Preparation and Infrared Studies of Hydroxy Bridged Chromium (III) Complexes of L-Glutamic Acid

MOHAMMAD RASUL JAN* AND HAROON AL RASHID**

**Department of Chemistry, University College Dublin, Belfield Dublin 4, Ireland*

***Department of Chemistry, University of Peshawar, Pakistan*

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Summary: A new series of hydroxy bridged Chromium (III) complexes of glutamic acid has been prepared, in addition to the previously prepared tris glutamic acid and tris cobalt (III) glycine complexes. For the hydroxy bridged complexes, a number of hydration isomers of different colours were also isolated. These compounds were characterized by using Infrared, U. V-Visible spectra and magnetic moment determinations. Infrared criteria have been adduced from a critical study of the Infrared spectra of fac $Cr(L\text{-}gly)_3H_2O$ and $[Cr(L\text{-}gly)_2OH]\ 1/2H_2O$ and applied to these L- glutamic acid complexes. These L-glutamic acid complexes with the exception of $Cr(L\text{-}glu)_3.\ 2H_2O$ are dihydroxy bridged. L-glutamic acid is coordinated through the γ-COOH group in the case of the tris complexes, and through the α-COOH group in the case of the hydroxy bridged complexes.

Introduction

A previous attempt to prepare Chromium (III) complexes of L-glutamic acid resulted in the formation in solution of two species $Cr(glu)_2(H_2O)^-_2$ and $Cr(glu)_2(H_2O)^+_2$[1]. The preparative method adopted in the present paper yielded amorphous products with satisfactory metal, carbon, hydrogen and nitrogen composition.

L-glutamic acid has in principle two carboxylic acid functions available for coordination to the metal and consequently is a potential terdentate, bidentate or unidentate ligand[2]. As no products suitable for X-ray single crystal analysis were obtained in these studies, infrared studies were of great value in their characterization. To this end, the Infrared Spectra of fac $Cr(gly)_3H_2O$ and $[Cr(gly)_2O\ H]$ both amenable to structural X-ray analysis[3,4], were examined in detail to develop diagnastic structural criteria applicable to these new amino acid complexes. In addition the established mer and fac isomers of $Co(gly)_3$[5] were reexamined.

Experimental

L-glutamic acid and L-glycine were obtained from Sigma Chemicals, while Chromium (III) nitrate and Sodium Hydroxide were obtained from BHD. No further purification was carried out.

Physical Methods:

Infrared Spectra were recorded as KBr and CsI discs on a Perkin-Elmer 283B Instrument. Solid State U.V/Vis. Spectras were recorded on a Perkin-Elmer 552 Spectrophotometer equipped with a PE 350 data station attachment. Variable temperature magnetic moment studies were carried out on a Newport Instruments Govy balance.

Preparation of Complexes:

The Mizouchi method[6] was modified for the synthesis of tris complexes. For example to a solution of L-glutamic acid and L-glycine (0.3 mole) an aqueous solution of Chromium (III) nitrate (0.1 mole) was added. The pH of the solution was adjusted to 6-7 by the addition of sodium hydroxide and the mixture was then heated on a water bath until it turned a pink colour and a pink powder was pricipitated. The mixture was cooled to room temperature and filtered.The product was washed several times with water and finally with dry acetone.The resulting powder was stored in a descicator over calcium chloride. For the preparation of compounds containing one hydroxyl group and two molecules of L- glutamic acid or L-glycine, the metal ligand ratio of 1:2 was taken and pH of the solution was adjusted to pH 7.5. While for the

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*Present Address: Department of Chemistry, University of Peshawar (Pakistan).

Table 1: Analytical and physical data.

		Analysis %					
S.No.	Complex	C	H	N	M	Colour	M.Wt.
1i	$Cr(glu)_3 2H_2O$	33.99 (34.20)	5.30 (5.29)	7.78 (7.94)	9.83 (9.82)	Pink	529.00
2i	$Cr(glu)_2OH\ 4H_2O$	27.54 (27.71)	3.97 (5.01)	5.85 (6.46)	11.52 (12.00)	Pink.	433.00
2ii	$Cr(glu)_2OH\ 5H_2O$	26.60 (26.61)	5.43 (5.54)	5.76 (6.21)	11.53 (11.52)	Blue	451.00
2iii	$Cr(glu)_2OH\ 6H_2O$	25.55 (25.58)	5.75 (5.54)	6.04 (5.97)	10.82 (11.08)	Purple.	469.00
3i	$[Cr(glu)\ (OH)_2]_2$	26.00 (25.88)	4.37 (4.31)	6.08 (6.04)	25.51 (25.41)	Pink	232.00
3ii	$[Cr(glu)\ (OH)_2]H_2O$	23.89 (24.00)	5.03 (4.80)	5.56 (5.60)	20.72 (20.80)	Grey-Blue.	250.00
3iii	$[Cr(glu)\ (OH)_2]2H_2O$	22.61 (22.39)	5.14 (5.22)	5.33 (5.22)	19.25 (19.4)	Grey-Blue.	268.00
3iv	$[Cr(glu)\ (OH)_2]\ 3H_2O$	21.33 (20.89)	5.37 (5.59)	4.97 (4.97)	18.16 (18.18)	Blue	286.00
4i	$Cr(gly)_3H_2O$	23.94 (24.84)	4.64 (4.48)	13.97 (14.49)	19.80 (20.33)	Red	298.93
4ii	$Cr(gly)_3$-1/2 H_2O	24.96 (24.84)	4.27 (4.48)	14.38 (14.49)	20.42 (20.33)	Violet	289.83
5i	$Cr(gly)_3H_2O$	24.17 (24.65)	4.88 (4.80)	14.24 (14.38)	17.91 (17.81)	Red	292.00
5ii	$Cr(gly)_3 1$-1/2H_2O	24.00 (23.92)	4.88 (4.98)	13.87 (13.95)	17.19 (17.28)	Purple	300.00
5iii	$Cr(gly)_3 2$-1/2H_2O	22.53 (22.57)	4.68 (5.33)	12.95 (13.17)	16.29 (16.30)	Red.	319.00
6i	$[Cr(gly)_2OH]$1/2H_2O	21.23 (21.23.)	4.20 (4.43)	12.12 (12.39)	22.98 (23.00)	Red.	319.00
6ii	$[Cr(gly)_2OH]$1/2H_2O	21.01 (21.23)	4.29 (4.42)	12.32 (12.39)	23.01 (23.00)	Purple	226.00
6iii	$[Cr(gy)_2\ OH]$ Hygroscopic	22.56 (22.2)	4.50 (4.20)	12.90 (12.90)	23.92 (23.96)	Purple	217.00
6iv	$[Cr(gly)_2OH]2H_2O$	18.99 (18.97)	4.50 (5.13)	11.17 (11.07)	20.23 (20.55)	Deep Pink	253.00
7i	$Cr(gly)_2\ (OH)_2\ H_2O$	14.76 (22.20)	4.80 (4.20)	12.90 (12.90)	23.92 (23.96)	Purple	160.00

preparation of compounds containing two hydroxyl group and one molecules of L-glutamic acid or L-glycine, the metal ligand ratio of 1:1 was maintained and the pH of the solution was adjusted to 8. The remaining procedure was the same as for the tris complexes.

Results and Discussion

Analytical data for the prepared complexes is presented in Table-I. In the case of the bridged compounds both cis and trans as well as a number of hydration isomers, pink, blue and purple were

Table 2(a): Infrared Data and its qualitative assignments Compound:- $Cr(gly)_3 2H_2O$

Band cm^{-1}	Assignment	Band cm^{-1}	Assignment
3440	H_2O absorption	800	NH_3^+ rocking
3050	NH_3^+ (stretch)	750	CH_2 rocking
2960 2920	CH_2 (Stretching).	710	COO^- (Wagging).
2090	NH_3^+ Stretch		
1635	COO^- Asy stretch	535	C-C-O (in plane bending)
1615	NH_3^+ (asy def:)	508	NH_3^+ twisting
1510 1500	NH_3^+ (Sym def:)	415	M-O Stretch.
1435	CH_2 (bending)		
1405	COO^- Sym stretch		
1300	CH_2 Wagging		
1255	CH_2 twisting.		
1150 1120	NH_3^+ rocking		
1055	C-N stretch.		
942	CO_2 + C-C (Combination).		
910	CO_2 + CH_2 (rocking).		

isolated. Because of the lack of a full infrared analysis of fac Cr(gly)$_3$, we decided to study its infrared spectra in detail and extend our conclusions to the present complexes. The infrared data and its qualitative assignments are given in Table- 2. In the case of tris Cr(gly)$_3$n-H_2O a red and a purple isomers were isolated. The fac Cr(gly)$_3$$H_2O$ (red) isomer is structurally known[3]. Deuteration experiment were carried out on this compound to confirm the assignments of certain bands. Complete deuteration was not achieved. The band at 3480 cm^{-1} and 3420 cm^{-1} disappear on deuteration, so these must be either due to OH or NH stretchings. New bands occur at 2600 cm^{-1} and 2520 cm^{-1} respectively, with deuteration ratio of 1.33 and 1.35 respectively. The appearance of a new band at 850

Table 2(a): Infrared data and its qualitative assignment Compound:- Co (glycine) $_3$-1/2 H_2O (mer form).

Band cm-1	Assignments	Band cm-1	Assignments
3440 3390	H_2O (absorption)	550 530	M = N (Splitted).
3200	NH_2 (Aymmetric Stretch)	355 335	M-O (Splitted)
2980 2940	CH_2 (Stretch)		
1680	OH (bending)		
1635 1615	COO^- (Asymmetric Stretch).		
1590	NH_2 (bending)		
1380 1360	COO^- (Symmetric Stretch)		
1330 1305	CH_2 Wagging.		
1040	C-N Stretch		
960 955	CO_2 + C-C (combination).		
915	CO_2 + CH_2 (rocking).		
775	H_2O (rocking).		
748	CO_2 + CH_2 + NH_2		
710	NH_2 rocking.		

Table 2(a): Infrared data and its qualitative assignments: Compound: Cr. (gly) 3.

Band cm-1	Assignment	Band cm-1	Assignment
3480 3420	H_2O absorption	770	H_2O (rocking)
3260 3230	NH_2 Asymetric Stretch	750	$CO_2 + CH_2 + NH_2$
31440	NH_2 (Symetric).	700	$NH._2$ rocking
2940	CH_2 (Stretching)	630	H_2O libration.
1685	OH bending	585	CO2 wagging and ring deformation
1660 1640	COO$^-$ (Antisymetric) Stretch.	530	Cr-O (Stretch).
1590	NH_2 bending	390	Cr-N (Stretch)
1425	CH_2 bending	325	Water
1380 1360	COO$^-$ (Symetric Stretch)		
1315	CH_2 (wagging).		
1200	CH2 (twisting)		
1160 1140	NH_2 wagging		
1030	C-N Stretch.		
960	CO + C-C (Combination) (Bending + Stretch).		
920	$CO_2 + CH_2$ (rocking).		

cm^{-1} in the deuterated compound was identified as a CD_2 twisting mode. The band at 380 cm^{-1} remains un-changed. The Cr-O band is most likely to occur at 530 cm^{-1}. In the deuterated spectra it is overlapped by a band at 520 cm^{-1} possibly due to water. The appearance of a new band in the deuterated spectra at 1525 cm^{-1} could be due to the change in the NH_2 deformation mode, caused by the new hydrogen bonding system.

The infrared spectra of $Cr(glu)_3 2H_2O$ (II) differ from compound(2) in that the zwitterion is present with bonding taking place through the γ-COOH group, which if bidentate, gives an octahedrally coordinated CR (III) entity. The infrared spectra and assignments are given in Table-2(a). The NH^+_3 group exhibits four charactaris bands, υNH^+_3 asym, υNH^+_3 sym, ρNH^+_3 and a combination band (NH^+_3 ciss ρNH^+_3) at 2070 cm^{-1}. The similarity with the solid state spectra of L-glutamic acid is immediately apparant. However additional bands occur at 510 and 415 cm^{-1} attributable to predominantly metal oxygen modes. The disappearance of the 1660 cm^{-1} band in L-glutamic acid indicates that coordination has occurred through the γ-COOH group, bidentate behaviour of the -c-o group is indicated by the appearance of bands at 1500 and 1405 cm^{-1} attributed to asym and sym mode $\Delta = 95$ cm^{-1}. Some caution is necessary in applying this criteria.

In contrast to I the infrared spectra of (2) is similar to those of the metal glycine complex and an analogue of this type $Cr[(gly)_2 OH]_2$ has been reported[3]. The detail infrared spectra and its assignments of both(2) and (6i) are given in Table-2(b). In case of (2) extensive overlapping in the 3500-2800 cm^{-1} precludes discussion of the NH_2 stretching modes. Coordination of the α-NH_2 group is indicated by the absence of NH^+_3 func-

Table 2(b): Infrared data and its qualitative assignments. Compound:- $[Cr(gly)_2 OH\}$ n. H_2O.

Band cm-1	Assignment
2920 2830 2740	CH_2 (Stretches).
1445 1435	CH_2 bending
1345	COOH (Stretch).
1310	CH_2 wagging.
1250	CH_2 twisting
1135 1150	NH_2 (wagging).
910	C-C (twisting).
860	Cr-OH Bending of hydroxy bridge.
540	Cr-O stretch

Table 2(c): Infrared data and its qualitative assignments. Compound: Cr(gly)$_2$ OH.H$_2$O.

Band cm-1	Assignments	Band cm-1	Assignments
3450	H_2O (absorption)	922 910	CO_2 + CH_2 (rocking)
3260 3220	NH_2 (Asymmetric Stretch).	750	CO_2 + CH_2 + NH_2
3150	NH_2 (Symmetric Stretch)	690	NH_2 (rocking).
2990 2960	CH_2 Stretching	645	H_2O
1670	OH Bending	585	Co_2 (Wagging and ring deformation).
1635 1608	COO^- (Asymmetric Stretch)	542 525	Cr-O (Stretch).
1570	NH_2 Bending		
1430 1420	CH2 Bending		
1390 1360	COO^- (Symmetric Stretch)	350 320	Cr-N
1320	CH_2 (twisting)		
1130 1050	NH_2 wagging.		
1032	C N Stretch.		
955	CO + C-C (Combination).		

Table 2(d): Infrared data and its qualitative assignments. Compound: $[Cr(gly)(OH)_2]\,2H_2O$

Band cm-1	Assignments
2920 2830 2740	CH_2 (Stretches)
1445 1435	CH_2 (bending)
1400	NH_2 (Stretch)
1250	CH_2 (Twisting)
860	Cr-O (Bending)
560	Cr-O (Stretch-brindings).

tion.Chromium nitrogen and chromium oxygen stretching bands may be attributed to a shouldring at 475 cm^{-1} and a broad band at 350 cm^{-1} respectively. The presence of OH bridging is established by a broad shouldered band at 540 cm^{-1} attributed to O-Cr-O stretchings, a week band at 955 cm^{-1} may be a bridging Cr-OH bending mode. The symmetrical stretching carbonyl mode of the γ- COOH group is observed at 1350 cm^{-1}. The 1600 cm^{-1} region is heavily overlapped. The bands in the infrared spectrum of compound[3] are broad, presumably due to extensive hydrogen bonding effects. The $NH^+{}_3$ group is not present. The presence of a free carboxylic acid functional group is indicated by a band at 1340 cm^{-1}. A characteristic Cr-O-Cr mode is observed at 535 cm^{-1} and a weak peak at 946 cm^{-1} corresponds to the bridging OH bending mode. The postulated structure of this complex is shown in the Fig.IV. to the best of our knowledge this is the first reported example of this class of complex.

U.V-Visible absorption Spectra:

Basolo[7] has correlated the U.V-Visible Spectrum of octahedrally coordinated Cr (III) with change in molecular summetry. For this d^3 system three bands are expected.

(a) $4A_{2g}$ (F) --------- $4T_{2g}$ (F).
(b) $4A_{2g}$ (F) --------- $4T_{1g}$ (F).
(c) $4A_{2g}$ (F) --------- $4T_{1g}$ (P)

The excited state split in energy on reduction of Symmetry. Thus the spectrum of fac $Cr(gly)_3$ shows no discernible splitting of bands (a) and (b), mer $Cr(gly)_3$ as yet unprepared would be expected to have splittings of these two bands. In the Co analogues this behaviour is substantiated. By analogy sample I shows no splitting in Band (a) and consequently is identified as a fac isomer. The assignment of the U.V-Visible bands and classification into cis and trans from is given in Table-3.

In the case of the hydroxy-bridged isomers, we have considered coordination about each chromium in the bis (glutamic acid) case.

Fig (i) and (iii) possess C_2 axes of symmetry, whilst (ii) does not. The two isomers of compound[2] prepared, one shows splitting of bands (a) and (b), while the other does not. Our consideration indicate that the structure of the isomer displaying splitting must be that of (ii), it is not possible to distinguish between (i) and (iii) which could apply to the remaining isomer.

Table 3: U.V-Visible band and its qualitative assignments

Compound	Isomer	Wavelength	Band	Assignments
$Cr(glu)_3\ 2H_2O$	Trans	18587 24355 45881	$4A_{2g}$ $4A_{2g}$ $4A_{2g}$	AT_{2g} (F). AT_{1g} (F). $4\ T_{1g}$ (P)
$Cr(glu)_3H_2O$	Cis	14592 14912 15458	Spin firbidden transition.	
		19642	$4A_{2g} \longrightarrow$	$4T_{2g}$ (F).
		25713	$4A_{2g} \longrightarrow$	45_{1g} (F).
		36536	$4A_{2g} \longrightarrow$	$4T_{1g}$ (P)
$Co(gly)\ _3H_2O$	Fac	19380	$1A_{1g} \longrightarrow$	$3T_{2g}$
		26589	$1A_{1g} \longrightarrow$	$1T_{1g}$
		34783	$1A_{lg} \longrightarrow$	$1T_{2g}$
$Co(gly)_3 1/2H_2O$	Mer	18618	$1A_{1g} \longrightarrow$	$3T_{2g}$
		26781	$1A_{1g} \longrightarrow$	$1T_{1g}$
		34880	$1A_{1g} \longrightarrow$	$1T_{2g}$
$Cr(gly)_2\ OH$	Cis	14493	$4A_{2g} \longrightarrow$	$2T_{2g}$ $2E_g$
		18983	$4A_{2g} \longrightarrow$	$4T_{2g}$
		25773	$4A_{2g} \longrightarrow$	$4T_{1g}$ (F).
		36670	$4A_{2g} \longrightarrow$	$4T_{1g}$ (P)
$Cr(gly)\ _2OH$	Trans	14535	$4A_{2g} \longrightarrow$	$2T_{2g}$ $2E_g$
		18584	$4A_{2g} \longrightarrow$	$4T_{2g}$
		25374	$4A_{2g} \longrightarrow$	$4T_{1g}$ (F).
		35625	4A2g $\longrightarrow$	4T1g (P)

Continued Table 3:

Compound	Isomer	Wavelength	Band	Assignments
Cr (glu)$_2$ OH 4H$_2$O	Cis	13850	$4A_{2g}$ →	$2T_{2g}$ $2E_g$
		17756	$4A_{2g}$ →	$4T_{2g}$
		23923	$4A_{2g}$ →	45_{1g} (F).
		35638	$4A_{2g}$ (F) →	45_{1g} (P)
Cr(glu)$_2$ OH 6H$_2$O	Trans	14633	$4A_{2g}$ →	$2T_{2g}$ 2Eg
		17756	$4A_{2g}$ →	$4T_{2g}$
		20189	$4A_{2g}$ →	$4T_{2g}$
		23782		
		27384		
		24782	$4A_{2g}$ (F) →	$4T_{1g}$ (P)
Cr(glu) (OH)$_2$ 2H$_2$O	Cis	18038	$4A_{2g}$ →	$4T_{2g}$
		24588	$4A_{2g}$ →	$4T_{1g}$ (F)
		36166	$4A_{2g}$ →	$4T_{1g}$ (P)
Cr(glu) (OH)$_2$ 2H$_2$O	Trans	14556	$4A_{2g}$ →	$2T_{2g}$ $2E_g$
		17709	$4A_{2g}$ →	$4T_{2g}$
		24108	$4A_{2g}$ →	$4T_{1g}$ (F)
		36258	$4A_{2g}$ (F) →	$4T_{1g}$ (P)

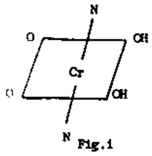
Fig.i

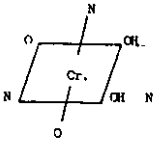
Fig.ii

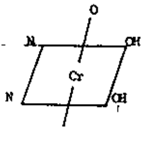
Fig.iii.

For the mono (glutamic acid) case, at least eight possibilities arise using this type of model. In all cases when an OH group is axial like in Fig-IV, three OH group occur on one face (Fac isomer) as in fac Cr(gly). Thus when no splitting of bands (a) and (b) is observed, we believe the OH group to be axial. Our isomers are thus distinguished on the basis of axial (Fac) and non-axial (mer) configuration of the OH group. Although the absolute sterochemistry can only be derived from the U.V-Visible in the case of tris (Cr(L-glu)$_3$. The values of 10 Dq for complexes I, and 3 have been used to construct a spectrochemical series using rule of average environment. A value of 17,400 cm^{-1} for

H_2O [taken for Cr^{3+} $(H_2O)_6$] was assumed, yielding glu = 37134 cm^{-1}, OH^- bridging = 16133 cm^{-1}, OH^- terminal = 19154 cm^{-1}. Thus the spliting ability of the ligand is in the order OH^- bridging < water < OH^- terminal < glu^-. It is interesting that the spin forbidden transition is observed more strongly in the Cis (fac) compounds as compared to the trans (mer) complexes. The classification of the prepared compounds on the basic of U.V- visible studies and their assignments are given in Table-3.

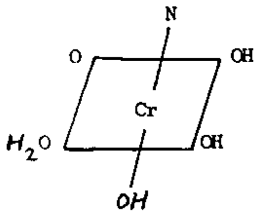

Fig. iv.

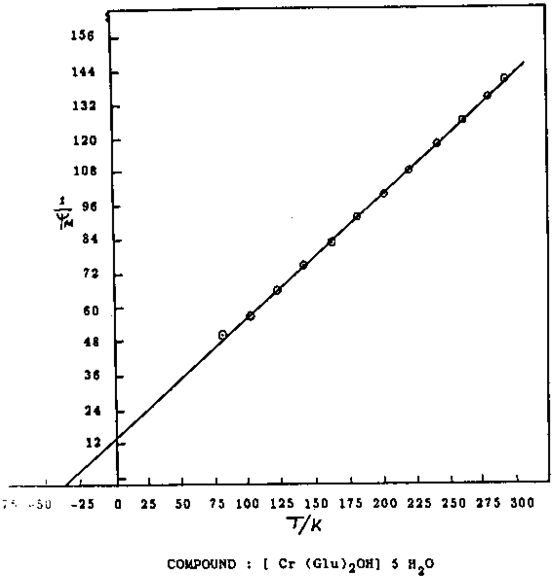

Fig. 1: A plot showing the effect of temperature on $\frac{1}{\Psi}$

Magnetochemical Properties:

Variable temperature magnetic moment measurements were obtained for the compounds fac $[Cr(glu)_3]$ $2H_2O$, $[Cr(glu)_2OH]$ $5H_2O$ and $[Cr(glu)\ (OH)_2]$ $3H_2O$ over the range 83-293°K. plots of $1/\Psi m$ against T°K were drawn.A representative plot is shown in Fig- 1. In all cases the room temperature magnetic moment is observed to decrease with temperature indicating interaction between adjacent chromium ions. There is a slight curvature of the plot and consequently the value of θ in the expresion $\mu_{eff} = 2.841\ \Psi_m\ (T + Q^{1/2}]$ is not exact.A value of 35° is obtained for both dihydroxybridged molecules and is in the range previously obtained for some Cr-dihydroxybridged systems[4].

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