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Synthesis and Spectroscopic Study of Platinum, Copper and Magnesium Coordination Compounds with 2′-Deoxyguanosine-5′-monophosphate

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2′-Deoxyguanosine-5′-monophosphate disodium (5′-dGMPNa$_2$) salt reacts with divalent platinum, magnesium and copper to give compounds of the type Pt(5′-dGMP)$_n$Cl$_2$·xH$_2$O, cis- *and* trans-*[Pt(NH$_3$)$_2$(5′-dGMP)$_2$]Cl$_2$, Mg(5′-dGMP)·xH$_2$O and Cu(5′-dGMP)·xH$_2$O, where n = 1, 2, 3 and x = 2–6.*

Due to the distinct spectral similarities of these compounds with the structurally known N$_7$-bonded Ni(II)– and Co(II)–dGMP compounds, Pt(II), Mg(II) and Cu(II) are also found to be N$_7$-coordinated in this series of mononucleotide compounds. Furthermore, spectroscopic evidence shows that there is no direct Pt–phosphate interaction in the Pt(II) nucleotide coordination compounds, whereas such a direct metal–phosphate bonding has been observed in the Cu(II) and Mg(II) compounds, discussed here.

Introduction

Since the discovery of the antitumor activity of *cis*-Pt(NH$_3$)$_2$Cl$_2$ and related compounds [1], the interaction of the Pt(II) ion with nucleic acids and their constituents has been the subject of intensive investigation, both in the solid state [2] and in solution [3–10]. Although Raman and NMR spectroscopy have been widely used to investigate the metal–nucleotide coordination compounds [3–8] reliable correlation data between structural properties and spectral information is still missing.

Infrared spectroscopy is the least used technique to demonstrate the bonding mode in the metal–nucleotide compounds. Recently, we reported [11, 12] the IR spectra of a series of Pt(II) and Mg(II) compounds with adenosine-5′-monophosphate (5′-AMP) and guanosine-5′-monophosphate (5′-GMP). In the present paper, we wish to discuss the synthesis, characterization and properties of several Pt(II)–, Mg(II)– and Cu(II)–5′-dGMP coordination compounds by elemental analysis, molar conductivity and Fourier Transform infrared spectroscopy (FT-IR).

Having unambiguous crystallographic structural information [13] on some N$_7$-bonded [Ni(5′-dGMP)·5H$_2$O]·3H$_2$O and [Co(5′-dGMP)·5H$_2$O]·3H$_2$O compounds, we examined their FT-IR spectra and compared them to that of the newly synthesized Pt(II), Mg(II) and Cu(II) compounds obtained in this work in order to establish a correlation between spectral changes and N$_7$-coordination site perturbation on the 5′-dGMP molecule.

Experimental

Materials

K$_2$PtCl$_4$ was purchased from Johnson Matthey and Mallory Ltd. The *cis* and *trans*-Pt(NH$_3$)$_2$Cl$_2$ were prepared from K$_2$PtCl$_4$ according to routine methods [14, 15]. The nucleotide 5′-dGMP in acid and sodium salt forms was purchased from the Sigma Chemical Company.

Synthesis of Pt(II) compounds

The platinum(II) coordination compounds of 5′-dGMP were prepared by addition of a stoichiometric amount of K$_2$PtCl$_4$ or *cis-* and *trans* Pt(NH$_3$)$_2$Cl$_2$ to a solution of the nucleotide in 200 ml of water, in the presence of an appropriate amount of NaCl at room temperature. 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. Ethanol (50 ml) was then used to precipitate the compounds. The precipitate (yellowish-white) was redissolved in a small amount of water and reprecipitated by the addition of ethanol, then dried in a desiccator over CaCl$_2$ and analyzed to have the empirical formula of Pt(5′-dGMP)$_n$Cl$_2$·xH$_2$O, where n = 1, 2, 3 and x = 4–6. The compounds are soluble in H$_2$O and acidic water solutions only and not in the common organic solvents. Their colour varies from

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TABLE I. Analytical Data and Millimolar Conductance of Pt(II)–, Mg(II)– and Cu(II)–dGMP Complexes.

		M	C	H	N	Cl	Color	Conductivity (Ω^{-1} cm^2 mol^{-1})
1. $K[Pt(dGMP)Cl_3]\cdot 4H_2O$	found	23.79	15.03	2.53	7.92	12.90	yellow	230
	calc.	23.98	14.77	2.46	8.62	13.10		
2. $K[Pt(dGMP)Cl_3]\cdot C_2H_5OH$		24.55	18.39[a]	3.50	9.29	13.40	pale yellow	200
		24.78	18.30	2.29	8.90	13.53		
3. $Pt(dGMP)_2Cl_2\cdot 6H_2O$		16.45	20.30[a]	4.11	11.55	5.90	yellow	260
		16.61	20.44	3.07	11.92	6.04		
4. $[Pt(dGMP)_3Cl]Cl\cdot 6H_2O$		12.25	23.52	3.97	12.77	4.35	white	300
		12.39	22.88	3.05	13.35	4.51		
5. *cis*-$[Pt(dGMP)_2(NH_3)_2]Cl_2\cdot 6H_2O$		15.95	20.00	4.11	13.50	5.70	white	240
		16.15	19.98	3.48	13.90	5.88		
6. *trans*-$[Pt(dGMP)_2(NH_3)_2]Cl_2\cdot 6H_2O$		16.25	19.45	4.62	14.16	5.90	white	260
		16.15	19.98	3.48	13.90	5.88		
7. $MgdGMP\cdot 4H_2O$		5.28	27.27	4.42	15.05	–	white	160
		5.43	26.65	4.44	15.53	–		
8. $MgdGMP\cdot 2H_2O$		5.69	29.88	4.70	16.56	–	white	120
		5.90	28.92	3.85	16.86	–		
9. $CudGMP\cdot 3H_2O$		13.50	25.38	4.26	14.58	–	pale green	80
		13.65	25.44	3.82	14.86	–		

[a] The high hydrogen values found for compounds 2 and 3 are due to their hygroscopic nature; dGMP is the disodium salt ($dGMPNa_2$) except in compounds 7, 8 and 9 in which the sodium ions have been replaced by the metal cations, Mg(II) and Cu(II).

yellow (1:1) to white for the 3:1 compounds. They show high values of molar conductivity, and this is mainly due to the presence of Na^+ ions associated with the monocleotide [16]. The analysis and millimolar conductances for these Pt(II)–$dGMPNa_2$ compounds are given in Table I.

Preparation of Mg(II) Compounds

The magnesium(II) compounds were synthesized at two different pH ranges, namely 7–4 and 7–9. 1 mmol of nucleotide (5′-$dGMPNa_2$) was dissolved in 30 ml of H_2O, then added to a solution of 1 mmol of $MgCl_2\cdot 6H_2O$ in 20 ml of solution and adjusted to the pH values mentioned above with 0.1 N HNO_3 or 0.1 N NaOH, then it was heated at 60 °C for 30 minutes. After cooling down to room temperature, a white precipitate appeared, which was filtered off and washed with cold water and air dried. The Mg(II) compounds of the nucleotide are soluble in hot water and slightly soluble in hot alcohol. They can be recrystallized from 0.1 N HCl or 0.1 N HNO_3 solution. The compounds show a conductivity value of 120–160 Ω^{-1} cm^2 mol^{-1}, corresponding to 2:2 electrolytes. The analytical data and millimolar conductances are given in Table I.

Cu(II) Compound

Hydrated copper nitrate (1 mmol) in 20 ml of H_2O was added to a solution of 5′-$dGMPNa_2$ (1 mmol) in 20 ml H_2O. The pH was adjusted to 4 and the solution was heated at 60 °C for 30 minutes. After cooling down the crystalline Cu(5′-dGMP)·$3H_2O$ was isolated, washed with cold water several times and air dried. The analytical results are given in Table I. The structurally known Co(II) and Ni(II)-dGMP compounds were prepared by published methods [13].

Physical Measurements

FT-IR have been recorded on a DIGILAB FTS-15/C Fourier Transform Michelson Infrared Interferometer, equipped with a high sensitivity HgCdTe detector and a KBr beam splitter with a spectral resolution of 2 to 4 cm^{-1}. Conductance measurements were carried out on a conductoscope, E365B MEROCHM. X-ray powder photographs were taken for comparative purposes by using a powder camera (Philips, Debye-Scherre) with copper Kα radiation and nickel filters.

Elemental Analysis

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

Results and Discussion

The X-ray structural analysis of [Ni(5′-dGMP)·$5H_2O$]$3H_2O$ and [Co(5′-dGMP)·$5H_2O$]$3H_2O$ has shown [13] an octahedral arrangement around the Ni(II) and Co(II) metal ions completed by the N_7 nitrogen atom of the guanine ring together with the five water molecules. Two of the water molecules are strongly hydrogen-bonded to a phosphate group. Three H_2O molecules in the outer coordination sphere of the said metal cations are waters of crystallization. The FT-IR spectra of these compounds are recorded and compared with those of the corresponding Pt(II), Mg(II) and Cu(II) compounds synthesized here. It should be noted that our discussion is largely based on the normal modes of vibration calculation by Tsuboi *et al.* [17–20] and the observations made by Lord and Thomas [21], Novak [22] and Chinsky *et al.* [23], being in good agreement with their observations.

Region 3600–2700 cm^{-1}

In this region, the symmetric and antisymmetric stretching frequencies of NH_2, NH, H_2O, OH, CH_2 and CH of the free 5′-dGMP (related to the base residue and the sugar moiety) have appeared [18, 21] and showed no considerable changes in the spectra of the metal compounds (Table II). The small shifts of the bands observed are mainly due to the rearrangement of the strong hydrogen-bonding network of the free ligand [24] upon formation of the coordination compounds. Due to the presence of such a hydrogen-bonding system in the free nucleotide and its metal compounds, one cannot draw a conclusion as to the nature of the metal–ligand bonding based on the observations made in this region of the spectra. The main features relevant to this region with possible assignments are given in Table II.

Region 1800–400 cm^{-1}

(a) CO stretching, NH$_2$ bending and skeletal vibrations

A strong, broad absorption band at 1697 cm^{-1} in the spectrum of the free 5′-dGMPNa_2 mainly assigned to the $C_6{=}O$ stretching vibration [17] showed intensity changes but no considerable displacement in the spectra of the structurally known N_7-bonded Ni(II) and Co(II) compounds. The small shift of the $C_6{=}O$ stretching frequency, observed in the spectra of the N_7-bonded metal compounds (Table II), is mainly due to the hydrogen bonding of the carbonyl group, through a coordinated water molecule [13] and not to a direct metal–carbonyl interaction. It is worth noting that the crystal structure of free 5′-dGMPNa_2 shows [24] sodium–carbonyl interaction with Na–O distances of 2.559 and 2.355 Å. Since the $C_6{=}O$ stretching vibration of the free 5′-dGMP acid (at 1705 cm^{-1}) does not show any major alteration in 5′-dGMPNa_2 salt (1697 cm^{-1}), this indicates that the sodium–carbonyl interaction, observed in the said compound, is largely electrostatic.

A shoulder absorption band at 1665 cm^{-1} in the spectra of the free ligand, related to the scissoring motion of the NH_2 group [17], gained intensity and split into a doublet shifting to a lower frequency in the spectra of Ni(II)– and Co(II)–5′-dGMP compounds (Table II). The shift of the NH_2 bending mode to a lower frequency, together with the shift of the NH_2 stretching frequency at 3400 cm^{-1} to a higher frequency, is indicative of the weakening of the hydrogen-bonding network of the NH_2 group on N_7-metal coordination and not to a direct metal–NH_2 binding, since metalation or deprotonation of the NH_2 group would cause considerable changes in the said absorption frequencies [25].

The other three absorption bands with medium intensities in the free base spectra at 1606, 1580 and 1532 cm^{-1}, mainly assigned to C_4–N_3, C_4–C_5 and C_4–N_9 stretching frequencies [17] (Table II), appeared as strong absorption bands at about the same position in the spectra of the structurally known N_7-bonded Ni(II) and Co(II) compounds. The small changes observed are probably due to the inductive effects caused by the metal electrophile bound at the N_7-coordination site, which induces less electron delocalization and finally less contribution to the skeletal vibration of the ring system. Similar spectral changes were observed in the region 1700–1530 cm^{-1} in the spectra of the Pt(II), Cu(II) and Mg(II) compounds studied here (Table II).

(b) Purine ring vibrational frequencies

An absorption band with medium intensity at 1481 cm^{-1} in the spectrum of the 5′-dGMPNa_2 assigned to C_8–H bending and N_7–C_8 stretching frequencies [26] appeared as a doublet at higher (1485–1500 cm^{-1}) and lower (1450–1455 cm^{-1}) frequencies, in the spectra of the structurally known N_7-bonded Ni(II), Co(II) and the other unknown Cu(II), Pt(II) and Mg(II) compounds (Table II). It has been demonstrated experimentally [27] that the $C{=}N^+$ groups have in general higher frequencies than the parent C=N groups; thus, protonation [28] or metalation [29] of the C=N groups causes an increase in the C=N stretching frequencies. Therefore, N_7-metalation of the purine ring system could increase in the N_7–C_8 stretching frequencies in these series of metal–dGMP compounds.

The absorption bands at 1330, 1275, 1241 and 1175 cm^{-1} in the spectra of the free nucleotide show considerable changes (shifting and splitting) in the spectra of the N_7-bonded Ni(II), Co(II) and the other metal ion compounds studied here (Table II). Since these absorption bands are mainly assigned [17, 23] to N_7–C_5, N_7–C_8, N_7–C_8–N_9 stretchings and C_8–H bending vibrations, it seems that

TABLE II. FT-IR Absorption Bands (cm^{-1}) of the Free 5'-dGMP and Its Metal Complexes with Possible Assignments.

5'-dGMP-Na_2	Ni(dGMP)·$8H_2O$	Cu(dGMP)·$5H_2O$	*cis*-$Pt(NH_3)_2$-$(dGMP)_2Cl_2$	*trans*-$Pt(NH_3)_2$-$(dGMP)_2Cl_2$	$Pt(dGMP)_2Cl_2$	$Pt(dGMP)_3Cl_2$	Mg(dGMP)·$4H_2O$	Possible Assignment
3440s	3460s	3440s	3450s	3440s	3440bs	3440s	3440s	νNH_2 asymmetric [17–21]
3320s	3340s	3340s	3330s	3320bs	3340bs	3340vs	3320s	νNH_2 symmetric [17–21]
3250b	3270s	3270s	3230s	3240m	3240s	3240	–	νOH (hydrogen-bonded) [19, 21]
3120bs	3140s	3140bs	3130bs	3120bs	3130s	3140s	3140bs	$\nu C_8{-}H$ [17]
3020s	–	3030s	3050s	3040s	3050s	3040m	3000s	νNH [17]
2940s	2940s	2940s	2950s	2950s	2950s	2940s	2940m	νCH_2 [19, 21]
2880s	2860s	2860m	2870m	2860m	2880m	1860m	2860m	
2780m	2760m	2750m	2750w	2750w	2750w	2750w	2750w	νCH [19, 21]
1697vs	1695s	1687vs	1690s	1684s	1696vs	1690vs	1698bs	$\nu C_6{=}O + \nu C_6{=}C_5$ [17]
1665sh	1650sh	–	1655sh	1650sh	–	1655sh	1655sh	$\delta NH_2 + \nu C_2{-}N_2$ [17]
	1640s	1640vs	1641vs	1640vs	1641s	1641vs	–	
1608s	1600s	1608s	1601vs	1601vs	1596s	1600vs	1606s	$\nu C_4{-}N_3 + \nu C_4{-}C_5 + \nu C_5{-}N_7$ [17]
1580m	1578sh	1580sh	1582sh	1585sh	1588s	1585sh	1585sh	$\nu C_5{-}C_4 + \delta N_1{-}H + \nu C_6{-}N_1$ [17]
1532s	1542m	1536m	1540m	1541m	1538s	1539s	1534s	$\nu C_4{-}N_9 + \nu C_6{=}O + \nu C_2{-}N_1$ [17]
1481m	1488m	1486m	1500m	1499s	1500s	1502s	1483m	$\delta C_8{-}H + N_7{-}C_8$ [26]
	1451w	1450vs	1457w	1563w	1452w	1555vw	1455sh	
1411w	1418w	1413m	1410vw	–	1410sh	1410vw	1412m	$\nu CH_2 + \delta CH$ [19]
1372m	1395m	–	1383sh	1394m	1383m	1394m	1380sh	ν(pyrimidine ring) [22]
1358s	1356s	1362s	1350s	1340s	1354m	1350m	1361s	
1330m	1320m	1320sh	1325sh	1330m	1320sh	1320sh	1325sh	$\nu C_8{-}C_9 + \nu N_7{-}C_8 + \delta N_1{-}H + \nu C_2{-}N_2$ [17, 23]
	1330sh	–	–	–	–	–	–	
1275m	1280sh	1280w	1285vw	1280vw	1280sh	1285m	1275w	$\nu C_6{-}N_1 + \nu N_7{-}C_5$ [17]
	1260sh	1260w	–	–	1260w	–	1260w	
1258m	1251s	1252w	1252vw	1255vw	1251w	1250sh	1242sh	$\delta C_8{-}H + \nu N_7{-}C_8$ [17]
1241m	1218s	1214m	1209w	1212sh	1220w	1215sh	1216m	
1175m	1174s	1176s	1173m	1181s	1177s	1177s	1175s	$\nu N_7{-}C_8 + \nu N_9$–sugar $+ \nu C_4{-}N_3$ [17]
1112sh	1112s	–	1110sh	1112sh	1110sh	1112sh	1110sh	$\nu C{-}O$ of sugar [19]
1077bs	1093s	1106s	–	–	–	–	1095sh	νPO_3^- deg. [19, 20]
	1075vs	1078vs	1083bs	1081bs	1067bs	1070bs	1069bs	
1022sh	1047sh	–	–	–	–	–	–	$\nu C{-}O$ [19]
976s	992s	944vs	–	–	–	–	1020sh	νPO_3^{2-} symmetric [19, 20]
	972s	–	978s	972s	976s	975s	990sh	

943vw	940sh	953m	–	–	–	–	936s	ribose ring + ribose–phosphate stretching [35]
990vw	–	900vw	900sh	890w	900vw	900w	900vw	
860w	889s	877m	886w	870w	877vw	880vw	870vw	
800sh	808s	825w	796sh	796sh	810sh	805sh	797sh	
780s	775s	778m	779s	779s	780s	780s	778s	νP–O stretching [19, 20]
740vw	728w	740w	735w	736vw	730w	735vw	735vw	ribose–phosphate stretching [35]
713vw	–	–	710vw	–	712vw	710vw	710sh	
695m	705s	698m	705m	705m	706m	705m	698m	ring breathing mode [17]
670sh	665w	660w	685vw	683w	680w	680sh	670vw	ring deformation [17]
647m	645m	640w	634w	640m	635w	640w	638m	NH out-of-plane def. [17]
575m	580w	580m	589w	580sh	575m	576sh	575w	PO_3^{2-} symmetric def. [19, 20]
531s	530w	540m	530m	529s	530m	528s	530sh	skeletal def. [17]
500sh	510w	510m	510sh	512sh	510sh	516s	510sh	
450vw	450vw	450vw	450w	450sh	460w	460w	450sh	PO_3 deg. def. [19, 20]

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

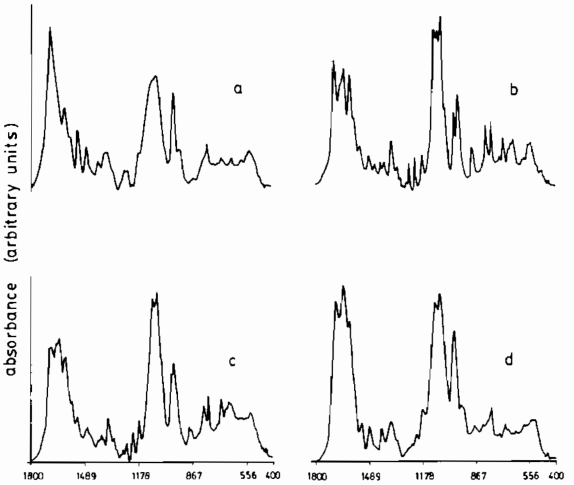


Fig. 1. FT-IR spectra of 5′-dGMPNa$_2$ and its N$_7$-bonded metal compounds in the region of 1800–400 cm^{-1} for a, 5′-dGMPNa$_2$; b, Ni(5′-dGMP)·8H$_2$O; c, Co(5′-dGMP)·8H$_2$O and d, Cu(5′-dGMP)·3H$_2$O.

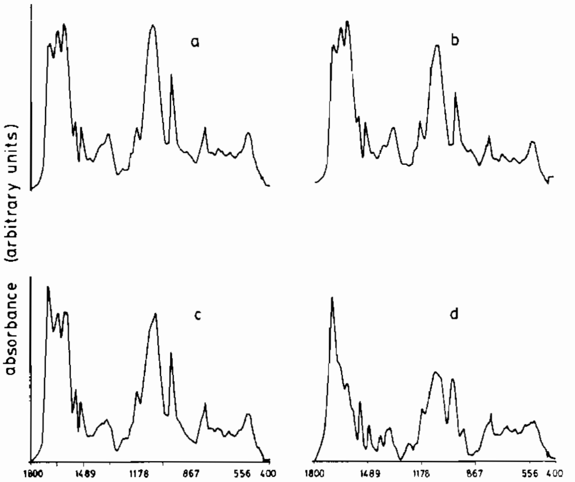


Fig. 2. FT-IR spectra of metal–5′-dGMP compounds in the region 1800–400 cm^{-1} for a, *cis*-[Pt(5′-dGMP)$_2$(NH$_3$)$_2$Cl$_2$·6H$_2$O; b, *trans*-[Pt(5′-dGMP)$_2$(NH$_3$)$_2$Cl$_2$·6H$_2$O; c, [Pt(5′-dGMP)$_2$Cl$_2$]·6H$_2$O and d, Mg(5′-dGMP)·4H$_2$O.

the N$_7$-coordination could change the electron distribution of the purine ring system, where the vibrations are mostly localized and finally induce a distortion of the imidazol ring system.

Mg–dGMP Compounds

The spectra of the Mg(II) compounds synthesized at different pH values show marked similarities with those of the structurally known N$_7$-bonded Ni(II) and Co(II) compounds except in the region of 1700–1600 cm^{-1} where the C$_6$=O stretching and NH$_2$

bending mode are known [17] to absorb. The carbonyl stretching frequency appeared as a strong broad absorption band at 1698 cm^{-1} and the NH_2 bending as a shoulder absorption at 1655 cm^{-1} in the spectra of Mg(II) compounds (similar to those of the corresponding free ligand absorptions) (Figs. 1 and 2), which is rather different from those of the other compounds described here. The dissimilarities observed in this region (1700–1600 cm^{-1}) are mainly due to the different hydrogen-bonding network of the $C_6{=}O$ and NH_2 groups, rather than to different coordination sites involved in bonding. The crystal structures of *Z* and *B* DNA, containing magnesium ions, show [30] that Mg(II) is bonded to the N_7 nitrogen atom of the guanine residue and to five water molecules.

Phosphate Vibrational Frequencies

The IR spectra of the mononucleotide phosphate groups together with their metal derivatives have been reported earlier [11, 12]. The IR spectrum of 5′-$dGMPNa_2$ shows five absorption bands in the region of 1100–400 cm^{-1} assignable to the PO_3^{2-} vibrational frequencies [19, 20]: 1077 cm^{-1} (broad and strong) assigned to PO_3^{2-} degenerate stretching; 976 cm^{-1} (strong) assigned to PO_3^{2-} stretching frequency; 780 cm^{-1} (medium intensity) assigned to P–O stretching frequency and two other absorption bands with medium intensities at about 570 and 450 cm^{-1}, assigned to the symmetric and degenerate deformation modes of the PO_3^{2-} group, respectively. Three of these absorption bands at 1077, 976 and 780 cm^{-1} show drastic changes upon direct or indirect metal–phosphate interaction.

The Cu(II) ion is directly bonded to the phosphate group, as well as to the N_7 atom in the $Cu_3(5'\text{-GMP})_3\cdot 8H_2O$ compound [31]. The phosphate vibrational frequencies at about 1070, 972 and 800 cm^{-1}, in the spectra of the free 5′-GMP show [12] shifting and splitting in the spectra of the copper(II) compound. Similar alterations occurred [12] in the spectra of the free 5′-IMP (inosine-5′-monophosphate) upon phosphate coordination in Cu(II)– and Zn(II)–IMP compounds [32, 33].

The phosphate vibrational frequencies at 1080, 984 and 820 cm^{-1} in the spectra of 5′-CMP (cytidine-5′-monophosphate) also exhibited [12] shifting and splitting upon direct metal–phosphate bonding in $Co(5'\text{-CMP})\cdot H_2O$ and $Cd(5'\text{-CMP})\cdot H_2O$ compounds [34].

In the present work, the absorption bands at 1077, 976 and 780 cm^{-1} in the spectrum of the free 5′-$dGMPNa_2$ show considerable changes (shifting and splitting), in the spectra of $[Ni(5'\text{-dGMP})\cdot 5H_2O]$ and $[Co(5'\text{-dGMP})\cdot 5H_2O]$ compounds (Figs. 1 and 3). Since the X-ray structural analysis shows [13] that the phosphate group is indirectly bonded to Ni(II) and Co(II) metal ions, via two water molecules, it seems therefore that this indirect metal–phosphate interaction causes considerable changes in the phosphate vibrational frequencies.

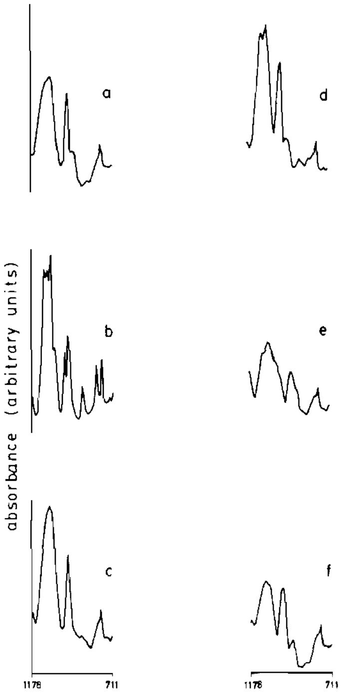


Fig. 3. FT-IR spectra of 5′-$dGMPNa_2$ and its metal compounds in the region of 1178–711 cm^{-1} (phosphate region) for a, 5′-$dGMPNa_2$; b, $Ni(5'\text{-dGMP})\cdot 8H_2O$; c, *cis*-$[Pt(5'\text{-dGMP})_2(NH_3)_2]Cl_2\cdot 6H_2O$; d, $Cu(5'\text{-dGMP})\cdot 3H_2O$; e, $Mg(5'\text{-dGMP})\cdot 2H_2O$ (pH = 4) and f, $Mg(5'\text{-dGMP})\cdot 4H_2O$ (pH = 7).

The absorption bands at 1077, 976 and 780 cm^{-1} in the spectrum of 5′-$dGMPNa_2$ exhibited considerable changes in the spectrum of the $Cu(5'\text{-dGMP})\cdot 3H_2O$ compound (Fig. 3). Since the IR spectra and the X-ray powder photograph of this compound show marked similarities with that of the structurally known $Cu_3(5'\text{-GMP})_3\cdot 8H_2O$ [31] the Cu(II) ion must also be directly bonded to the phosphate group, as well as to the N_7-atom of the guanine residue of 5′-dGMP with a possible polymeric structure in the $Cu(5'\text{-dGMP})\cdot 3H_2O$ compound.

The IR spectra of the Mg(II) compounds obtained in acidic media show a resemblance to that of the $Cu(5'\text{-dGMP})\cdot 3H_2O$ compound by exhibiting splitting and shifting of the absorption bands at 1077, 976 and 780 cm^{-1}, containing direct $Mg{-}OPO_3$ bonding, whereas the Mg(II) compounds synthesized at basic pH values do not show any considerable changes in the said absorption frequencies (Fig. 3), thus indicating no direct metal–phosphate interaction. The Pt(II)–dGMP compounds discussed here show no large perturbation of the absorption bands at 1077, 976 and 780 cm^{-1} (related to the phosphate stretching frequencies) and therefore, the direct Pt(II)–phosphate interaction does not occur in the Pt(II)–dGMP compounds (Fig. 3) studied here.

It is worth mentioning that the X-ray analysis [24] of 5′-dGMPNa$_2$ shows direct Na–phosphate interaction with Na$^+$–O distances of 2.34 and 2.39 Å. Since the absorption bands of the phosphate group, in the region of 1100–780 cm^{-1} in 5′-dGMPNa$_2$ do not show any major differences from that of the free 5′-dGMP acid, this Na–phosphate interaction should be largely ionic.

Sugar Vibrational Frequencies

As well as the strong broad absorption bands in the region of 3600–2700 cm^{-1} related to the sugar vibrations [19, 21], the ribose ring also contains several sharp fine absorption bands in the region of 1400–400 cm^{-1} which are mainly obscured by the strong broad absorption bands of the phosphate group and the base moiety. The band at 1112 cm^{-1} in the spectra of the free 5′-dGMPNa$_2$ assigned to C–O stretching of the ribose ring [19] shows no changes in the spectra of the metal compounds (Table II), thus indicating no direct metal–sugar interaction. The absorption bands in the region 943–800 cm^{-1} in the spectrum of the free ligand related to the ribose–phosphate stretching frequencies [35], naturally exhibit some intensity changes and shifting in the spectra of the metal compounds. The changes observed may be due to the conformational changes around the ribose–phosphate bond [36, 37], which come about upon direct or indirect metal–phosphate interaction.

An absorption band with medium intensity at 695 cm^{-1} in the spectrum of the free ligand related to the guanine ring breathing mode [17] shifted to higher frequencies in the spectra of the metal compounds (Table II). A similar shift was observed in the spectra of the structurally known N$_7$-bonded metal–5′-GMP compounds [12], which is characteristic of N$_7$-bonding in this series of metal–mononucleotide compounds.

Conclusion

Atomic motions in the ring system of 5′-dGMP are strongly coupled and the vibrations are spread over the entire molecule. Metalation of the ring system does not simplify the vibrational problem. Using the spectroscopic and structural properties of the structurally known N$_7$-bonded Ni(II)– and Co(II)–dGMP compounds and the other Pt(II), Mg(II) and Cu(II) compounds studied here the following statements can be made:

(1) Similar spectral changes occurred for the C$_6$=O stretching, NH$_2$ bending and skeletal vibrations of the ring system in the region 1700–1540 cm^{-1} in the complexes,

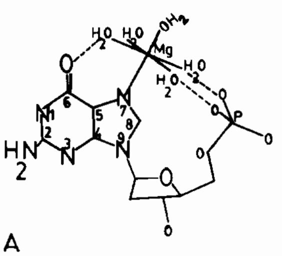
(2) shifting and splitting of the band at 1481 cm^{-1} assigned to C$_8$–H bending and N$_7$–C$_8$ stretching frequencies) was observed,

(3) considerable spectral changes in the absorption band at 1330, 1275, 1241 and 1175 cm^{-1} (assigned mainly to N$_7$–C$_8$, N$_7$–C$_5$, N$_9$–C$_8$ stretching and C$_8$–H bending mode) were found,

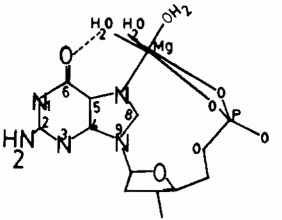
(4) the absorption band at 695 cm^{-1}, due to the breathing mode of the ring system, shifted to a higher frequency and

(5) shifting and splitting of the bands at 1077, 976 and 780 cm^{-1} (related to the PO$_3^{2-}$ vibrational frequencies) are indicative of direct or indirect metal–phosphate coordination, whereas the lack of any considerable changes in the said absorption bands may indicate a metal–phosphate ionic interaction.

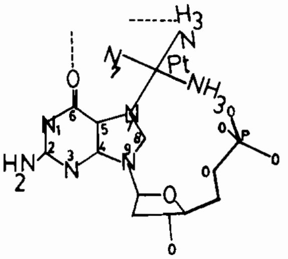
It is worth noting that the Mg(II) ion shows a soft acid character by binding to the soft base nitrogen N$_7$-atom of the ring system in the Mg–dGMP complexes obtained in basic solution (A), while the hard acid character of the Mg(II) ion predominates in the compounds synthesized in acidic media by binding to hard base oxygen atoms of the phosphate group as well as to the N$_7$-atom (B). No direct metal–carbonyl bonding was observed in the solid state com-



A



B



C

pounds studied, here, whereas an indirect metal–carbonyl interaction *via* H_2O or NH_3 cannot be ruled out for these metal–nucleotide compounds. Pt(II) compounds are only N_7-bonded and show no direct or indirect Pt–phosphate interaction (C). The Cu(II) ion also shows N_7-bonding, as well as a direct Cu–phosphate interaction in Cu(5′-dGMP)·$3H_2O$, similar to the structurally known $Cu_3(5'\text{-}GMP)_3\cdot 8H_2O$ complex.

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