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Meridional Coordination of Diethylenetriamine to Chromium(III)

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Although meridional coordination of diethylenetriamine (dien = *N*-(2-aminoethyl)-1,2-ethanediamine) is apparently accompanied by more steric strain than facial coordination [1], meridional complexation does occur with a variety of metal ions [2, 3]. Very few chromium(III) examples are known, all of them derived from *mer*-[Cr(dien)Cl$_3$] [4], which is itself prepared from the Cr(IV) peroxo complex [Cr(dien)(O$_2$)$_2$] [5–8], in which the diethylenetriamine appears to be forced into meridional coordination by the coplanar arrangement of the four oxygen atoms [9]. Direct meridional coordination to Cr(III) through ligand substitution by dien has yet to be shown; this is a reflection of the tendency of Cr(III) to exhibit a high degree of stereospecificity towards the thermodynamically most favorable isomer.

Many dipeptides are known to adopt meridional coordination as tridentate ligands, in which the coordinating atoms are constrained to approximate planarity [10–13]. Thus it is possible to use a mono(dipeptide) complex of Cr(III) to synthesize meridional complexes with tridentate ligands that usually coordinate facially. We report here an example of such a procedure using diethylenetriamine.

Experimental

[Cr(glygly)(dien)]ClO$_4$·H$_2$O

Glycylglycine (H$_2$glygly) (1.32 g; 0.010 mol) and Cr(ClO$_4$)$_3$·6H$_2$O (4.58 g; 0.010 mol) were dissolved in methanol (75 cm^3). Diethylenetriamine (1.10 g; 0.010 mol) was added and the solution was refluxed for 1.5 h. KOH (1.12 g; 0.020 mol) was then added in small portions. Refluxing was resumed for an additional 23 h, then the brownish red solution was cooled and the KClO$_4$ that had settled out was removed by filtration. After standing for several days at 5 °C, water-soluble brownish red crystals were collected, washed with ethanol, and air-dried. *Anal.* Calc. for Cr(C$_8$H$_{19}$N$_5$O$_3$)ClO$_4$·H$_2$O: C, 23.86; H, 5.26; N, 17.39; Cr, 12.91. Found: C, 24.17; H, 5.34; N, 17.24; Cr, 12.46%.

Infrared spectra were recorded on a Mattson Cygnus 25 FTIR spectrometer using KBr discs. UV–Vis absorption spectra were measured in aqueous solution with a Hewlett-Packard 8451A diode array spectrometer. Conductivity measurements were taken with a Digital Model 1481-60 conductivity meter.

Results and Discussion

The absorption spectrum of [Cr(glygly)(dien)](ClO$_4$) in water is shown in Fig. 1. The $^4A_{2g} \rightarrow {}^4T_{2g}$ band at 488 nm is two to three times more intense than is usual in Cr(III) spectra ($\epsilon = 160$), while the second band, representing the $^4A_{2g} \rightarrow {}^4T_{1g}$ transition, is less intense than usual. This behavior is quite characteristic of the meridional complexes of Cr(III) and Co(III) with tridentate ligands known thus far [11, 12, 14, 15] and may be diagnostic for meridional coordination. Table 1 gives some comparative data for some meridional tridentate complexes.

Table 2 lists important frequencies from the infrared spectrum of [Cr(glygly)(dien)]ClO$_4$ that relate to the coordination of the two ligands to the metal. Schmidtke and Garthoff [2] have studied in detail the IR spectra of geometric isomers of diethylenetriamine complexes of several metal ions, and concluded that facial and meridional isomers, for either mono- or bis(dien) complexes, may be distinguished by certain features of the spectrum: the CH$_2$ bending region (1400–1500 cm^{-1}) tends to consist of three bands for facial isomers and 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 [2].

With respect to Schmidtke and Garthoff's scheme, the IR spectrum of [Cr(glygly)(dien)]ClO$_4$ has a single band at 1440 cm^{-1} and the NH wagging band at 1288 cm^{-1}. Two bands occur near 850 cm^{-1} (825 and 855 cm^{-1}), while the one band between 700 and 800 cm^{-1} (730 cm^{-1}) is from the glycylglycinate ligand. Another diagnostic band is the N–H stretching mode near 2850 cm^{-1} for the secondary amine in diethylenetriamine. Yoshikawa and Yamasaki found that this band occurs with medium intensity for meridional isomers, but is weak in facial isomers [16]. The weak 2868 cm^{-1} band in [Cr(glygly)(dien)]ClO$_4$ confirms the meridional coordination. The IR spectrum also confirms

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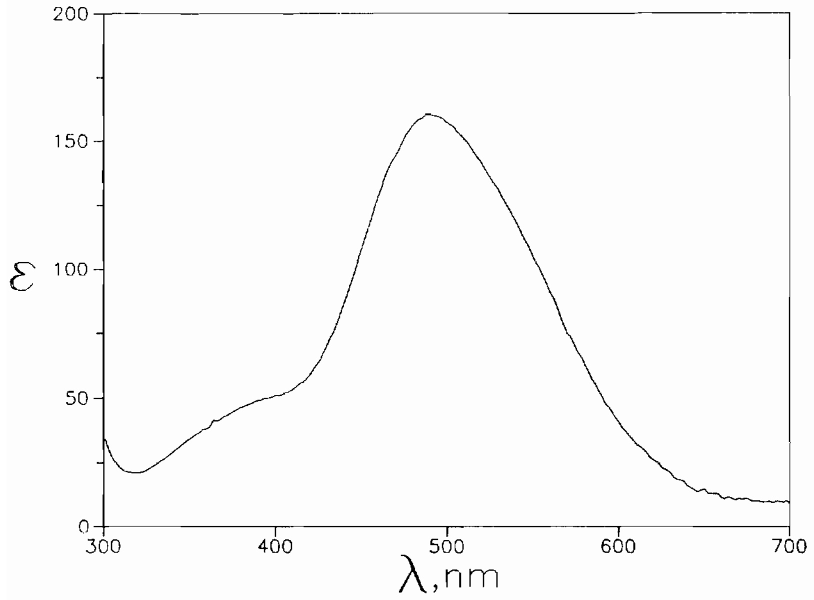

Fig. 1. Electronic absorption spectrum of [Cr(glygly)(dien)]ClO_4 in aqueous solution.

TABLE 1. Electronic Spectral Data for [Cr(glygly)(dien)]$^+$ and Other Meridionally Coordinated Complexes in Aqueous Solution

Complex	λ_1 (nm) (ϵ_{max})	λ_2 (nm) (ϵ_{max})
[Cr(glygly)(dien)]$^+$	488 (160)	362sh
[Co(glygly)(dien)]$^+$	482 (284)	340 (97)
mer-[Co(dien)$_2$]$^{3+}$	466 (137)	341 (105)
[Cr(glygly)$_2$]$^-$	548 (216)	420 (48)
[Cr(PDC)$_2$]$^-$	552 (235)	sh

sh = shoulder.

TABLE 2. Selected Frequencies and Assignments from the IR spectrum of [Cr(glygly)(dien)]$^+$ (cm^{-1})

$\bar{\nu}$	Assignment
3561s	ν(O–H) H_2O
3304s	ν(N–H) –NH_2 (dien)
3258s	ν(N–H) –NH_2 (glygly^{2-})
3158s	ν(N–H) –NH_2 (glygly^{2-})
2868m	ν(N–H) >N–H (dien)
1645vs	ν(C=O) imide (glygly^{2-})
1617s	δ(H–N–H) (glygly^{2-})
1585s	ν_s(CO_2) (glygly^{2-})
1559s	δ(H–N–H) (dien)
1440m	δ(CH_2) (dien)
1288s	ω(NH_2) (dien)
855w	ρ(NH_2)
825w	ρ(NH_2)

the coordination of the deprotonated peptide nitrogen of glycylglycine, through the appearance of the characteristic carbonyl stretching frequency at 1645 cm^{-1} [17]. The glycylglycine carboxylato symmetric stretching frequency is found at 1585 cm^{-1}, indicating that the carboxylate is indeed coordinated [17].

When dissolved in water, [Cr(glygly)(dien)]$^+$ eluted as a single band from an SP-Sephadex cation exchange column, using 0.3 M $NaClO_4$ as the eluent. That eluent concentration is consistent with a unipositive complex. The molar conductance Λ in aqueous solution was 134 Ω^{-1} cm^2, which is characteristic of a 1:1 electrolyte.

All measurements thus clearly support the meridional coordination of tridentate diethylenetriamine in the complex [Cr(glygly)(dien)]$^+$.

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