate binding). The shift of the ring breathing mode to higher frequencies is characteristic of N_7-bonding, since similar behaviour was observed in the spectra of a series of N_7-bonded transition metal complexes [21] and it may indicate a change in the sugar conformation.

Phosphate Binding Modes

The characteristic features of the infrared vibrational frequencies of the mononucleotide phosphate group have been reported [21]. The PO_3^{2-} group exhibits five absorption bands in the region 1100–350 cm^{-1} [21, 26]. In the present work the infrared spectrum of the 5'-$XMPNa_2$ molecule shows four absorption bands in the region 1100–400 cm^{-1} which are given below (Fig. 1 and Table II).

(a) 1090 cm^{-1} (bs) related to the PO_3^{2-} degenerate stretching;

(b) 976 cm^{-1} (s) assigned to the PO_3^{2-} symmetric stretching;

(c) 783 cm^{-1} (m) related to the P–O stretching vibration and

(d) 592 cm^{-1} (m) assigned to the PO_3^{2-} symmetric deformation.

The other absorption band related to the PO_3^{2-} degenerate deformation was not observed in this region. The two absorption bands at 1090 cm^{-1} and 976 cm^{-1} are sensitive to the metallation or protonation of the phosphate group.

The infrared spectra of the structurally known [27] $Cu_3(5'\text{-GMP})_3 \cdot 8H_2O$ showed [21] splitting and shifting of the phosphate bands at about 1070 and 970 cm^{-1}, which is a result of direct Cu–OPO_3 bonding. Similar behaviour was observed [21] in the infrared spectra of the structurally known Cu(IMP)·H_2O [28], Zn(IMP)·H_2O [29], Cd(IMP)·H_2O [30] and Ca(IMP)·H_2O [31] where direct metal–phosphate coordination was shown.

In the present work the two absorption bands at 1090 and 976 cm^{-1} in the free 5'-$XMPNa_2$ showed no considerable changes upon platination (Fig. 1 and Table II) and this is indicative of an indirect Pt–OPO_3 bonding. The small shifts of the bands observed are mainly due to the indirect Pt(II)–phosphate interaction *via* water or NH_3 groups (in *cis*- and *trans*-Pt–$XMPNa_2$). Similar changes were observed in the spectra of Mg(II) compounds synthesized at neutral pH values (Table II), indicating an indirect Mg–OPO_3 interaction through coordinated water molecules. Such indirect interaction *via* bonded water molecules was observed in the crystal structures of a series of transition metal–nucleotide complexes [21]. It is interesting to note that the spectra of Mg(II) and Cu(II) XMP complexes obtained from acidic solution (pH = 4) showed considerable changes in the phosphate vibrational frequencies. The bands at 1090 and 976 cm^{-1} in the spectra of the Mg(II) compound lost intensity and showed splitting and shifting towards higher frequencies (Fig. 1). Similar shifting was also observed for these vibrational frequencies in the spectra of the Cu(II) complex (Fig. 1). These shifting and spectral changes which occur for the bands at 1090 and 976 cm^{-1} in the spectra of these two complexes are indicative of a direct metal–phosphate interaction, since such spectral changes were also observed [21] in the spectra of the Cu(II) and Mg(II) GMP complexes, obtained from acidic media in which a direct metal–OPO_3 binding was suggested.

Sugar Vibrational Frequencies

The sugar hydroxyl and CH frequencies appear as broad and strong absorption bands in the region 3500–2700 cm^{-1} and several other medium sharp absorption bands in the region 1400–500 cm^{-1} [26]. The latter are overlapped almost completely by the strong and broad absorption bands of the phosphate and base vibrations [21].

An absorption band at 1109 cm^{-1} in the spectrum of the free base attributed to the C–O stretching of the sugar moiety [21, 26] exhibited no changes upon ligand metallation and this is indicative of a non-sugar–metal interaction. Other bands at about 900–600 cm^{-1} related to the ribose–phosphate stretchings [32] showed modifications in the spectra of the metal complexes. The changes observed in these vibrational frequencies could be related to conformational changes around the ribose–phosphate bond [33] due to the direct or indirect metal–OPO_3 interaction and the rearrangement of the sugar hydrogen bonding upon nucleotide metallation.

Conclusion

On the basis of the spectroscopic and structural properties of the Pt(II), Cu(II) and Mg(II) XMP complexes studied here the following statements can be made:

(a) The free nucleotide exists in the keto–imine form (A) in the solid state, while in the metal complexes the enol ($C_2 \cdots O{-}{-}H$) form is predominant (B, C);

(b) Due to the marked spectral changes of the bands at 1573, 1529, 1477, 1389, 1319, 1290, 1205 and 1171 cm^{-1} in the spectra of all the metal complexes, the metal–nucleotide binding is suggested to be through the N_7-atom of the imidazole ring, since these absorption bands are assigned mainly to the purine ring vibrational frequencies;

(c) The direct metal $C_6{=}O$ interaction was not observed for these metal–XMP complexes, but an indirect metal carbonyl interaction *via* a coordinated water molecule can be proposed for Cu(II) and Mg(II) complexes and

(d) A direct metal–phosphate interaction is suggested for Mg(II) and Cu(II) complexes obtained from acidic media (pH = 4), due to considerable spectral changes observed in the phosphate vibrational frequencies at 1090 and 976 cm^{-1}. The indirect metal–phosphate binding through water or NH_3 molecules is indicated by the spectra of all the metal–XMP compounds synthesized at neutral pH values.

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