Ternary Chromium(III)–Nucleotide–Cysteine Complexes

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Abstract

The first ternary chromium(III)–nucleotide–cysteine complexes with purine and pyrimidine nucleotides are reported. A cysteine molecule of the starting complex is removed in some cases. With 5'ATP, ternary compounds have not been obtained because of total substitution of cysteine molecules from the starting chromium(III)–cysteine complex. The complexes have been characterized by elemental analyses, conductivity measurements, infrared and electronic spectroscopy and EPR. Distortions from octahedral geometry appear to be very small ($D < 0.1$ cm^{-1}).

Introduction

The role of chromium in biological systems is still imperfectly understood. Chromium(III) is involved in the glucose tolerance factor [1–5] but there is also abundant evidence that chromium can have deleterious effects. The mediation of such effects depends upon the oxidation state of the chromium and the facility with which it is transported *in vivo*; these in turn, are interrelated. The ultimate bound form is considered to be Cr(III), which complexes with small cellular molecules, protein and DNA [6]. It is believed that these complexes inhibit normal cellular functions and disrupt replication, transcription and translation processes. 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 complexes of Cr(III), nucleotides and amino acids, such as histidine [7]. We have now extended this work to cysteine, as that is known to bind to Cr(III) [8], and is an important reductant for the conversion of Cr(VI) to Cr(III) in natural systems. Nucleotide and cysteine structures and abbreviations used are given in Fig. 1.

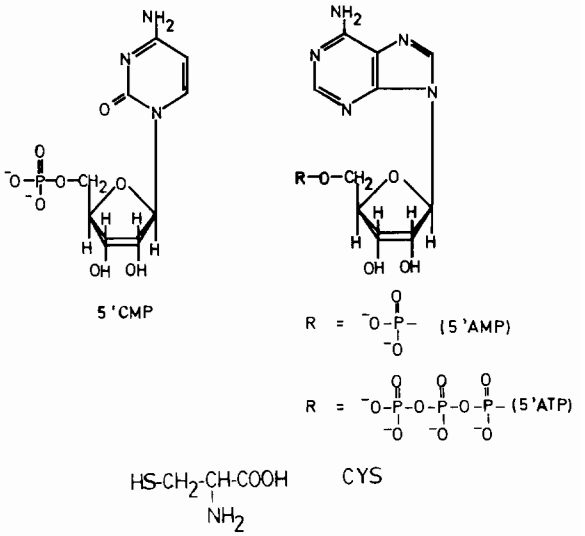

Fig. 1. Nucleotide and cysteine structures and abbreviations used.

Experimental

Carbon, hydrogen, nitrogen and sulfur analyses were carried out with Carlo Erba microanalysers at the Institute of Bio-organic Chemistry in Barcelona and with a Perkin-Elmer 240 B at the Faculty of Chemistry in Tarragona. Chloride was determined by the Schoniger method. Chromium [9] and phosphorus [10] 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.

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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 were Merck. The starting $Cr(urea)_6Cl_3 \cdot 3H_2O$ complex was prepared according to the literature [11].

$Cr(Cys)Cl_2 \cdot 2H_2O$

A 10 ml water solution containing 1 mM of $Cr(urea)_6Cl_3 \cdot 3H_2O$ and pH adjusted to 5.5 was added to a solution of 2 mM of cysteine in 10 ml water with the pH adjusted with 2 N NaOH to 8.2 (pK_2 of cysteine is 8.33). The resultant solution was placed in a thermostated bath at 50 °C for 5 h, by which time a violet solution with pH = 3.1 was obtained. This was concentrated in a rota-vapor and then eluted through a Sephadex G-10 column (diameter = 1 cm, length = 40 cm) to give a single F_1 violet fraction. The precipitate obtained on evaporating the solution was vacuum dried over P_4O_{10}.

Anal. for $Cr(C_3H_6NO_2S)Cl_2 \cdot 2H_2O$. Found (calc.): C, 13.26 (12.90); H, 3.53 (3.58); N, 5.83 (5.02); Cl 24.43 (25.45); S, 11.92 (11.47)%. The violet complex decomposes at 260 °C and is soluble in water with a molar conductivity of 239 Ω^{-1} cm^2 mol^{-1}.

$Cr(Cys)_2Cl \cdot 2H_2O$

This was obtained by an analogous method but using a 1:3 Cr:cysteine stoichiometry.

Anal. for $Cr(C_3H_6NO_2S)_2Cl \cdot 2H_2O$. Found (calc.): C, 19.93 (19.81); H, 4.07 (4.40); N, 7.65 (7.70); S, 17.49 (17.61)%. The violet complex decomposes at 225–230 °C and has a molar conductivity in water of 190 Ω^{-1} cm^2 mol^{-1}.

$Cr(5'CMPH)_2(L\text{-}Cys) \cdot 7H_2O$

A 5 ml water solution containing 1 mM of Na_2-5'CMP (pH = 4.3 adjusted with 2 N HCl) was added dropwise to a 5 ml water solution containing 1 mM of $Cr(L\text{-}Cys)Cl_2 \cdot 2H_2O$. The mixture, which had pH = 3.76, was maintained at 40 °C for 3.5 h. The final solution (pH = 3.3) was concentrated to 5 ml and eluted through a Sephadex G-10 column to give a single grey-blue fraction. The precipitate obtained by evaporating this fraction was washed with ethanol and vacuum dried over P_4O_{10}.

Anal. for $Cr(C_9H_{13}N_3O_8P)_2(C_3H_6NO_2S) \cdot 7H_2O$. Found (calc.): C, 26.23 (26.75); H, 4.66 (4.88); N, 10.95 (10.40); Cr, 6.06 (5.52); P, 6.80 (6.58); S, 3.60 (3.40)%. The complex is grey–blue, decomposes at 260–265 °C and is insoluble in water.

$Cr(5'CMP)(L\text{-}Cys) \cdot 4H_2O$

A 5 ml water solution containing 1 mM of Na_2-5'CMP (pH adjusted to 7.0) was added dropwise to a 5 ml solution containing 1 mM of $Cr(L\text{-}Cys)_2Cl \cdot 2H_2O$. The resulting solution (pH = 5.9) was maintained at 40 °C for 6 h. The final solution (pH = 5.8) was concentrated to 5 ml and eluted through a Sephadex G-10 column to give a single blue–grey fraction. Addition of ethanol gave a blue–grey precipitate which was filtered off, washed with ethanol and vacuum dried over P_4O_{10}.

Anal. for $Cr(C_9H_{12}N_3O_8P)(C_3H_6NO_2S) \cdot 4H_2O$. Found (calc.): C, 25.31 (25.49); H, 4.29 (4.60); N, 9.82 (9.91); Cr, 8.85 (9.20); P, 5.51 (5.49); S, 5.54 (5.66)%. The complex decomposes at 259 °C and is soluble in water with a molar conductivity of 101 Ω^{-1} cm^2 mol^{-1}.

$Cr(5'AMP)(L\text{-}Cys) \cdot 7H_2O$

A 5 ml water solution containing 1 mM of Na_2-5'AMP (pH adjusted to 4.2) was added dropwise to an aqueous solution $Cr(L\text{-}Cys)Cl_2 \cdot 2H_2O$ (1 mM in 5 ml). After 3 h at 40 °C a green precipitate was formed. This was filtered off, washed with ethanol and vacuum dried over P_4O_{10}.

Anal. for $Cr(C_{10}H_{12}N_5O_7P)(C_3H_6NO_2S) \cdot 7H_2O$. Found (calc.): C, 24.54 (24.26); H, 4.18 (4.98); N, 13.47 (13.06); Cr, 7.66 (8.09); P, 5.48 (4.82); S, 3.50 (4.98)%. The grey–green complex decomposes at 258 °C and is insoluble in water.

$Cr(5'AMP)(L\text{-}Cys) \cdot 3H_2O$

This was prepared as for the Cr(5'CMP)(L-Cys)·$4H_2O$ complex.

Anal. for $Cr(C_{10}H_{12}N_5O_7P)(C_3H_6NO_2S) \cdot 3H_2O$. Found (calc.): C, 27.32 (27.32); H, 4.08 (4.20); N, 14.11 (14.71); Cr, 8.85 (9.11); P, 5.23 (5.43); S, 5.25 (5.60)%. The complex decomposes at 245 °C; it is soluble in water with a molar conductivity of 97 Ω^{-1} cm^2 mol^{-1}.

$NaCr(5'ATP) \cdot 7H_2O$

Two forms of this compound were obtained depending on the starting material employed.

(a) To an aqueous solution of $Cr(L\text{-}Cys)Cl_2 \cdot 2H_2O$ (1 mM in 5 ml) a 5 ml water solution containing 1 mM of $Na_2$5'ATP was added dropwise. The resultant solution (pH = 2.7) was maintained at 40 °C for 3 h (final pH = 2.5) and then concentrated in a rota-vapor to 5 ml. Elution through a Sephadex G-10 column gave a single fraction, which afforded a blue–grey precipitate on adding ethanol. The precipitate was filtered off, washed with ethanol and vacuum dried over P_4O_{10}.

Anal. for $NaCr(C_{10}H_{12}N_5O_{13}P_3) \cdot 7H_2O$ (a). Found (calc.): C, 17.00 (17.05); H, 3.57 (3.69); N, 9.34 (9.94); Cr, 6.20 (7.39); P, 13.69 (13.21); Na, 3.93 (3.27)%. The blue–grey complex decomposes at 228 °C. It is soluble in water with a molar conductivity of 99 Ω^{-1} cm^2 mol^{-1}.

(b) A 5 ml water solution containing 1 mmol of $Na_2$5'ATP with pH adjusted with dilute NaOH

to 7.1 was added dropwise to a 5 ml water solution containing 1 mM of $Cr(L\text{-}Cys)_2Cl\cdot 2H_2O$. The resulting solution (pH = 6.34) was kept at 40 °C for 6 h. After a day a white precipitate appeared in the solution. This precipitate was removed and found to be L-cysteine. After filtering off the cysteine, ethanol was added to the solution, when a grey–blue precipitate appeared. This was filtered off, washed with ethanol and dried over P_4O_{10}.

Anal. for $NaCr(C_{10}H_{12}N_5O_{13}P_3)\cdot 7H_2O$ (b). Found (calc.): C, 17.44 (17.05); H, 3.86 (3.69); N, 10.23 (9.94); Cr, 7.20 (7.39); P, 13.42 (13.21); Na, 3.52 (3.27)%. The blue–grey complex decomposes at 218 °C and has a molar conductivity of 145 Ω^{-1} cm^2 mol^{-1} in water.

Results and Discussion

The chromium(III) cysteine binary complexes, $Cr(L\text{-}Cys)Cl_2\cdot 2H_2O$ and $Cr(L\text{-}Cys)_2Cl\cdot 2H_2O$, were used as starting compounds in order to obtain the ternary complexes. In these complexes, the cysteine S–H stretching band at 2546 cm^{-1} disappears, γ_p-NH_3^+ at 1205 cm^{-1} does not change and the symmetric stretching $-COO^-$ band at 1395 cm^{-1} shifts to 1415 cm^{-1} in both complexes [12–14].

The soluble ternary compounds show a molar conductivity greater than expected for a non-electrolyte [15]. This may be explained as protonation or dissociation equilibria either from the nucleotide base or the amino acid. Both forms of $NaCr(5'ATP)\cdot 7H_2O$ have molar electrolytic conductance values consistent with the 1:1 ionic formula proposed.

Some pertinent infrared data for the 5′CMP complexes are given in Table 1 with appropriate band assignments [16–20]. The S–H stretching band [12–14] disappears in the complex $Cr(5'CMPH)_2(L\text{-}Cys)\cdot 7H_2O$. A new band appears at 1727 cm^{-1} owing to a free carboxylic group or hydrogen bonding of cytidine carboxylic groups. The amino acid bands at 1346 and 883 cm^{-1} are observable. The symmetric phosphate group band increases its frequency by 20 cm^{-1}. Some weak bands at 455 and 351 cm^{-1} may be due to Cr–N or Cr–O stretching modes.

TABLE 1. Infrared Data for the Ternary Complexes Chromium–5′CMP–Cysteine (cm^{-1})

Tentative assignment	L-Cys	$Na_2$5′CMP	$Cr(5'CMPH)_2(L\text{-}Cys)\cdot 7H_2 7H_2O$	$Cr(5'CMP)(L\text{-}Cys)\cdot 4H_2O$
ν-SH	2546s			2550m
νC=O			1727s	
			1717s	
νC_2=O		1663vs	1660s	
δ-NH_2 + νC=N + νC=C	1611s	1650vs	1645s	1645s
		1615sh		1636s
				1618s
ν_a-COO^-	1586s			
ν ring		1531m	1528m	1513s
		1498s	1488m	1492s
δCH_2	1426s			1425m
ν_s-COO^-	1395s		1412m	1396m
δCCH	1361m			
	1347m		1346m	1348m
γCH_2 + νPO_2^-	1328m			
	1293s	1296m	1285m	1294s
ν_a-PO_3^{2-} + C–O (sugar)		1115vs,br	1110s,br	1113s,br
		1082vs,br	1081s,br	1072s,br
ν_s-PO_3^{2-}		977vs	997s	985s
ν skeleton	874m		883w	878m
	816m			
δ-COO^-	775m			
	742w			
νC–S	661s			662m
	617m			
γ_w-COO^-	533s		525w	535m
	515s			517w
νCr–O or νCr–N			455w	457w
	376s			383m
				375m
νCr–N			351w	

TABLE 2. Infrared Data for the Ternary Complexes Chromium–5′AMP–Cysteine (cm^{-1})

Tentative assignment	L-Cys	$Na_2$5′AMP	Cr(5′AMP)(L-Cys)·$7H_2O$	Cr(5′AMP)(L-Cys)·$3H_2O$
ν-SH	2546s			
νC=O			1691m	
δ-NH_2 + νC=N		1663vs		1660vs
		1646vs	1642s	1644vs
	1611s	1608s	1609m	
ν_a-COO^-	1586s			
$\nu C_8{=}N_7$ + $\delta C_8{-}H$		1506w	1504w	
$\delta C_8{=}N_7$ + $\delta C_8{-}N_9$ + $\delta C_8{-}H$ + $\delta C_2{-}H$		1484s	1480m	1482m
δCH_2	1426s	1425m	1418m	1422m
ν_s-COO^-	1395s		1382w	1384m
γCH_2	1328m		1336m	1338m
	1293s			
$\delta C_8{-}H$ + $\nu N_7{=}C_8$		1307m	1303w	1305m
ν_a-PO_3^{2-} + νC–O (sugar)		1120s,br	1112s,br	1111s,br
		1094vs,br		1080s,br
ν_s-PO_3^{2-}		977vs	996s	992s
ν skeleton + νC–O–P		901m	903w	908w
	874m	879m	886w	881w
	816m	820sh	820m	820sh
νP–O		797s	798m	798m
δ-COO^-	775m			
	742w		724m	725m
νC–S	661s		641w	648m
	617m			
γ_w-COO^-	533s		overlapped	overlapped
	376s			

The complex Cr(5′CMP)(L-Cys)·$4H_2O$ has the S–H stretching band at 2550 cm^{-1} showing that there is no coordination of chromium(III) to sulfur in the solid complex. The deprotonation of this group in water could be responsible for the observed conductivity values. Also the C–S stretching band at 662 cm^{-1} shows no shift in comparison with free cysteine. The bands at 1425, 1396, 1348 and 878 cm^{-1} are due to cysteine vibration modes. The phosphate group symmetric band increases also its frequency. Some weak bands at 535–517 and 457 cm^{-1} may be due to Cr–N or Cr–O stretching bands.

The infrared data of 5′AMP derivatives are collected in Table 2. In both complexes the S–H stretching band at 2546 cm^{-1} disappears [12–14]. This fact does not necessarily imply coordination with the metal. In Cr(5′AMP)(1-Cys)·$7H_2O$ a band appears at 1691 cm^{-1} possibly owing to protonation of the adenine ring. The symmetric carboxylic band is shifted to lower frequencies. The phosphate group symmetric band increases its frequency suggesting interaction with the chromium in both complexes.

The infrared data of 5′ATP derivatives are shown in Table 3. No band assignable to cysteine appears, in agreement with the total substitution of the amino acid from the starting complexes. Some ring bands show shifts in comparison with the frequencies of the free nucleotide and a coordination with the N(7) of the base may not be disregarded. The most significant changes are the variation of phosphate group bands [21–26]. A weak band at 323 cm^{-1} may be due to a Cr–N stretching band combined with a ring mode.

When the synthesis of analogous complexes was attempted using 5′ATP instead of 5′CMP or 5′AMP there was complete displacement of the cysteine and the formation of NaCr(5′ATP)·$7H_2O$. A related complex, but insoluble in water, has been described previously [27].

The electronic data of the cysteine, the ternary and the 5′ATP complexes are recorded in Table 4. These data are in agreement with coordination of chromium(III) in a pseudooctahedral geometry.

To provide further information about the ligand field environments of the Cr(III) ions in these compounds we have examined their X-band (*ca.* 9.6 GHz) EPR spectra using polycrystalline samples of the soluble compounds. Two of the complexes, Cr(L-Cys)Cl_2·$2H_2O$ and Cr(5′AMP)(L-Cys)·$3H_2O$, gave only a broad featureless band in the g_{eff} = 2 region, attributable to the effects of strong dipolar broadening of the resonances expected from the Cr(III) centers. This could arise if the compounds have polynuclear structures.

The remaining compounds gave complex spectra with several overlapping bands in the range 0.15–0.4

TABLE 3. Infrared Data for the 5'ATP Complexes (cm^{-1})

Tentative assignment	$H_4$5'ATP	NaCr(5'ATP)·7H_2O (a)	NaCr(5'ATP)·7H_2O (b)
νC=N	1712vs	1693s	
δ-NH_2 + νC=N	1646m	1660m	1663vs
		1645m	1646vs
νC=C + νC=N	1615m	1614m	1633vs
νC=C	1552w	1505m	1517w
$\delta C_8{=}N_7 + \nu C_8{-}N_9 + \delta C_8{-}H + \delta C_2{-}H$	1481m	1480w	1486m
δCH_2	1420m	1420m	1408s
νPO_2^- (α and β)	1258s,br		1251s
	1230s,br	1237s	
νP–O–C	1136s,br		
	1123s,br		
ν_a-PO_3^{2-} + νC–O(sugar)	1110s,br	1083s,br	1093s,br
	1070s,br	1075s,br	
ν_s-PO_3^{2-}	990s	988sh	992m
	966s		
νP–O–P	905s	910s	913s
νC–O–P	811m	820m	825w
δCH (ring)	720m	722m	723m
	645s	634w	645w
PO_3^{2-}	519s	518w	537w

TABLE 4 Electronic Spectral Data for the Complexes

Compound	$^4T_{2g} \leftarrow {}^4A_{2g}$ λ (nm)	$^4T_{1g} \leftarrow {}^4A_{2g}$ λ (nm)
Cr(L-Cys)Cl_2·2H_2O	548 (ϵ = 32)	402 (ϵ = 82)
Cr(L-Cys)$_2$Cl·2H_2O	548 (ϵ = 62)	402 (ϵ = 103)
Cr(5'CMPH)$_2$(L-Cys)·7H_2O[a]	610, 570	433, 392
Cr(5'AMP)(L-Cys)·7H_2O[a]	610, 564	431, 387
NaCr(5'ATP)·7H_2O (a)	582 (ϵ = 56)	402 (ϵ = 125)
Cr(5'CMP)(L-Cys)·4H_2O	576 (ϵ = 27)	402 (ϵ = 62)
Cr(5'AMP)(L-Cys)·3H_2O	574 (ϵ = 56)	424 (ϵ = 73)
NaCr(5'ATP)·7H_2O (b)	584 (ϵ = 18)	402 (ϵ = 57)

[a]Diffuse reflectance spectra.

Tesla (Fig. 2; in each case the measurements were extended to applied fields of 1 Tesla, but no additional bands were observed). Such spectra may, in general, be described by the spin Hamiltonian for $S = 3/2$ systems [28]:

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

The second and third terms in the Hamiltonian are the axial and rhombic zero-field splittings (zfs) respectively.

The individual band components in the spectra shown in Fig. 2 are insufficiently resolved for accurate evaluation of the zfs parameters D and E. However the facts that the strongest transition is in the $g_{eff} = 2$ region, that the bands below 0.2 T are very weak, and that no bands were observed in the 0.5–1 T range all point to a relatively low value for D, probably <0.1 cm^{-1} [29–31]. This suggests that there is no major departure from an octahedral geometry of the ligand field around Cr ions in these compounds.

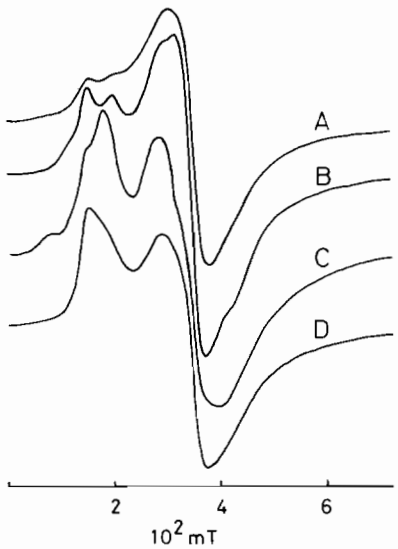

Fig. 2. EPR spectra: (A) NaCr(5'ATP)·7H_2O (b); (B) Cr(L-Cys)$_2$Cl·2H_2O; (C) Cr(5'CMP)(L-Cys)·4H_2O; (D) NaCr(5'-ATP)·7H_2O (a).

Measurements were also made at Q-band frequency (*ca.* 36 GHz) on Cr(L-Cys)$_2$Cl·2H_2O and NaCr-

(5′ATP)·$7H_2O$ (b) and the results are in accord with the above conclusions. In each case there was a very strong band in the g_{eff} = 2 region accompanied by two very weak bands at *ca.* 0.48 and *ca.* 0.61 T.

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