

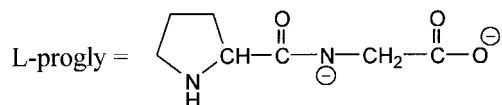
Synthesis and Spectral Properties of [N-(2-Aminoethyl)-1,2-ethanediamine] (L-prolylglycinato)chromium(III) Perchlorate

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A number of metal complexes with various peptides have been studied as model for biological processes.^{1,3} Coordination behaviors of dipeptides to metal ions are delicately different among metals and peptides. The L-prolylglycine (H₂-progly) may coordinate to a metal as bidentate or tridentate. Recently, it has been reported that the carboxyl group of the L-prolylglycine in platinum(II) complex is protonated and does not participate in the coordination.² However, the chromium(III) ion is coordinated *via* the N(imino), N(peptide) and O(carboxylate) atoms of the prolylglycinate.³ The three donor atoms of the progly are located in meridional disposition.



Diethylenediamine [dien = N-(2-aminoethyl)-1,2-ethanediamine] can adopt both facial and meridional dispositions in coordinating to metals, but the dipeptides generally form meridionally coordinated complexes as tridentate ligand because the coordinating peptide nitrogen atom is constrained to approximate coplanarity.^{4,6} Thus they can act as strong template ligands to synthesize meridionally coordinated complexes with other tridentate ligands. While the three nitrogens of the dien are not constrained to planarity, it should serve as a much weaker template ligand.

Here, we report the synthesis and spectral properties of newly prepared [Cr(L-progly)(dien)]ClO₄. The objective of the work was to acquire spectroscopic data that would help to recognize and assign the meridional coordination of Cr(III) complex with two mixed tridentate ligands.

Experimental Section

The chemicals were of reagent grade or better quality and used without further purification. The complex [Cr(L-progly)(dien)]ClO₄ · H₂O was prepared by a method analogous to the synthesis of *mer*-[Cr(glygly)(dien)]ClO₄ · H₂O.⁷ L-prolylglycine (H₂-progly) (0.376 g, 2.18 mmol) and [Cr(ClO₄)₃] · 6H₂O (1.0 g, 2.18 mmol) were dissolved in methanol (16 cm³). Diethylenediamine (0.225 g, 2.18 mmol) was added to the solution. The reaction mixture was heated with continuous stirring for 1.5 hr at 65 °C. And then KOH (0.245 g, 4.36

mmol) dissolved in methanol (4 cm³) was added. After additional heating for 23 hr, the solution was cooled and KClO₄ that had settled out was removed by filtration. The solution was then evaporated to dryness. The residue was dissolved again in a minimum amount of water and passed through a Sephadex G-10 column. It eluted as two bands. The first violet band eluted was identified as [Cr(L-progly)₂]⁺ by comparing electronic spectral data.³ The second brownish red band was collected and concentrated. After standing for several days, water-soluble brownish red precipitate was collected by filtration, washed with ethanol, and air-dried. **Caution!** Although we have experienced no difficulty with the present perchlorate salt, this should be regarded as a potentially explosive compound and treat with care. *Anal.* Found: C, 30.09; H, 6.01; N, 16.21. Calcd. for Cr(C₁₁H₂₃N₅O₃)ClO₄ · H₂O: C, 29.84; H, 5.68; N, 15.82. Analysis for C, H, and N was performed by a Carlo Erba 11080 Elemental Vario EL analyzer at Taegu division of KBSI. The mid-infrared spectrum was obtained with a Mattson Infinities series FT-IR spectrometer using a KBr pellet. The room-temperature visible absorption spectrum was recorded by using a Cary 5e spectrometer. The emission and excitation spectra at 77 K were measured on a Spex Fluorolog-2 spectrofluorometer as described previously.⁸

Results and Discussion

The UV-visible electronic spectra of transition metal complexes with many meridional tridentate dipeptide and pyridine carboxylate appear to exhibit a very intense first band and a weak second band. This is unusual property and can be used for structure elucidation.⁹ The absorption spectrum of [Cr(L-progly)(dien)]ClO₄ in aqueous solution is shown in Figure 1.

The two main bands at 488 and 370 nm are assignable to ⁴A_{2g} → ⁴T_{2g} and ⁴A_{2g} → ⁴T_{1g} transitions, respectively. These transitions are indicative of a pseudo-octahedral configuration for the chromium(III) complexes.¹⁰ The ⁴A_{2g} → ⁴T_{2g} band was two to three times more intense than usual in chromium(III) spectra, while the second band, representing the transition ⁴A_{2g} → ⁴T_{1g}, was less intense than usual, as was observed for the meridional complexes, [Cr(glygly)(dien)]⁺ and [Cr(glygly)(dpt)]⁻.^{4,5} The first energy maximum appeared at the same positions in these spectra. This may be attributed to

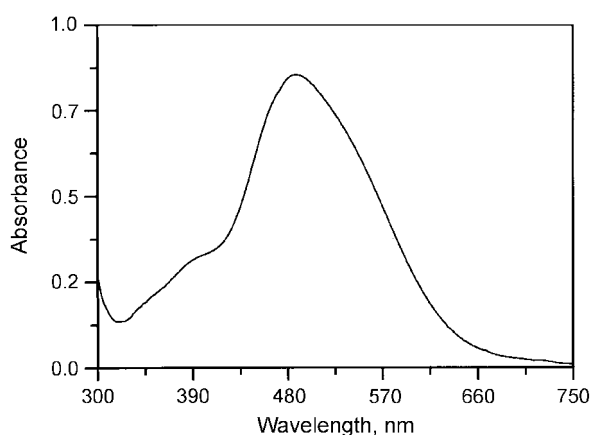


Figure 1. Electronic absorption spectrum of $[\text{Cr}(\text{L-progly})(\text{dien})]^-$ (2×10^{-3} mol dm^{-3}) in aqueous solution.

Table 1. Electronic spectral data for some meridional chromium (III) complexes with tridentates

Complex	λ_1/nm	λ_2/nm	h_1^a	h_2^a	h_1/h_2	Ref.
$[\text{Cr}(\text{glygly})_2]^-$	548	420	200	32	6.20	3
$[\text{Cr}(\text{L-alaala})_2]^-$	545	418	211	53	3.98	9
$[\text{Cr}(\text{L-alagly})_2]^-$	548	416	213	55	3.87	13
$[\text{Cr}(\text{gly-L-ala})_2]^-$	547	419	124	35	3.54	13
$[\text{Cr}(\text{L-progly})_2]^-$	556	425	254	89	2.85	3
$[\text{Cr}(\text{pdc})_2]^-$	552	sh	206	12	17.50	9
$[\text{Cr}(\text{glygly})(\text{dpt})]^+$	490	370	151	21	7.17	5
$[\text{Cr}(\text{glygly})(\text{dien})]^+$	488	362sh	177	49	3.61	7
$[\text{Cr}(\text{L-alaala})(\text{dpt})]^+$	490	380	144	37	3.90	9
$[\text{Cr}(\text{L-progly})(\text{dpt})]^-$	489	375	135	40	3.38	13
$[\text{Cr}(\text{L-progly})(\text{dien})]^-$	488	370sh	82	25	3.28	This work

^a h_1 and h_2 are estimated from heights of the first and second bands in units of absorption coefficients (ϵ), respectively.

identical ligand field strength for glygly and progly. Table 1 summarizes the visible spectral data for some chromium(III) complexes with meridional tridentate ligand. The estimation of relative intensities of shoulder or weak bands were obtained by subtracting the assumed baseline extrapolated from neighboring bands.

The ratio of h_1 and h_2 heights of the first and second bands is 3.28. This confirms to expectations for meridional coordination of the prolylglycinate. In addition to spin-allowed transitions, two spin-forbidden transitions were observed at 667 nm, a weak band assigned to a transition to the ${}^2T_{1g}$ level, and at 720 nm, assigned to a transition to the 2E_g level. The components of higher energy ${}^4A_{2g} \rightarrow {}^2T_{2g}$ transition were also found at 465, 481 and 492 nm from the second derivative of the solution absorption spectrum. In case of $[\text{Cr}(\text{glygly})(\text{dpt})]\text{ClO}_4$, these components were observed at 469, 476 and 487 nm by using the antiresonance effect due to the close-lying states ${}^2T_{2g}$ and ${}^4T_{2g}$.¹¹

The 77 K excitation (left) and emission (right) spectra of $[\text{Cr}(\text{L-progly})(\text{dien})]\text{ClO}_4$ are shown in Figure 2.

A mirror image relationship between the emission and excitation spectra was observed. The complex exhibits at 77 K a sharp line emission spectrum typical of ${}^2E_g \rightarrow {}^4A_{2g}(O_h)$

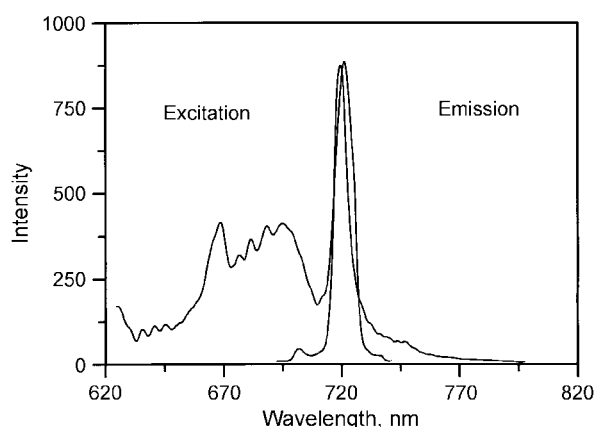


Figure 2. The 77 K excitation (left) and emission (right) spectra of $[\text{Cr}(\text{L-progly})(\text{dien})]\text{ClO}_4$.

phosphorescence in chromium(III) complexes.¹² The very strong peak at 719.7 nm (13895 cm^{-1}) in the emission spectrum can be assigned to the 0-0 band because a corresponding strong peak is found in the excitation spectrum. The vibrational intervals occurring in the emission spectrum can be presumed to involve primarily ring torsion, angle-bending and metal-ligand stretching modes with frequencies below 517 cm^{-1} . The $[\text{Cr}(\text{L-progly})(\text{dien})]\text{ClO}_4$ and $[\text{Cr}(\text{glygly})(\text{dien})]\text{ClO}_4$ had very similar sharp line emission and excitation spectra, so that structural similarity is also likely. The strong peak at 721.2 nm (13866 cm^{-1}) in the excitation spectrum is assigned to the ${}^4A_{2g} \rightarrow {}^2E_g$ transition. Other peaks were found with strong intensities 527, 665, 805, 914, 1091, 1628, 1744 and 1867 cm^{-1} from the lowest-energy zero phonon line. In general, it is not easy to locate positions of the other electronic components because the vibronic sidebands of the 2E_g levels overlap with the zero phonon lines of ${}^2T_{1g}$. The detailed spectral assignment, crystal structure and ligand field analysis are now in progress and will be the subject of our future publications.¹³

Infrared spectra can be used diagnostically to identify the meridional isomer of complexes with tridentate ligands which have coordinating atoms constrained to approximate coplanarity. An absorption peak at 3450 cm^{-1} can be assigned to the O-H stretching of H_2O molecule in the hydrate complex. The strong bands in the regions of $2800\text{-}3300 \text{ cm}^{-1}$ are due to the symmetric and antisymmetric N-H and C-H stretching modes. The very strong absorption at 625 cm^{-1} and strong broad band at 1106 cm^{-1} are assigned to ionic perchlorate.¹⁴ In some cases stretching and bending modes of amino groups in metal-amino acid complexes are sensitive to the stereochemistry of the complexes. Meridional coordinated ligands have different stretching, bending and rocking frequencies in the infrared region than facially coordinated ligands. The carboxylate stretching frequency of the progly is found at 1594 cm^{-1} and amide carbonyl stretching frequency at 1652 cm^{-1} indicating that both the carboxylate and the deprotonated amide nitrogen of prolylglycine are coordinated.^{9,14} As described in Schmidtke and Garthoff's scheme,¹⁵ the infrared spectrum of $[\text{Cr}(\text{L-progly})(\text{dien})]\text{ClO}_4$ has two NH_2

rocking peaks between 700 and 850 cm^{-1} as 717 and 832 cm^{-1} . The N-H wagging motion near 1250 cm^{-1} in the dien is another diagnostic band of meridional isomer. The N-H wagging mode appears at 1246 cm^{-1} as a weak band. There is a corresponding medium intense peak at 1251 cm^{-1} in *mer*-[Cr(dien)Cl₃].¹⁵ These are consistent with meridional coordination. This confirms that the bands can be used to distinguish meridional from facial isomers.¹⁶ The configuration of similar glycyglycinate in [Cr(glygly)(dpt)ClO₄ · H₂O] was established as meridional geometry by our single crystal X-ray structure determination.⁹

All measurement thus clearly support the meridional coordination of the tridentate polyglycinate in the title complex. Since dipeptides are present in biological systems further research ought to be directed towards the possible role of such compounds in biological processes. Meridional coordination at active sites may be possible in reactions catalyzed by metalloenzymes.

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