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Ternary Chromium(III)–Nucleotide–Amino Acid Complexes III. L-Glutamic Acid Derivatives

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Summary

The first ternary chromium(III)–nucleotide–glutamic acid complexes with purine (5'ATP, 5'AMP, 5'GMP, 5'IMP) and pyrimidine (5'CMP) nucleotides are reported. The compounds were prepared by reaction of Cr_2(L-Glu)$_3(OH)_2Cl\cdot 4H_2O$ or Na_3Cr(L-Glu)$_3\cdot 4H_2O$ with the nucleotide in water medium. One or two glutamic acid molecules of the starting Cr(III)–amino acid complex are removed during reaction. These facts are similar to those previously reported in the cases of histidine and cysteine ternary complexes. The complexes have been characterized by elemental analyses, conductivity measurements, infrared and electronic spectra and EPR.

Introduction

As part of a programme to investigate the ways in which Cr(III) binds to biologically relevant molecules, we have studied the formation of ternary chromium(III)–nucleotide–L-glutamic acid complexes. The ternary histidine and cysteine ternary chromium(III) complexes have been reported previously [1, 2].

There are very few chromium(III)–L-glutamic acid complexes in the literature [3–6]. In this paper, a new synthetic method of two derivatives is described using $Cr(urea)_6Cl_3\cdot 3H_2O$ as starting material. Interest in the reaction properties of metal urea complexes has recently been pointed out [7]. The L-glutamic acid promotes the total substitution of the urea molecules from the chromium(III) coordination sphere, as was observed previously for L-cysteine and L-histidine [1, 2].

Experimental

Carbon, hydrogen and nitrogen analyses were carried out with a Carlo Erba microanalyser at the Institute of Bio-organic Chemistry in Barcelona. Chlorine was determined by the Schoniger method. Chromium [8] and phosphorous [9] were determined colorimetrically. Conductivities were measured with a Crisom 525 conductimeter at 20.0 °C in 10^{-3} M aqueous solution. The infrared spectra were obtained in the solid state (KBr pellets) on a Perkin-Elmer 693 spectrophotometer connected to a Perkin-Elmer 3600 data station. Solid state reflectance spectra were recorded on a Perkin-Elmer 552 UV–Vis spectrophotometer with an integrating sphere attachment. The UV–Vis solution spectra were recorded in water on the same apparatus. The EPR spectra were measured on polycrystalline samples at room temperature on a Varian model E-12 spectrometer at X band frequency.

Preparation

The sources of nucleotides were Serva and Merck. The other products used such as L-glutamic acid were Merck. The starting $Cr(urea)_6Cl_3\cdot 3H_2O$ complex was prepared according to the literature [10].

Syntheses of the Complexes

Cr_2(L-Glu)$_3(OH)_2Cl\cdot 4H_2O$

A 10 ml water solution containing 2 mmol of L-glutamic acid was raised to pH = 4.3 with the addition of a 2 N NaOH solution. This solution was added drop by drop to a dissolution of 1 mmol of $Cr(urea)_6Cl_3\cdot 3H_2O$ dissolved in 5 ml of water. The resultant solution was placed in a thermostatted bath at 50 °C for 10 h. This was concentrated in a rotavapor to 5 ml and eluted through a Sephadex G-10 column (diameter = 1 cm, length 40 cm) to give a single violet fraction. The precipitate obtained on evaporating the solution or adding 50 ml of ethanol was vacuum dried over P_4O_{10}. The product is insoluble in water and usual organic solvents, and presents a μ_{eff} = 3.47 BM.

Na_3Cr(L-Glu)$_3\cdot 4H_2O$

L-Glutamic acid (3 mmol) was dissolved in 15 ml water and the pH of the solution raised with diluted

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2 N NaOH to 9.9. A solution containing 1 mmol of $Cr(urea)_6Cl_3 \cdot 3H_2O$ in 5 ml of water and pH adjusted to 7.6 by adding diluted NaOH was prepared. The two solutions were mixed (pH = 9.74) and placed in a thermostatted bath at 50 °C for 3.5 h. At the end, a violet solution of pH = 6–8 was obtained. This was concentrated to 5 ml and eluted through a Sephadex G-10 column. A single violet fraction was obtained. Addition of 50 ml of ethanol gave a violet precipitate which was filtered off and vacuum dried over P_4O_{10}. The complex is soluble in water but during the solution of 1 mmol in a litre of distilled water the pH increased by one unit due to protonation of the complex making no conductivity studies feasible. At pH = 4.2 the triprotonated compound $Cr(L\text{-}GluH)_3 \cdot 4H_2O$ can be isolated.

$Na_2Cr_2(5'CMP)(L\text{-}Glu)(OH)_4 \cdot 7H_2O$, $Na_2Cr(5'GMP)(L\text{-}Glu)(OH) \cdot 6H_2O_4$ and $Na_2Cr_2(5'AMP)(L\text{-}Glu)_2(OH)_2 \cdot 8H_2O$

A 10 ml solution containing 1 mmol of $Na_3Cr(L\text{-}Glu)_3 \cdot 4H_2O$ and 1 mmol of XMP (XMP = 5'CMP, 5'GMP or 5'AMP) in 10 ml of water and pH comprised between 6.8 and 7.0 was placed in a thermostatted bath at 40 °C for 7 h. The resultant solution was concentrated in a rota-vapor to 5 ml and eluted through a Sephadex G-10 column. Only a single fraction appeared which was evaporated to dryness and vacuum dried over P_4O_{10} in the case of 5'CMP and 5'AMP. For the 5'GMP derivative a precipitate appeared before elution. The complexes were filtered and dried as the former ones.

$Cr(XMP)(L\text{-}Glu) \cdot nH_2O$ and $Cr_2(5'ATP)(L\text{-}Glu)_2(OH)_2 \cdot 7H_2O$, where XMP = 5'CMP, 5'AMP, 5'IMP and 5'GMP

A solution of 1 mmol of the complex $Cr_2(L\text{-}Glu)_3(OH)_2Cl \cdot 4H_2O$ in 10 ml H_2O was mixed with 1 mmol of either 5'CMP, 5'AMP, 5'GMP, 5'IMP and 5'ATP (pH = 3.6–3.7), in 5 ml of water. The mixture was placed in a thermostatted bath at 50 °C for 2 h. In some cases (5'GMP and 5'ATP derivatives) a precipitate appeared and was filtered off and washed with water. Elution through the Sephadex G-10 column and addition of ethanol to precipitate the complex was carried out in the other compounds. All the complexes were insoluble in water and usual organic solvents.

The elemental analyses and the g_{eff} values are displayed in Table 1. The formulae of the ligands and abbreviations used in the paper are shown in Fig. 1.

Results and Discussion

The infrared data for the amino acid complexes are indicated in Table 2. The assignments have been made according to the literature [11–16].

Noticeable changes in the bands related to νCOO^- and δNH_2 areas are observed by comparison with those of L-Glu. The peak corresponding to $\nu_a COO^-$

TABLE 1. Analytical data and some properties of the complexes

Compound	Analysis, found (calc.) (%)							g_{eff}	Colour	Melting point (°C)
	C	H	N	Cr	Cl	Na	P			
$Cr_2(L\text{-}Glu)_3(OH)_2Cl \cdot 4H_2O$	26.54 (26.34)	5.02 (4.97)	6.71 (6.14)	15.11 (15.22)	5.78 (5.19)			1.94	violet	330
$Na_3Cr(L\text{-}Glu)_3 \cdot 4H_2O$	28.01 (28.66)	4.65 (4.62)	6.73 (6.69)	8.34 (8.28)		10.70 (10.99)		1.94	volet	340
$Na_2Cr_2(5'CMP)(L\text{-}Glu)(OH)_4 \cdot 7H_2O$	20.36 (20.74)	4.47 (4.57)	6.24 (6.91)	12.86 (12.84)		5.70 (5.68)	3.47 (3.83)		violet	253–255
$Na_2Cr(5'GMP)(L\text{-}Glu)(OH) \cdot 6H_2O$	24.28 (24.69)	3.50 (4.39)	11.67 (11.52)	6.62 (7.13)		7.19 (6.31)	4.65 (4.25)		violet	265
$Na_2Cr_2(5'AMP)(L\text{-}Glu)_2(OH)_2 \cdot 8H_2O$	25.02 (24.92)	4.61 (4.57)	8.69 (10.68)	11.70 (10.80)		4.39 (4.78)	3.32 (3.22)		violet	205–207
$Cr(5'CMP)(L\text{-}Glu) \cdot 6H_2O$	26.72 (26.79)	5.03 (5.10)	9.15 (8.93)	7.99 (8.29)			5.49 (4.94)	1.94	gray	265–270
$Cr(5'GMP)(L\text{-}Glu) \cdot 7H_2O$	26.58 (26.28)	4.75 (4.96)	11.59 (12.26)	7.49 (7.59)			4.54 (4.53)	1.93	gray	260
$Cr(5'IMP)(L\text{-}Glu) \cdot 5H_2O$	28.66 (28.39)	4.74 (4.57)	10.50 (11.04)	8.25 (8.20)			4.84 (4.89)	1.94	gray	258–260
$Cr(5'AMP)(L\text{-}Glu) \cdot 5H_2O$	27.81 (28.44)	4.54 (4.74)	13.24 (13.27)	8.00 (8.21)			5.36 (4.90)	1.99	green	255
$Cr_2(5'ATP)(L\text{-}Glu)_2(OH)_2 \cdot 7H_2O$	22.40 (22.62)	4.36 (4.34)	8.69 (9.24)	9.90 (9.80)			8.61 (8.76)	1.94	gray	240

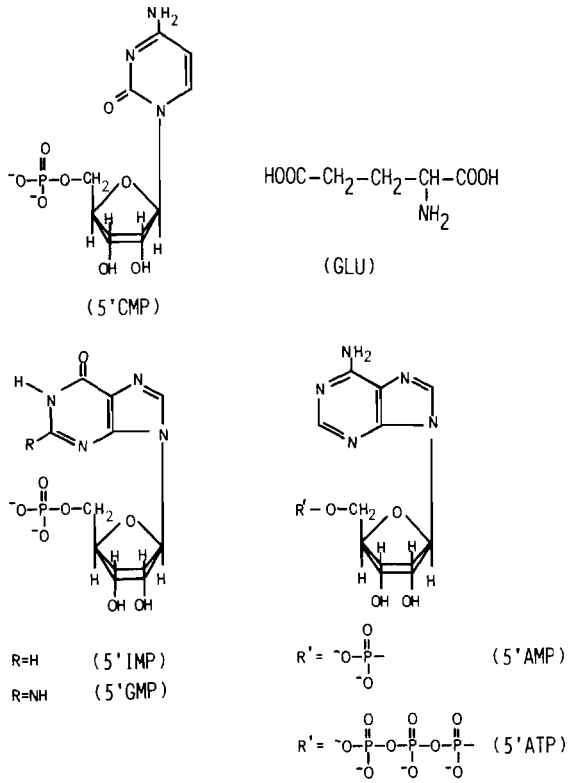

Fig. 1. Nucleotide structures and abbreviations used.

(1616 cm^{-1}) is shifted to higher frequencies in both complexes, whereas the peak appearing at 1422 cm^{-1} assignable to $\nu_s COO^-$ shows the opposite tendency. Other bands due to $\gamma_\rho COO^-$, $\gamma_w COO^-$ and δCOO^- show variations in the lower area of the spectra [11]. The peaks appearing at 1583 ($\delta_d NH_3^+$) and 1515 ($\delta_s NH_3^+$) cm^{-1} and the three absorptions ($\tau_\rho NH_3^+$) between 1000–1150 cm^{-1} undergo noticeable modifications in frequency and intensity in both complexes. All these data agree with chelate bonding between Cr(III) carboxylate and amino groups [6, 18, 19]. The presence of the 1724 cm^{-1} band assignable to free $\tau COOH$ [16] for $Cr_2(L\text{-}Glu)_3(OH)_2Cl \cdot 4H_2O$ shows that carboxylate bonding occurs through the αCOO^- group [17]. This absorption may be masked by the $\nu C{=}O$ broad band in the other complex.

The electronic data (Table 3) are in agreement with coordination of Cr(III) to O and N donors. The two complexes present g_{eff} values (Table 1) corresponding to Cr(III) in pseudo octahedral geometry.

The IR spectra of L-Glutamic–nucleotide compounds show less definition of peaks in comparison with those of histidine [1] and cysteine [2] previously described. Broad bands and some apparent shifts are in fact due to overlapping between L-Glu and nucleotide peaks. The spectra of the free nucleotide

TABLE 2. Infrared data for the binary complexes chromium–L-glutamic acid (cm^{-1})

Tentative assignment	L-Glu	$Cr_2(L\text{-}Glu)_3(OH)_2Cl \cdot 4H_2O$	$Na_3Cr(L\text{-}Glu)_3 \cdot 4H_2O$
$\nu C{=}O$		1724w	
	1665s	1713w	1659s
	1645s		1644s
$\nu_a–COO^-$	1616m	1624s	1632s
		1613s	
$\delta_d–NH_3^+$	1583m		1568s
$\delta_s–NH_3^+$	1515s		
$\nu C–C$		1450s	1445m
$\nu_s–COO^-$	1422s	1404s	1401s
			1399s
δCCH	1356s	1346m	1343m
$\gamma_\rho–CH_2$	1260s		
$\nu(OH) + \delta(OH)$	1216m		
$\gamma_\rho–NH_3^+$	1129s	1149s	1152s
	1078s	1088w	1085w
	1058s	1035sh	1055w
$\gamma_\rho–CH_2$	969w	995w	
	948m	950w	941m
$\nu C–C$	869m		
δOH	810s	812m	818w
$\rho_r–NH_2$		767m	789w
$\delta–COO^-$	716s		
$\gamma_w–COO^-$	541s	579w	561w
		535w	
$\gamma_\rho–COO^-$	423m	452w	417w

TABLE 3. Diffuse reflectance spectra of the complexes

Compound	$^4T_{2g} \leftarrow {}^4A_{2g}$ λ (nm)	$^4T_{1g} \leftarrow {}^4A_{2g}$ λ (nm)	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	Δ_0 (cm^{-1})
Cr_2(L-Glu)$_3(OH)_2Cl \cdot 4H_2O$	608, 562	430, 390	250	17100
Na_3Cr(L-Glu)$_3 \cdot 4H_2O$[a]	548 (ε = 87)	402 (ε = 155)		18200
Na_2Cr_2(5'CMP)(L-Glu)$(OH)_4 \cdot 7H_2O$	604, 562	430, 390	270	17200
Na_2Cr(5'GMP)(L-Glu)$(OH) \cdot 6H_2O$	608, 564	430, 390	304, 270	17100
Na_2Cr_2(5'AMP)(L-Glu)$_2(OH)_2 \cdot 8H_2O$	610, 562	430, 370	322, 262	17100
Cr(5'CMP)(L-Glu)$\cdot 6H_2O$	608, 566	430, 388	306, 266	17100
Cr(5'GMP)(L-Glu)$\cdot 7H_2O$	606, 568	432, 392	304, 270	17100
Cr(5'IMP)(L-Glu)$\cdot 5H_2O$	608, 563	430, 388	287	17100
Cr(5'AMP)(L-Glu)$\cdot 5H_2O$	608, 568	432, 390	292, 252	17000
Cr_2(5'ATP)(L-Glu)$_2(OH)_2 \cdot 7H_2O$	608, 568	430, 392, 358	286, 256	17000

[a]Aqueous solution electronic spectra.

TABLE 4. Infrared data for the ternary complexes chromium–5'CMP–L-glutamic acid (cm^{-1})

Tentative assignement	L-Glu	$Na_2$5'CMP$\cdot 2H_2O$	Na_2Cr_2(5'CMP)(L-Glu)$(OH)_4 \cdot 7H_2O$	Cr(5'CMP)(L-Glu)$\cdot 6H_2O$
νC=O				1726s
	1665s	1663s	1661s	1645vs
	1645s			
δ-NH_2 + νC=N + νC=C		1650s	1647s	
ν_a-COO^-	1616m		1618sh	
δ_d-NH_3^+	1583m		1556s	
δ_s-NH_3^+	1515s		1494m	1538sh
νC–C			1449m	1451m
ν_s-COO^- + ν(ring)	1422s	1407w	1402w	1409m
		1372w,sh	1394m	
δCCH	1356s		1342w	1347w
ν-PO_2^-		1296m	1291w	1285m
γ_ρ-NH_3^+ + ν_a-PO_3^{2-} + νC–O(sugar)	1129s	1115vs,br	1129s,br	1110s,br
	1078s	1082vs,br	1064s,br	1081s,br
	1058s			1064s,br
ν_s-PO_3^{2-}		977vs	993s	996m
γ_w-COO^-	541s		561w	529w
			528w	

ligands are in agreement with data published [20–25] and papers cited therein. A clear new band at 1450 cm^{-1} appears in almost all spectra which is assignable to νC–C of the L-Glu chain [6].

In the case of 5'CMP derivatives (Table 4) a broad absorption appears between 1600–1560 cm^{-1} including some definite peaks corresponding to νC=O, $\nu_a COO^-$ (L-Glu) and νC_2=O, ring of the cytosine base. The band appearing at 1726 cm^{-1} for the Cr(5'CMP)(L-Glu)$\cdot 6H_2O$ complex is assigned to a free carboxylic group [16, 17]. The 1422 cm^{-1} peak due to $\nu_s COO^-$ shifts to lower frequencies in both complexes suggesting that the carboxylate group is involved in metal bonding [6], although in this case there is some contribution from the 1407 cm^{-1} of the cytosine ring. The band related to τ_wCOO also undergoes changes in frequency and intensity. The variations in the $\delta_d NH_3^+$ (1583 cm^{-1}) and $\delta_s NH_3^+$ (1515 cm^{-1}) bands [11] may indicate participation of the amino group in the bonding. On the other hand, the nucleotide seems to interact with the metal ion through the phosphate moiety as the νPO_3^{2-} sym. band at 977 cm^{-1} is clearly shifted to higher frequencies in both complexes [23].

Tables 5 and 6 show the IR data for the purine nucleotide ternary complexes. For the 5'GMP and 5'IMP derivatives, peaks due to the νCOOH free carboxylic group are not observed in the νC=O area. The $\nu_a COO^-$ (1616 cm^{-1}) band is shifted to lower frequency (1603 cm^{-1}) in the Cr(5'GMP)(L-Glu)$\cdot 7H_2O$ complex and disappears in the other two,

TABLE 5. Infrared data for the 5′GMP and 5′IMP ternary complexes (cm^{-1})

Tentative assignment	L-Glu	$Na_2$5′GMP	$Na_2$5′IMP	Na_2Cr(5′GMP)(L-Glu)(OH)·$6H_2O$	Cr(5′GMP)(L-Glu)·$7H_2O$	Cr(5′IMP)(L-Gllu)·$5H_2O$
$\nu C_6{=}O$		1691s,br	1692s	1696vs		1691s
			1683s			1682s
$\nu C{=}O$	1665s			1646s	1668s	1644s
	1645s			1635s	1660s	1633s
ν_a-COO^-	1616m				1603sh	
δ_d-NH_3^+ + $\nu C{-}N$ + $\nu C{-}C$	1583m	1577m	1594m	1577sh		1591s
			1551m			1552m
δ_s-NH_3^+ + $\nu C{-}N$ + $\nu C_6{=}O$	1515s	1538m	1521w	1537w		1516m
		1491m		1486m	1488m	
$\nu C{-}C$				1448m	1450w	1451s
ν_s-COO^- + ν(ring) + δCCH	1422s	1420m	1428m	1405m	1412m	1415m
	1356s	1366m	1383m	1395m	1360sh	1385w
		1331w	1349m			1349m
$\nu C_8{-}H$ + $\nu C_8{-}N_7$		1207m	1219s			1212s
γ_ρ-NH_3^+ + ν_a-PO_3^{2-} + $\nu C{-}O$(sugar)	1129s	1181m,br	1143s,br	1080s,br	1111s,br	1120s,br
	1078s	1117s,br	1119s,br		1081s,br	1083s,br
	1058s	1085s,br	1097s,br			
ν_s-PO_3^{2-}		979s	979s	979s	995s	993s
νPO		785m	793m	803w	802m	820m
				782w	782m	793m
δ-COO^- or ρ-NH_2				731sh	728w	719w
ring breathing mode		694m	719m	689w		
γ_w-COO^- + νskeleton	541s	539m	536m	531w	532w	533w

TABLE 6. Infrared data for the adenosine nucleotide ternary complexes (cm^{-1})

Tentative assignment	L-Glu	$Na_2$5′AMP	$H_4$5′ATP	Na_2Cr_2(5′AMP)(L-Glu)$_2$(OH)$_2\cdot 8H_2O$	Cr(5′AMP)(L-Glu)$\cdot 5H_2O$	Cr_2(5′ATP)(L-Glu)$_2$(OH)$_2\cdot 5H_2O$
νC=O + δ-NH_2 + νC=N	1665s	1663vs	1646m	1645vs	1691m	1693m
	1645s	1646vs		1609vs	1659s	1658sh
		1608s			1645vs	1642vs
ν_a-COO^-	1616m				1608vs	1616vs
δ_d-NH_3^+ + νC=C + νC=N	1583m	1584s	1615m	1576s	1578vs	
δ_s-NH_3^+	1515s				1510w	1505w
$\delta C_8{=}N_7$ + $\nu C_8{-}N_9$ + $\delta C_8{-}H$ + $\delta C_2{-}H$		1484s	1481m	1481m	1481m	
νC–C				1449m	1451m	
ν_s–COO^- + δCH_2	1422s	1425m	1420m	1394s	1424m	1416w
δCCH	1356s			1340m	1336m	1347m
γ_ρ-NH_3^+ + ν_a-PO_3^{2-} + νC–O(sugar)	1129s	1120s,br	1136s,br	1136s,br	1121s,br	1080s,br
	1078s	1094s,br	1123s,br	1085s,br	1083s,br	1077s,br
	1058s		1110s,br			
			1070s,br			
ν_s-PO_3^{2-}		977vs	990vs	992s	1012s,br	1002sh
			996vs		1001s,br	
νP–O–P			905vs			911s
νC–O–P		901m	811m	900w	904w	819m
		879m		882w	876w	
νP–O + δOH	810s	797s		819w	820w, 797w	
δ-COO^- + ρ-NH_2	716s			719sh	722w	722m
γ_w-COO^-	541s			562w	584w	524w

and $\nu_s COO^-$ (1422 cm^{-1}) is shifted to lower frequency in the three compounds. This might indicate that the L-Glu residue is interacting via the carboxylate group in the ternary complex. The bands related to δNH_3^+ of L-Glu are overlapped with the ring peaks of the purine base and no information can be drawn from these data. Metal–O(phosphate) bonding for the nucleotide moiety is inferred again in penta and hexahydrate derivatives owing to the changes on the νPO_3^{2-} sym. band. No direct bonding via phosphate seems to occur in the case of the $Na_2Cr(5'GMP)(L\text{-}Glu)(OH)\cdot 6H_2O$ complex [22].

In the case of 5'AMP/5'ATP complexes the νPO_3^{2-} sym. peak undergoes noticeable changes as well, suggesting the same interaction. The 977 cm^{-1} peak is shifted to 992 and 1012, 1001 cm^{-1} for the 5'AMP derivatives and the doublet at 990, 966 cm^{-1} is solved in a band at 1002 cm^{-1} (5'ATP compound). In the latter, complex phosphate bonding probably occurs through the P(β) and P(τ) oxygens [26]. No clear conclusion can be drawn about the mode of bonding of the L-Glu residue in these complexes due to overlap of $\nu_s COO^-$ and δNH_3^+ peaks with the corresponding purine ring bands of the nucleotide.

The electronic data (Table 3) and the EPR measurements (Table 1) are in agreement with a pseudo octahedral coordination of Cr(III) to oxygen (from carboxylic or phosphate groups) and nitrogen (from amino group) donors.

As a general trend, the nucleotide always removes one of the L-glutamic acid molecules of the coordination sphere of chromium(III). This also occurs in the syntheses of the previously described ternary complexes of histidine and L-cysteine [1, 2]. These facts may be important in understanding the behaviour of chromium(III) in biological systems because of the presence of L-glutamic acid in the glucose tolerance factor [4, 27], although some authors claim that chromium is not present in GTF [28, 29]. These data can also be important for the role of Cr(III) in molecular biology [30, 31].

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