Inorganica Chimica Acta, 138 (1987) 105–112

Chromium(III) Interactions with Nucleotides. III*

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(Received January 26, 1987)

Abstract

Some new derivatives of Cr(III) with 5′AMP, 5′ATP, 5′CMP, 5′GMP, 5′IMP and 5′UMP have been obtained by reaction of the starting complexes *cis* and *trans*-$[Cr(en)_2Cl_2]Cl$ with the above nucleotides.

The complexes were characterized by elemental analysis, conductivity, infrared and electronic spectroscopy, and EPR for the 5′UMP derivative.

In all cases, chlorine has been substituted and one ethylenediamine eliminated. The interaction of Cr(III) with the nucleotide seems to occur through the phosphate group and additional interaction through the heterocyclic ring especially for the 5′GMP and 5′IMP derivatives.

The 5′UMP complex seems to be a dimer and the other complexes are polymer.

Introduction

Obtaining inert derivatives of Cr(III) or Co(III) with nucleotides, which could be applied as allosteric activators of enzymes, by the substitution of the natural Mg(II)–nucleotide activator or inhibitor is a field of great interest [1–4].

The presence of Cr(III) in the glucose tolerance factor (GTF) has increased the synthesis of chromium(III) derivatives with natural products as bases, aminoacids and nucleotides [5–9]. Until now very few nucleotide Cr(III) complexes have been described in the solid state [10–14].

This paper refers to the synthesis and characterization of some new derivatives of chromium(III) obtained by reaction of *cis*- and *trans*-$[Cr(en)_2Cl_2]Cl$ and the disodium salts of 5′AMP, 5′ATP, 5′GMP, 5′IMP, 5′CMP and 5′UMP in water (Fig. 1).

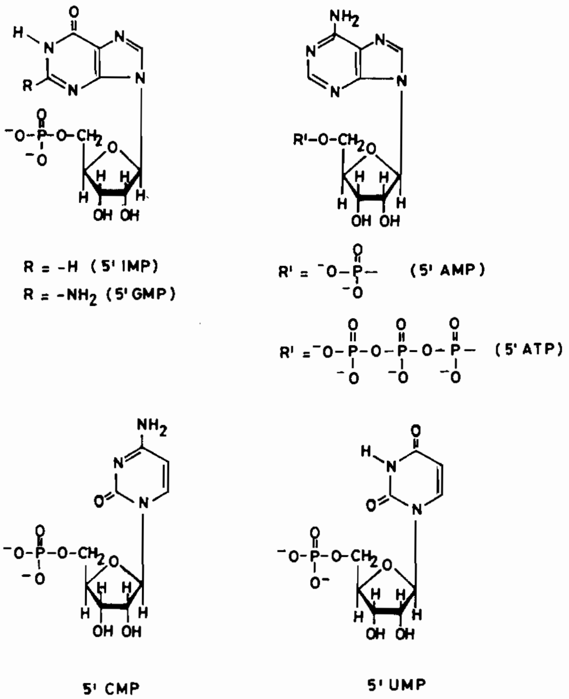

Fig. 1. Nucleotide structures and abbreviations used.

Experimental

The analyses of carbon, hydrogen and nitrogen were carried out with a Carlo Erba model 1106 microanalyzer at the Institute of Bio-organic Chemistry in Barcelona and with a Perkin-Elmer 240.B at the Faculty of Chemistry, Tarragona. The chlorine analysis was determined by the Schoniger method. Chromium was determined by using the colorimetric method for chromate [15]. The measurements were performed with a Perkin-Elmer 552 UV–Vis spectrophotometer at 375 nm and 2 nm slit. The phosphorus content was determined by using the colorimetric method for phosphomolibdovanadate [16]. The measurements were carried out at 390 nm and 2 nm

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0020-1693/87/$3.50

slit. The sodium content was determined by flame photometry on a Perkin-Elmer 703 spectrophotometer. The working conditions were: λ = 590 nm and 0.2 nm slit with an acetylene–air flame oxidant. The conductivities were measured with a Crison 525 conductimeter. The cell constant was determined by using a water solution of KCl 10^{-2} N (k = 1.08 cm^{-1}). The IR spectra were registered in the solid state (KBr pellets) on a Perkin-Elmer 683 IR spectrophotometer connected with a P.E.1600 data station. The reflectance spectra were recorded in the solid state on a P.E.552 UV–Vis spectrophotometer with an integrating sphere attachment. Visible–UV spectra were recorded in the same apparatus at 10^{-3}–10^{-4} M concentration.

The EPR spectra were registered in the solid state and in solution at room temperature and liquid nitrogen temperature, respectively, on a Varian model E-12 in the X-band (Imperial College, London). The modulation field frequency was 9.56 Hz.

The sources for nucleotides were Serva and Merck without further purification. The starting complexes *cis*- and *trans*-$[Cr(en)_2Cl_2]Cl$ were prepared according to literature procedures [17, 18].

All the complexes were obtained by the same procedure in water medium. *Cis*- and *trans*-$[Cr(en)_2Cl_2]Cl$ (0.5 mmol) were dissolved in 10 ml water and 0.5 mmol disodium salt of nucleotide in 5 ml water. Both solutions were mixed and the resulting solution placed in a thermostatic bath at approximately 55 °C with constant stirring between 5 and 7 h depending on the case. A precipitate was observed for the *cis*- and *trans*-5′GMP, 5′IMP and *cis*-5′AMP derivatives. In the other cases, the solution was concentrated at 50 °C until a 5 ml volume and passed through a Sephadex G-15 column. The complexes were precipitated by addition of ethanol, filtered, washed with ethanol and dried over silica gel.

The composition of the complexes and the analytical results are reported in Table I. All the complexes, obtained from *cis* and *trans* starting complexes with the same nucleotide, have very similar composition with slight variations in the number of water molecules. Except in the case of the 5′UMP complex, which is soluble in water, the remaining compounds are insoluble in water and common organic solvents.

Results and Discussion

It is interesting that the composition of the complexes obtained is consistent with the formula

TABLE I. Analytical Data and some Properties of the Complexes

Compound	Analysis, found (calc.) (%)						Colour	Melting point (°C)	Λ_M (Ω^{-1} cm^2 mol^{-1}) 10^{-3} M at 20 °C (H_2O)
	C	H	N	Cr	P	Na			
$Cr(en)(5'AMP)(5'AMPH)\cdot\frac{11}{2}H_2O$	29.71 (29.25)	5.39 (4.88)	17.90 (18.61)	 (5.76)	6.04 (6.87)		lilac	238–243(d)[a]	
$Cr(en)(5'AMP)(5'AMPH)\cdot 11H_2O$	26.99 (26.36)	5.48 (5.49)	16.42 (16.77)	4.99 (5.19)	6.25 (6.19)		lilac	230–236(d)	
$Cr(en)(5'ATPH_2)(OH)\cdot 2H_2O$	20.97 (21.48)	4.64 (4.03)	15.62 (14.62)	6.55 (7.76)	15.21 (13.88)		lilac	249–256(d)	
$Cr(en)(5'GMP)(OH)\cdot 4H_2O$	25.52 (25.61)	5.08 (5.16)	17.58 (17.43)	9.18 (9.25)	6.36 (5.69)		lilac	184–191(d)	
$Cr(en)(5'GMP)(OH)\cdot\frac{13}{2}H_2O$	23.36 (23.71)	4.90 (5.59)	16.03 (16.14)	8.07 (8.56)	5.30 (5.27)		lilac	179–184(d)	
$Na[Cr(en)(5'IMP)(OH)_2]\cdot 3H_2O$	24.96 (25.39)	4.74 (4.76)	15.08 (14.81)	9.15 (9.17)	6.05 (5.47)	5.50 (4.06)	lilac	141–155(d)	
$Na[Cr(en)(5'IMP)(OH)_2]\cdot 4H_2O$	24.82 (24.61)	4.69 (4.95)	13.97 (14.35)	9.31 (8.89)	5.41 (5.30)	4.24 (3.93)	lilac	144–157(d)	
$Cr(en)(5'CMP)(5'CMPH)\cdot EtOH\cdot 6H_2O$	28.70 (29.00)	5.45 (5.60)	12.63 (12.30)	5.54 (5.60)	6.72 (6.81)		lilac	146–152(d)	
$Cr(en)(5'CMP)(5'CMPH)\cdot 8H_2O$	26.59 (26.60)	5.56 (5.43)	13.57 (12.41)	6.34 (5.76)	6.54 (6.87)		lilac	141–147(d)	
$Cr(en)(5'UMP)(OH)\cdot 3H_2O$	25.74 (26.13)	5.15 (5.15)	11.37 (11.08)	10.11 (10.29)	6.28 (6.14)		lilac	154–161(d)	17

[a](d) - decomposition.

$[Cr(5'XMP)_x(en)(OH)_y(H_2O)_z]$ where 5'XMP is the nucleotide implied and $x = 1$ or $2, y = 0, 1$ or 2 and z is the number of water molecules needed to complete the coordination index plus hydration water. This implies the substitution of one 'en' group, or the presence of two subunits similar to the previously described $[Co(en)_2(OH_2)_2][Co(5'IMP)_2(OH_2)_4]Cl_2 \cdot 4H_2O$ [19].

Nevertheless, in recent work we have resolved the X-ray structure of a new complex obtained from $[Ni(en)_2Cl_2]Cl$ with 5'GMP. In this complex there is substitution of one ethylenediamine and coordination of two nucleotides to the metal ion [20].

Tables II, III and IV record the infrared data for the compounds obtained. In all cases, the spectra of *cis* and *trans* complexes with the same ligand are very similar: the differences in the ν(ring) and $\nu(PO_3^{2-})$ bands are minimal. As we have mentioned above, the only apparent difference in their compositions is the number of water molecules. The band related to ethylenediamine ($\nu(C\text{–}C) + \nu(C\text{–}N)$) [21] always appears at approximately 1054 cm^{-1} and the $\nu(M\text{–}Cl)$ and $\nu(NMCl)$ [22] bands in the lower area disappear.

For the 5'AMP complexes there are no important changes in the 1663, 1646 and 1608 cm^{-1} bands, corresponding to the bending mode of NH_2. Other bands corresponding to ν(ring) vibrations (1484, 1307 and 1255 cm^{-1}) show small shifts without splitting that may be due to the base pairing interaction $N_7base_1 \cdots NH_2base_2$ between the two nucleotides [23]. The $\nu(PO_3^{2-})_{asym} + \nu(C\text{–}O)_{sugar}$ band appears as a broad absorption overlapping with the 1054 cm^{-1} band assigned to the stretching vibrations of the ethylenediamine group and the 977 cm^{-1} band ($\nu(PO_3^{2-})_{sym}$) shifts to higher frequency which seems to indicate interaction of Cr(III) with the phosphate group.

The 5'ATP compound shows modifications on the bands at 1615 and 1420 cm^{-1} and disappearance of the 1552 cm^{-1} band assignable to vibrations of the purine ring. This is consistent with an interaction between Cr(III) and the adenine ring [24], although N(1) protonation may not be ruled out [23]. On the other hand, there are important changes in the ν(phosphate) area. The $\nu(PO_2^-)$ α and β doublet at 1258, 1230 cm^{-1} [25, 26] appears as a single band at 1225 cm^{-1} and $\nu(PO_3^{2-})_{sym}$ bands at 990, 966 cm^{-1} [23, 27] disappear. Moreover the absorptions related to $\nu(P\text{–}O\text{–}P)$ and $\nu(C\text{–}O\text{–}P)$ [23, 27] show noticeable shifts at higher frequencies. All this suggests that the phosphate group is involved in the metal coordination, possibly through $P(\beta)$ and $P(\gamma)$ oxygens [26, 28].

There are similar changes on the ν(ring) and ν(phosphate) bands for the 5'GMP and 5'IMP derivatives. The slight modifications of the stretching carbonyl bands, as well as the decrease in frequency in the $-NH_2$ bands, may be due to the participation of the O(6) atom and $-NH_2$ of the ring in hydrogen bonding upon complexation [23, 27].

Nevertheless, the more important changes occur in the 1484 cm^{-1}, 1331 cm^{-1} and 1207 cm^{-1} bands, related to $\nu(C_8{=}N_7)$ vibrations. In all cases, the 1484 cm^{-1} band splits into two absorption peaks at approximately 1480 cm^{-1} and 1465 cm^{-1}. In accordance with Tajmir–Riahi and Theophanides studies [29, 30] this implies $M\text{–}N_7$ coordination, as we have suggested in our previous papers [31, 32]. The 1331 cm^{-1} band also splits in the 5'GMP derivatives and disappears in the 5'IMP complexes.

The $\nu(PO_3^{2-})_{asym}$ band appears as a broad absorption in the nucleotide. This band appears in the complexes overlapping with $\nu(C\text{–}C)$ and $\nu(C\text{–}N)$ of the ethylenediamine bands. The $\nu(PO_3^{2-})_{sym}$ band shifts at higher frequencies in the complexes, indicating some kind of interaction with the phosphate group [30].

Table IV shows the infrared data for the complexes with pyrimidine nucleotides and their assignment.

There are no changes in the $\nu(C_2{=}O)$ band for the 5'CMP compound. Meanwhile, the $\nu(C_4{=}O)$ bands in the 5'UMP derivative shift slightly to higher frequencies. The ν(ring) bands in the 5'CMP derivative shift slightly to lower frequencies in general, and the 1368 cm^{-1} band shifts to higher frequency (1377 cm^{-1}). The complex $Co(en)_2(5'CMP)(5'CMPH) \cdot 6H_2O$ described in a previous paper [32] shows changes of ν(ring) bands similar to the Cr(III)–5'CMP complexes described here. The ^{13}C NMR study confirms for the Co(III) derivative the interaction N(3) for the two nucleotides of the molecule. The similarity of the infrared bands suggests also the interaction Cr–N(3) in the complexes with 5'CMP.

The infrared data of $Cr(en)(5'UMP)(OH) \cdot 3H_2O$ present very few changes for the ν(ring) bands which seems to indicate no direct interaction between the metal and the uracile ring. The changes of the bands $\nu(C_4{=}O)$ and $\nu(C_2{<}^{N}_{N})$ [27] could be due to some kind of interaction. This interaction could be a direct bonding metal–O(carboxylic) or the presence of a hydrogen bonding between water molecules coordinated to the metal and the carboxylic oxygen of the ring. The phosphate stretching bands (asymmetric) are very broad overlapping with the 1054 cm^{-1} band related to the $\nu(C\text{–}C) + \nu(C\text{–}N)$ of the ethylenediamine. The $\nu(PO_3^{2-})_{sym}$ band shifts to higher frequencies for the three pyrimidine nucleotide complexes owing to metal interaction through the phosphate group.

The diffuse reflectance data are collected in Table V. These data agree with a pseudooctahedral geometry for Cr(III). The ν_1 and ν_2 bands appear with several peaks due to splitting of $^4T_{2g}$ and $^4T_{1g}$ (F) terms owing to descending symmetry. The 10 *Dq* values have been calculated from Tanabe–Sugano

TABLE II. Infrared Data for the 5′AMP and 5′ATP Complexes (cm^{-1})[a]

Tentative assignment	$Na_2$5′AMP	[Cr(en)(5′AMP)-(5′AMPH)]·$\frac{11}{2}H_2O$ [b]	[Cr(en)(5′AMP)-(5′AMPH)]·$11H_2O$ [c]	$H_4$5′ATP [d]	[Cr(en)(5′ATPH_2)-(OH)]·$2H_2O$ [b]
$\delta(NH_2) + \nu(C_5-C_6) + \nu(C_6-NH_2)$	1663vs		1660vs		
	1646vs	1647vs	1646vs		
$\delta(NH_2) + \nu(C_5-C_6)$	1608s	1605s	1604s	1646m	1648s
$\nu(C_4{=}C_5) + \nu(N_3-C_4{=}C_5)$	1584s	1584s	1583s	1615m	1605m
$\nu(C{=}C)$				1552w	
$\nu(C_8{=}N_7) + \delta(C_8-H)$	1506w	1502w	1504w		
$\delta(C_8{=}N_7) + \nu(C_8-N_9) + \delta(C_8-H) + \delta(C_2-H)$	1484s	1479m	1479m	1481m	1480m
$\delta(CH_2)$	1425m	1423m	1422m	1420m	1423w
$\delta(C_8-H) + \nu(N_7{=}C_8)$	1307m	1301m	1302m		
$\nu(N_7{=}C_8-N_9) + \nu(C_2-H)$	1255m	1252m	1254m		
$\nu(PO_2^-)$ α and β				1258vs,br	1225s
				1230vs,br	
$\nu(PO_3)_{asym} + \nu(C-O)_{sugar}$	1120s,br	1119–1116vs,br	1123vs,br	1136–1123vs,br	1123vs
	1094vs,br	(overlapped)	(overlapped)	1110–1070vs,br	1107vs
$\nu(C-C) + \nu(C-N)(en)$		1054vs	1054vs		1054vs
$\nu(PO_3)_{sym}$	977vs	987vs	987vs	990vs, 966vs	
$\nu(P-O-P)$				905vs	919vs
$\nu(C-O-P)$ [e]	901m, 820sh	906m, 820sh	905m, 819sh	811m	823m
$\nu(Cr-O)$		365w	367w, 332w		361w
–		231w, 207w	257w, 241w, 222w		591m

[a] s = strong; m = medium; br = broad; sh = shoulder; w = weak; ν = stretching; δ = bending. [b] Obtained from *cis*-[Cr(en)$_2$Cl$_2$]Cl. [c] Obtained from *trans*-[Cr(en)$_2$Cl$_2$]Cl. [d] Precipitated at pH = 3.3. [e] With contribution of the δ(C–H)(ring) in the case of the 5′ATP derivative.

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

Tentative assignment	$Na_2$5'GMP	Cr(en)(5'GMP)-(OH)·$4H_2O$ [b]	Cr(en)(5'GMP)-(OH)·$\frac{13}{2}H_2O$ [c]	$Na_2$5'IMP	Na[Cr(en)(5'IMP)-$(OH)_2$]·$3H_2O$ [b]	Na[Cr(en)(5'IMP)-$(OH)_2$]·$4H_2O$ [c]
$\nu(C_6{=}O) + \nu(C_6{-}C_5)$	1694s,br	1692s,br	1692sh	1690s, 1681s	1694s	1692s
$\delta(NH_2) + \nu(C_2{-}N_2)$	1661sh		1663s			
		1643–1635s,br	1645–1635s,br			
ν(ring)	1603m	1600s	1600s	1592m	1591m	1592s
				1551m	1553m	1553m
	1536m	1534m	1536m	1521w	1518w	1517w
$\nu(C_8{=}N_7) + \delta(C_8{-}H)$	1484m	1486m 1466w,sh	1485m 1465w,sh	1483m	1479w 1466w	1480m 1473m
ν(ring)	1361s			1383m 1371m	1378w	1376w
				1347m	1348w	1347m
$\nu(C_8{=}N_7) + \nu(C_8{-}N_9)$	1331w	1363m 1289w	1364m 1289w	1330m		
	1309w			1308w		
$\delta(C_8{-}H) + \nu(C_8{=}N_7)$	1207m					
$\nu(C{-}O)_{sugar} + \nu(PO_3)_{asym}$	1122s,br	1120s,br	1120–1111s,br	1128s,br	1124–1115s,br	1120s
	1097–1066s,br	(overlapped)	(overlapped)	1098–1070s,br	(overlapped)	(overlapped)
$\nu(C{-}C) + \nu(C{-}N)$(en)		1051s	1053s		1052s	1053s
$\nu(PO_3)_{sym}$	975s	986s	988s	980s	986s	988s
ν(ribose-phospate)	908m	903w	905w	899m	877w,sh	876m,sh
$\nu(P{-}O)$	781m	784w	784m	793m,sp	793m,sp	793m,sp
ring breathing mode	694m	688m	688m	720m	718m	718m
NH out-of-plane def.	633m	642m	639m	647m	648m	649m
PO_3^{2-} sym def.	595m			603m		605m
$\nu(Cr{-}N)$			300w,sh; 267w		559s	560s
$\nu(Cr{-}O)$					324w	323w
–		225w	225w		289w, 222w,sp	225w,sp

[a] s = strong; m = medium; br = broad; sh = shoulder; w = weak; ν = stretching; δ = bending. [b] Obtained from *cis*-$[Cr(en)_2Cl_2]Cl$. [c] Obtained from *trans*-$[Cr(en)_2Cl_2]Cl$.

TABLE IV. Infrared Data for the 5'CMP and 5'UMP Compounds (cm^{-1})[a]

Tentative assignment	$Na_2$5'CMP	[Cr(en)(5'CMP)(5'CMPH)]·EtOH·$6H_2O$ [b]	[Cr(en)(5'CMP)(5'CMPH)]·$8H_2O$ [c]	$Na_2$5'UMP	Cr(en)(5'UMP)(OH)·$3H_2O$ [b]
$\nu(C_2{=}O)$ [d]	1661s	1663s	1662s	1704–1689br	1707–1696br
$\nu(C_4{=}O)$				1679br	1683br
$\delta(NH_2) + \nu(C{=}N) + \nu(C{=}C)$	1654s,sh	1650s	1653s		
	1610m,sh	1610s,sh	1610s,sh		
$\delta(NH) + \nu(C{=}C)$				1630w	(overlapped)
ν(ring)	1531m	1528m	1530m		
	1499m	1495s	1494s	1478m	(overlapped)
	1407w	1403w	1404w	1429m	1431m
	1368w,sh	1377w	1380w	1394m	1393m
				1349w	
				1330m	1330w
	1294m	1292m	1291m	1284m	1275m
				1267m	
	1214w,sh	(overlapped)	1208w,sh		
$\nu(PO_3)_{asym} + \nu(C{-}O)_{sugar}$	1115s,br	1113s,br	1115s,br	1125s,br	1130s,br
	1083s,br	(overlapped)	(overlapped)	1092s,br	(overlapped)
				1081s,br	(overlapped)
$\nu(C{-}N) + \nu(C{-}C)$(en)		1052s	1052s		1053s
$\nu(PO_3)_{sym}$	978s	988s	988s	981s	990s
$\nu(Cr{-}N)$					427m,sh
		372w,sh	364w,sh, 324w,sh		366w, 326w
		245w, 223w	264w, 246w, 226w		266w, 223w

[a] s = strong; m = medium; br = broad; sh = shoulder; w = weak; ν = stretching; δ = bending. [b] Obtained from *cis*-$[Cr(en)_2Cl_2]Cl$. [c] Obtained from *trans*-$[Cr(en)_2Cl_2]Cl$. [d] With contribution of the $\delta(NH_2)$ def. mode in the case of 5'CMP derivatives.

TABLE V. Diffuse Reflectance Spectra of the Complexes[a, b] (bands in nm)

Compound	$\pi \longrightarrow \pi^*$ $n \longrightarrow \pi^*$	$(\nu_2)^4T_{1g}(F) \longleftarrow {}^4A_{2g}$		$(\nu_1)^4T_{2g} \longleftarrow {}^4A_{2g}$		$10\,Dq$ (cm^{-1})
$Na_2$5'AMP	252s, 292.5s					
Cr(en)(5'AMP)(5'AMPH)·$\frac{11}{2}H_2O$	254s, 287s	370sh	average	460sh	average	18498
		384m	394	557s	541	
		429s		605s		
Cr(en)(5'AMP)(5'AMPH)·$11H_2O$	255s, 290s	370sh	average	460sh	average	18315
		384m	395	560s	546	
		429s		605s		
$H_4$5'ATP	268s,sh; 287s,sh					
Cr(en)(5'ATPH_2)(OH)·$2H_2O$	250s,sh; 272s,sh	386m	average	470sh	average	18315
		429s	407.5	560s	546	
				608s		
$Na_2$5'GMP	242s, 284–305s,sh					
Cr(en)(5'GMP)(OH)· $4H_2O$	250–277s,sh; 302s	386s	average	470sh	average	18382
		429s	408.5	557sh	544	
				604s		
Cr(en)(5'GMP)(OH)·$\frac{13}{2}H_2O$	260s,sh; 304s	387m	average	465sh	average	18394
		430s	408	560sh	544	
				606s		
$Na_2$5'IMP	240s, 290s					
Na[Cr(en)(5'IMP)$(OH)_2$]·$3H_2O$	242–250m,sh; 291m	365m,sh	average	470sh	average	18762
		384m,sh	393	495sh	533	
		430s		560s		
				607s		

(continued)

TABLE V. *(continued)*

Compound	$\pi \longrightarrow \pi^*$ $n \longrightarrow \pi^*$	$(\nu_2)^4T_{1g}(F) \longleftarrow {}^4A_{2g}$		$(\nu_1)^4T_{2g} \longleftarrow {}^4A_{2g}$		10 *Dq* (cm^{-1})
Na[Cr(en)(5'IMP)$(OH)_2$]$\cdot 4H_2O$	246s,sh; 288s	388m 429s	average 408.5	469sh 560s 606s	average 545	18349
$Na_2$5'CMP	260s, 308s					
Cr(en)(5'CMP)(5'CMPH)$\cdot$EtOH$\cdot 6H_2O$	272s, 310s	385m 430.5s	average 390	465sh 558s 607s	average 543	18411
Cr(en)(5'CMP)(5'CMPH)$\cdot 8H_2O$	298–270m,sh; 323m	363s 380sh 431s	average 391	470m 495m 561m 609s	average 534	18735
Solution UV Spectrum of the 5'UMP Derivative (bands in mn)[c]						
$Na_2$5'UMP	262s ($\epsilon = 10^4$)					
Cr(en)(5'UMP)(OH)$\cdot 3H_2O$	261.5s ($\epsilon = 8363$)	545m ($\epsilon = 46.3$)		401m ($\epsilon = 53.4$)		18349

[a] s = strong; sh = shoulder; m = medium; br = broad. [b] For the *cis*-[Cr(en)$_2$Cl$_2$]Cl complex bands at 365m, 430s, 465sh, 484sh, 495sh, 558m, 607m. For the *trans*-[Cr(en)$_2$Cl$_2$]Cl complex bands at 383m, 429s, 465m, 568s, 606s. [c] Bands of UV solution spectra of *cis*-[Cr(en)$_2$Cl$_2$]Cl at 399s, 515s,br.

diagrams [33]. These values are in agreement with chromium complexes bonded to N and O donors.

The ring bands π → π* and n → π* [34], except for the 5'AMP derivatives, present changes in intensity and wavelength. These data agree with a direct bonding Cr–purine ring, in accordance with the infrared data.

For the 5'GMP and 5'IMP derivatives, the UV band at 240 nm in the nucleotide shifts to a higher wavelength, with broadening for the complexes obtained from the *cis*-[Cr(en)$_2$Cl$_2$]Cl, which implies an electronic charge redistribution owing to coordination Cr(III)–N(7). For the 5'ATP compound bands at 250 nm and 272 nm are shifted to a lower wavelength in comparison with the nucleotide bands. This suggests a different kind of interaction between the metallic ion and the base or N(1)–H protonation. In the case of 5'AMP complexes, bands at 252 nm and 292.5 nm show little modification. This fact supports the N(heterocyclic) and NH_2 participation in the pairing base hypothesis.

For the 5'CMP derivatives (Table V) the changes on the UV ring bands agree with coordination between Cr(III)–N(3). For the 5'UMP complex there are no significant changes on the UV uracil band, which suggests no interaction between Cr(III) and O(carbonylic). The EPR spectra of Cr(en)(5'UMP)(OH)$\cdot 3H_2O$ were recorded at room and liquid nitrogen temperature. A *g* value of 1.981 was obtained at room temperature. The intensity of the signal decreases dramatically at liquid nitrogen tem-

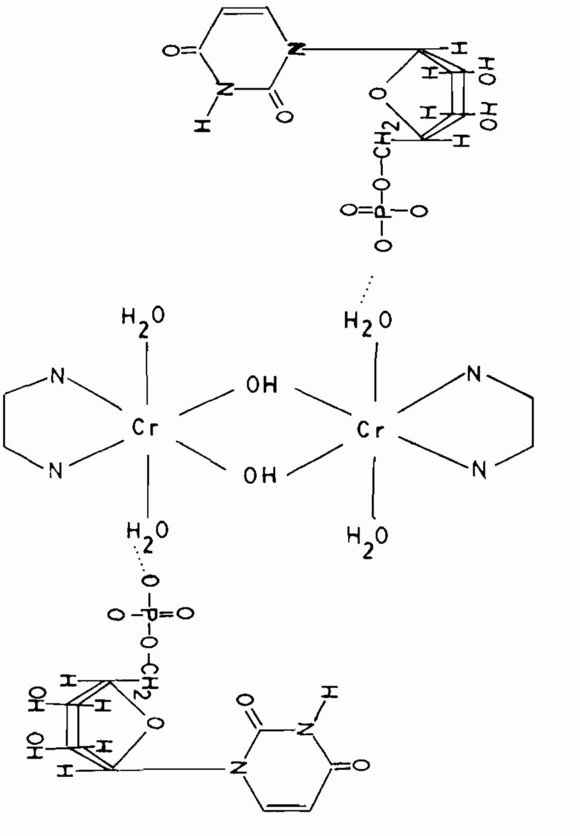

Fig. 2. Hypothetical dimeric structure for the Cr(en)(5'UMP)(OH)$\cdot 3H_2O$ complex.

perature which seems to indicate an antiferromagnetic interaction. The EPR and conductivity (Λ_M = 17) data suggest a dimer structure, consistent with the solubility and non-electrolyte character of this complex.

The data for this complex (IR, EPR, electronic spectra, and conductivity measurements) are in agreement with the structure of Fig. 2 or an isomeric-similar one. Nevertheless, an indirect Cr(III)–O(phosphate) interaction through a hydrogen bonded water molecule may not be ruled out because until now the structures studied by X-ray diffraction with a direct bond are very scarce [35]. Unfortunately it was not possible to obtain suitable crystals for a X-ray study.

Acknowledgements

We wish to express our thanks to Dr. D. M. L. Goodgame (Dept. Chemistry, Imperial College, London) for the EPR measurements. This work was partly financed by CAICYT (Madrid). Two of us wish to thank Ministerio de Educacion y Ciencia for a predoctoral fellowship (A.M.C.) and for a post-doctoral fellowship 'Bolsa de Estudios en el Extranjero' (A.T.).

References

1 I. Legg, *Coord. Chem. Rev., 25,* 103 (1978).
2 W. W. Cleland and A. S. Mildvan, *Adv. Inorg. Biochem., 1,* 163 (1979).
3 D. Dunaway-Mariano and W. W. Cleland, *Biochemistry, 19,* 1506 (1980).
4 P. Puig, A. Terrón and V. Moreno, *J. Inorg. Biochem., 25,* 175 (1985).
5 J. A. Cooper, B. F. Anderson, P. D. Buckley and L. F. Blackwell, *Inorg. Chim. Acta, 91,* 1 (1984).
6 E. Gonzalez Vergara, B. Candia, J. Hegenaver and P. Saltman, *Isr. J. Chem., 21,* 18 (1981).
7 J. A. Cooper, L. F. Blackwell and P. D. Buckley, *Inorg. Chim. Acta, 92,* 23 (1984).
8 C. E. Green, R. J. Bianchine and I. Legg, *Inorg. Chem., 23,* 2713 (1984).
9 W. E. Broderick, M. R. Pressprich, I. Legg, U. Geiser and R. D. Wilet, *Inorg. Chem., 25,* 3372 (1986).
10 J. J. Fiol, A. Terrón and V. Moreno, *Inorg. Chim. Acta, 83,* 69 (1984).
11 J. Campomar, J. J. Fiol, A. Terrón and V. Moreno, *Inorg. Chim. Acta, 124,* 75 (1986).
12 J. J. Fiol, A. Terrón and V. Moreno, *Polyhedron, 5,* 1125 (1986).
13 A. Terrón and V. Moreno, *Inorg. Chim. Acta, 56,* L57 (1981).
14 G. Brewer and C. M. Grisham, *Inorg. Chim. Acta, 106,* 37 (1985).
15 E. B. Sandell, 'Colorimetric Metal Analysis', Wiley, New York, 1959, p. 217.
16 F. Dee Snell, 'Encyclopedia of Industrial Analysis', Wiley, New York, Vol. 17, 1973, p. 67.
17 W. C. Fernelius (ed.), *Inorg. Synth., 2,* 200 (1978).
18 G. Brauer, 'Quimica Inorganica Preparativa', Reverté, Barcelona, 1958, p. 813.
19 M. Damodara Poojary and Hattikudur Manohar, *J. Chem. Soc., Chem. Commun.,* 533 (1982).
20 X. Solans, J. J. Fiol, A. Terrón and V. Moreno, unpublished results.
21 M. Baldwin, *J. Chem. Soc.,* 4369 (1960).
22 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, 22,* 759 (1966).
23 M. Tsuboi, in P.O.P. Ts'o (ed.), 'Basic Principles in Nucleic Acid Chemistry', Vol. 1, Academic Press, New York, 1974.
24 B. T. Khan, M. R. Somayajulu and M. M. Taqui Khan, *Indian J. Chem., 17,* 359 (1979).
25 P. G. Harrison and M. A. Healy, *Inorg. Chim. Acta, 80,* 279 (1983).
26 N. Katsaros, E. Vrachnou-Astra and J. Konstantatos, *J. Inorg. Biochem., 16,* 227 (1982).
27 J. Duchesne (ed.), 'Physicochemical Properties of Nucleic Acids', Vol. 2, Academic Press, London, 1973.
28 L. Kiss and J. Csaszar, *Acta Chim. Acad. Sci. Hung., 109,* 57 (1982).
29 H. Tajmir-Riahi and T. Theophanides, *Can. J. Chem., 61,* 1813 (1983).
30 E. Scherer, H. A. Tajmir-Riahi and T. Theophanides, *Inorg. Chim. Acta, 92,* 285 (1984).
31 J. J. Fiol, A. Terrón and V. Moreno, *Inorg. Chim. Acta, 125,* 159 (1986).
32 J. J. Fiol, A. Terrón, D. Mulet and V. Moreno, *Inorg. Chim. Acta, 135,* 197 (1987).
33 A. B. P. Lever, 'Inorganic Electronic Spectra', 2nd edn., Elsevier, Amsterdam, 1984.
34 L. B. Clark and I. Tinoco Jr., *J. Am. Chem. Soc., 87,* 11 (1965).
35 B. E. Fischer and R. Bau, *Inorg. Chem., 17,* 27 (1978).