Synthesis and Characterization of some Chromium(III) Complexes with Glutathione

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The glutathione (H_5L) complexes $K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$, $K_2[Cr(H_2L)(A)]\cdot nH_2O$ (A = the dianion of the amino acids L-cysteine, L-glutamic acid, or L-aspartic acid), and $K_2[Cr(H_2L)(gly)(OH)]\cdot 2H_2O$ [gly = glycinate(1−)] have been synthesized. All the complexes exhibit an intense u.v. charge-transfer band which is characteristic of a Cr–S bond. The sulphydryl to chromium linkage undergoes an acid-catalysed hydrolysis. The complexes have been characterized by elemental and thermogravimetric analyses, electronic and i.r. spectroscopy, and circular dichroism. Comparison of these properties with those of known chromium(III) complexes leads to the conclusion that glutathione is bound to chromium(III) by the terminal glycine group (*N,O*) and the deprotonated sulphur of cysteine. The glutamic acid residue of glutathione does not apparently interact with the chromium centre in these complexes.

Glucose tolerance factor is an unidentified complex of chromium(III) found in brewers' yeast, meat, and various other foods.[1,2] The compound is an insulin potentiating factor and believed to contain chromium(III), the amino acids glycine, cysteine, and glutamic acid, together with nicotinic acid.[3,4] The tripeptide glutathione H_5L [(**I**); shown as H_4L^-] contains the above amino acids. A synthetic complex of glutathione and chromium(III) of unknown structure, prepared by Anderson *et al.*,[5] is extremely active in *in vitro* glucose tolerance factor assays.

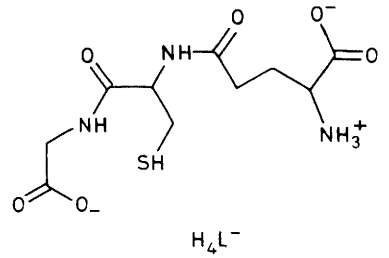
The biological significance of sulphydryl compounds has led to many studies on the interaction of sulphur-containing ligands with metal ions. de Meester and Hodgson[6] have demonstrated that sulphur co-ordinates to chromium(III) in (L-histidinato-*NN'O*)(D-penicillaminato-*NOS*)chromium(III) monohydrate, D-penicillamine and L-histidine both acting as tridentate ligands. The co-ordination is a monomeric distorted octahedron. The same workers[7] confirmed Cr–S bonding in the crystal-structure determination of $Na[Cr(cys)_2]$ [cys = L-cysteinate(2−)]. We have recently reviewed the chemistry of chromium(III) of relevance to the glucose tolerance factor.[8]

In this paper we report studies of a series of chromium(III)–glutathione–amino acid complexes. The biological importance of chromium(III) in glucose tolerance is well established, the more active glucose tolerance factor preparations known to date all involve glutathione or its constituent amino acids. As a starting point, for a better understanding of glucose tolerance factor, we have synthesized a number of glutathione complexes of chromium(III); these are the first chromium(III)–glutathione complexes to be characterized.

Experimental

Materials.—Glutathione and the amino acids used in this study were obtained from BDH (chromatographically homogeneous and of the L configuration). Chromium(III) perchlorate (Pfitz and Bauer Inc.) and chromium(III) nitrate (Strem Chemicals) were used without further purification. All other reagents were BDH AnalaR grade.

Equipment.—Electronic spectra were measured on Cary 17 or Perkin-Elmer 402 instruments. Infrared spectra were recorded either as KBr discs (100 mg, 2% sample) or Nujol mulls between CsI plates using a Perkin-Elmer 475 spectrometer. Thermogravimetric analysis was performed on a Stanton-Redcroft TG750 thermobalance (10 °C min^{-1}, N_2 10 cm^3 min^{-1}, to 200 °C). Circular dichroism (c.d.) was studied using a JASCO J40 instrument.



H_4L^-

(I)

Methods.—The complexes were analysed for chromium using 1,5-diphenylhexanohydrazide.[9] Microanalyses of K, C, H, N, and S were obtained from Butterworths Laboratories. Attempts were made to assay free sulphydryls by Ellmans' method.[10] Yields were somewhat variable, but substantial, and in the range 50—70% based on chromium.

Preparation of $K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$.—A solution of $Cr(ClO_4)_3\cdot 9H_2O$ (2×10^{-3} mol) in ethanol (25 cm^3) was heated under reflux on a boiling water-bath and glutathione (4×10^{-3} mol) was added. The mixture was heated with occasional shaking for 15 min. The colour of the solution was then blue-green (pH ~ 3). The condenser was removed and $KHCO_3$ (1 g) was added slowly with continued heating and stirring. This was followed by H_2O (3 cm^3), which dissolved most of the remaining bicarbonate. The mixture was heated with stirring to evaporate off most of the ethanol. Red-violet crystals appeared on the inner wall of the flask, water (3 cm^3) was introduced to dissolve any solid material, and heating was continued until a red-violet solution was formed (pH ~ 7—8). The resulting solution was cooled to room temperature and then cooled on ice and filtered to remove any unreacted material and K_2CO_3 formed. The filtrate was evaporated to dryness in an evaporating dish, either by heating the dish on a water-bath or allowing evaporation to proceed at room temperature overnight. The red-violet crystals were washed with ethanol and

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then with acetone or diethyl ether. The corresponding sodium salt of the complex can be prepared by following the same procedure but using $NaHCO_3$ instead of $KHCO_3$. This produced the more hygroscopic sodium salt.

The complex can also be prepared from chromium(II) acetate monohydrate. To a degassed solution (25 cm^3) of freshly prepared $[Cr_2(O_2CMe)_4]\cdot 2H_2O$, a stoicheiometric amount of glutathione (2×10^{-3} mol) was added. The colour of the mixture changed from red-brown to blue. The pH was increased to 8 by adding $KHCO_3$ with stirring and complete aerial oxidation of the red-violet solution was then effected by exposing it to the atmosphere. The solution was evaporated to obtain a solid. The solid residue was washed with ethanol and then acetone. It had identical properties to the complex prepared from chromium(III) perchlorate.

Preparation of $K_2[Cr(H_2L)(A)]\cdot nH_2O$ [*where* A = L-*cysteinate*(2−) (cys), L-*aspartate*(2−) (asp), *or* L-*glutamate*(2−) (glu) *and* $K_2[Cr(H_2L)(A)(OH)]\cdot 2H_2O$ [*where* A = *glycinate*-(1−) (gly)].—The procedure followed was essentially similar to that for the preparation of $K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$ reported above. To a solution of $Cr(ClO_4)_3\cdot 9H_2O$ (2×10^{-3} mol) in ethanol (25 cm^3) glutathione (2×10^{-3} mol) was added. The mixture was refluxed for 15 min on a water-bath.

$KHCO_3$ (1 g) was added, in small portions, with stirring, to a hot solution of the potassium salt of the amino acid (2×10^{-3} mol) in water (3 cm^3). The resulting mixture was heated to evaporate off the ethanol. Crystals appeared on the inner wall of the flask and water (3 cm^3) was added to dissolve any soluble material which had formed. A red-violet solution was formed in the case of glycine, glutamic acid, and aspartic acid while in the case of cysteine the colour was dark violet. After cooling and filtering, the filtrate was evaporated to dryness in an evaporating dish on a steam-bath. The solid residue was washed with ethanol and then with acetone or diethyl ether. The sodium salt may be prepared by using $NaHCO_3$ instead of $KHCO_3$.

Preparation of $Na[Cr(cys)_2]\cdot 2H_2O$.—This complex was prepared by a slight modification of the method of de Meester *et al.*[7] A solution of $Cr(NO_3)_3\cdot 9H_2O$ or $KCr(SO_4)_2\cdot 12H_2O$ (2.5×10^{-3} mol) in H_2O (15 cm^3) was mixed with cysteine (7.5×10^{-3} mol) in water (10 cm^3). The resulting mixture was heated to boiling for a few minutes and then $NaHCO_3$ (0.02 mol) (or $KHCO_3$ to prepare the potassium salt) was added until the pH reached 7—8, at which pH the solution was blue. The solution was cooled on ice and the blue precipitate filtered off. The precipitate was washed with ethanol and then with acetone or diethyl ether.

Following the de Meester[7] procedure which used NaOH to neutralize the solution and leaving the mixture overnight to crystallize, the blue precipitate formed was contaminated with a red-violet precipitate, which was difficult to separate from the desired complex.

Results and Discussion

The complexes all had satisfactory microanalyses for their proposed compositions; these results are summarized in Table 1. The complexes were confirmed to be anionic by ion-exchange chromatography on Sephadex A-25 in the Cl^- form; they were all homogeneous on 25-cm columns of this resin.

Electronic Spectra.—The electronic spectra of all the complexes prepared in this study are tabulated both for the solution and the solid state in Table 2. The band positions for each complex occurred in the region expected for chromium(III) complexes with *N*, *O*, and *S* donors.

The electronic spectra of the cysteine-containing complexes $Na[Cr(cys)_2]\cdot 2H_2O$ and $K_2[Cr(H_2L)(cys)]\cdot 2H_2O$ are shown in Figure 1. In the bis-cysteine complex the lower energy band (T_{2g} in octahedral symmetry) is unsymmetrical and has a shoulder which suggests a low-symmetry arrangement; for tris complexes of non-equivalent bidentate ligands such spectra are often associated with *mer* complexes.[11,12] In $K_2[Cr(H_2L)(cys)]\cdot 2H_2O$ the same lower-energy band is very broad, which suggests a similar arrangement of ligands to that possessed by the bis-cysteine complex. This is confirmed by the c.d. spectra (see later).

The electronic absorption bands in the complexes $K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$, $K_2[Cr(H_2L)(gly)(OH)]\cdot 2H_2O$, $K_2[Cr(H_2L)(glu)]\cdot 3H_2O$, and $K_2[Cr(H_2L)(asp)]\cdot 3H_2O$ are nearly symmetrical and appear to be very similar; notably there is no splitting of the lowest energy ligand-field band. These complexes may be of higher symmetry.

Table 2 shows a difference in band position for the solid reflectance spectra and those recorded in solution for the complexes $K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$ and $K_2[Cr(H_2L)(cys)]\cdot 2H_2O$. This may arise either from pH effects upon dissolution, an isomerization reaction in solution, or by a solid-state effect. Upon acidification of basic or neutral solutions of both complexes the spectra change, shifting to higher energy with a colour change from red-violet to pink.

The u.v. spectra of all the complexes exhibit an intense absorption in solution and the solid state. Two bands were observed in the solid state (290—300 and 250—265 nm), while in solution only one band is observed at around 250—265 nm

Table 1. Analytical results (%)

	C		H		N		S		Cr		K	
Compound (empirical formula)	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$ ($C_{20}H_{35}CrK_2N_6O_{15}S_2$)	30.25	(30.25)	4.5	(4.45)	10.2	(10.6)	8.25	(8.05)	6.45	(6.55)	10.1	(9.85)
$K_2[Cr(H_2L)(cys)]\cdot 2H_2O$ ($C_{13}H_{23}CrK_2N_4O_{10}S_2$)	26.6	(26.5)	4.15	(3.95)	9.15	(9.5)	11.2	(10.85)	9.1	(9.15)	12.5	(13.25)
$K_2[Cr(H_2L)(gly)(OH)]\cdot 2H_2O$ ($C_{12}H_{23}CrK_2N_4O_{11}S$)	25.5	(25.65)	4.25	(4.1)	9.85	(10.0)	5.6	(5.7)	9.45	(9.25)	13.5	(13.9)
$K_2[Cr(H_2L)(glu)]\cdot 3H_2O$ ($C_{15}H_{27}CrK_2N_4O_{13}S$)	28.7	(28.45)	4.65	(4.25)	9.0	(8.85)	5.2	(5.05)	8.25	(8.2)	12.4	(13.2)
$K_2[Cr(H_2L)(asp)]\cdot 3H_2O$ ($C_{14}H_{25}CrK_2N_4O_{13}S$)	26.85	(27.15)	4.25	(4.05)	8.95	(9.05)	5.4	(5.15)	8.35	(8.4)	12.6	(12.65)
$K[Cr(cys)_2]\cdot 2H_2O$ ($C_6H_{14}CrKN_2O_6S_2$)	20.75	(20.6)	4.05	(4.0)	8.12	(8.02)	19.25	(18.25)	15.15	(14.9)		

Table 2. Electronic spectra and circular dichroism

Sample	State	$\lambda_{max.}$*/nm Visible	Ultraviolet
$K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$	Solution	546 (62.4) 408 (69.5)	262 (4.04 × 10^3)
	Solid	550 420	300 258
	C.d.	612 (+0.0404), 503 (−0.244), 402 (+0.0189)	
$K_2[Cr(H_2L)(cys)]\cdot 2H_2O$	Solution	560 (62.5) 418 (67.0)	260 (7.02 × 10^3)
	Solid	571 438—440	300 264
	C.d.	697 (−0.0274), 584 (+0.507), 530 (sh) (+0.307), 457 (−0.226), 424 (−0.0329), 372 (+0.0233)	
$K_2[Cr(H_2L)(gly)(OH)]\cdot 2H_2O$	Solution	550 (53.4) 407 (58.4)	254 (3.46 × 10^3)
	Solid	550 403	292 258
	C.d.	610 (+0.0425), 504 (−0.123), 394 (+0.0225)	
$K_2[Cr(H_2L)(glu)]\cdot 3H_2O$	Solution	550 (68.5) 412 (65.6)	254 (3.00 × 10^3)
	Solid	552 420	300 264
	C.d.	625 (+0.0381), 520 (−0.218), 408 (+0.0148)	
$K_2[Cr(H_2L)(asp)]\cdot 3H_2O$	Solution	542 (57.0) 405 (53.8)	259 (2.64 × 10^3)
	Solid	545 412	292 260
	C.d.	592 (+0.0762), 493 (−0.1914), 383 (+0.0443)	
$K[Cr(cys)_2]\cdot 2H_2O$	Solution	606 (89.5) 540 (67.9), 460 (sh), 408 (89.1)	258 (1.04 × 10^4)
	Solid	620 541 (sh), 460	408 300
	C.d.	691(−0.206), 604 (+1.491), 523 (+0.842), 454 (−0.388), 424 (sh) (−0.778), 380 (+0.216)	

* Molar absorption coefficient ε (dm^3 mol^{-1} cm^{-1}) or differential absorption coefficient ΔE (dm^3 mol^{-1} cm^{-1}) given in parentheses.

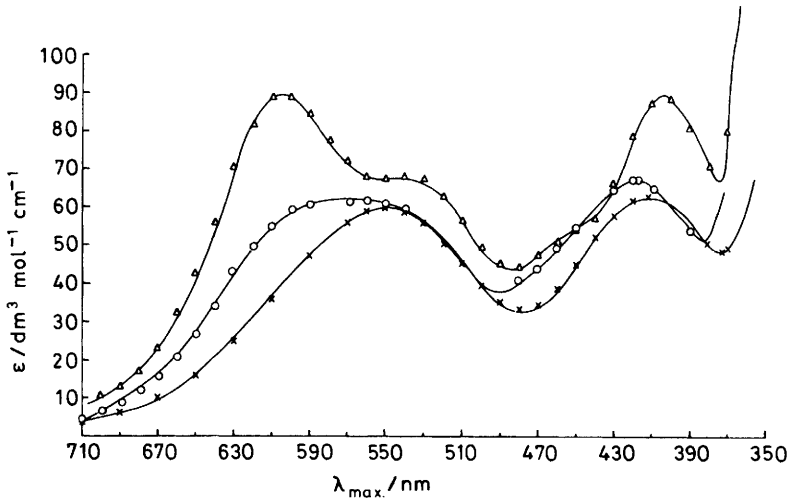


Figure 1. Typical electronic spectra: $[Cr(cys)_2]^-$ (△), $[Cr(H_2L)(cys)]^{2-}$ (○), $[Cr(H_2L)(glu)]^{2-}$ (×)

(Table 2). This may be compared with the results reported for other complexes with a Cr–S bond.[13] A band in this region of the spectrum may also appear as a shoulder and has been identified in chromium(III) thiolato-complexes.[13,14] This intense band is usually attributed to S→Cr ligand-to-metal charge transfer. The band was observed to diminish slowly in basic media, its rate of disappearance was acid catalysed.

The absorption coefficients of the charge-transfer bands are also of interest. The charge-transfer bands in $K[Cr(cys)_2]\cdot 2H_2O$ and $K_2[Cr(H_2L)(cys)]\cdot 2H_2O$ are almost twice the intensity (ε *ca.* 7.0 × 10^3 compared to 3.5 × 10^3 dm^3 mol^{-1} cm^{-1}) of the related bands in the other complexes (Table 2). There is hence the possibility than in $K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$ only one sulphur is co-ordinated to chromium.

Circular Dichroism.—The circular dichroism results are summarized in Table 2. The complexes $K_2[Cr(H_3L)(H_2L)]\cdot 2H_2O$, $K_2[Cr(H_2L)(gly)(OH)]\cdot 2H_2O$, $K_2[Cr(H_2L)(glu)]\cdot 3H_2O$, and $K_2[Cr(H_2L)(asp)]\cdot 3H_2O$ all showed similar c.d. spectra in terms of sign, position, and intensity (Figure 2). In these complexes the low-energy octahedral 'T_{2g}' band of the electronic spectra (see Table 2) showed two c.d. bands, with a positive band followed by a negative one. This pattern has previously been found in the c.d. spectra of facial (β) isomers of the C_3 chromophores of $[M(ab)_3]$ complexes (ab = ambidentate ligand), *e.g.* (+)-$[M(ala)_3]$ [M = Co^{III} or Cr^{III}, ala = alaninate(1−)].[15] Complexes of polydentate ligands with a cobalt(III) ion, *e.g.* $[Co(edta)]^-$ (H_4edta = ethylenediaminetetra-acetic acid) and $[Co(pdta)]^-$ (H_4pdta = propane-1,3-diaminetetra-acetic acid),[16] also have similar patterns of sign in the c.d. spectrum, with a large positive band followed by a small negative band. A similar pattern is observed in the c.d. spectrum of $[M(asp)_2]^-$ (M = Cr^{III} or Co^{III}; *cis*-N_5, *trans*-O_5 isomer).[12,17,18] The c.d. spectra of even relatively

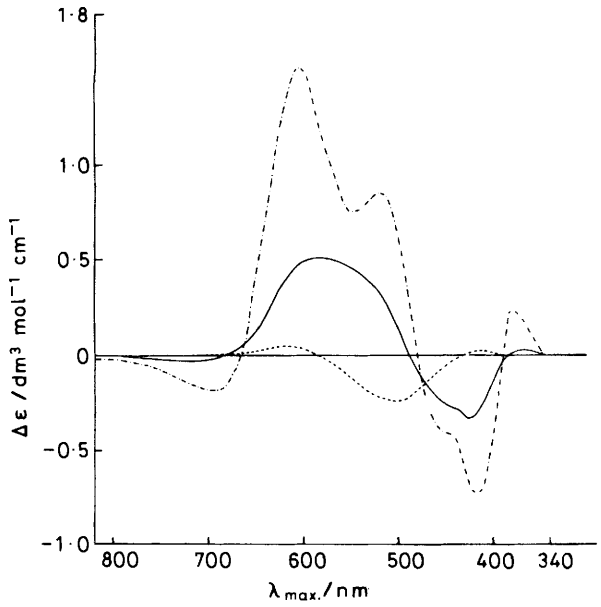
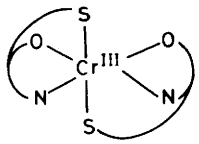


Figure 2. Typical circular dichroism: $[Cr(cys)_2]^-$ (· — · — · —), $[Cr(H_3L)(H_2L)]^{2-}$ (– – – –), $[Cr(H_2L)(cys)]^{2-}$ (——)



trans-S

(II)

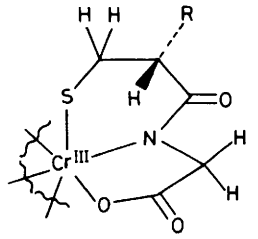
simple amino acid complexes of chromium(III) are poorly understood.

The c.d. spectrum of $K_2[Cr(H_2L)(cys)]\cdot 2H_2O$ differs from those of the other mixed glutathione–amino acid complexes but is very similar to that of $Na[Cr(cys)_2]\cdot 2H_2O$. In both these complexes, the c.d. corresponding to the low-lying electronic transitions has a (−),(+),(−) pattern. The structure of a bis-cysteine complex of chromium(III) has been determined [7] and is shown by (II). A similar structure can be suggested for $K_2[Cr(H_2L)(cys)]\cdot H_2O$, based on the c.d. results, *i.e.* two mutually *cis* Cr–O and Cr–N bonds and a *trans* Cr–S bond.

Discussion

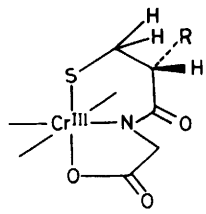
The most compelling evidence concerning donor atoms is the observation of the charge-transfer band characteristic of sulphur co-ordination in the electronic spectrum. We shall hence concentrate our discussion of the co-ordination of glutathione on the sulphur of cysteine and the adjacent N,O atoms of the glycine residue. The simultaneous co-ordination of the glutamic acid residue and the sulphur of cysteine would require the formation of eight-membered chelate rings.

There are two geometric isomers possible for such *N,O,S* co-ordination by glutathione and we designate these as facial (III) and meridional (IV). The facial isomer has two skew chelate rings, the absolute configuration of the chromium centre may thus be designated as Δ or Λ.[19] The optical activity arising in the case of two skew non-equivalent chelate rings on a tridentate ligand has received scant attention. The structure (III) shows the Λ-L arrangement (Λ at Cr^{III}, L at cysteine); for

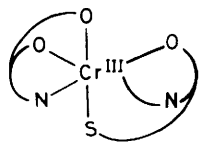


R = $NHC(O)CH_2CH_2CH(NH_2)COOH$

(III)



(IV)



'pseudo-facial O'

(V)

this diastereoisomer the glutamyl residue points away from the chelate ring and lies across the vacant face of the chromium(III) octahedron. The configuration of the chromium centre hence determines whether the γ-glutamyl residue of the glutathione lies across the vacant co-ordination sites of the octahedron or away from these vacant sites. In the complexes reported in this study a second ligand, the amino acid, adds to the complex, suggesting that the co-ordination of glutathione may be stereospecific and Δ.

The complexes prepared in this study are all chromatographically homogeneous on Sephadex A-25. This suggests, but does not prove, that we are dealing with single isomerically pure complexes in the subsequent spectroscopic studies.

Distinction between the many isomers possible for the complexes described in this study is difficult, a crystal structure is really needed to clarify the situation. Extensive efforts to crystallize the complexes have so far been unproductive, glasses and/or microcrystalline samples have been obtained, but no samples suitable for a structure determination are yet available. However, we can draw a number of tentative conclusions. The c.d. and electronic spectra of $K[Cr(cys)_2]\cdot 2H_2O$ and $K_2[Cr(H_2L)(cys)]\cdot 2H_2O$ are similar and we hence suggest that co-ordination in these complexes is *cis-N,O* and *trans-S*,[7] see (II). The high intensity of the c.d. may suggest stereospecific co-ordination at chromium and it seems most probable that the glutathione–chromium centre is Δ.

The other complexes are all similar in their spectroscopic properties. The lowest energy ('T_{2g}' in O_h) band in the electronic spectrum is much more symmetrical than in either $K[Cr(cys)_2]\cdot 2H_2O$ or $K_2[Cr(H_2L)(cys)]\cdot 2H_2O$. This suggests a complex of higher symmetry, a more symmetrical set of donor groups being obtained by a facial arrangement of the oxygen donors as in structure (V). We tentatively suggest that in the mixed glycine, aspartic and glutamic acid complexes an isomer or isomers of the complexes involving facial *O*-donors (V) describes the product of our reaction. The complex $K_2[Cr(H_3L)(H_2L)]\cdot 3H_2O$ may well involve two different modes of co-ordination for glutathione, with one molecule bonding (*N,S,O*) as discussed above, and the other *via* the *O*-terminal glutamic acid residue. This may explain the similarity of its spectra with those of the mixed glutathione–amino acid complexes. The low value of ε for the Cr–S charge-transfer band is in accord with such a conclusion. The c.d. spectra of these complexes are difficult to interpret, the similarity of all the spectra may suggest a similar

co-ordination sphere and the same mode of co-ordination (*N,O* of an amino acid) for all these complexes. The weak c.d. may be the result of the contributions from the two halves of the molecule effectively cancelling.

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