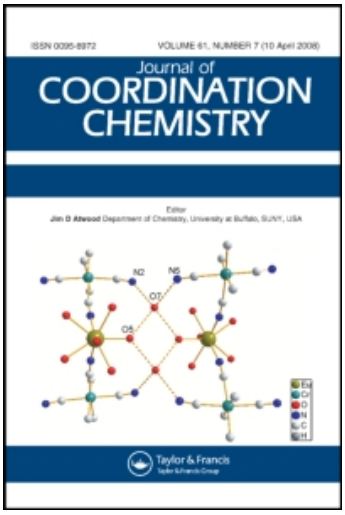

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AMINO ACID COORDINATION TO CHROMIUM(III) WITH MERIDIONAL GEOMETRY

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L-lysine and L-glutamic acid can be made to coordinate as tridentate ligands with meridional geometry in octahedral mixed ligand complexes where the other ligand is tridentate and has a preference for meridional coordination. Both $[Cr(dpt)(L\text{-}lys)]^{2+}$ (*Hlys* = lysine, *dpt* = di(3-aminopropyl)amine) and $[Cr(glygly)(L\text{-}glu)]^{-}$ ($H_2glygly$ = glycylglycine, H_2glu = glutamic acid) exhibit meridional geometry.

KEYWORDS: Chromium III, meridional, amino acid

INTRODUCTION

Tridentate amino acids tend to coordinate facially to metal ions because of the tripodal disposition of the coordinating groups around the α-carbon.[1] The residues on some amino acids, however, are long enough and flexible enough that they should be able to coordinate meridionally. Lysine (*HLys* = $H_2N_\omega - (CH_2)_4 - CH(N_\alpha H_2) - COOH$) and glutamic acid ($H_2glu$ = $HO_\alpha OC - CH(NH_2) - (CH_2)_2 - COO_\gamma H$) are among these. The objective of this work was to force meridional coordination on these two amino acids by synthesizing mixed complexes with a tridentate ligand that prefers meridional coordination, which we refer to as a template ligand.

Near planarity among the three coordinating groups is a strong inducement to meridional coordination of a tridentate ligand. Among the ligands that have a strong preference for meridional geometry for this reason are 2,2′,2″-terpyridine,[2] pyridinedicarboxylate,[3] and glycylglycinate.[4,5] In this study we use glycylglycinate ($glygly^{2-}$) to induce meridional coordination by forming an initial 1:1 complex with the metal ion, leaving the second ligand no alternative if it is to coordinate through three groups.

Tridentate coordination by lysine and glutamic acid cannot be taken for granted. The larger ring sizes necessary to coordinate the γ-carboxylate (7- and 8-membered rings) in a glutamate complex or the ω-amine (8- and 9-membered rings) in a lysinate complex make coordination of the residue less favorable than in smaller

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analogs. We have found no reports of tridentate coordination of lysine, and only weak evidence of tridentate glutamate.[6-12] By contrast, a number of complexation studies with both lysine and glutamic acid have suggested bidentate coordination, even when there was opportunity for the third group to coordinate.[1] There are well-characterized examples of tridentate coordination by aspartic acid[13,14] and ornithine (all facial),[15] the next smaller analogs.

We have also used di(3-aminopropyl)amine (*dpt*) as a template ligand. This ligand adopts a meridional geometry in most mononuclear complexes,[16,17] though it coordinates facially in at least one dinuclear complex.[18] Since the three nitrogens are not constrained to planarity, it should serve as a much weaker template. The *mer*-[Cr(*dpt*)Cl_3] complex is a convenient starting material.[17]

Chromium(III) complexes are relatively inert, which it was hoped would hinder both intramolecular rearrangement and intermolecular ligand exchange to products that might be favored thermodynamically. The lability increases with temperature, allowing some measure of control of ligand association and dissociation processes.

EXPERIMENTAL SECTION

Materials

Di(3-aminopropyl)amine and $CrCl_3 \cdot 6H_2O$ were obtained from Aldrich Chemical Co., glycylglycine, L-lysine, and L-glutamic acid from Sigma, and chromium(III) perchlorate from G.F. Smith. *mer*-[Cr(*dpt*)Cl_3] was prepared by the method of House and Robinson.[17]

[Cr(dpt)(L-lys)]$Cl_2 \cdot C_2H_5OH \cdot 0.5KCl$

L-lysine hydrochloride (0.91 g; 0.0050 mol) was added to a suspension of [Cr(*dpt*)Cl_3] (1.44 g; 0.0050 mol) in ethanol (75 mL). The mixture was heated at 55–60°C for 90 min with constant stirring. KOH (0.56 g; 0.0100 mol) was then added in small portions and heating was continued for another 90 min. The red solution was cooled and KCl that had settled out was removed by filtration. After standing for 24 h at 5°C a hygroscopic red solid was collected by filtration under a nitrogen atmosphere. It was washed with ether and dried in vacuo. Anal. Calcd. for $Cr(C_{12}H_{30}N_5O_2)Cl_2 \cdot C_2H_5OH \cdot 0.5KCl$: C, 35.42; H, 7.69; N, 14.52; Cr, 10.53. Found: C, 34.84; H, 7.47; N, 14.52; Cr, 10.78.

K[Cr(glygly)(L-glu)]$\cdot xH_2O$

H_2glygly (1.32 g; 0.0100 mol) and $Cr(ClO_4)_3 \cdot 6H_2O$ (4.58 g; 0.0100 mol) in methanol (75 cm^3) were heated at 60°C until the *H_2glygly* dissolved. Then L-glutamic acid (1.47 g; 0.0100 mol), dissolved in 1:1 methanol/water, was added and heating was continued for 2 h with constant stirring. $KHCO_3$ (4.00 g; 0.0400 mol), dissolved in a minimum amount of water, was then added in small portions, and heating was resumed for an additional hour. The violet solution was filtered hot and concentrated in a rotary evaporator. The solution was loaded onto a Sephadex DEAE anion exchanger (Cl^- form), washed with water, and eluted with a 0.3 M KCl

solution as a single band. A very hygroscopic product was obtained by this and other methods tried.

Ba[Cr(glygly(L-glu)]$_2$·xH$_2$O

H_2glygly (1.32 g; 0.0100 mol) and L-glutamic acid (1.47 g; 0.0100 mol) were dissolved in water. Barium hydroxide (6.30 g; 0.0200 mol) was added, and then, once it was dissolved, $Cr(ClO_4)_3 \cdot 6H_2O$ (4.58 g; 0.0100 mol). The solution was heated on a water bath and maintained at 80°C for 2 h. The violet solution was filtered hot and allowed to cool. After reducing its volume it was loaded onto a Sephadex G-10 column. A violet band separated ahead of a red band. The violet eluate was evaporated in a rotary evaporator, then ethanol was added to precipitate a violet substance, which was collected by filtration under a nitrogen atmosphere and dried in vacuo. This complex was also extremely hygroscopic and an elemental analysis was not carried out.

Measurements

IR spectra were recorded on a Mattson Cygnus-25 FTIR spectrometer on samples suspended in KBr discs. UV-visible absorption spectra were measured with a Hewlett-Packard Model 8451A diode array spectrometer. Conductivity measurements were taken with a Cole-Parmer Model 1481-60 conductivity meter. X-ray powder diffraction spectra were collected on a Philips Model 3600 automated diffractometer to check the crystallinity of the products. A Kevex Model 5100 energy-dispersive X-ray fluorescence (EDXRF) spectrometer with Mo Kα radiation was used to detect the elements present in solid samples.

Molecular Modeling

Molecular mechanics calculations were done with the program PCMODEL[19] on a Silicon Iris computer. PCMODEL uses the MMX force field,[20] which does not apply bending constants to ligand-metal-ligand angles, assuming that van der Waal's forces will constrain the six coordinating atoms (in the complexes studied here) to approach octahedral orientation.

RESULTS AND DISCUSSION

Methods of Characterization

Coordination of carboxylate can be verified from the asymmetric -CO_2 stretching band, which is normally intense and easily located. The frequencies fall in the order protonated > coordinated > anionic carboxylate, and coordinated carboxylate tends to occur near 1630 cm^{-1}.[21] In crystalline L-glutamic acid there is one anionic and one protonated carboxylate (it is a zwitterion), and $\nu_{as}(CO_2)$ is found at 1577 and 1681 cm^{-1}.[22] This band is at 1572 cm^{-1} in the spectrum of L-lysine, in which only deprotonated carboxylate is present.

Amine coordination may be established by shifts in the frequencies of the amine stretching, bending, and twisting bands near 2900, 1500, and 1100 cm^{-1},

respectively.[23,24] Stretching modes for individual amines in the metal complexes were not distinguishable, but the other two modes were, and they could be identified by comparison with the IR spectra of similar complexes.

The most important question is whether the amino acid ligands are meridionally coordinated. Chromium(III) is six-coordinate except under circumstances of extreme steric hindrance. Coordination of a particular group may often be inferred simply from the lack of an alternative. Assuming both ligands in the complex are tridentate, only one of them need be established as meridional or facial.

Schmidtke and Garthoff have studied in detail the IR spectra of geometric isomers of diethylenetriamine (dien) complexes of several metal ions, and found certain features diagnostic of meridional coordination.[25] The CH_2 bending region between 1400 and 1500 cm^{-1} usually consists of three bands for facial isomers, but just a single band for meridional isomers. A band near 1250 cm^{-1}, representing an NH wagging motion, appears for meridional but not for facial isomers, and the NH_2 rocking motions result in one or two bands between 700 and 800 cm^{-1} for facial isomers, but two bands near 850 cm^{-1} for meridional isomers.[25] Another diagnostic band is the N-H stretching mode near 2850 cm^{-1} for the coordinated secondary amine. Yoshikawa and Yamasaki found that this band occurs with medium intensity for meridional isomers, but is weak in facial isomers.[26] Each of these features is presumed to be valid for di(3-aminopropyl)amine as well.

[Cr(dpt)(lys)]$^{2+}$

Each ligand has only three groups that can coordinate. The only other possible ligands are chloride ions or ethanol, both of which are in the formula of the compound isolated. The charge on the complex was determined by loading an aqueous solution onto a Sephadex SP cation exchange column, from which it was eluted with a 0.6 M KCl solution; it was moved only very slowly by a 0.3 M solution. This has been found empirically in our laboratory to indicate a +2 charge on the complex. The molar conductance was 213 $Ohm^{-1} \cdot cm^2 \cdot mol^{-1}$, which corresponds to a 1:2 electrolyte. This effectively precludes Cl^- coordination.

The visible and near-UV absorption spectrum of $[Cr(dpt)(lys)]^{2+}$ consists of bands at 522 nm (ε = 53 $M^{-1}cm^{-1}$) and 390 nm (ε = 55 $M^{-1}cm^{-1}$), representing the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4T_{1g}$ transitions, in O_h notation. The spectrum is nearly identical in aqueous and ethanolic solution, which is evidence that ethanol is not coordinated, since it should be readily displaced by water, altering the absorption spectrum. We thus conclude that each ligand is tridentate.

There are four possible isomers, shown in Figure 1 [coordinating atom designations: dpt(N^1, primary amine; N^2, secondary amine), lys^- (O, N_α, N_ω)]. PCMODEL calculations predicted the meridional isomer to be the most stable, 20 kJ/mol lower in energy than the facial *trans*(N^2, O) isomer. Chromium(III) complexes reported with di(3-aminopropyl)amine and a bidentate amine (with meridional geometry) have first band maxima in the visible absorption spectrum between 489 and 492 nm when the sixth ligand is H_2O, and between 521 and 527 nm when it is Cl^-.[16] If the sixth ligand were carboxylate, the complex would resemble $[Cr(dpt)(L\text{-}lys)]^{2+}$, and a similar spectrum would be expected. A suitable complex has not been made, but the ligand field strength of carboxylate (on which the first band position depends) is closer to that of water than to that of chloride ion. Thus the spectrum of $[Cr(dpt)(L\text{-}lys)]^{2+}$ ought to be closer to that of the aquo complexes. The opposite is

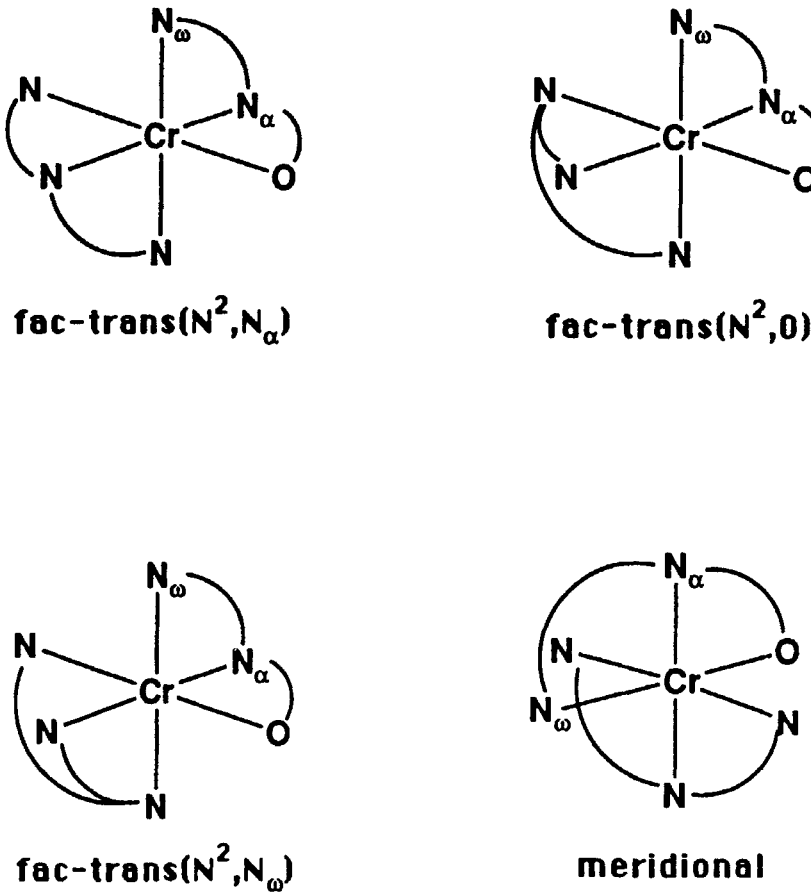

Figure 1 Geometric isomers of $[Cr(dpt)(L\text{-}lys)]^{2+}$.

true, however, so the UV-visible spectrum cannot be used to support meridional coordination.

The infrared spectrum, however, does indicate meridional coordination. A peak at 2865 cm^{-1} of medium intensity corresponds to ν(N-H) of a meridionally coordinated *dpt* secondary amine.[26] Two peaks near 850 cm^{-1} are present as expected for meridional coordination of di(3-aminopropyl)amine. The absence of peaks in the 700–800 cm^{-1} region is strong evidence against facial coordination. The CH_2 bending criterion developed for dien complexes[25] was not useful. There were no peaks between 1400 and 1500 cm^{-1}, though it is possible that one was obscured by the carboxylate symmetric stretching band at 1400 cm^{-1}.

The asymmetric carboxylate stretching band is at 1653 cm^{-1}, similar to other lysine complexes,[9] confirming carboxylate coordination. The IR spectrum is consistent with coordinated α- and ω-amine groups, lacking the bend and twist modes of the uncoordinated amino acid, and exhibiting the coordination-shifted frequencies at 1576 and 1150 cm^{-1}.

We conclude that $[Cr(dpt)(lys)]Cl_2 \cdot C_2H_5OH \cdot 0.5KCl$ incorporates tridentate lysine with meridional geometry, as predicted by the molecular mechanics calculation. This assignment relies primarily on the distinctions between meridional and facial diethylenetriamine in the IR spectrum found to be diagnostic by Schmidtke and Garthoff.[25]

[Cr(glygly)(L-glu)]$^-$

The products obtained in the synthesis were very sensitive to the base used. In all cases four equivalents of base were used to completely deprotonate both ligands. Using sodium or potassium hydroxide, only $[Cr(glygly)_2]^-$ was obtained,[27] with none of the mixed-ligand complex. With $Ba(OH)_2$ the product was approximately 50% $[Cr(glygly)(L\text{-}glu)]^-$. With $KHCO_3$ the only significant product was the mixed-ligand complex.

When loaded onto a Sephadex DEAE anion exchange column, the complex was eluted with 0.3 M KCl, consistent with a uninegative charge. The UV-visible spectra in water and in ethanol were very similar, from which we infer that no solvent molecules are coordinated. Both ligands must then be tridentate for lack of alternative donors.

Further confirmation is provided by the IR spectrum (see Table 1). Coordination of the glycylglycinate peptide nitrogen is shown by the appearance of a characteristically intense peak near 1600 cm^{-1}.[28] The glycylglycine carboxylate stretching band is found at 1595 cm^{-1}, similar to its position in $K[Cr(glygly)_2]$,[5] but lower than in simple coordinated amino acids because of conjugation with the peptide function. Glutamate carboxylate coordination is shown by the asymmetric carboxylate stretch at 1642 cm^{-1}, while the ν(N-H) peak at 2900 cm^{-1} and the $\rho(NH_2)$ peak at 1148 cm^{-1} are indicative of amine coordination.

There are seven possible geometric isomers, one meridional and six facial. PCMODEL calculations predicted that the meridional isomer would be the most stable, 29 kJ/mol lower in energy than the most stable facial isomer. This is in accord with the expected tendency of the glycylglycinate ion to remain planar upon coordination because of sp^2 hybridization at the peptide nitrogen and adjacent carbon.

An analysis of the UV-visible spectrum was undertaken to test the isomer assignment. The angular overlap model (AOM) has proven to be beneficial in finding the correct isomer assignment from absorption spectra.[29,30] The basis for this analysis is that energies of the three components of the $^4A_{2g} \rightarrow {}^4T_{2g}$ band in Cr(III) spectra correspond to the average values of the ligand field splitting

Table 1 Infrared spectral data for $Ba[Cr(glygly)(L\text{-}glu)]_2$ and related complexes.

H_2glu	$Ba[Cr(glygly)(L\text{-}glu)]_2$	$[Cr(glygly)(dien)]^+$[a]	$K[Cr(L\text{-}glu)_2]$[b]	Assignment
1724	1642		1642	$\nu_{as}(CO_2)(glu)$
	1602		1617	$\nu(C{=}O)_{peptide}$
	1595	1585	1582	$\nu_{as}(CO_2)(glygly)$
1420	1400		1390	$\nu_s(CO_2)(glu)$
1110	1148		1138	$\delta(NH_2)(glu)$
	533		551	ν(Cr-O)(*glu*)

[a]Ref. 34
[b]Ref. 27

parameters (Δ = 10Dq) of the four coordinating groups in the three Cartesian planes, one plane for each component.[31] Some of these transition energy expressions are shown in detail in Table 2.

The UV-visible absorption spectrum of [Cr(*glygly*)(*L-glu*)]$^-$ does not show any obvious splitting of either band. A Gaussian resolution was performed to locate the band maxima of the component transitions. The spectrum was fit very well by two components per band, thus a resolution into three components would be invalid. The inability to resolve a pair of components in the $^4A_{2g} \rightarrow {}^4T_{2g}$ band is common, because the band width is much larger than the separation of the components, especially the separation of the closest pair.[32,33]

Ligand field splitting parameters for the six coordinating groups were taken from a similar analysis of the UV-visible spectra of isomers of [Cr(*L-glu*)$_2$]$^-$,[27] and from a more detailed analysis of the broad band and sharp-line electronic spectrum of K[Cr(*glygly*)$_2$] at low temperature.[27] The approximation is made that similar values can be assigned in other complexes with the same groups. These values were used to evaluate the expressions illustrated in Table 2 and the transition energies of the pair of components closest in energy were averaged in order to make comparisons with the resolved experimental spectrum. The results are shown in Table 3. The calculations lend support to the meridional assignment, though the facial *trans*(N_g, O_γ; N_p, N) assignment works just as well.

CONCLUSIONS

The bulk of the evidence indicates that L-lysinate is tridentate and meridionally coordinated in [Cr(*dpt*)(*L-lys*)]$Cl_2 \cdot C_2H_5OH \cdot 0.5KCl$, and that it is feasible to induce meridional coordination by starting with *mer*-[Cr(*dpt*)Cl_3] and displacing the

Table 2 $^4A_{2g} \rightarrow {}^4T_{2g}$ Transition energy expressions for several isomers of [Cr(*glygly*)(*L-glu*)]$^-$.

Meridional Isomer
$E_1 = 1/4(\Delta_N + \Delta_{O\gamma} + \Delta_{O\alpha} + \Delta_{Np})$
$E_2 = 1/4(\Delta_N + \Delta_{Og} + \Delta_{Ng} + \Delta_{Np})$
$E_3 = 1/4(\Delta_{O\alpha} + \Delta_{O\gamma} + \Delta_{Og} + \Delta_{Ng})$
Facial *trans*(N_g, O_α; N_p, N) Isomer
$E_1 = 1/4(\Delta_N + \Delta_{O\alpha} + \Delta_{Ng} + \Delta_{Np})$
$E_2 = 1/4(\Delta_N + \Delta_{O\gamma} + \Delta_{Og} + \Delta_{Np})$
$E_3 = 1/4(\Delta_{O\alpha} + \Delta_{O\gamma} + \Delta_{Og} + \Delta_{Ng})$
Facial *trans*(N_g, O_γ; N_p, N) Isomer
$E_1 = 1/4(\Delta_N + \Delta_{Og} + \Delta_{O\alpha} + \Delta_{Np})$
$E_2 = 1/4(\Delta_{Ng} + \Delta_{O\gamma} + \Delta_N + \Delta_{Np})$
$E_3 = 1/4(\Delta_{O\alpha} + \Delta_{O\gamma} + \Delta_{Og} + \Delta_{Ng})$
Facial *trans*(N_g, N; N_p, O_α) Isomer
$E_1 = 1/4(\Delta_N + \Delta_{O\alpha} + \Delta_{Ng} + \Delta_{Np})$
$E_2 = 1/4(\Delta_{Og} + \Delta_{O\gamma} + \Delta_{O\alpha} + \Delta_{Np})$
$E_3 = 1/4(\Delta_{Ng} + \Delta_{O\gamma} + \Delta_{Og} + \Delta_N)$

Ligand designations. L-glutamate: Oα, Oγ, N; glycylglycine: Ng (amine), Np (peptide), Og.

Table 3 Calculated[a] and experimental[b] $^4A_{2g} \rightarrow {}^4T_{2g}$ component band maxima (cm^{-1}) for $[Cr(glygly)(L\text{-}glu)]^-$

Isomer	Component I[c]	Component II	Splitting
meridional	17830	18802	972
fac-trans(N, N_g; N_p, O_α)	18089	19256	1167
fac-trans(N, N_g; N_p, O_γ)	17776	18829	1053
fac-trans(N, O_γ; N_p, N_g)	17830	18802	972
fac-trans(N, O_α; N_p, N_g)	18089	19256	1167
fac-trans(N, O_γ; N_p, O_α)	18406	18623	217
fac-trans(N, O_α; N_p, O_γ)	18379	18667	298
Experimental[b]	17990	18740	750

[a]from equations like those in Table 2. Values used (cm^{-1}):[27] Δ_N, 19362; $\Delta_{O\alpha}$, 18118, $\Delta_{O\gamma}$, 17014; Δ_{Ng}, 20400; Δ_{Np}, 19145; Δ_{Og}, 16827.
[b]After Gaussian deconvolution.
[c]Underlined energies are averages from two components.

chloro groups under mild conditions. L-glutamate is also coordinated as a tridentate ligand with meridional geometry in barium and potassium salts of $[Cr(glygly)(L\text{-}glu)]^-$. It is thus feasible to use glycylglycinate to induce meridional coordination, but considerable care, including control of the basicity, must be exercised to prevent the formation of the homochelates.

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