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Some New Derivatives of Ni(II) with Uracil, Uridine and Nucleotides

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Abstract

This paper describes the synthesis of compounds of Ni(II) with uracil, uridine and the nucleotides 5'UMP, 5'CMP, 5'GMP and 5'IMP, and their characterization, carried out by elemental analysis, by studying the infrared spectra, diffuse reflectance and conductivity measurement.

In the complexes of Ni–URA (and Ni–URD) with acetate, direct coordination of the metal ion to the C_4=O group of the pyrimidine ring is inferred from the changes observed on the infrared spectrum of the corresponding bands at νC=O. The variations in frequency of the νCOO symmetric and asymmetric bands of the acetate group together with the conductivity and reflectance results seem to indicate the dimer structure of the compounds.

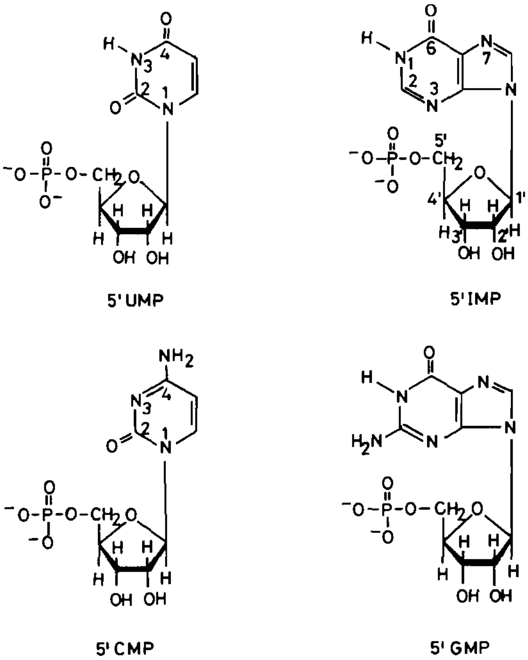
In the compounds of Ni–URA (and Ni–URD) with ethylenediamine indirect bonding of Ni(II) to the pyrimidine ring is inferred, probably established through hydrogen bonds involving the C_4=O groups in the base or nucleoside and the $-NH_2$ groups in the ethylenediamine.

In the complexes of Ni–nucleotide, bonding seems to occur through the heterocyclic ring (C_4=O for 5'UMP, N(3) for 5'CMP, N(7) for 5'GMP and 5'IMP) together with additional interactions through the phosphate group.

Introduction

In the field of interactions between metal ions and nucleotides, it is interesting to study complexes of Ni(II) with uracil, uridine and nucleotides because the well-known presence of a constant amount of Ni(II) in ribonucleic acids suggests it plays an important role, which has not yet been discovered. Also of interest is the synthesis and characterization of these compounds which, being relatively labile, may be found balanced in different ways in solution, depending on the temperature, pH and concentrations, and which offer many possibilities as far as control of enzyme activity is concerned [1].

In comparison with other bases and nucleosides the formation of uracil and uridine complexes proved more difficult because the heterocyclic nitrogens were protonated in a wide area of pH, making coordination by nitrogen possible only in basic conditions different from those found in biological systems [2–4]. Another alternative for bonding is coordination by carbonyl oxygen, which may be promoted by using a suitable dissolving agent [5–8]. Parallel to this type of study, a lot of work has been carried out on uracil and bases related to Pt and Pd, encouraged by the well-known anti-tumor action of platinum blues, both in solution and in the solid state [9–12].


5'UMP

5'IMP

5'CMP

5'GMP

Fig. 1. Complexes of 5'UMP, 5'IMP, 5'CMP and 5'GMP.

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In the complexes of 5′UMP, the presence of the phosphate group alters the bonding problem and the phosphate oxygens are the main point for coordination [13–15]. In the complexes of 5′CMP, 5′GMP and 5′IMP coordination occurs mainly through the heterocyclic nitrogens (Fig. 1).

Experimental

The analyses of carbon, hydrogen and nitrogen were carried out in a Carlo Erba model 1106 microanalyzer in the Institute of Bio-Organic Chemistry in Barcelona and in a Perkin Elmer 240.B in the Faculty of Chemistry, Tarragona.

The chlorine analysis was determined by the Schoniger method using a 638 Metrohm Titro Processor, by burning the sample in O_2 over sodium dissulphite. Dissolutions was assessed by Volhard.

The sodium content was determined by flame photometry in a Perkin Elmer 703 spectrophotometer. The working conditions were: $\lambda = 590$ nm and slit = 0.2 nm with an oxidant acetylene–air flame.

Nickel was determined by atomic absorption in a Perkin Elmer 703 spectrophotometer. The working conditions were: $\lambda = 232$ nm and slit = 0.2 nm with an oxidant acetylene–air flame.

The phosphorous content was determined by using the colorimetric method of phosphomolibdovanadate [16]. The measurements were carried out in a Perkin Elmer 552 UV–Vis spectrophotometer at 390 nm and slit 2 nm.

The conductivities were measured with a Crisom 525 conductimeter. The cell constant was determined by using a water solution of KCl 10^{-2} N ($k = 1.04$ cm^{-1}).

The infrared spectra were registered in the solid state (KBr pellets) on a Perkin Elmer 683 infrared spectrophotometer with an infrared data station.

The reflectance spectra were registered in solid state on a Perkin Elmer 552 UV–Vis spectrophotometer with an integrating sphere attachment.

The complexes were prepared using uracil (URA), uridine (URD) and nucleotides (Serva), $Ni(AcO)_2 \cdot 4H_2O$ (Merck) without further purification. The starting complex $Ni(en)_2Cl_2 \cdot H_2O$ was prepared by the method described in the literature [17].

Magnetic susceptibility was measured (at the Institute of Applied Organic Chemistry of Barcelona) by Faraday's method.

Synthesis of $Ni(en)_2Cl_2(URA)_2 \cdot H_2O$, $Ni(en)_2Cl_2(URD)_2 \cdot H_2O$, $(Ni(URA)(AcO)_2 \cdot H_2O)_2$ *and* $(Ni(URD)(AcO)_2 \cdot H_2O)_2$

These four complexes were obtained in an ethyl acetate medium in a similar way to that described by Goodgame [7, 8]. 0.5 mmol of the $Ni(en)_2Cl_2 \cdot H_2O$ complex and 1 mmol of uracil or uridine finely powdered were mixed and about 15 ml ethyl acetate were added. (For the acetate complexes 1 mmol of nickel acetate and 1 mmol of uracil or uridine were mixed.) The mixture was then reflux heated by constant stirring between 9 and 24 h depending on the case, until the reaction was complete. The product was filtered, washed with ethyl acetate (2.5 ml) and dried over P_4O_{10}.

Synthesis of $Ni(5'UMP) \cdot 7.5H_2O$

To a solution of 1 mmol of nickel acetate tetrahydrate in 10 ml distilled water was added 1 mmol of dissodium salt of 5′UMP in 5 ml water. The greenish solution obtained (pH = 7.5) was placed in a thermostatic bath at 50 °C and began to precipitate a green product after 15 min. The solution was left soaking in the presence of ethanol steam for two days. The precipitate was washed repeatedly with cold water and dried over P_4O_{10}.

Synthesis of $Na_3\{Ni(en)_2(5'CMP)(5'CMPH)Cl_2\} \cdot 11H_2O$, $Ni(en)_2(5'GMP)(5'GMPH_2) \cdot 10H_2O$, $Ni(en)_2(5'IMP)(5'IMPH_2)_2 \cdot 10H_2O$

$Ni(en)_2Cl_2 \cdot H_2O$ (0.5 mmol) was dissolved in 10 ml distilled water and 1 mmol dissodium salt of 5′CMP (0.5 mmol $Na_25'GMP$, 0.5 mmol $Na_25'IMP$) in 5 ml water. Both solutions of pH = 7.5 (8.1 and 7.7) were mixed and the resulting solution was concentrated in a rotating evaporator at 70 °C for 8 min. Heating was continued at 60 °C in a thermostatic bath with constant stirring for about 2 h. The solution was left to stand for 24 h and bluish products were obtained, which in the case of 5′GMP derivatives were crystals. With the filtrate of the 5′IMP complex the process was repeated and this time crystals similar to those from 5′GMP were obtained. They were dried over P_4O_{10}.

The composition of the complexes and the analytical results appear in Table I.

Results and Discussion

Table II records the infrared data for the compounds obtained with uracil and uridine. The assignment was carried out according to the literature [18–20].

For the compounds prepared from the aminated complex, interaction of the uracil with the metal ion, probably through the ligands, is reflected in slight variations in frequency and intensity of the bands belonging to the uracil and the starting complexes. In general, significant shiftings are only observed on the bands due to $\nu C_4{=}O$ of the uracil ring, and these decrease in frequency possibly due a charge transfer from the carbonyl group to the metal [6, 7].

TABLE I. Analytical Data and some Physico-chemical Properties of the Complexes

Compound	Found (Calc.)%							Colour	Melting point[a] (°C)	μ_{eff} (BM)
	C	H	N	Cl	Ni	P	Na			
$Ni(en)_2Cl_2(URA)_2 \cdot H_2O$	29.41 (29.26)	5.32 (5.28)	23.20 (22.76)	14.80 (14.40)	12.07 (11.93)			blue	298(d)	3.138
$Ni(en)_2Cl_2(URD)_2 \cdot H_2O$	35.09 (34.9)	5.72 (5.55)	15.22 (14.80)	9.52 (9.37)	7.33 (7.76)			blue	165(d)	
$[Ni(URA)(AcO)_2 \cdot H_2O]_2$	30.25 (31.27)	3.81 (3.90)	10.08 (9.12)		18.75 (19.12)			green	340(d)	
$[Ni(URD)(AcO)_2 \cdot H_2O]_2$	35.33 (35.53)	4.49 (4.55)	6.70 (6.37)		13.62 (13.37)			green	168(d)	2.90
$Ni(5'UMP) \cdot 7.5H_2O$	20.53 (20.90)	4.08 (4.90)	5.19 (5.42)		12.01 (11.37)	6.17 (6.00)		green	193(d)	1.58
$Na_3[Ni(en)_2(5'CMP) \cdot (5'CMPH)Cl_2] \cdot 11H_2O$	22.77 (22.75)	5.28 (5.40)	12.40 (12.06)	5.94 (6.11)	4.60 (5.05)	5.95 (5.34)	6.18 (5.94)	blue	210(d)	3.22
$Ni(en)_2(5'IMP) \cdot (5'IMPH_2)_2 \cdot 10H_2O$	29.39 (29.10)	5.51 (5.20)	15.57 (15.90)		4.02 (4.10)	6.90 (6.62)		blue	185(d)	3.37
$Ni(en)_2(5'GMP)(5'GMPH_2) \cdot 10H_2O$	26.35 (26.69)	5.23 (5.72)	17.45 (18.09)		5.51 (5.42)	6.40 (5.72)		blue	220(d)	3.02

[a] d, decomposition.

TABLE II. Infrared Data for the Uracil and Uridine Compounds (cm^{-1})[a]

Tentative assignment	URA	$Ni(en)_2Cl_2 \cdot (URA)_2 \cdot H_2O$	$(Ni(URA)(AcO)_2 \cdot H_2O)_2$	URD	$Ni(en)_2Cl_2 \cdot (URD)_2 \cdot H_2O$	$(Ni(URD)(AcO)_2 \cdot H_2O)_2$
$\nu C_2=O$	1715s,br	1715s,br	1715s	1694s,br		1694s
$\nu C_4=O + \nu C=C$	1671s,br	1661s,br	1662s	1682s,br	1681s,br	1679s
		1644s,br	1643s	1670s,br	1667s,br	1665s
				1615m	1615m	1615m
δNH_2		1590s[b]			1591m[b]	
νCOO^- (asymm.)			1583–1574s[c]			1583–73br[c]
$\delta N-H + \nu$(ring)	1508m	1507m				
ν(ring)				1470s,sp	1470s,sp	1466m
	1452s,sp	1452s,sp	1451m			
ν(ring) +	1417s,sp	1417s,sp	1417s[d]	1421s,sp	1421m	1422m[d]
νCOO^- (symm.)	1389s,sp	1390s,sp	1392m,sp	1396s,sp	1396m	1396m
$\nu CN + \nu$(ring)	1237s	1236s	1237s	1271s	1271s	1271s
ν(sugar) + $\nu C-O$ +				1098s	1098s	1098s
$\nu C-C$				1076s	1076s	1076m
$\nu M-N$		351w			351w	
		308–302w			312w	
		272w			287w	

[a] s, strong; m, medium; b, broad; sh, shoulder; w, weak; ν, stretching; δ, bending. [b] δNH_2 of $Ni(en)_2Cl_2 \cdot H_2O$ at 1583 cm^{-1}. [c] νCOO^- (asymm.) of $Ni(AcO)_2 \cdot 4H_2O$ at 1547 cm^{-1}. [d] νCOO^- (symm.) of $Ni(AcO)_2 \cdot 4H_2O$ at 1420 cm^{-1}.

The bands due to νring (δNH and νC–N) do not vary noticeably, and those of the starting-complex $Ni(en)_2Cl_2 \cdot H_2O$ do not show shifting either, in general, overlapping in some cases with the uracil bands, although the one appearing at 1583 cm^{-1}, assigned at δNH_2, shifts in both complexes, suggesting some kind of interaction. Analogously, permanence is observed in the bands appearing at 351, 308–302 and 272 cm^{-1}, assignable at νNi–N [21], which in the case of the uridine complex overlap with those of ν(ribose) [8]. From all this it may be inferred that the initial complex of Ni(II) does not vary its coordination environment and there is possibly interaction by hydrogen bonding between the uracil

TABLE III. Infrared Data for the 5′CMP and 5′UMP Complexes (cm^{-1})[a]

Tentative assignment	$Na_25'CMP$	$Na_3(Ni(en)_2(5'CMP)(5'CMPH)Cl_2)\cdot 11H_2O$	$Na_25'UMP$	$Ni(5'UMP)\cdot 7.5H_2O$
$\nu C_2{=}O$	1659s	1669–1662s,br	1704–1689br	1702–1682br
$\nu C_4{=}O$			1679br	1644sh
$\delta NH_2 + \nu C{=}N + \nu C{=}C$	1652s,sh	1646s,br		
	1610m,sh	1611s,br		
$\delta NH + \nu C{=}C$			1630w	
	1528w	1526s	1478m	1529m
	1495m	1492s	1429m	1467m
	1412w	1417m	1394m	1424–1388br,m
ν(ring)	1383–73w	1375m,1347m,1328m	1349w	
	1294m	1297s	1330m	
	1250w	1254m	1284m	1275m
	1216w	1218m	1267m	
νPO_3 (asymm.) + $\nu C{-}O$ (sugar)	1112s,br	1119s,br	1125s,br	
	1084s,br	1066s,br	1092s,br	1112s,br
			1081s,br	1073s,br
νPO_3(symm.)	979s	981s,951s,916m	981s	992s
$\nu C{-}O$(sugar) + ν(ring)	876w	876w	939s	
$\delta NH + \nu P{-}O$ +	787m	819,786s	874w	
PO_3 symm. def. + deg. def.	714w	722,694s,br	818s	815m
	626w	652,634s,br	779w	786m
	600w,535w	600s,543,521s,br	763m,565, 534m	572m
$\nu Ni{-}N$		427,350,330,297w		

[a] s, strong; m, medium; b, broad; sh, shoulder; w, weak; ν, stretching; δ, bending.

$C_4{=}O$ groups and NH_2 of the coordinated ethylenediamine.

For the two acetate complexes, shifting is observed at lower frequencies (1662, 1643 cm^{-1} and 1679, 1665 cm^{-1}) for the band assigned at $C_4{=}O$, indicating coordination through this group. On the other hand, activation is observed on the band appearing at $\nu C{=}O$ (ν–COO asymmetric). This band shifts at 1583–74 cm^{-1}. Slight shifting is also observed on the band corresponding to νCOO symmetric of the acetate group, overlapping with the ring band which appears in the same area. Separation between the two bands is consistent with coordination of the acetate groups as a bridge between two atoms of nickel [20] so the complexes may have a dimer structure.

Table III records the infrared data for the complexes with pyrimidine base nucleotides and their tentative assignment by comparison with the corresponding dissodium salt spectra.

For the 5′UMP compound there are variations in frequency and intensity on the bands appearing mainly in the $\nu C{=}O$, νring, νPO_3^{2-} areas. The 1679 cm^{-1} band corresponding to $\nu C_4{=}O + \nu C{=}C$ shifts at 1644 cm^{-1}, which seems to indicate interaction through this group. The bands related to ring stretching also shift as a consequence of restructuring the ring charge. The bands corresponding to phosphate stretching (symmetric and asymmetric or degenerate) also shift significantly. The increase in frequency on the 981 cm^{-1} band indicates coordination through the phosphate group [23].

For the 5′CMP compound there is strong widespread absorption in the $\nu C{=}O$, δNH_2, $\nu C{=}N$ and $\nu C{=}C$ area, which indicates an important alteration in these groups. The peak assigned at $\nu C_2{=}O$ stretching as the main vibration appears at greater frequencies and loses its definite character. The 1652 cm^{-1} band due to coupling of δNH_2, $\nu C{=}N$ and $\nu C{=}C$ shifts at 1646 cm^{-1} and the 1610 cm^{-1} band intensifies significantly. The ring stretching bands also vary in frequency and intensify significantly. Two new bands appear at 1347 and 1328 cm^{-1} which may correspond to the ethylenediamine altered by the presence of the nucleotide. The 1294 and 1250 cm^{-1} bands, assignable according to Tsuboi [18] at $\nu C{-}N$ and $\nu O{=}C(2)_N{}^N$ respectively, shift at higher frequencies. In the area between 1200–900 cm^{-1} bands appear due to the stretching vibrations of the phosphate group which are also altered. The bands corresponding to asymmetric stretching coupled with the stretching C–O from the ribose group lose their definite character and appear as a strong broad absorption with peaks at 1119, 1066 and 1028 cm^{-1}. The band due to symmetric stretching of the phosphate group splits and two new bands appear at 951 and 916 cm^{-1}. In the lower area of the spectrum changes are also observed; four weak intensity bands appear at 427, 350, 330 and 297 cm^{-1}, tentatively assignable at $\nu Ni{-}N$, perhaps coupled with bands due

TABLE IV. Infrared Data for the 5'GMP and 5'IMP Complexes (cm^{-1})[a]

Tentative assignment	$Na_2$5'GMP	Ni(en)$_2$(5'GMP)(5'GMPH$_2$)$\cdot$ 10H$_2$O	$Na_2$5'IMP	Ni(en)$_2$(5'IMP)(5'IMPH$_2$)$_2$$\cdot$ 10H$_2$O
$\nu C_6{=}O$	1694s		1690s,sh,1681s	1679m
δNH_2	1661sh	1662s,1644s		
	1603m	1574m,sh	1592m	1588m
	1585m,sh		1550m	1553m
ν(ring)	1536m	1537w	1519m	
	1484m	1490,1461w	1482m	1487m,1461w
	1412m	1419w	1425m	1428m,1407w
	1361s	1395w,1368m,1357m	1381m	
	1331w	1322w,1275m	1347m	1367m
	1238m	1250w,1215m	1330m	1340m
			1216s,sp	1221s,sp
νPO_3(asymm.) + νC–O(sugar)	1097s,br	1113s	1128s,br	1113s
	1066s,br	1072s,1039s	1098s,br	
			1070s,br	1072s,1045sh
			1034s,sp	
νPO_3(symm.)	975s	975s,960s	980s	977s,961s
νC–O(sugar) + ν(ring) +	811m	798s	830s	823m
δNH + νP–O +	781m	778m,761m	793m,sp	791m
PO_3 symm. def. + deg. def.	730m	721m	720m	719m
	577br	590w,551w	644m,603m	650m,612m
	515br	528m,sh,508m	533m	557w,506m
νNi–N		427w,381sh		417w

[a] s, strong; m, medium; b, broad; sh, shoulder; w, weak; ν, stretching; δ, bending.

to vibrations of the ring skeleton. All this infers the existence of bonding of Ni(II) to the cytosine ring, probably through N(3), and also interaction with the phosphate group, although it does not rule out the possibility of the modification observed in the latter being due to interactions through the NH_2 groups of the ethylenediamine. The second nucleotide could join the coordinate through hydrogen bonds.

In the infrared spectra of the complexes with purine base nucleotides (Table IV) important changes in frequency are observed on the bands corresponding to ring and phosphate stretching in comparison with those of the corresponding dissodium salts. In both cases, the bands related to stretching vibrations νC=N(7) which appear at about 1480 and 1330 cm^{-1} undergo variations; the former splits in a similar way to that of the other complexes described with 5'dGMP [23], which indicates an important alteration in the bonds adjacent to N(7) probably as a consequence of coordination with the metal.

The bands corresponding to phosphate group symmetric and asymmetric or degenerate stretching are also modified; various peaks are resolved both for νPO_3 + νC–O ribose and for νPO_3 (sym), and the intensity of some of them is changed. The band appearing at 980 cm^{-1} splits in both complexes, and this indicates a direct or otherwise interaction of the metal ion with the phosphate group [23]. Equally, the band appearing around 780 cm^{-1} assigned at νP–O is shifted. In the lower area of the spectrum, a great number of bands corresponding to ring skeleton vibrations coupled to bands related to the phosphate group are resolved. The 427 cm^{-1} (5'GMP) and 417 cm^{-1} (5'IMP) peaks are tentatively assigned at νNi–N.

All this indicates interaction of a nucleotide with the metal ion through N(7) and with the phosphate group, either directly or through hydrogen bonds.

The other nucleotides will probably be maintained associated with the coordinate nucleotide by weak bonds, as according to the conductivity measurements they are liberated in water solution.

The diffuse reflectance spectra of the compounds obtained are consistent with approximately octahedral geometries of Ni(II). The values of the 10*Dq*, *B'* and β parameters were found using Tanabe and Sugano's diagram [24]. In most of the spectra, bands are observed corresponding to ν_2 and ν_3 transitions and bands due to the purine or pyrimidine ring ($\pi \rightarrow \pi^*$) in the 240–300 nm area (Table V).

For the compounds of uracil and uridine the most significant variations both for the d → d and the $\pi \rightarrow \pi^*$ bands correspond to the acetate compounds. The 10*Dq* value is consistent with bonding to donor oxygen. The variations in frequency on the uracil ring bands are probably the result of alteration of the charge due to bonding. The complexes with ethylenediamine present spectra very similar to that

TABLE V. Diffuse Reflectance Spectra for the Complexes (bands in nm)

Compound	$\pi \rightarrow \pi^*$	$(\nu_3)\ ^3A_{2g} \rightarrow {}^3T_{1g}$ (P)			$(\nu_2)\ ^3A_{2g} \rightarrow {}^3T_{1g}$			10*Dq* (cm^{-1})	*B'* (cm^{-1})	β
URA	244s,290sh									
$Ni(en)_2Cl_2(URA)_2 \cdot H_2O$[a]	245s,288sh	366m		418vw	601m			9357	985	0.94
$(Ni(URA)(AcO)_2 \cdot H_2O)_2$[b]	248s,284s	392m 423m	average 407.5m		608m,br		757m	7930	933	0.89
URD	247s,290sh									
$Ni(en)_2Cl_2(URD)_2 \cdot H_2O$[a]	252s,289sh	365m		418vw	576m 600m	average 587m		9650	965	0.92
$(Ni(URD)(AcO)_2 \cdot H_2O)_2$[b]	255s,289s	390m 424m	average 407m		680m 704m	average 692m,br	756m	7800	975	0.93
$Na_2$5'UMP	250s,292s									
Ni(5'UMP)·7.5H_2O	250s,290s	390m 426m	average 408m		680m,br		758m	8330	980	0.94
$Na_2$5'CMP	260s,308s									
Na_3(Ni(en)$_2$(5'CMP)(5'CMPH)Cl_2)·11H_2O[a]	267s,br,300s	362m		423vw	565m 608m	average 585m		10185	970	0.93
$Na_2$5'IMP	240s,290s									
Ni(en)$_2$(5'IMP)(5'IMPH$_2$)$_2$·10H_2O[a]	250s,289s	366m		416vw	611m		760w	8964	996	0.95
$Na_2$5'GMP	242s,284–305s									
Ni(en)$_2$(5'GMP)(5'GMPH$_2$)·10H_2O[a]	243s,305s	365m		417vw	609m		760w	8982	998	0.95

[a] For the $Ni(en)_2Cl_2 \cdot H_2O$ complex bands at 260m, 364s, 421w, 567s, 608s.

[b] For the $Ni(AcO)_2 \cdot 4H_2O$ compound bands at 390s, 418s, 660s,br.

TABLE VI. Conductivity Data for the Complexes

Compound	Λ_M (Ω^{-1} cm^2 mol^{-1}) 10^{-3} M in H$_2$O (20 °C)		10^{-3} M in MeOH (25 °C)		Electrolyte type
Ni(en)$_2$Cl$_2$(URA)$_2$•H$_2$O	261				1:2
Ni(en)$_2$Cl$_2$(URD)$_2$•H$_2$O	233		144		1:2
(Ni(URA)(AcO)$_2$•H$_2$O)$_2$	255				1:2
(Ni(URD)(AcO)$_2$•H$_2$O)$_2$	236				1:2
Na$_3$(Ni(en)$_2$(5'CMP)•(5'CMPH)Cl$_2$•11H$_2$O	420				1:3
Ni(en)$_2$(5'IMP)(5'IMPH$_2$)$_2$•10H$_2$O	230				1:2
Ni(en)$_2$(5'GMP)(5'GMPH$_2$)•10H$_2$O	144				1:1
	Solvent	Temperature	Λ_o (Ω^{-1})	$\Lambda_o - \Lambda_e/\sqrt{c_e}$	Ion type
Ni(en)$_2$Cl$_2$•H$_2$O	water	20.4 °C	126.1	234	1:2
Ni(en)$_2$Cl$_2$(URD)$_2$•H$_2$O	water	20.4 °C	127	187.5	1:2
Ni(en)$_2$Cl$_2$(URD)$_2$•H$_2$O	Me•OH	25 °C	95	500	1:2

of Ni(en)$_2$Cl$_2$•H$_2$O, which supports the hypothesis of indirect metal–uracil (uridine) bonding. The ring bands shift only slightly.

In the case of the complexes with nucleotides, variations on the ring bands are in general more noticeable and reflect restructuring of the charge as a consequence of bonding, except in the case of the 5'UMP complex where shiftings are slight. Here the 10*Dq* value is consistent with Ni(II)–O bondings, while in the other pyrimidine base 5'CMP complex bonding probably occurs through N(3). For the purine base complexes the spectra are very similar; shifting of the ring bands is observed in both cases. The very similar 10*Dq* values indicate the less covalent character of the Ni(II) bondings in comparison with the 5'CMP complex, which implies weakening of the Ni(II) bondings with ethylenediamine as a consequence of entering the greater volume nucleotide as a second ligand. According to the $\pi \rightarrow \pi^*$ shiftings and the 10*Dq* value, coordination through N(7) of the purine base seems likely.

Magnetic susceptibility studies are in agreement with an octahedral geometry for the Ni(II) derivatives with the exception of the formula complex Ni(5'UMP)•7.5H$_2$O. The abnormally low value for this complex could be due to a magnetic exchange in a bi- or polynuclear structure.

The water solubility of the complexes made calculation of the Λ_M conductivity of 10^{-3} M solutions at 20 °C possible and the type of electrolyte for each compound could be determined [25, 26]. Results are shown in Table VI.

Values were obtained for the aminated complexes of uracil and uridine Λ_M confirming the results of the infrared and reflectance spectra, as they indicated in all cases the presence of types of electrolytes coinciding with those of the starting complexes. This implied permanence of the initial environment of the metallic ion in the compound obtained, and indirect bonding of the base or nucleoside to the metal. In the case of the compounds obtained from acetate of Ni(II), the dimer structure of the compounds was confirmed as the type of electrolyte found corresponded to total breaking of the Ni–O=C bonds resulting in a 1:2 electrolyte. Given the weak interaction existing in these compounds, separation of uracil or uridine in solution is very likely, a fact already observed in complexes of the same type [6].

The Λ_M value for the 5'GMP and 5'IMP complexes implies freeing of the associated nucleotides in water solution, while the 5'CMP complex corresponding to a 1:3 electrolyte, is interpreted by assuming a strong association between the associated and coordi-

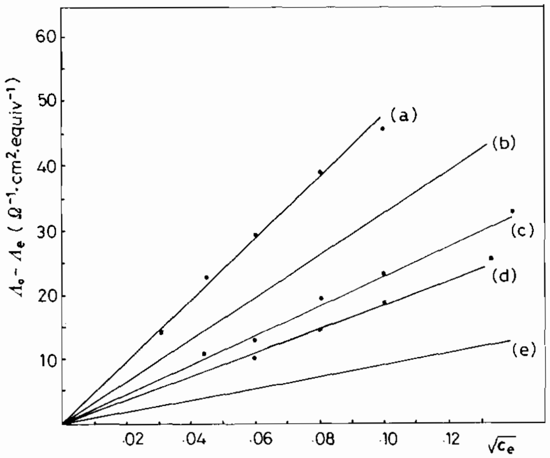

Fig. 2. (a) For the Ni(en)$_2$Cl$_2$(URD)$_2$•H$_2$O compound in MeOH at 25 °C; (b) for ion type 1:3 [25]; (c) for the Ni(en)$_2$Cl$_2$•H$_2$O complex in water at 20.4 °C; (d) for the Ni(en)$_2$Cl$_2$•(URD)$_2$•H$_2$O in water at 20.4 °C; (e) for ion type 1:1 [25].

nated nucleotides with participation of the chlorine atoms.

Conductivities for the $Ni(en)_2Cl_2 \cdot (URD)_2 \cdot H_2O$ compound were measured in the interval of 10^{-2}–3.10^{-4} N concentrations in water solution at 20.4 °C and in methanol at 25 °C; these were compared to the starting compounds and similar results were obtained. The equivalent conductivity Λ_e was first plotted graphically as a function of $\sqrt{c_e}$, where c_e is the equivalent concentration, and the Λ_o value was found by extrapolation. Next, $\Lambda_o - \Lambda_e$ was plotted as a function of $\sqrt{c_e}$, and the slope found in both cases was peculiar to 1:2 electrolytes, implying freeing of the two chlorides in solution and probably of the two nucleosides. The results are shown in Table VI and Fig. 2.

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