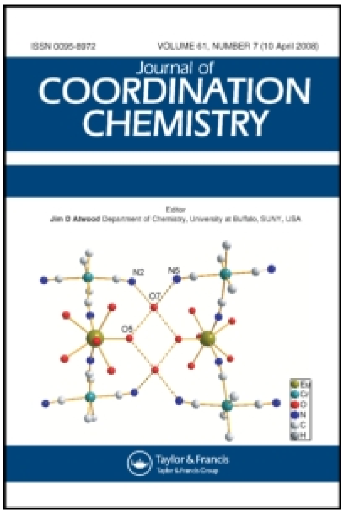

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IDENTIFICATION AND CHARACTERIZATION OF SOME RHODIUM(III) COMPLEXES CONTAINING EDDDA AND 1,3-PDTA LIGANDS

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IDENTIFICATION AND CHARACTERIZATION OF SOME RHODIUM(III) COMPLEXES CONTAINING EDDDA AND 1,3-PDTA LIGANDS

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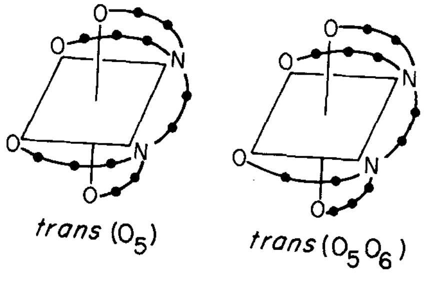
The sexidentate complexes of rhodium(III) with ethylenediamine-N,N′-diacetic-N,N′-di-3-propionic acid (H_4EDDDA) and with 1,3-propanediaminetetraacetic acid (1,3-PDTA) have been prepared and characterized using ^{1}H and ^{13}C nmr and infrared spectra. Two isomers of [Rh(EDDDA]$^-$ were separated and identified as the *trans*(O_5) and *trans*(O_5O_6) isomers.

Key words: Circular dichroism spectra
Nuclear magnetic resonance spectra

INTRODUCTION

A series of yellow rhodium(III) complexes has been obtained from the individual reactions of rhodium(III) chloride with aqueous solutions of neutralized H_4EDDDA (ethylenediamine-*N,N′*-diacetic-*N,N′*-di-3-propionic acid) and with H_4(1,3-PDTA), (1,3-propanediaminetetraacetic acid) using the sealed-tube technique employed by Dwyer and Garvan.[1] A number of complex anions with different charges were isolated via anion exchange chromatography (QAE-Sephadex, A-25, strong acid anion exchanger in the chloride form) and gel filtration (G-10 Sephadex). This paper describes the characterization of complexes bearing a 1 charge by means of ^{13}C and ^{1}H magnetic resonance and infrared spectra. These complexes include sodium salts of two sexidentate isomers of [Rh(EDDDA)]$^-$ and sexidentate [Rh(1,3-PDTA)]$^-$ (see Figure 1). On the basis of the data reported here, the two isomers involving the EDDDA ligand can be assigned the *trans* (O_5) and *trans* (O_5O_6) geometries in accordance with convention described in earlier papers dealing with cobalt(III)[2,3] complexes of EDDA.

The elemental analyses of the complexes are consistent with the following formulations: *trans* (O_5)-Na[Rh(EDDDA)] ·$2H_2O$; *trans* (O_5O_6)-Na[Rh(EDDDA)] ·$3H_2O$; and Na[Rh(1,3-PDTA)] ·2 H_2O.



trans (O_5) *trans* (O_5O_6)

FIGURE 1 Isomers of a sexidentate complex [M(EDDDA)].

Small amounts of complexes with higher charges were separated from the reaction mixtures. These are quinquedentate and/or quadridentate complexes. However, since only small quantities were available their geometries have not yet been determined.

Carbon-13 nmr

High quality carbon-13 nmr spectra were obtained using a JEOL PFT-100 spectrometer operating at *ca.* 25 MHz in the noise decoupled mode. For the two EDDDA complexes, approximately 0.4 M solutions in D_2O were used in 10.0 mm tubes. Owing to the lower stability of the 1,3-PDTA complex only a solution of about 0.2 M concentration in D_2O could

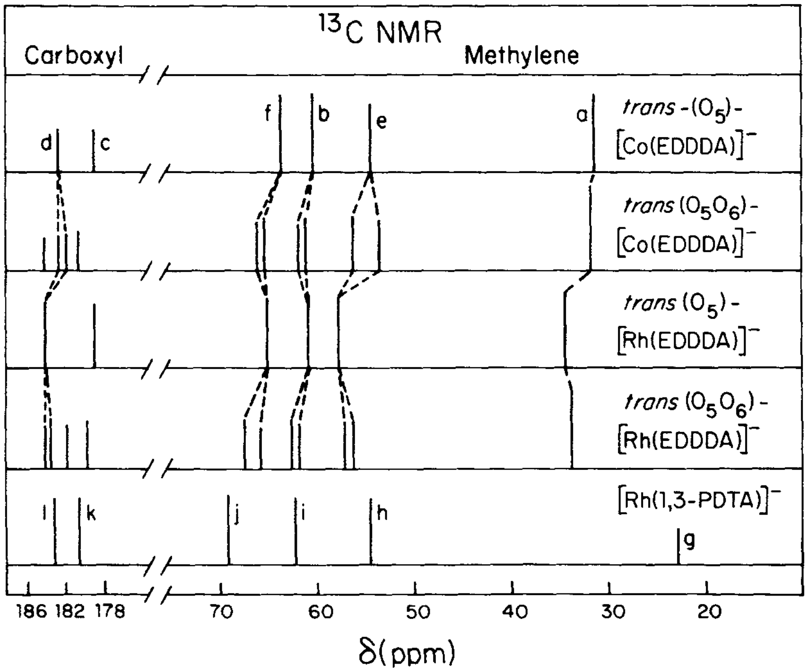


FIGURE 2 Carbon-13 nmr spectra of sexidentate complexes of Co(III) and Rh(III).

be prepared at room temperature. All spectra were measured relative to external TMS dissolved in benzene. The results are shown in stick diagram form in Figure 2 and tabulated in Table I. For comparison the ^{13}C spectra[4] of the corresponding Co(III) isomers of the EDDDA complexes are also given. The similarity between the spectra of the rhodium and cobalt complexes of EDDDA is evident and assignments of resonances for corresponding complexes are the same. Selective decoupling and deuterium exchange studies of *trans* (O$_5$)[Co(EDDDA)]$^-$ have allowed the assignments[4] of the peaks labeled *a*, *b*, *c*, *d*, as follows: *a* – the carbons α to the carboxyl group of the two (in-plane) alaninate (6-membered) rings; *b* – the methylene carbons of the two (out-of-plane) glycinate (5-membered) rings; *c* – the two equivalent carboxyl carbons of the alaninate rings; and *d* – the two carboxyl carbons of the glycinate rings.

The methylene resonance labeled *e* is assigned to the two carbons of the ethylenediamine backbone in accordance with assignments for analogous carbons in a number of Co(III)-EDDDA complexes,[5] and Co(III)-EDTA complexes[6,7] which show that the ethylenediamine methylene resonances appear at higher field (lower ppm) than those of the methylene carbons of the carboxylate arms.[8,9] Finally, the resonance labeled *f* must be associated with the carbons which are β to the carboxyl group of the alaninate rings.

The resonances associated with both *trans* (O$_5$O$_6$) isomers appear in the same regions as those of the *trans* (O$_5$) isomers. But since the *trans* (O$_5$O$_6$) complexes have in-plane and out-of-plane alaninate rings and in-plane and out-of-plane glycinate rings, each carbon should be magnetically distinct. Thus, two resonances result in the *trans* (O$_5$O$_6$) spectra in regions where only one appears in the *trans* (O$_5$) spectra. The α carbons of the alaninate rings are exceptions in that they give rise to only one broad, intense resonance for the *trans* (O$_5$O$_6$) complexes. Under the experimental conditions used for the JEOL PFT-100 the resolution was 1.52 Hz or 0.06 ppm, i.e., peaks separated by 0.06 ppm or more should be clearly separated. This suggests that the α carbons of the alaninate rings are the least affected of all the carbons of the EDDDA ligand by changing the geometry from *trans* (O$_5$) to *trans*-(O$_5$O$_6$) for both Co(III) and Rh(III) complexes.

The most notable differences between the *trans*-(O$_5$O$_6$)-[Rh(EDDDA)]$^-$ and *trans* (O$_5$O$_6$)-[Co-(EDDDA)]$^-$ spectra occur in the carboxyl region. The two lowest field resonances in the *trans* (O$_5$O$_6$)-rhodium spectrum (183.66 and 183.78 ppm) are nearly degenerate, separated by only 0.12 ± 0.03

TABLE I
^{13}C resonance positions[a]

Complex	Carboxyl	Methylene
trans(O_5)-[Co(EDDDA)]$^-$	182.54, 178.88	63.80, 60.31, 54.54, 31.49
trans(O_5O_6)-[Co(EDDDA)]$^-$	183.11, 182.46, 182.13, 180.75	66.15, 65.50, 61.85, 61.12, 56.25, 53.73, 31.82
trans(O_5)-[Rh(EDDDA)]$^-$	183.54, 178.91	65.26, 60.94, 57.71, 34.31
trans(O_5O_6)-[Rh(EDDDA)]$^-$	183.78, 183.66, 181.84, 179.70	67.46, 65.93, 62.76, 61.91, 57.22, 56.37, 34.12
[Rh(1,3-PDTA)]$^-$	183.30, 180.74	69.59, 62.64, 54.84, 23.03

[a] δ (ppm) relative to external TMS dissolved in benzene.

ppm and are very close to the position of the lowest field (glycinate carboxyl) resonance of *trans* (O_5)-[Rh(EDDDA)]$^-$ (183.54 ppm). The closeness of the two resonances in the *trans* (O_5O_6) spectrum to each other and to the *trans* (O_5) resonance suggests the liklihood that all are associated with the glycinate carboxyl carbon. The results also suggest that these carbons do not experience much of a difference in magnetic environment between the two geometrics for the rhodium complexes. However, assuming the aforementioned assignments correct, the alaninate carboxyl carbons, which show resonances separated by 2.14 ppm in the *trans* (O_5O_6)-[Rh(EDDDA)]$^-$ isomer, experience significantly different environments. Similar effects have been observed for methylene resonances in the ^{13}C nmr spectra of various symmetrical-*cis* and unsymmetrical-*cis* isomers of Co(III)-TMDDA (TMDDA = trimethylenediamine-N,N′-diacetate) complexes. In these cases, the correctness of assignments of resonances was verified by deuterium exchange and selective decoupling techniques.

The carboxyl carbon resonances of *trans* (O_5O_6)-[Co(EDDDA)]$^-$, taken alone, are not easily assigned as their pattern differs from that of *trans*-(O_5O_6)-[Rh(EDDDA)]$^-$. However, if the preceding assignments of *trans* (O_5O_6)-[Rh(EDDDA)]$^-$ carboxyl resonances are correct, it would be expected that the glycinate carboxyl resonances of the *trans*-(O_5O_6) cobalt complex would be only slightly separated and quite close to the corresponding resonance in the spectrum of *trans* (O_5)-[Co(EDDDA)]$^-$. It can be seen that the two middle carboxyl resonances (182.13 and 182.46 ppm) are only separated by 0.33 ppm and are very close to the lowest field (glycinate carboxyl) resonance in the *trans* (O_5)-[Co(EDDDA)]$^-$ spectrum. The outer two carboxyl resonances of *trans*-(O_5O_6)-(Co(EDDDA)]$^-$ would then be assigned to the alaninate carboxyls. The resonances assigned to glycinate carboxyl carbons are connected by dashed lines in Figure 2 and the alaninate carboxyl resonances remain unconnected.

The peaks associated with [Rh(1,3-PDTA)]$^-$ are labeled *g* through *l*. The highest field methylene resonance, *g*, is due to the middle carbon of the propylenediamine backbone since this carbon is in the greatest shielding environment. As expected, it is only half as intense as the other methylene resonances. Resonance *h* is assigned to the two terminal carbons of the propylenediamine backbone. These assignments are consistent with those of the carbons of the propylenediamine backbone in a series of Co(III)-TMDDA complexes[5] and in [Co(1,3-PDTA)]$^-$.[10]

It is well known that the x-ray crystal structure[11] of [Co(EDTA)]$^-$ indicates that the in-plane glycinate rings are more strained than those coordinated out-of-plane. The situation is presumed to be similar for complexes of 1,3-PDTA, but with the strain relieved somewhat. X-ray analysis of K[Co(1,3-PDTA)][12] shows that its in-plane glycinate rings are under greater strain than its out-of-plane rings, although the differences are not as great as in the [Co(EDTA)]$^-$ ion.

Treatment of a solution of Na[Rh(1,3-PDTA)] in D_2O with 38% DCl in D_2O and heating for 2 hours at pD∿0.5 results in a solution whose ^{13}C nmr spectrum differs from that of the neutral complex in that some new peaks appear in addition to those of the original sample. Most of the original peaks are shifted slightly (0.15–0.30 ppm) due to the acidic environment. One of the new peaks which appears in the carboxyl region is well upfield of the others, at 169.89 ppm, strongly suggesting the presence of a quinquedentate species[6,7] in addition to the sexidentate complex. However, the peak corresponding to *j* in the spectrum of the neutral complex is considerably broadened and has lost relative intensity. This indicates that the carbon responsible for this resonance has undergone deuterium exchange of its slightly acidic hydrogens. Its ^{13}C resonance is thus decreased in relative intensity since the resonanating ^{13}C nuclei can no longer relax by transferring energy to bound, resonating hydrogen atoms. Deuterium exchange has been used as a means of identifying the methylene groups of the less strained rings of aminopolycarboxylate metal complexes[4,5,8] since Terrill and Reilley postulated on the basis of proton nmr work[13] that the methylene groups adjacent to the carboxyl groups of the less strained rings of EDTA-type metal complexes undergo deuterium exchange more readily than those of the more strained rings. Thus, peak *j* is assigned to the in-plane glycinate methylene carbon and *i* is assigned to the out-of-plane methylene carbon. This result is contrary to the result obtained from the ^{13}C nmr spectrum of [Co(1, 3-PDTA)]$^{-}$[10] after acid-catalyzed deuterium exchange, from which it was determined that the R-ring carbons are more shielded (at higher field) than the G-ring carbons in [Co(1, 3-PDTA)]$^{-}$. However, while this behavior cannot be easily explained, it can be rationalized since it would be expected that [Rh(1,3-PDTA)]$^{-}$ is more strained than [Co(1,3-PDTA)]$^{-}$. It has been found[10] from ^{13}C nmr studies of cobalt (III) complexes structurally related to [Co(EDTA)]$^{-}$ that the more strained complexes seem to have less shielded R-ring methylene carbons. The two carboxyl carbon peaks in the [Rh(1,3-PDTA)]$^{-}$ spectrum, *k* and *l*, are difficult to assign conclusively and assignments will not be attempted here.

Proton nmr

Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer (60 MHz). Approximately 0.2 M solutions of the complexes in D_2O were used with 1% sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DDS) as standard. The spectra of *trans* (O_5)-[Rh(EDDDA)]$^{-}$ and *trans*-(O_5O_6)-[Rh(EDDDA)]$^{-}$ are shown in Figure 3 and that of [Rh(1,3-PDTA)]$^{-}$ is shown in Figure 4. Results are tabulated in Table II. Resonances marked "x" in Figure 3 are spinning side bonds.

The spectra of the two EDDDA isomers are very similar to those of the corresponding cobalt complexes.[2,3] The identification of AB patterns associated with the methylene protons of in-plane (G) glycinate rings and out-of-plane (R) glycinate rings in EDTA-type complexes has been very useful in determining coordination geometries. In general, the AB patterns of the in-plane glycinate methylene protons for complexes of this type have geminal proton coupling constants in the vicinity of 16 Hz and the out-of-plane protons about 18 Hz.[14]

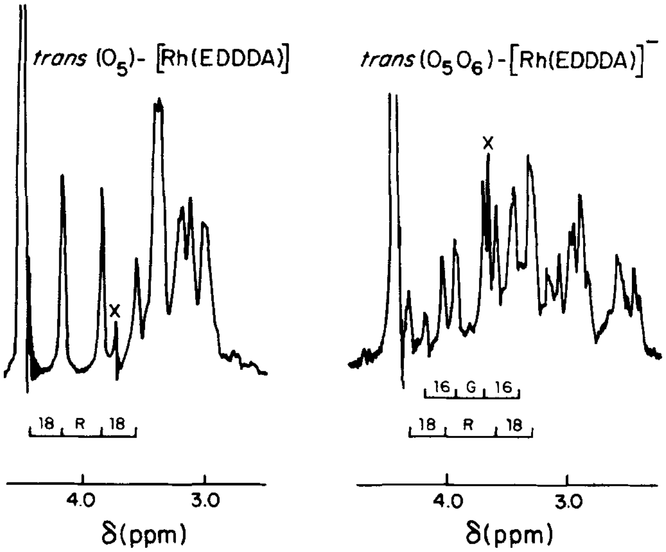


FIGURE 3 Proton nmr spectra of the isomers of [Rh(EDDDA)]$^{-}$.

The spectrum of the rhodium complex assigned the *trans* (O_5) geometry is shifted to lower field than that of *trans*O_5-[Co(EDDDA)]$^{-}$ but otherwise looks quite similar, indeed. This shifting downfield, unfortunately, causes the lowest field member of the only AB pattern (J_{AB} = 18.8 Hz) to be masked by an overlapping intense water resonance. Two AB

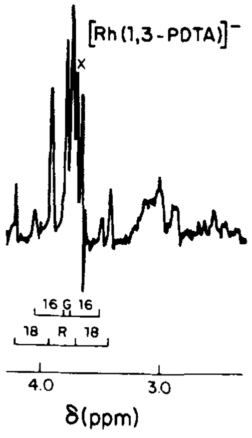


FIGURE 4 Proton nmr spectrum of [Rh(1,3-PDTA)]$^{-}$.

TABLE II
AB patterns of 60 MHz pmr spectra of sexidentate M(III)-EDTA type complexes

Complex	δ_A (ppm)	δ_B (ppm)	δ_A-δ_B (ppm)	J_{AB} (Hz)	R or G[c]
trans(O_5)-[Co(EDDDA)]$^{-}$[a]	4.25	3.52	0.73	18.4	R
trans(O_5)-[Rh(EDDDA)]$^{-}$	4.34[b]	3.68	0.66[b]	18.8	R
trans(O_5O_6)-[Co(EDDDA)]$^{-}$[a]	4.15	3.40	0.75	18.4	R
	4.03	3.43	0.61	16.4	G
trans(O_5O_6)-[Rh(EDDDA)]$^{-}$	4.26	3.51	0.75	17.5	R
	4.12	3.64	0.48	16.0	G
[Rh(1,3-PDTA)]$^{-}$	4.11	3.55	0.56	18.2	R
	3.96	3.64	0.32	15.8	G

[a] From references 2 and 3.

[b] Estimated due to masking of lower field A resonance by water resonance.

[c] R and G denote out-of-plane and in-plane glycinate rings, respectively.

patterns, J_{AB} = 16.0 Hz and 17.5 Hz, are found in the glycinate region of the spectrum of *trans*(O_5O_6)-[Rh(EDDDA)]$^{-}$, as expected, corresponding to in-plane and out-of-plane glycinate rings.

Of course, since only one structural possibility exists for sexidentate [Rh(1,3-PDTA)]$^{-}$ there are two glycinate rings in-plane and two out-of-plane. Thus, two AB patterns appear, one with J_{AB} = 15.8 Hz and one with J_{AB} = 18.2 Hz.

Infrared spectra

It has been found[15–19] that protonated carboxylate groups may be distinguished from coordinated carboxylate groups on the basis of the positions at which infrared absorption bands occur in the carboxylate asymmetric stretch region. In addition, it has been established for *tris*(aminoacidato)cobalt(III) complexes that the asymmetric stretching frequencies of carboxylate groups of five-

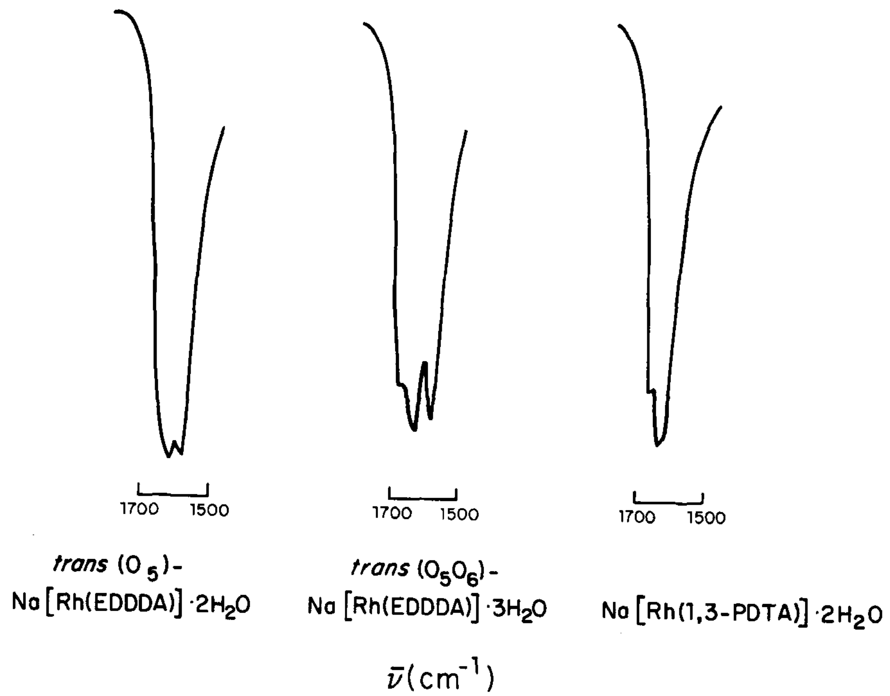


FIGURE 5 Infrared spectra (carboxylate region) of Rh(III) complexes.

TABLE III
The asymmetric carboxyl region for Rh(III)-1,3-PDTA, Rh(III)-EDDDA and some sexidentate M(III)-EDTA type complexes (cm^{-1})[a]

Complex	COOM $\bar{\nu}$ (cm^{-1})	Chelate ring size	$\Delta\bar{\nu}$ (cm^{-1})	Ref.
Na[Co(EDTA)]·2H$_2$O	1638	5		15, 18
Na[Rh(1,3-PDTA)]·2H$_2$O	1640; 1690	5		This work
trans(O$_5$)-Na[Co(S,S-EDDS)]·H$_2$O	1640 1560	5	80	22
trans(O$_5$)-Ag[Cr(S,S-EDDS)]·H$_2$O	1652 1570	5 6	82	24
trans(O$_5$)-Na[Rh(S,S-EDDS)]·H$_2$O	1635 1600	5 6	35	22
trans(O$_5$)-K[Co(EDDDA)]·2H$_2$O	1644 1580	5 6	64	24
trans(O$_5$)-K[Cr(EDDDA)]·2H$_2$O	1618 1590	5 6	28	24
trans(O$_5$)-Na[Rh(EDDDA)]·2H$_2$O	1622 1596	5 6	26	This work
trans(O$_5$O$_6$)-K[Co(EDDDA)]·3H$_2$O	1685; 1630 1612; 1585	5 6		24
trans(O$_5$O$_6$)-Na[Rh(EDDDA)]·3H$_2$O	1680; 1635 1585	5		This work

[a] All spectra obtained from Nujol mulls.

membered[20] chelate rings lie at higher energy (1600–1650 cm^{-1}) than those of six-membered rings.[21] Recent studies[2,3,22–25] of sexidentate complexes with EDTA-type ligands having mixed carboxylate arms of different sizes, *S,S*-EDDS, and EDDDA, support the above trends. The complexes of known *trans*(O$_5$) geometries configuration exhibit two strong bands in the expected region. The higher energy bands have been assigned to the carboxylate groups of the five-membered rings, and the lower energy bands to the six-membered (less strained) rings. The asymmetric carboxylate regions of the ir spectra of the rhodium complexes reported here are shown in Figure 5. The results are tabulated in Table III along with the absorption maxima of previously investigated sexidentate complexes, for comparison.

The [Rh(1,3-PDTA)]$^-$ complex shows one very strong band (1640 cm^{-1}) and one weaker one (1690 cm^{-1}). The higher energy peak is assigned to the carboxyl groups of the more strained rings, which according to the ^{13}C nmr results are the in-plane rings. Thus, the 1640 cm^{-1} peak is assigned to the out-of-plane carboxyl groups. Since protonated carboxyl groups should absorb in the 1700–1750 cm^{-1} region, this is consistent with the idea that the complex is sexidentate. Only one broad band was obtained for [Co(EDTA)]$^-$.[15,18] The [Rh(EDTA)]$^-$ is sexidentate only in the pD range 4–8.[22,26] The sexidentate [Rh(1,3-PDTA)]$^-$ and [Rh(EDDDA)]$^-$ complexes are probably less strained due to their six-membered chelate rings and therefore more resistant to acid or base hydrolysis.

The *trans*(O$_5$)-[Rh(EDDDA)]$^-$ complex, with C$_2$ symmetry, exhibits the expected two peaks, at 1622 cm^{-1} and 1596 cm^{-1} corresponding to carboxyl groups of five-membered (more strained) and six-membered rings, respectively.

The *trans*(O$_5$O$_6$)-[Rh(EDDDA)]$^-$ complex, with only C$_1$ symmetry, does not clearly show four distinct peaks associated with each of the non-equivalent carboxylate groups. However, the region is obviously more complicated than that of the *trans*(O$_5$) complexes. The only other possible sexidentate geometry would be *trans*(O$_6$),[2,3] with C$_2$ symmetry, having two in-plane glycinate rings and two out-of-plane alaninate rings. But this coordination would be expected to give rise to only two ir bands in this region and also would be inconsistent with the ^{13}C and proton nmr spectra obtained.

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