Spectroscopic Studies of Co(III)–Tripeptide Complexes

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(Received January 17, 1986)

Abstract

Absorption, CD, ^{1}H and ^{13}C NMR spectroscopy techniques have been used to study Co(III)–tripeptide complexes. Results are compared with previous studies.

Introduction

Recent works of Howkins *et al.* [1, 2] have shown that tripeptide molecules are coordinated to Co(III) ion as quadridentate chelates through the terminal NH_2, two peptide N^- and terminal COO^- donors. The NMR conformational analysis have shown that in $[Co(NH_3)_2(Gly–Gly–Phe)]$ and similar tyrosine containing complexes the aromatic ring adopts a conformation adjacent to NH_3 ligand. The similar side-chain conformation of the aromatic amino acid residues in tripeptide ligands were also established in Ni(II) and Pd(II) planar complexes [3] as well as Cu(II) [4] though in these cases the direct metal–aromatic ring interaction was suggested.

In this work we have tried to prepare Co(III)–tripeptide complexes having a bulky imidazole ring bound in apical position. The complexes obtained were studied by absorption, CD, ^{1}H and ^{13}C NMR spectroscopy.

Experimental

$Co(imidazole)_2$ complex was prepared as described earlier [5]. The preparation of Co(III)–tripeptide complexes was undertaken similarly to Evans *et al.* [1, 2]. $Co(imidazole)_2$ complex (0.2 mM) was added with constant stirring to tripeptide (0.4 mM) solution. After 8 h of oxygen bubbling the brown solution containing peroxo complexes were transferred to a refrigerator for approximately 15 h. The solution was filtered prior to being chromatographed on a Dowex column (50–100 mesh, 20 × 600 mm) with water. Three fractions were separated: fraction 1 (pink) eluted rapidly, fraction 2 (orange) was the complex desired, fraction 3 (pink) adhered to the top of the column. The desired compound was rechromatographed twice to ensure purity.

Spectroscopic Measurement

Circular dichroism (CD) spectra were recorded on a JASCO-J-20 automatic recording spectropolarimeter. The absorption spectra were measured on a Beckman UV 5420 spectrophotometer. ^{13}C NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer and ^{1}H NMR spectra on a 500 MHz Bruker spectrometer at 300 ± 2 K. Simulation of the ^{1}H NMR spectra were done as described earlier [3].

Results and Discussion

Absorption and Circular Dichroism Spectra

The visible absorption spectra of the complexes studied have maxima at ≃454 nm ($^{1}A_{1g} \rightarrow {}^{1}T_{1g}$) and at ≃350 nm ($^{1}A_{1g} \rightarrow {}^{1}T_{2g}$) with a low energy shoulder around 525 nm (Table I).

The metal chromophore has a rhombic symmetry under which the triply degenerate cubic d–d transitions $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$, are each split into three components. From the shape of the $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ band it would appear that the low energy transition at 525 nm may be assigned to $^{1}A_{1g} \rightarrow {}^{1}B_{3g}$ (see ref. 2). The energy pattern corresponds well to the results obtained earlier by Evans *et al.* for the diamminecobalt(III)tripeptide complexes [2], and it suggests the quadridentate coordination of tripeptide ligands to Co(III) ion via NH_2, $2N^-$ and COO^- donors.

Also CD spectra in the visible region are similar to those of diammine–Co(III)–tripeptide complexes reported in ref. 2. Two strong Cotton effects associated with the $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ transition are observed in the 530–550 nm and 470–450 nm regions (Table II). The Co–Tyr–Gly–Gly complex has a strong negative

0020-1693/86/$3.50

TABLE I. Absorption Spectra of Cobalt(III) Complexes with Tripeptides[a]

Complex	$^1A_{1g} \rightarrow {}^1T_{1g}$ (B_{3g})		$^1A_{1g} \rightarrow {}^1T_{1g}$		$^1A_{1g} \rightarrow {}^1T_{2g}$	
	λ	ε	λ	ε	λ	ε
Co–imidazole–Gly–Gly–Gly	526sh	75	454	205	350sh	175
Co–Tyr–Gly–Gly			454	206	350sh	217
Co–Leu–Gly–Leu	520sh	34	454	86	345sh	72

[a]λ (nm), ε (M^{-1} cm^{-1}).

TABLE II. Circular Dichroism Spectra of Cobalt(III) Complexes with Tripeptides[a]

Complex	$^1A_{1g} \rightarrow {}^1T_{1g}$ (B_{3g})		$^1A_{1g} \rightarrow {}^1T_{1g}$		$^1A_{1g} \rightarrow {}^1T_{2g}$		$CT_N \rightarrow Co(III)$		$CT_{NH_2} \rightarrow Co(III)$	
	λ	Δε	λ	Δε	λ	Δε	λ	Δε	λ	Δε
Co–Tyr–Gly–Gly	552	−0.81	453	+0.64	355	−0.21	293	+0.48	245sh	−1.59
Co–Leu–Gly–Leu	530	−1.22	470	−0.86	380	+0.01	295	+0.49	240	−1.80

[a]λ (nm), Δε (M^{-1} cm^{-1}).

TABLE III. ^1H Chemical Shifts[a] of Ligands and Cobalt(III) Complexes

Form	CH–Gly	CH–Tyr	CH_2–Tyr	CH–imidazole
Gly–Gly–Gly (pH 9.5)	3.42 4.00 3.78			
Imidazole				7.16 7.78
Complex	3.27 4.23 3.71			6.80 7.25 7.64
Tyr–Gly–Gly (pH 9.5)	3.86 3.72	3.64	2.82	
Complex	3.74 3.59	3.70	2.79 2.85	

[a]In ppm from DSS.

Cotton effect at 552 nm and positive one at 453 nm under the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption band, and a negative peak occurs under the $^1A_{1g} \rightarrow {}^1T_{2g}$ band at 355 nm.

As presented in Table II, three Co(III)–tripeptide complexes exhibit two other Cotton effects in the UV region, *i.e.* positive at ≃295 nm and negative around 240–250 nm. Because the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition is magnetic dipole forbidden for an octahedral complex it is likely that the 295 nm band which is relatively strong as well as the 250 nm Cotton effect correspond to ligand to metal charge transfer transitions, e.g. $N^- \rightarrow Co(III)$ and $NH_2 \rightarrow Co(III)$ transitions, respectively.

The aromatic ring $^1L_b \pi \rightarrow \pi^*$ transitions also occur in this region but close similarity of the spectra of the tyrosine containing complexes to that of Co–Leu–Gly–Leu (Table II) allow us to assign the 295 nm band as a complex transition.

^1H and ^{13}C NMR Data

These are given in Table III and IV. The assignment of both the ^1H and ^{13}C resonances were done similarly to those described earlier [1, 3]. Detailed analysis of the NMR spectra has shown that imidazole remains in the coordination sphere of the metal ion only in the Co–Gly–Gly–Gly complex. The bulky

TABLE IV. ^{13}C Chemical Shifts[a] of Peptides and Cobalt Complexes

Species	COO^-	CO	CH_2	Other
Gly–Gly–Gly (pH 9.5)	177.23	171.62 170.21	43.81 42.99 41.80	
Complex	187.08	179.80 177.38	51.06 48.27 47.91	137.09[b] 126.53[b] 119.38[b]
Tyr–Gly–Gly	176.93	177.53 171.55	56.82 43.75 42.93 39.94	155.42[c] 131.29[d] 128.98[e] 116.20[f]
Complex	187.01	186.21 179.54	60.03 56.83 52.03 48.63	155.42[c] 126.88[d] 126.28[e] 116.27[f]

[a]In ppm from dioxane. [b]CH imidazole. [c]C4 phenyl. [d]C2, 6 phenyl. [e]C1 phenyl. [f]C3, 5 phenyl.

TABLE V. Tyrosine Residue Rotamer Populations

Peptide	Form	J_{AB} (Hz)	J_{AC} (Hz)	J_{BC} (Hz)	n_I[a]	n_{II}[a]	n_{III}[a]
Tyr–Gly–Gly	anion		14.2		0.82		0.18
	complex	−13.7	7.3	6.7	0.45	0.39	0.16

[a]n_I, n_{II} and n_{III} rotamer populations for the isomer notation used for example in refs. 1, 3.

Tyr residue in the Co–Tyr–Gly–Gly species leads to formation of a complex without a large base ring bound to Co(III) ion which in such case is most likely substituted by the solvent molecules. The other interacting feature of the latter complex is that the side-chain conformation of the Tyr residue in the complex is considerably different than that found in diammine–Co(III)–tripeptide complexes [1]. The isomer **III** being most stable in $[Co(NH_3)_2(Tyr–Gly–Gly)]$ complex (n_{III} = 75%) is quite unstable in our species (n_{III} = 16%, Table V).

Both ^1H and ^{13}C chemical shift variations upon Co(III) coordination (Table III) clearly indicate the quadridentate coordination of tripeptide ligand as it was established by X-ray and spectroscopic methods by Evans *et al.* [1, 2].

Acknowledgements

The authors wish to thank the Polish Academy of Sciences for financial support (Problem MR-I-9).

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