

# Preparation and $^{13}\text{C}$ NMR Study of Carbonato–, Bicarbonato– and Oxalato–Tetraamminecobalt(III) Complexes

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## Abstract

A series of diamagnetic carbonato–, bicarbonato– and oxalato–tetraamminecobalt(III) complexes have been prepared, where the amines are: ammonia, 1,2-diaminoethane (en), 1,3-diaminopropane (tn), 2,2',2''-triaminotriethylamine (tren), and 3,3',3''-triaminotripropylamine (trpn), and the  $^{13}\text{C}$  NMR spectra for these complexes have been examined.  $^{13}\text{C}$  NMR provides a valuable diagnostic probe for the complexes, and assignments of chemical shifts to specific carbons are in most cases readily made. Results for  $[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})]^{2+}$  indicate the presence of both geometric isomers. The studies have relevance to the use of  $^{13}\text{C}$  NMR in examining metal–ligand interactions in systems of biological interest.

## Introduction

There has been recent interest in the roles of simple anions in the binding of metal ions to the transferrins [1, 2]. In particular, carbonate and/or bicarbonate, and also a number of other bifunctional anions such as oxalate, are required in order for the transferrins to bind metal ions; hence these anions have been labeled 'synergistic anions' [3, 4]. Recent  $^{13}\text{C}$  NMR studies of Al(III), Ga(III) and Zn(II) derivatives of both transferrin and ovotransferrin have shown that substitution of bicarbonate by oxalate, although modifying the systems, allows opportunity to analyze the interaction of the synergistic anion with both the protein chain and the metal [2].

In the present study we have prepared a series of diamagnetic tetraamminecobalt(III) complexes of the above mentioned 'synergistic anions', namely carbonate, bicarbonate and oxalate, and we have examined the free ligands and the complexes by  $^{13}\text{C}$  NMR spectroscopy. This systematic study allows

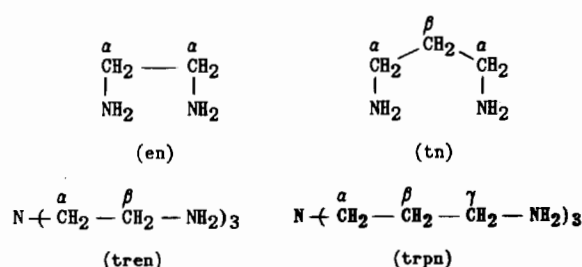


Fig. 1. Amine ligands.

us to compare anion binding in these complexes, and to examine changes as the amine ligands are varied from the simple monodentate amine  $\text{NH}_3$ , to the linear bidentate amines 1,2-diaminoethane (en) and 1,3-diaminopropane (tn), to the tripodal amines 2,2',2''-triaminotriethylamine (tren) and 3,3',3''-triaminotripropylamine (trpn). The carbon skeletons for these ligands and their letter indices are shown in Fig. 1.

## Experimental

1,2-Diaminoethane (en), 1,3-diaminopropane (tn), and 2,2',2''-triaminotriethylamine (tren) were purchased from Aldrich Chemical Co. and were used without further purification. The 3,3',3''-triaminotripropylamine tetrahydrochloride hemihydrate ( $\text{trpn} \cdot 4\text{HCl} \cdot \frac{1}{2}\text{H}_2\text{O}$ ) was supplied by Strem Chemical Co. All other chemicals were reagent grade quality.

**Caution:** Potential hazards of compounds containing both perchlorate and organic ligands always require precautions, including limitations in the amounts handled!

### $[\text{Co}(\text{trpn})(\text{CO}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$

The complex was obtained in a modification\*\* of the method used for the tren cobalt complex

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\*\* First prepared in our laboratory at Boston University by Dr Markus Hediger.

described by Scheidegger [5]. Fifteen mmol (5.14 g) of  $\text{trpn} \cdot 4\text{HCl} \cdot \frac{1}{2}\text{H}_2\text{O}$  was dissolved in 40 ml of water, and 13.52 g of  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  (60 mmol), dissolved in 15 ml of water, was added at 5–10 °C with stirring. The resulting solid was collected by filtration and washed with 10 ml of water. The pH of the filtrate was quickly adjusted to 6.0 by addition of 5 M NaOH. At a temperature of 5 °C, 7.2 g  $\text{PbO}_2$  (30 mmol) and 6.3 g of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (16.4 mmol) in 20 ml of water was added slowly over a period of 15 min under stirring. The temperature was increased to 60–65 °C and maintained for ~4.5 h, then increased to 70–75 °C and maintained for 1.5 h. The mixture was then cooled, filtered through celite using filter paper (Fisher P2, qualitative fine), and 0.6 g  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  (3 mmol) was added to the filtrate. After filtration (to remove  $\text{AgCl}$  and  $\text{Ag}_2\text{CO}_3$ ) the dark violet filtrate was concentrated on a rotary evaporator to a volume of ~30 ml. Ethanol (100 ml) was added and a nitrogen stream was passed through the resulting solution for 15 min. After standing at 0 °C, the resulting dark red crystals were filtered off. The product was dissolved in the minimum volume of water at 70 °C; then 80 ml of ethanol was added and the solution was cooled and stirred at 0 °C and placed in the refrigerator for crystallization (yield 2.0 g, 32%).

*Preparation of  $[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$*

The carbonato complex was converted to the bicarbonato complex by treating 200 mg of finely powdered  $[\text{Co}(\text{trpn})(\text{CO}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$  dropwise and carefully with 60%  $\text{HClO}_4$  (400  $\mu\text{l}$ ). During the addition the red color of the carbonato complex changed to violet. The product was stirred for a few minutes and then filtered off, washed with 25 ml ether, and dried *in vacuo* over  $\text{P}_4\text{O}_{10}$  for 24 h (yield 200 mg, 80%).

$[\text{Co}(\text{en})_2(\text{CO}_3)]\text{Cl}$  and  $[\text{Co}(\text{tn})_2(\text{CO}_3)]\text{Cl} \cdot \text{H}_2\text{O}$  were prepared by reported methods [6, 7], and each was converted to the perchlorate complex by treating a cold solution with a saturated solution of sodium perchlorate. Literature methods were used to prepare  $[\text{Co}(\text{tren})(\text{CO}_3)]\text{ClO}_4$  [8],  $[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$  [9] and  $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{NO}_3$  [10].

A general method was used to prepare all the oxalato complexes, in which the carbonato complex (0.5 mmol), dissolved in the minimum volume of water, was acidified by 0.6 ml of 6 M  $\text{HClO}_4$ , followed by heating on a steam bath for 15 min to expel  $\text{CO}_2$ . Oxalic acid dihydrate (0.5 mmol) was added and the resulting solution was heated for 30 min at 60 °C. On cooling to room temperature, a pink solid separated; this was collected by filtration, washed with methanol and ether, and dried *in vacuo* over  $\text{P}_4\text{O}_{10}$  for two days. The yields varied from 65 to 85%.

The elemental analysis for the oxalato complexes together with  $[\text{Co}(\text{trpn})(\text{CO}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$  and  $[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  are given in Table I. The purities of the other synthesized complexes were checked by comparing their electronic spectra with those reported in the literature.

The elemental analyses for the  $\text{trpn}$  cobalt(III) complexes were performed by Galbraith Laboratories, Knoxville, Tenn., U.S.A., while those for the oxalato complexes were carried out at Ciba-Geigy AG, Basel, Switzerland. Electronic spectra were recorded with a Cary 210 spectrophotometer.  $^{13}\text{C}$  NMR spectra were recorded with a Jeol FX 90Q FT spectrometer operating at 22.49 MHz with a deuterium internal lock. 1,4-Dioxane was used as the internal reference with  $\text{D}_2\text{O}$  as solvent. The  $^{13}\text{C}$  NMR chemical shifts are recorded in ppm relative to TMS.

TABLE I. Analytical Data

Complex	C (%)		H (%)		N (%)		Cl (%)		X (%)	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
$[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl} \cdot 2\text{H}_2\text{O}$	21.28	21.29	5.95	5.94	16.55	16.52	10.47	10.25		
$[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)]\text{ClO}_4 \cdot 3\text{H}_2\text{O}$	17.13	17.29	5.27	5.23	13.32	13.52	8.43	8.50		
$[\text{Co}(\text{tn})_2(\text{C}_2\text{O}_4)]\text{ClO}_4$	24.35	24.17	5.11	5.19	14.20	14.27	8.98	8.77		
$[\text{Co}(\text{tren})(\text{C}_2\text{O}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$	23.40	23.44	4.91	4.99	13.64	13.67	8.63	8.53		
$[\text{Co}(\text{trpn})(\text{C}_2\text{O}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$	29.18	29.51	5.79	5.78	12.38	12.47	7.83	7.92		
$[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	8.39	8.79	4.58	4.71	24.48	23.07			3.15	3.13 <sup>a</sup>
$[\text{Co}(\text{trpn})(\text{CO}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$	28.28	28.28	6.17	6.02	13.19	12.99			13.88	13.79 <sup>b</sup>
$[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	22.48	22.46	5.28	5.22	10.49	10.50	13.27	13.34		

<sup>a</sup>%  $\text{H}_2\text{O}$ . <sup>b</sup>%  $\text{Co}$ .

## Results and Discussion

We have prepared a series of previously known cobalt(III) amine-carbonato and amine-oxalato complexes where the amines are  $(\text{NH}_3)_4$ ,  $(\text{NH}_3)_5$ ,  $\text{en}_2$ ,  $\text{tn}_2$  and  $\text{tren}$  [5–10], as well as the cobalt(III)  $\text{trpn}$ -carbonato and the new cobalt(III)  $\text{trpn}$ -aquabarbonato and  $\text{trpn}$ -oxalato complexes, and we have examined these and the free ligands by  $^{13}\text{C}$  NMR. Complexes with the quadridentate tripodal ligands  $\text{trpn}$  and  $\text{tren}$ , which require the remaining two coordination positions in octahedral complexes to assume *cis* geometry [11, 12], have been of special value in studies of metal ion promoted reactions of polyphosphates and phosphate esters [13]. For the  $\text{Co}(\text{trpn})^{3+}$  complexes examined here, electronic

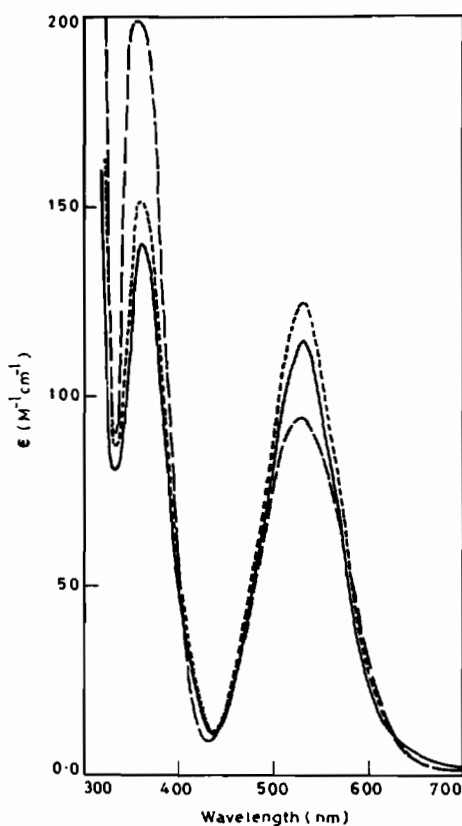


Fig. 2. Electronic spectra for aqueous solutions of: ----  $[\text{Co}(\text{trpn})(\text{CO}_3)]^+$ , —  $[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})]^{2+}$ , - · -  $[\text{Co}(\text{trpn})(\text{C}_2\text{O}_4)]^+$ .

spectra are shown in Fig. 2 and molar absorptivity coefficients are given in Table II.

For  $[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})]^{2+}$  the presence of just two low intensity bands in the visible–near UV region, and the great similarity of the spectrum to those for the carbonato and oxalato complexes, argues for a *cis* relation between the coordinated  $\text{H}_2\text{O}$  and  $\text{OCO}_2\text{H}^-$  [14]. However, these electronic spectra provide no guidance on whether our preparation represents one or both of the possible geometric isomers [15] which are shown in Fig. 3.

$^{13}\text{C}$  NMR chemical shifts for ligands in diamagnetic metal complexes are readily observed, although the magnitudes and even directions of the shifts are not easy to predict. On the other hand, empirical observations and comparisons of spectra can provide considerable information about the complexes, including detail about geometrical isomers. A variety of such studies have been made on organometallic and metal carbonyl complexes [16, 17]. Studies of special relevance to the present work, using  $^{13}\text{C}$  NMR, have been carried out on the binding mode of oxalate in some cobalt(III) complexes [18], on the characterization of some  $\mu$ -carboxylato complexes of cobalt(III) [19], on tris(diamine)-cobalt(III) complexes containing five- and six-membered rings [20], and, as mentioned before, on Al(III), Ga(III) and Zn(II) derivatives of transferrin and ovotransferrin [2], here using  $^{13}\text{C}$  enriched bicarbonate and oxalate. In their study of  $[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)(\text{NO}_2)]$ , Cooper *et al.* [18] observed two signals: one of these, at 170 ppm, was assigned to the bound carboxylate, and the other, at 178 ppm, was assigned to the dangling carboxylate.

The  $^{13}\text{C}$  NMR chemical shifts obtained in the present study for the free ligands (the amines,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{C}_2\text{O}_4^{2-}$ ) and for their cobalt(III) com-

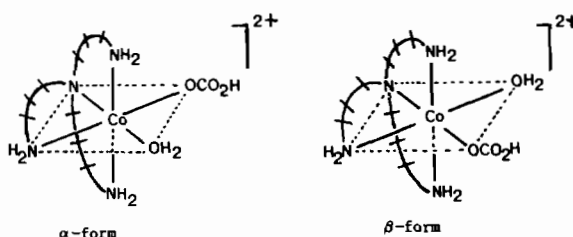


Fig. 3. Possible isomers for  $[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})]^{2+}$ .

TABLE II. Electronic Spectra of Cobalt(III) Complexes of 3,3',3''-Triaminotripropylamine in Water at 25 °C

Complex	$\lambda_{\text{max}}(\epsilon)^a$	$\lambda_{\text{min}}(\epsilon)$	$\lambda_{\text{max}}(\epsilon)$	$\lambda_{\text{min}}(\epsilon)$
$[\text{Co}(\text{trpn})(\text{CO}_3)]\text{ClO}_4 \cdot \text{H}_2\text{O}$	532(125)	434(11.2)	363(153.3)	334(86.7)
$[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})](\text{ClO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	532(108.5)	436(11.7)	362(139.3)	335(88.9)
$[\text{Co}(\text{trpn})(\text{C}_2\text{O}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$	530(94.1)	430(9.6)	363(198.6)	330(89.3)

<sup>a</sup> $\lambda$  in nm;  $\epsilon$  in  $\text{M}^{-1} \text{cm}^{-1}$ .

TABLE III.  $^{13}\text{C}$  NMR Chemical Shifts<sup>a</sup> for Ligands and Cobalt(III) Complexes<sup>b</sup>

Ligand of complex	Chemical shift, $\delta$ (ppm)			
	$\text{CO}_n$	$\alpha\text{-C}$	$\beta\text{-C}$	$\gamma\text{-C}$
$\text{HCO}_3^-$	161.4			
$\text{CO}_3^{2-}$	169.4			
$\text{C}_2\text{O}_4^{2-}$	174.1			
en		44.1		
tn		39.4	36.1	
tren		57.2	38.8	
trpn		51.0	37.3	22.4
$[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]^+$	168.2			
$[\text{Co}(\text{NH}_3)_4(\text{CO}_3)]^+$	166.1			
$[\text{Co}(\text{en})_2(\text{CO}_3)]^+$	163.1	45.5, 44.4		
$[\text{Co}(\text{tn})_2(\text{CO}_3)]^+$	167.9	39.6	26.5	
$[\text{Co}(\text{tren})(\text{CO}_3)]^+$	164.1	59.9, 56.2	41.9, 41.6	
$[\text{Co}(\text{trpn})(\text{CO}_3)]^+$	163.3	53.8, 51.7	34.1, 33.2	19.5, 17.1
$[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})]^{2+}$	168.2	61.5, 58.4	39.0, 38.1	24.1, 22.5
		57.5, 56.6	37.8, 37.6	21.7
$[\text{Co}(\text{NH}_3)_4(\text{C}_2\text{O}_4)]^+$	169.6			
$[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)]^+$	169.5 <sup>c</sup>	44.6, 44.9		
$[\text{Co}(\text{tn})_2(\text{C}_2\text{O}_4)]^+$	177.5	39.0	26.1	
$[\text{Co}(\text{tren})(\text{C}_2\text{O}_4)]^+$	170.1	62.8, 58.4	46.8, 44.9	
$[\text{Co}(\text{trpn})(\text{C}_2\text{O}_4)]^+$	168.9	58.8, 56.9	38.4, 37.3	24.0, 21.6

<sup>a</sup>The  $^{13}\text{C}$  NMR chemical shifts are reported as ppm relative to TMS. <sup>b</sup>pH values: for carbonato complexes, 7–9; for oxalato complexes, ~4.5. <sup>c</sup>Reported as 169 ppm in ref. 18.

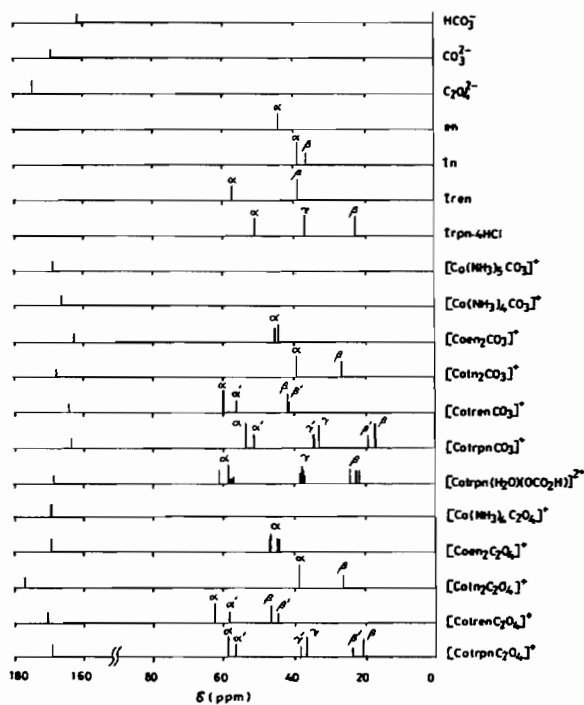


Fig. 4. Positions of  $^{13}\text{C}$  NMR signals for the free ligands and their cobalt(III) complexes.

plexes are presented in Table III and in Fig. 4. Assignments for carbons in the free amines follow from literature assignments [21]. Although there

have been reports that chelation results in down-field chemical shifts for carbons in the vicinity of the coordination site [22, 23], we see (Table III, Fig. 4) that coordination can result in upfield shifts, of 1–6 ppm for carbonate and of 4–5 ppm for oxalate, although for  $[\text{Co}(\text{tn})_2(\text{C}_2\text{O}_4)]^+$  a down-field shift of 3.4 ppm is observed.

The  $^{13}\text{C}$  NMR signals for the methylene carbons in the complexes  $[\text{Co}(\text{en})_2(\text{CO}_3)]^+$  and  $[\text{Co}(\text{en})_2(\text{C}_2\text{O}_4)]^+$  ions consist of two closely separated signals of equal intensity, shifted very slightly down-field, which we ascribe to methylene carbons bound to the nitrogens *cis* to both coordinated oxygens, and to methylene carbons bound to the nitrogens *cis* to one and *trans* to the other coordinated oxygen. For the corresponding  $[\text{Co}(\text{tn})_2(\text{CO}_3)]^+$  and  $[\text{Co}(\text{tn})_2(\text{C}_2\text{O}_4)]^+$ , the signals for the two types of methylene carbon directly bound to nitrogen ( $\alpha, \alpha'$ )

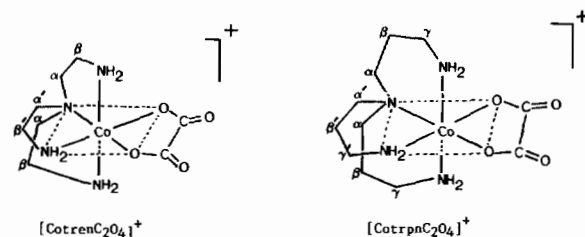


Fig. 5. Schematic drawing for  $[\text{Co}(\text{tren})(\text{C}_2\text{O}_4)]^+$  and  $[\text{Co}(\text{trpn})(\text{C}_2\text{O}_4)]^+$ .

are just distinguishable for the carbonato complex but not for the oxalato complex; for both complexes the signals for the  $\beta$ -carbons are well separated from those for the  $\alpha$ -carbons, more so than in the free trn ligand (see Fig. 4).

For  $[\text{Co}(\text{tren})(\text{CO}_3)]^+$  and  $[\text{Co}(\text{tren})(\text{C}_2\text{O}_4)]^+$  comparison with the free ligand and the 2:1 intensity ratios lead to unambiguous assignments for the four geometrically distinct tren carbons (Figs. 4 and 5). Extension of this analysis to  $[\text{Co}(\text{trpn})(\text{CO}_3)]^+$  and  $[\text{Co}(\text{trpn})(\text{C}_2\text{O}_4)]^+$  is straightforward: thus, for each complex there are two  $\alpha$ -carbons, two  $\beta$ -carbons and two  $\gamma$ -carbons in the arms which include the primary amine nitrogens that are *cis* to both coordinated oxygens; the other three carbons,  $\alpha'$ ,  $\beta'$  and  $\gamma'$ , each of which is unique, are in the arm which includes the primary amine nitrogen which is *cis* to one coordinated oxygen and *trans* to the other.

Finally, we will comment on the result for  $[\text{Co}(\text{trpn})(\text{H}_2\text{O})(\text{OCO}_2\text{H})]^{2+}$ . Here we see a more complex pattern for the trpn carbons. The simplest expectation is a pattern of six signals for each of the two isomers, similar to that seen for  $[\text{Co}(\text{trpn})(\text{CO}_3)]^+$  or  $[\text{Co}(\text{trpn})(\text{C}_2\text{O}_4)]^+$  (Fig. 4, or Table III). However, more complex patterns would not be unlikely, since no two of the nine trpn carbons can be fully equivalent without rapid ring conformational changes. The observed spectra can in fact be understood on the assumption that we are seeing a superposition of spectra due to the two geometric isomers, with some additional splitting due to ring conformational differences. Detailed analysis, however, must await further experimentation on these and related systems.

In conclusion, the present studies show ways in which  $^{13}\text{C}$  NMR can provide valuable information about the environments of the carbons in some simple diamagnetic metal chelates.

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