Synthesis and Characterization of new Hydroxybridged Chromium (III) Complexes with L-Aspartic acid and L-Serine

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Summary: A new series of Chromium(III) hydroxybridged compounds of general formula $[Cr(L)_n(OH)_m]$ x H_2O (n,m=1,2,x=1-4) have been synthesised. The infrared spectra have been systematically examined. The existence of cis and trans isomers was established by the use of the solid state U.V-Visible studies. Low temperature magnetic moment studies of these compounds confirm hydroxy bridging. In addition to hydroxybridged compounds, the tris aspartic and tris serine compounds were also prepared. The tris serine compound is anhydrous in contrast to the tris aspartic acid compound. The compound $[Cr(Serine)NO_3OH]_2$ was also prepared.

Introduction

In the solid state, amino acids generally exist in the Zwitterion form. On co-ordination, chelation may take place through the amino or carboxylic acid functions giving a variety of co-ordination.

L-aspartic acid has three binding sites for protons or metal ions. Three chelate rings are formed when this ligand is tridentate, one glycine like five membered ring and rather unusual six, seven or eight membered ring (1). As no product suitable for X-ray single crystal analysis were obtained in these studies, infrared and U.V-Visible studies were of great value in their characterization.

Experimental

L-aspartic acid and L-serine were obtained from sigma chemicals while chromium(III) chloride and sodium hydroxide were obtained from BDH. All were used as obtained without further purification.

Physical Methods

Infrared spectras were recorded as KBr and CSI discs on a Perkin-Elmer 283 B instrument. Solid state U.V-Visible spectra were recorded on a Perkin - Elmer 552 Spectrophotometer equipped with diffuse reflectance and data station attachments. Magnetic moment studies were carried out on a Newport Variable temperature susceptibility apparatus.

Preparation of Complexes

The Mizuochi method [2] was modified for the synthesis of tris complexes. To a solution of L-aspartic acid or L-serien (0.3 mol), an aqueous solution of Chromium(III) chloride hexahydrate

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(0.1 mol) was added. The pH value of the solution was adjusted to 6.7 by the addition of sodium hydroxide and the mixture was heated on a water bath until it turned to pink and after an hour a pink powder precipitated. The mixture was cooled to room temperature, filtered and washed several times with water and finally with dry acetone. The resulting powder tris amino acid complexes were stored over $CaCl_2$ in a desiccator. For the preparation of compounds containing one hydroxy groups and two molecules of the ligand, the metal ligand ratio of 1:2 was taken and pH of the solution was adjusted to 7.5. While for the preparation of compounds containing two hydroxyl groups and one molecule of the ligand, the metal-ligand ratio of 1:1 was maintained and the pH of the solution was adjusted to pH 8 as already reported for hydroxybridged glutamic acid complexes [3]. The remaining procedure was the same as for the tris complexes.

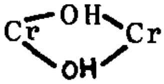
Table-1: Analytical data of the prepared compounds.

S.No.	Formula of the Complex	Element	Theory %	Found %
1	$[Cr(ASP)_3]\ H_2O$	C	30.9	31.1
		H	4.5	4.9
		N	9.1	9.4
II	$[Cr(ASP)_3]\ 2H_2O$	C	29.7	29.5
		H	4.5	4.5
		N	8.7	8.7
III	$[Cr(ASP)_2(OH)]\ 4H_2O$	C	23.7	24.4
		H	5.18	4.70
		N	6.91	6.6
		M	12.83	12.55
IV	$[Cr(ASP)_2\ (OH)]\ 3H_2O$	C	24.8	24.9
		H	4.9	4.00
		N	7.2	6.5
		M	13.44	13.25
V	$[Cr(ASP)\ (OH)_2]\ H_2O$	C	20.25	19.88
		H	4.20	4.04
		N	5.90	6.66
		M	22.00	21.98
VI	$Cr(Serine)_3$	C	29.67	29.83
		H	4.95	5.00
		N	11.54	11.52
		M	14.29	14.32
VII	$[Cr(Serine)_2OH]H_2O$	C	24.40	24.2
		H	5.08	5.2
		N	9.4	9.5
		M	17.6	17.3
VII	$[Cr(Serine)_2OH]\ 2H_2O$	C	23.0	22.5
		H	5.4	4.92
		N	8.9	8.8
		M	16.6	16.26
IX	$[Cr(Serine)NO_3OH]_2$	C	15.2	15.15
		H	3.39	3.58
		N	11.8	11.5

Results and Discussion

Analytical data for the prepared complexes is presented in table 1. Detailed infrared studies of these compounds were carried out in the region of 4000 cm^{-1} - 200 cm^{-1}. The infrared data and its qualitative assignments of the prepared compounds are given in table 2. In case of the tris aspartic acid compound, bidentate chelation occurs solely through one of the acid groups. The presence of the NH_3^+ group is indicated by bands assigned to NH_3^+ deg; NH_3^+ sym and NH_3^+ rocking modes and a combination mode at 2080 cm^{-1}. The COO^- group region is complicated due to the overlapping of a coordinated and a free COO^- group. In sharp contrast, the tris serine complex exhibits chelation through both the COO^- group and the amino group. Coordination through the amino group is indicated by the absence of the NH_3^+ stretching, rocking and combination mode mentioned above. Characteristic NH_2 group frequencies are present. The metal nitrogen and metal oxygen bands are observed at 360 cm^{-1} and 520 cm^{-1} respectively.

In case of the hydroxybridged compounds the spectras are complicated by extensive hydrogen bonding, which is more pronounced in the case of dihydroxy bridged compounds.

Characteristic CH_2 group bands are present, the CH_2 rocking, twisting and wagging modes being observed at 772 cm^{-1}, 1240 cm^{-1} and 1304 cm^{-1} respectively in all cases. The CH_2 bending occurs at 1445 cm^{-1} and CH_2 stretching modes appear at 2940 cm^{-1} (Asymmetric) and 2850 cm^{-1} (Symmetric). In the case of aspartic acid, confirmation of bonding of one carboxylic acid group is provided by bands at 1340 and 1600 cm^{-1}. A free carboxylic acid band, C-OH bending mode is observed at 1408 cm^{-1}. The NH_2 scissoring occurs at 1600 cm^{-1}. The band at 1050 cm^{-1} may be a water librational mode. A band at 870 cm^{-1} assigned to a  bending mode band a broad band centered at 550 cm^{-1} is observed in all the hydroxy bridged compounds.

In case of $[Cr(serine)(NO_3)(OH)]_2$, a deuteration experiment was carried out to assign the bands. The weak band at 986 cm^{-1} is shifted to 713 cm^{-1} giving H/ D ratio of 1.38. The ratio in the Copper compound is reported to be 1.35(4). Other bands which changes on deuteration area:-

a. 864 $cm^{-1} \longrightarrow$ 842 cm^{-1} ratio 1.35

b. 1150 cm^{-1} $(NH_2) \longrightarrow$ 850 cm^{-1} (broad).

c. and the 650 cm^{-1} (NH_2) band is shifted to 489 cm^{-1}.

The NO_3^- group absorbs at 1380 cm^{-1} rather than 1350 cm^{-1} from the intensity distribution. Some of the aliphatic CH_2 group in serine also exchanges on deuteration (occurrence of

Table-2(a): Infrared data and its qualitative assignments Compounds: $Cr(ASP)_3\ H_2O$

Band cm^{-1}	Assignment
3430	H_2O Absorption
3000	NH_3^+ stretch
2730	CH_2 stretching
2660	NH_3^+ strech
2090	
1690	COOH Dimer
1645	COO^- Asymetric stretch
1595	NH_3^+ Asym degenerate deformation
1505	NH_3^+ sym deg deformation
1420	CH_2 bending + COO^- sym. stretching
1320	CH_2 wagging
1245	CH_2 twisting
1150	NH_3^+ rocking
1080	NH_3^+ inflexion
1040	C-C-N Asym. Stretch.
930	CH_2 rocking
900	C-CN sym stretch
870	C-C strech
750	CH_2 rocking
650	COO^- in plane bending
600	COO^- wagging
550	C-C=O in plane bending
460	COO^- rocking
410	M-O stretch

Table-2(b): Infrared data and its qualitative assignments. Compound: Cr (Serine)$_3$

Band cm^{-1}	Assignment
3450	OH absorption
3100	NH_3^+ stretch
1630	NH_2 Asym.def.
1465	CH_2 bending.
1405	COO^- Sym.Stretch.
1380	OH absorption
1340	
1300	CH_2 wagging
1220	CH_2 twisting
1120	NH_2 rocking
1080	
1050	CH_2 rocking
1010	OH in Plane deformation
910	COO^- + CH_2 rocking
800	CH_2 rocking
600	COO^- wagging
520	Cr-O splitting
360	Cr-N splitting

Table-2(c): Infrared data and its qualitative assignments. Compound: $[Cr(ASP)_2\ OH]3H_2O$

Band cm^{-1}	Assignment
3450	H_2O absorption
2940	CH_2 stretch
2820	
1600	COOH stretch
1445	CH_2 bending
1410	COO^- free
1400	NH_2 bending
1350	COOH stretch
1300	CH_2 wagging
1230	CH_2 twisting
1250	
1150	NH_2 wagging
990	H_2O
900	C-C stretch
870	Cr-OH bending
775	CH_2 rocking
550	Cr-O bridging

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

Band cm^{-1}	Assignment
3450	H_2O absorption
1600	COOH Asy:stretch
1445	CH_2 bending
1400	COO^- Free
1350	COOH Sym.stretch
1310	CH_2 wagging
1230	CH_2 twisting
1150	NH_2 wagging
870	Cr(OH) bending of hydroxy bridge
550	Cr-O Bridging

Table-2(e): Infrared data and its qualitative assignments. Compound: $[Cr(Serine)_2\ 2H_2O]\ NO_3H_2O$

Band cm^{-1}	Assignment	Band	Assignment
3440	H_2O (absorption)		
1630	H_2O (bending)	900	C-C stretch
1500	NO_3^- (unidentate)	870	Cr-OH (bending)
1440	CH_2 (bending)	550	Cr-C (Cr-o-bridging)
1380	COO^- (stretch)		
1350			
1330	CH_2 wagging		
1250	NH_2 wagging		
1050	C-N (stretch).		

Table-2(f): Infrared data and qualitative assignments.
Compound: $[Cr(Serine)OH]NO_3$

Band	Assignment	Band	Assignment
1760	Some unidentate NO_3^-	825	NO_3^- unidentate
		652	NH_2 rocking
1620	COO^- Asym.stretch	550	Cr-O bridging
1580	COO^- Sym.stretch		
1350	NO_3^- Unidentate		
1140	NH_2 wagging		

bands at 2020-2040 cm^{-1} region). The evidence for the hydroxybridged species are the broad band occurring in the 630-500 cm^{-1} region corresponding to the Cr-O vibration mode. The nature of the unidentate NO_3^- group is substantiated by both bands at 825 cm^{-1} and 1380 cm^{-1} being unchanged. The combination band at 1760 cm^{-1}, which shows a very small splitting also indicates a unidentate NO_3^- group.

U.V.-Visible absorption spectra

Basolo [5] has correlated the U.V.-Visible spectrum of octahedrally coordinated Cr(III) with changes in molecular symmetry. For this d^3 system, three bands are expcted.

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

The excited states split in energy on reduction of symmetry. Thus the spectrum of the cis isomers should show no discernible splitting of bands (A) and (B), while the trans compounds would be expected to display splittings or shouldering of these bands.

In the case of the tris serine compound, two isomers fac (cis) and mer (trans) are possible. In contrast to tris aspartic acid only one form is possible. There is variation in the amount of water of crystallization in the molecules giving two different hydration isomers. The U.V-Visible band of tris aspartic acid compounds and their assignments are given in table 3. On the basis of the U.V.-Visible spectra, the tris serine compound was assigned the trans form.

In the case of the hydroxy-bridged isomers we have considered coordination of chromium in the bis (aspartic acid) and bis (serine) case. Structure (1) and (3) posses a C_2 axis of symmetry while structure (2) does not. Our considerations indicate that the structure of the isomer displaying splitting must be that of (2). It does not seem possible to distinguish between case (1) and (3) on the basis of U.V.-Visible spectroscopy. Using this criteria compound (IV) and (VI) were assigned as trans form, while compound (V) was assigned as a cis form.

For the mono (aspartic acid) case at least eight possibilities arise using this type of model. In all cases when an OH^- group is axial as in Fig. 4.

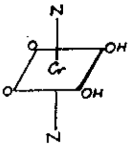


Fig. (1)

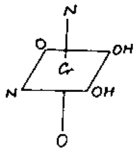


Fig. (2)

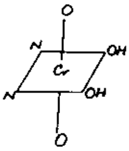


Fig. (3)

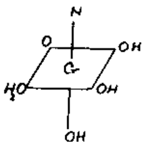


Fig. (4)

Three OH^- groups occur on one face (Fac isomer, cis form). Thus when no splitting of bands (a) and (b) is observed, we believe the OH^- group

Table-3: Electronic spectral data for Cr(III) amino acid compounds in solid state.

			Band			
	Isomer	nm	cm^{-1}	Intensity	Assignment	
$[Cr(ASP)_3]$ H_2O	Cis	550	18152	6354	$4A_{2g}$	$4T_{2g}$
		512	19497	5316	$4A_{2g}$	$4T_{1g}(F)$
		271	36900	9391	$4A_{2g}$	$4T_{1g}(P)$
$[Cr(ASP)_3]2H_2O$	Cis	597	16750	3945	$4A_{2g}$	$4T_{2g}$
		542	18450	3763		
		459	21786	3551		
		415	24096	4634	$4A_{2g}$	$4T_{1g}(F)$
		279	35842	5362	$4A_{2g}$	$4T_{1g}(P)$
$Cr(Serine)_3$	Trans	553	18070	4522	$4A_{2g}$	$4T_{2g}$
		411		24331	$4A_{2g}$	$4T_{1g}(F)$
		385		25974	$4A_{2g}$	$4T_{1g}(P)$
$[Cr(ASP_2OH]4H_2O$	Trans	690	14493	3583	$4A_{2g}$	$4T_{2g}$
		568	17599	6851	$4\ A_{2g}$	$4T_{2g}$
		416	24039	6045	$4A_{2g}$	$4T_{1g}(F)$
		279	35842	2708	$4A_{2g}$	$4T_{1g}(P)$
$[Cr(ASP)_2OH)]3H_2O$	Cis	577	17331	7051	$4A_{2g}$	$4T_{2g}$
		418	23952	4452	$4A_{2g}$	$4T_{1g}(F)$
		276	36140	4484	$4A_{2g}$	$4T_{1g}(P)$
$\{Cr(Serine)_2OH]H_2O$	Trans	689	14507	2098	$4A_{2g}$	$2T_{2g}$ 2Eg
		523	25451	8278	$4A_{2g}$	$4T_{1g}(F)$
		392	25451	8278	$4A_{2g}$	$4T_{1g}(F)$
		274	36403	9158	$4A_{2g}$	$4T_{1g}(P)$

Table-3 Cont.

	Isomer	nm	Band cm^{-1}	Intensity	Assignment	
$[Cr(Serine)2OH]2H_2O$		689	14514	1481	$4A_2g$	$2T_2g$
		526	19011	6450	$4A_2g$	$4T_{2g}$
		391	25575	5566	$4A_2g$	$4T_{1g}$(F)
		276	36232	7632	$4A_{2g}$	$4T_{1g}$(P)
$[Cr(Serine)_2OH$ $2H_2O$		689	14514	1481	$4A_{2g}$ $2E_g$	$2T_{2g}$
		526	19000	6450	$4A_{2g}$	$4T_{2g}$
		391	25575	5566	$4A_{2g}$	$4T_{1g}$
		276	36127	7632	$4A_{2g}$	$4T_{1g}$

to be axial. Using the same type of model system and applying the criteria of splitting of bands, the nitrate bridged compound serine was assigned to be the trans form. The U.V-Visible bands, its assignment and classification into cis and trans form on the basis of the above criteria are given in table-3.

Magnetochemical Properties

The compounds $[Cr(ASP)_2OH]3H_2O$, $[Cr(Ser)_2OH]H_2O$ and $[Cr(ASP)(OH)_2]H_2O$ were chosen as representative and their magnetic moments were studied in the range of 83-293 ^oK. The susceptibility plots showed the existence of metal-metal interaction and Θ values of 40.35 and 36 respectively were obtained.

Conclusion

$Cr(Asp)_3$ has been characterized as the cis isomer from the analysis of both its infrared and electronic spectrum. In this compound bidentate chelation occurs only through one of the carboxilic acid functional group, while the amino group does not take part in chelation. While the tris serine complex which has been assigned as the trans isomer, exhibits chelation through both the acidic group and the amino group as substantiated from the infrared studies.

In case of hydroxybridged compounds, the chelation of aspartic acid resemble that of serine. Chelation in both ligands occurs through amino and carboxilic acid functional groups. The existance of metal-metal interaction is substantiated by low temperature magnetic moment studies.

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