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Ternary Chromium(III)–Nucleotide–Amino Acid Complexes: L-Methionine, L-Serine and Glycine Derivatives

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Abstract

The first ternary Cr(III)–nucleotide–amino acid complexes (nucleotide: 5′AMP, 5′CMP; amino acid: L-serine, L-methionine, glycine) are described. The complexes have been characterized by elemental and thermogravimetric analyses, IR and electronic spectroscopy and EPR measurements. In all cases the interaction of Cr(III) with the nucleotide seems to occur mainly through the phosphate group, whereas the amino acid binds to Cr(III) through the carboxylic and amino groups. Some of the complexes show distortions from octahedral geometry, but these distortions appear to be small resulting in values of the zero field splitting parameter $D < 0.1$ cm^{-1}.

Introduction

Although the role of chromium in biological systems is not perfectly known, there is abundant evidence that Cr(III) is present in the glucose tolerance factor (GTF) [1, 2]. For this reason, interest in derivatives of Cr(III) with amino acids has increased during recent years [2–5]. There is also great interest in obtaining inert derivatives of Cr(III) with nucleotides, which could be used as enzymatic labels of allosteric enzymes [6] and for the study of the role of chromium in transcription processes and RNA and DNA interactions [7]. In this paper we describe the syntheses and characterization of the first ternary complexes of Cr(III) with L-methionine, L-serine and glycine and the nucleotides 5′AMP and 5′CMP.

Experimental

Carbon, hydrogen, nitrogen and sulphur analyses were carried out with a Carlo Erba model 1106 microanalyzer at the Centro de Investigación y Desarrollo-C.S.I.C. in Barcelona. Chlorine was determined by the Schöniger method. Chromium was determined by atomic absorption with a Perkin-Elmer 703 spectrophotometer using $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ solutions as a standard. The phosphorus content was determined using the colorimetric method with phosphomolybdovanadate [8]. Thermogravimetric analyses were carried out with a Perkin-Elmer TGS-2 system with oxygen atmosphere at a velocity rate of 5 or 10 °/min depending on the cases. Conductivities were measured with a Crison 525 conductimeter at 25 °C in 10^{-3} M aqueous solution. The IR spectra were recorded in solid state (KBr pellets) on a Perkin-Elmer 683 IR spectrophotometer connected to a Perkin-Elmer 3600 data station. The reflectance spectra were obtained with a Perkin-Elmer UV–Vis spectrophotometer with an integrating sphere attachment. UV–Vis spectra were recorded in the same apparatus at 10^{-3}–10^{-4} M concentration. The EPR spectra were measured using polycrystalline samples at room temperature. X-band spectra were obtained with a Varian E 12 spectrometer and Q-band spectra with a Bruker ER 200 D-SRC spectrometer and an ER 078 15-inch electromagnet (Imperial College, London).

The nucleotides and amino acids (Fig. 1) were from Serva and Merck and used without further purification. The starting complex $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ was prepared according to the literature [9].

Preparation

$Cr(L\text{-}met)(L\text{-}metH)Cl_2 \cdot 3H_2O$, $Cr(L\text{-}ser)_2(H_2O)_2Cl \cdot H_2O$ and $Cr(glyH)_2(gly)Cl_2 \cdot 3H_2O$

A 10 ml water solution containing 1 mmol of $[Cr(urea)_6]Cl_3 \cdot 3H_2O$ (pH adjusted to 6.3) was added to a solution of amino acid (2 mmol in the case of L-methionine and L-serine and 3 mmol for glycine)

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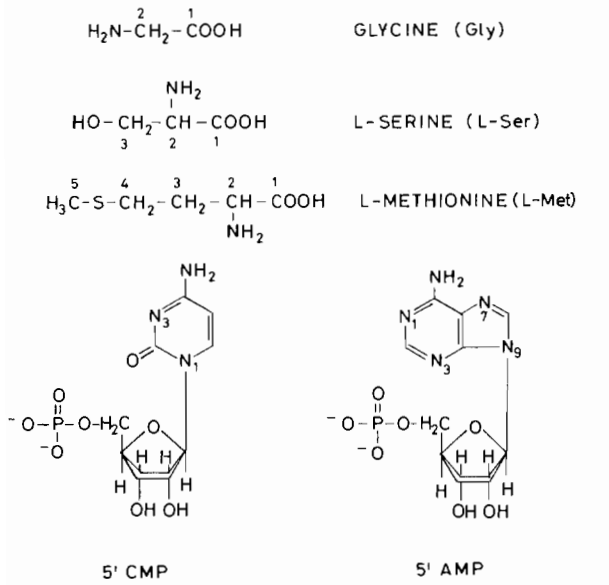

Fig. 1. Nucleotide and amino acid formulae and abbreviations used.

in 10 ml water [pH adjusted to 9.2 (met and ser) and 9.8 (gly)]. The resultant green solution [pH = 9.2 (met), 9.3 (ser) and 9.7 (gly)] was placed in a thermostated bath at 50 °C, with constant stirring, for 10 h (5 h in the case of methionine complex), by which time a lilac–violet solution [pH = 3.7 (met), 3.3 (ser) and 3.9 (gly)] was obtained. This was concentrated in a rota-vapor and then eluted through a Sephadex G-10 column to give two fractions: the first one, violet, corresponding to the binary complex, and the second one, green, corresponding to unreacted starting complex. In the case of the glycine complex, there were three fractions: the first one, blue, in a very small quantity; the second, violet, corresponding to the binary complex; the third, green, corresponding to unreacted starting complex. A precipitate corresponding to the violet fraction was obtained on evaporating the solution or adding ethanol (for the L-serine complex). This was vacuum dried over P_4O_{10}. The three complexes are hygroscopic and soluble in water.

Cr(L-ser)$_2$(L-serH)$Cl\cdot 3H_2O$

This was obtained by the same procedure as $Cr(\text{L-ser})_2(H_2O)_2Cl\cdot H_2O$, but using a 1:3 Cr:L-ser stoichiometry.

Cr(L-met)(5′AMP)$\cdot\frac{11}{2}H_2O$ and
Cr_2(L-met)(5′CMP)$_2OH\cdot 10H_2O$

Ten ml of an aqueous solution (pH approx. 7) containing 0.75 mmol of $Na_2$5′XMP were added dropwise to a solution of $Cr(\text{L-met})(\text{L-metH})Cl_2\cdot 3H_2O$ (0.75 mmol in 10 ml H_2O, pH 3.9–4.2). The violet mixture (pH 5.6–5.7) was maintained at 50 °C, with constant stirring, for 1.5–2.5 h. A grey precipitate was formed. It was filtered off, washed with cold water and vacuum dried over P_4O_{10}.

Cr_2(L-ser)(5′AMP)$_2Cl\cdot 16H_2O$ and
Cr_2(L-ser)$_2$(5′CMP)$OHCl\cdot 7H_2O$

To an aqueous solution of $Cr(\text{L-ser})_2(H_2O)_2Cl\cdot H_2O$ (0.94 mmol in 10 ml) was added dropwise a solution of $Na_2$5′XMP (0.94 mmol in 10 ml water, pH = 7). The violet resultant solution (pH = 4.5–4.7) was placed in a thermostated bath at 50 °C with constant stirring for 20 h (for the 5′AMP complex) or 8 h (in the case of the 5′CMP derivative). The final violet solution (pH = 3.4–3.6) was concentrated to 5 ml and then eluted through a Sephadex G-10 column to give two fractions: the first grey–blue, and the second violet. Addition of ethanol to the blue fraction and further evaporation gave $Cr_2(\text{L-ser})(5'\text{AMP})_2Cl\cdot 16H_2O$ and $Cr_2(\text{L-ser})_2(5'\text{CMP})(OH)Cl\cdot 7H_2O$, which are insoluble in water. These precipitates were vacuum dried over P_4O_{10}.

$Cr_2(gly)_2(5'AMP)(OH)_2\cdot 6H_2O$ and
$Cr_2(gly)_2(5'CMP)(OH)_2\cdot 6H_2O$

Ten ml of an aqueous solution containing 0.64 mmol $Na_2$5′XMP (pH adjusted to 7.0) was added dropwise to an aqueous solution of $Cr(gly)(glyH)_2Cl_2\cdot 3H_2O$ (0.64 mmol in 10 ml). The violet solution (pH 5.5 or 6.1) was maintained at 50 °C with continuous stirring for 5 or 8 h, depending on the nucleotide. By this time a precipitate was formed. This was filtered off, washed with cold water and then vacuum dried over P_4O_{10}.

The composition of the complexes and the analytical results are reported in Table 1. The elemental analyses were confirmed by the thermogravimetric studies, which are summarized in Table 2.

Results and Discussion

The Cr(III)–amino acid binary complexes are very hygroscopic and soluble in water. Their molar conductivities are consistent with non-coordination of the chlorine atoms to chromium [10]. The fact that the molar conductivity value of $Cr(\text{L-met})(\text{L-metH})Cl_2\cdot 3H_2O$ is greater than expected for an electrolyte 1:2 may be explained as a result of dissociation equilibrium from the amino acid.

The infrared spectra of these complexes show in all cases, modifications of the bands related to vibrations of the carboxylic group suggesting that this group is involved in the coordination to Cr(III) [11–13]. The most important changes occur in the $\nu_s(COO^-)$ bands (1412, 1420 and 1416 cm^{-1} for L-met, L-ser and gly respectively) which are shifted 20–30 cm^{-1} to lower frequencies. There are also noticeable modifications in the (500–600) cm^{-1}

TABLE 1. Analytical data and some properties of the complexes

Compound	Analysis: found(calc.) (%)							Colour	Melting point (°C)	Λ_M (Ω^{-1} cm^2 mol^{-1})
	C	H	N	Cr	Cl	P	S			
Cr(L-met)(L-metH)$Cl_2 \cdot 3H_2O$	25.19 (25.29)	5.07 (5.69)	6.82 (5.90)	10.00 (10.96)	15.95 (14.97)		12.64 (13.49)	violet	160–170(d)	307
Cr(L-met)(5′AMP)$\cdot 11/2H_2O$	27.14 (27.93)	4.61 (5.12)	13.46 (13.03)	7.91 (8.07)			4.12 (4.96)	grey–blue	254–258(d)	
Cr_2(L-met)(5′CMP)$_2$(OH)$\cdot 10H_2O$	24.70 (25.26)	4.63 (5.03)	8.73 (8.97)	10.91 (9.52)		4.22 (5.68)	3.12 (2.93)	grey–blue	260–264(d)	
Cr_2(L-serH)$_2$(L-ser)$_4Cl_2 \cdot 6H_2O$	23.75 (23.79)	5.50 (5.01)	9.23 (9.11)	11.43 (10.57)	9.04 (9.13)			lilac	250–255(d)	278
Cr(L-ser)$_2(H_2O)_2Cl \cdot H_2O$	21.28 (20.59)	5.19 (5.15)	8.26 (8.01)	14.66 (14.87)	10.81 (10.15)			lilac	205–210(d)	130
Cr_2(L-ser)(5′AMP)$_2Cl \cdot 16H_2O$	22.30 (22.59)	4.12 (5.07)	11.56 (12.60)	8.68 (8.51)	3.19 (2.90)	4.35 (5.07)		grey	300(d)	
Cr_2(L-ser)$_2$(5′CMP)(OH)$Cl \cdot 7H_2O$	21.67 (22.16)	4.04 (4.80)	8.28 (8.62)	13.48 (12.80)	4.35 (4.37)	3.34 (3.82)		grey–blue	190–195(d)	
Cr(glyH)$_2$(gly)$Cl_2 \cdot 3H_2O$	17.91 (17.94)	4.72 (4.98)	10.94 (10.47)	13.13 (12.96)	17.42 (17.69)			violet	156–165(d)	251
Cr_2(gly)$_2$(5′AMP)(OH)$_2 \cdot 6H_2O$	22.38 (22.72)	3.87 (4.59)	12.68 (13.25)	14.90 (14.07)		4.44 (4.19)		grey–blue	284–289(d)	
Cr_2(gly)$_2$(5′CMP)(OH)$_2 \cdot 7H_2O$	21.25 (21.26)	3.96 (4.90)	8.79 (9.54)	14.29 (14.17)				grey–blue	270–274(d)	

TABLE 2. Thermogravimetric data for the complexes

Compound	Temperature (°C)	Weight loss (%)		Tentative assignment
		Calc.	Found	
Cr(L-met)(L-metH)$Cl_2 \cdot 3H_2O$	30–130	3.79	3.82	H_2O
	130–980	85.46	86.65	$2H_2O$ + 2Cl + 2met
	residue			chromium oxide
Cr(L-met)(5'AMP)$\cdot 11/2H_2O$	30–120	9.78	10.28	$\frac{7}{2}H_2O$
	120–980	70.21	68.31	$2H_2O$ + met + ado
	residue			chromium phosphate (esp.)
Cr_2(L-met)(5'CMP)$_2$(OH)$\cdot 10H_2O$	30–110	8.24	8.33	$5H_2O$
	110–980	66.43	66.54	met + 2cyd + $5H_2O$
	residue			chromium phosphate (esp.)
Cr_2(L-serH)$_2$(L-ser)$_4Cl_2 \cdot 6H_2O$	30–110	5.94	6.25	$3H_2O$
	110–380	73.28	73.26	6ser + $2H_2O$
	380–670	9.78	9.10	H_2O + 2Cl
	residue			chromium oxide
Cr(L-ser)$_2$(H_2O)$_2$Cl$\cdot H_2O$	30–90	5.15	5.21	H_2O
	90–550	80.55	79.23	$2H_2O$ + 2ser + Cl
	residue			chromium oxide
Cr_2(L-ser)$_2$(5'CMP)(OH)Cl$\cdot 7H_2O$	30–120	6.65	6.67	$3H_2O$
	120–980	69.05	71.13	$4H_2O$ + 2ser + cyd + Cl
	residue			chromium phosphate (esp.)
Cr_2(L-ser)(5'AMP)$_2$Cl$\cdot 16H_2O$	30–110	7.36	7.29	$5H_2O$
	110–980	71.44	71.72	$11H_2O$ + Cl + 2ser + ado
	residue			chromium phosphate (esp.)
Cr(glyH)$_2$(gly)$Cl_2 \cdot 3H_2O$	30–600	87.27	85.57	$3H_2O$ + 3gly + 2Cl
	residue			chromium oxide
Cr_2(gly)$_2$(5'AMP)(OH)$_2 \cdot 6H_2O$	30–110	9.74	9.72	$4H_2O$
	110–980	61.32	60.80	$2H_2O$ + 2gly + ado
	residue			chromium phosphate (esp.)
Cr_2(gly)$_2$(5'CMP)(OH)$_2 \cdot 7H_2O$	30–120	7.36	7.22	$3H_2O$
	120–980	63.56	62.76	$4H_2O$ + 2gly + cyd
	residue			chromium phosphate (esp.)

bands due to $\delta(COO^-)$, $\gamma_r(COO^-)$ and $\gamma_w(COO^-)$. The modifications of the $\delta_s(NH_2)$ bands at 1505–1514 cm^{-1} may be due to the interaction with Cr(III) or to the participation of this group in hydrogen bonding [12]. The small variations in the bands arising from vibrations π(OH) at 805 cm^{-1} and $\nu(S-CH_3)$ at 1319 cm^{-1} do not necessarily imply coordination of these groups to Cr(III). For Cr(L-met)(L-metH)$Cl_2 \cdot 3H_2O$, the bands at 578 and 450 cm^{-1} have been tentatively assigned to ν(Cr–O) and ν(Cr–N) respectively. There is no evidence of the presence of ν(Cr–Cl) bands, in agreement with the conductivity measurements.

Table 3 records the electronic spectral data which are in agreement with coordination of chromium to N and O donors in a pseudooctahedral geometry. These results are confirmed by EPR measurements. The X-band EPR spectra of the complexes Cr(L-met)(L-metH)$Cl_2 \cdot 3H_2O$ and Cr(L-ser)$_2$(H_2O)$_2$Cl$\cdot H_2O$, gave a broad featureless band in the $g_{eff} = 2$ region, characteristic of Cr(III) in a pseudooctahedral environment. However, Cr(glyH)$_2$(gly)$Cl_2 \cdot 3H_2O$ and Cr(L-ser)$_2$(L-serH)Cl$\cdot 3H_2O$ gave EPR spectra comprising several overlapping bands in the range 0.15–0.4 T (Fig. 2). Such spectra may be described by the spin Hamiltonian for $S = \frac{3}{2}$ systems of the form

$$\mathcal{H} = \beta(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + D(S_z^2 - 5/4) + E(S_x^2 - S_y^2)$$

in which the second and third terms are the axial and rhombic zero field splittings (zfs) respectively [14].

Although the individual band components are insufficiently resolved for accurate evaluation of D and E parameters, the facts that the strongest transition appears in the $g_{eff} = 2$ region, the bands below 0.2 T are very weak, and no bands are observed between 0.5–1 T indicate a relatively low value for

TABLE 3. Electronic spectral data for the complexes (bands in nm)[a]

Compound	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	$(\nu_2)^4T_{1g}(F) \leftarrow {}^4A_{2g}$	$(\nu_1)^4T_{2g} \leftarrow {}^4A_{2g}$	10 Dq (cm^{-1})
Cr(L-met)(L-metH)$Cl_2 \cdot 3H_2O$		404(89)	548(41)	18200
Cr(L-ser)$_2(H_2O)_2Cl \cdot H_2O$		403(110)	541(60)	18500
Cr_2(L-serH)$_2$(L-ser)$_4Cl_2 \cdot 6H_2O$		401(152)	541(105)	18500
Cr(glyH)$_2$(gly)$Cl_2 \cdot 3H_2O$		403(84)	544(51)	18400
$Na_2$5'AMP [b]	252s, 293s			
Cr(L-met)(5'AMP)$\cdot 11/2H_2O$ [b]	255s, 295s	435s 395s	610s 570s 470sh	18200
Cr_2(L-ser)(5'AMP)$_2Cl \cdot 16H_2O$ [b]	270br, 325s	440s 395s	610s 565s 500sh 465sh	18700
Cr_2(gly)$_2$(5'AMP)$(OH)_2 \cdot 6H_2O$ [b]	255s, 290s	435s 395s	610s 570s 470sh	18200
$Na_2$5'CMP [b]	260s, 308s			
Cr_2(L-met)(5'CMP)$_2(OH) \cdot 10H_2O$ [b]	270s, 310s	435s 395s	610s 570s	17000
Cr_2(L-ser)$_2$(5'CMP)$(OH)Cl \cdot 7H_2O$ [b]	280sh, 325s	435s 395s 365sh	615s 560s 500sh 465sh	18700
Cr_2(gly)$_2$(5'CMP)$(OH)_2 \cdot 7H_2O$ [b]	270s, 310s	435s 400s	610s 575s 500sh 470sh	18600

[a]s = strong, m = medium, br = broad, sh = shoulder, sp = sharp, w = weak. [b]Diffuse reflectance spectra.

D (<0.1 cm^{-1}) [15–17]. These results suggest little distortion from octahedral geometry. Q-band spectra of both compounds (Fig. 3) are in agreement with the previous conclusions. There is a strong band in the $g_{eff} = 2$ region and weak transitions between 0.5 and 0.8 T.

All the ternary complexes are insoluble in water. In all cases, elemental and thermogravimetric analyses (Tables 1 and 2) are consistent with the ternary formulation. Only the serine derivatives contain chloride, but no bands assignable to ν(Cr–Cl) were observed in their IR spectra. The weak band that appears at 380–390 cm^{-1} in some complexes has been tentatively assigned to ν(Cr–O) [12]. In all cases, bonding with the nucleotide through the phosphate group is inferred. As in the case of the binary complexes, the carboxylic and amino groups of the amino acid seem to participate in the interaction with chromium.

For the methionine ternary derivatives, the bands corresponding to ν(S–CH_3), ν_a(C–S) and ν_s(C–S) at 1319, 766 and 681 cm^{-1} respectively in the free ligand are not observed. However, this fact does not necessarily imply coordination through sulphur atom. In both complexes, the $\nu_s(COO^-)$ band is shifted by 20–30 cm^{-1} to lower frequencies. The bands assignable to amino group vibrations are modified in the spectra of the complexes or overlap with nucleotide bands. With regard to nucleotide vibrations, there are small variations in some ν(ring) bands (1600–1200 cm^{-1}). In the case of the 5'CMP compound, a new band appears at 1720 cm^{-1} which may be due to a free carboxylic group or to participation of C=O in hydrogen bonding upon complexation [18, 19]. Nevertheless, the most important changes occur in the phosphate bands, especially that of $\nu_s(PO_3)$ band (978 cm^{-1}), which is shifted by 20–25 cm^{-1} to higher frequencies in both cases. Therefore, IR data suggest that methionine interacts with chromium through its carboxylic and amino groups [11, 12] and the phosphate group of 5'AMP and 5'CMP is involved in metal coordination [18, 20].

In the case of serine ternary compounds again there are important changes in the bands correspond-

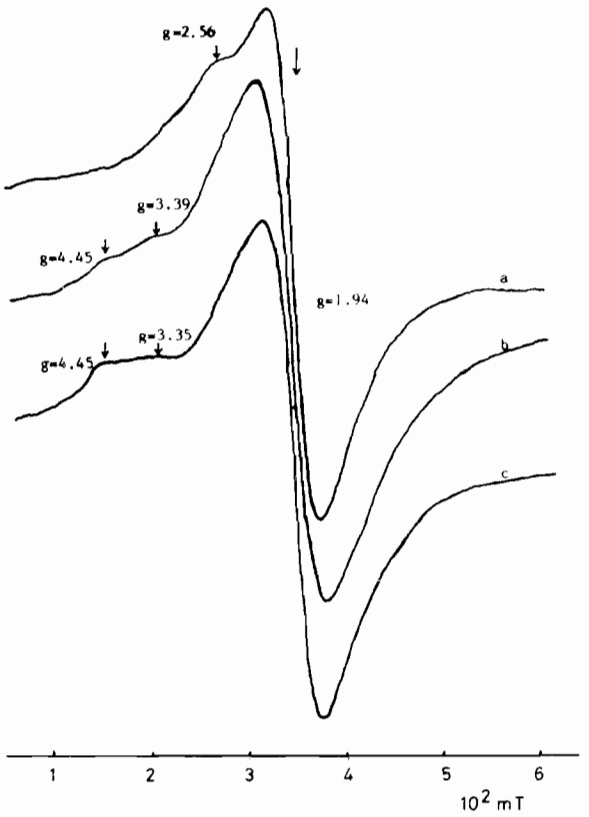

Fig. 2. X-band EPR spectra of polycrystalline samples of: (a) Cr_2(L-ser)(5'AMP)$_2$Cl·16H_2O; (b) Cr_2(L-serH)$_2$(L-ser)$_4$-Cl_2·6H_2O; (c) Cr(glyH)$_2$(gly)Cl_2·3H_2O.

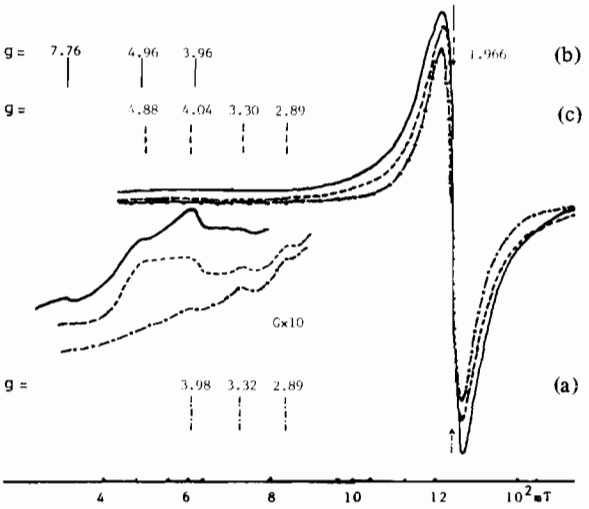

Fig. 3. Q-band EPR spectra of polycrystalline samples of: (a) (– · –) Cr_2(L-ser)(5'AMP)$_2$Cl·16H_2O; (b) (——) Cr_2(L-serH)$_2$(L-ser)$_4$Cl$_2$·6H_2O; (c) (- - - -) Cr(glyH)$_2$(gly)Cl_2·3H_2O.

ing to carboxylic vibrations. The band assignable to $\nu_s(COO^-)$ shifts 25–30 cm^{-1} to lower frequencies, overlapping with $\gamma_w(CH_2) + \nu(C{-}O)$ of the serine (1384 cm^{-1}). The carboxylic bands at lower frequency, $\delta(COO^-)$ at 612 cm^{-1} and $\gamma_w(COO^-)$ at 526 cm^{-1}, are also modified as well as the $\delta_s(NH_2)$ (1513 cm^{-1}) and $\gamma_r(NH_2)$ (1128 cm^{-1}) bands of the amino group. All this seems to indicate that the carboxylic and amino groups are involved in the coordination with Cr(III) [12]. With respect to the bands corresponding to vibrations of the hydroxyl group, most of them overlap with nucleotide bands and no information can be inferred from these data. Although some of the ν(ring) bands show slight modifications, the most noticeable changes are observed in the phosphate group vibrations, especially in the symmetric stretching PO_3 vibration which is shifted to higher frequencies suggesting interaction with chromium [21].

The infrared spectra of glycine ternary derivatives show important changes for the COO^- vibrations bands which seem to indicate direct interaction between the chromium and this group. The 1416 cm^{-1} ($\nu_s(COO^-)$) and 507 cm^{-1} ($\gamma_r(COO^-)$) bands shift in both complexes to lower and higher frequencies respectively, whereas other carboxylic bands show slight modifications. The bands related to the amino group vibrations overlap in some cases with nucleotide bands and are not observable. With relation to the phosphate bands, the noticeable shift at higher frequencies (997 cm^{-1}) for the symmetric stretching band suggests coordination through this group [18, 19]. The IR data for the 5'AMP derivative show slight variations in the bands corresponding to ν(ring), but no clear conclusion can be drawn from these data. In the case of $Cr_2(gly)_2$(5'CMP)$(OH)_2$·7H_2O, the bands assignable to ν(ring) (1531, 1499 and 1407 cm^{-1}) shift to lower frequencies and the band at 1368 cm^{-1} is not observed. These changes are similar to that of Co(en)$_2$(5'CMP)(5'CMPH)·6H_2O of which the ^{13}C NMR spectrum suggested coordination through N(3) [22]. For this reason, participation of the cytosine ring in bonding may not be ruled out.

The diffuse reflectance spectra are collected in Table 3. These data agree with a pseudooctahedral geometry for Cr(III) bonded to N and O donors. The ν_1 and ν_2 bands appear with several peaks which may be ascribed to splitting of $^4T_{2g}$ and $^4T_{1g}$(F) terms owing to distortions from *Oh* symmetry. For the 5'CMP derivatives the changes in the ring bands $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ [23] agree with participation of cytosine ring in coordination to Cr(III). Except for the serine derivative, the other 5'AMP complexes show only very small changes on the UV ring bands, which suggests no direct interaction between Cr(III) and the adenine ring. In the case of Cr_2(L-ser)-(5'AMP)$_2$Cl·16H_2O, the UV bands at 252 and 293 nm in the nucleotide shift to a higher wavelength, which implies an electronic charge redistribution owing to the participation of the adenine ring in the bonding to Cr(III).

In an attempt to provide further information about the ligand field environments of Cr(III) in the ternary complexes we have studied their EPR spectra. However, all these complexes, except Cr_2(L-ser)-$(5'AMP)_2Cl \cdot 16H_2O$, had only a broad band in the $g_{eff} = 2$ region, which suggests a polynuclear structure, with consequent dipolar broadening. The compound Cr_2(L-ser)$(5'AMP)_2Cl \cdot 16H_2O$ gave a spectrum with several overlapping bands in the range 0.15–0.4 T, a result which suggests distortion from octahedral geometry, as indicated by the electronic spectrum.

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References

1 J. Barrett, P. O'Brien and J. Pedrosa de Jesus, *Polyhedron, 4* (1985) 1.
2 J. A. Copper, L. F. Blackwell and P. D. Buckley, *Inorg. Chim. Acta, 92* (1984) 23.
3 E. W. Toepfer, W. Mertz, M. M. Polansky, E. E. Roginski and W. R. Wolf, *J. Agric. Food Chem., 25* (1977) 162.
4 M. Vicens, J. J. Fiol, A. Terron, V. Moreno and D. M. L. Goodgame, *Inorg. Chim. Acta, 157* (1989) 127.
5 M. Vicens, M. Prats, J. J. Fiol, A. Terron and V. Moreno, *Inorg. Chim. Acta, 158* (1989) 59.
6 D. Dunaway-Mariano and W. W. Cleland, *Biochemistry, 19* (1980) 1506.
7 S. Okada, N. Suzuki and H. Ohba, *J. Inorg. Biochem., 19* (1983) 95.
8 F. Dee Snell, *Encyclopedia of Industrial Analysis,* Vol. 17, Wiley, New York, 1973, p. 67.
9 G. Brauer, *Química Inorgánica Preparativa,* Reverté, Barcelona, 1958, p. 815.
10 G. R. Brubaker, M. K. Yoo and J. R. Thuot, *Gov. Rep. Announce Index, 78* (1978) 114.
11 C. A. McAuliffe, J. V. Quagliano and L. M. Vallarino, *Inorg. Chem., 5* (1966) 1996.
12 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Wiley, New York, 4th edn., 1978.
13 V. I. Spitsyn, S. V. Mozgin, M. G. Felin, N. A. Subbotina and A. I. Zhirov, *Russ. J. Inorg. Chem., 27* (1982) 386.
14 B. Bleaney and K. W. H. Stevens, *Rep. Prog. Phys., 16* (1953) 108.
15 E. Pedersen and H. Toftlund, *Inorg. Chem., 13* (1974) 1603.
16 E. Pedersen and H. Toftlund, *Inorg. Chem., 14* (1975) 85.
17 W. T. M. Andriessen and M. T. Groenewege, *Inorg. Chem., 15* (1976) 621.
18 M. Tsuboi, in *Basic Principles in Nucleic Acid Chemistry,* Vol. 1, P.O.P. TS'O, Academic Press, New York, 1974.
19 K. A. Hartman, R. C. Lord and G. J. Thomas, Jr., in J. Duchesne (ed.), *Physicochemical Properties of Nucleic Acids,* Vol. 2, Academic Press, London/New York, 1973.
20 H. A. Tajmir-Riahi and T. Theophanides, *Inorg. Chim. Acta, 80* (1983) 183.
21 K. Maskos, *Acta Biochimica Polonica, 26* (1979) 249.
22 J. J. Fiol, A. Terron, D. Mulet and V. Moreno, *Inorg. Chim. Acta, 135* (1987) 197.
23 L. B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc., 87* (1965) 11.