

An Interpretation of ^1H and ^{13}C Chemical Shifts of the Glycinato Ligand in Mixed-Ligand Cobalt(III) Complexes

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The influence of magnetic anisotropy of the cobalt(III) ion on ^1H and ^{13}C chemical shifts of the glycinato ligand was calculated for the $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ complexes (oxH₂ = oxalic acid; glyH = glycine; en = ethylenediamine). It was shown that magnetic anisotropy determines chemical shifts of the glycinato methylene protons throughout the series. It also significantly influences the ^{13}C chemical shifts of the carboxylato carbon. After correction of the ^{13}C chemical shifts for the contribution from magnetic anisotropy, the influence of trans ligands on carboxylato and methylene carbons of the glycinato chelate is clearly demonstrated.

Introduction

The interpretation of chemical shifts of the nuclei of ligands in cobalt(III) complexes is important for practical as well as for theoretical reasons, and it has been the subject of study by numerous authors.¹⁻¹³ The influence of magnetic anisotropy of the cobalt(III) ion on chemical shifts of nuclei in ligands^{1-3,6-10} received their greatest attention. Especially studied were the pentaamminecobalt(III) complexes where proton chemical shift data pointed to the influence of cobalt d-electron magnetic anisotropy^{2,3} upon the former, as confirmed later by detailed calculations.^{7,9,10} In this case a theoretical relation between the proton and ^{59}Co chemical shielding was successfully applied for calculating proton chemical shifts.⁷⁻¹⁰ Recent measurements of the anisotropy of the magnetic susceptibility in a single crystal of the complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ ¹³ have also confirmed the influence of such anisotropy upon chemical shifts of ammine protons, although the agreement of calculated and experimentally obtained values was not quite satisfactory. Differences in chemical shifts of methylene protons of geometrically nonequivalent amino-carboxylato chelates were also successfully explained through the influence of cobalt ion anisotropy.⁸

For chemical shifts of other examined nuclei (^{13}C , ^{14}N , ^{15}N , ^{19}F) a correlation between them and cobalt(III) magnetic anisotropy has not yet been found. However, the considerable influence of ligands in the trans position upon these shifts was noticed.^{4,5,13-16} This influence is mainly attributed to a change in the paramagnetic term of the nuclear shielding due to electronic charge changes or changes of the average electronic excitation energy. The importance of the electric field effect on these shifts was also considered.¹¹⁻¹³

In this study, continuing our earlier NMR examinations of mixed cobalt(III) complexes containing the glycinato ligand,^{12,17} we have undertaken to investigate ^1H and ^{13}C glycine chemical shifts in the $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ complexes. This series is very suitable since it may be looked upon as a $\text{CoN}_{6-x}\text{O}_x$ complex type which has a very well-defined ligand field symmetry,¹⁸ thus enabling the study of the influence of magnetic anisotropy on methylene protons of the glycinato ligand through the whole series. Moreover, these complexes contain ligands suitable for the study of trans influences. Since the series comprises complexes with charges ranging from 2- to 2+, as well as neutral complexes, the examination of the influence of the electric field on chemical shifts under investigation is also made possible. Furthermore, the chelate five-membered ring which glycinato ligand forms with the cobalt(III) ion has a relatively stable geometry. Finally, in these complexes proton and carbon nuclei are sufficiently distant from the cobalt nucleus for the point-dipole approximation to be applied in the consideration of the influence of magnetic anisotropy.

Data for ^1H and ^{13}C chemical shifts for the majority of complexes of the $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ series are reported in the literature.^{8,12,18-20} However, since in our study it was indispensable to compare only values obtained under identical experimental conditions, chemical shifts of complexes under investigation have been determined anew.

Experimental Section

The synthesis of the complexes under consideration is described elsewhere (see Table I).

For NMR measurement, complexes were dissolved in D₂O at concentrations ranging from 5 to 20 mg cm⁻³; at such low concentrations (~10⁻² M) no concentration dependence on chemical shifts was observed. $[\text{Co}(\text{gly})_3]$, a practically undissolvable complex in water, was dissolved in a D₂O solution of 20 mg cm⁻³ of LiNO₃. Measurements were carried out on a Bruker SXP-100 Fourier transform spectrometer at a temperature of 25 ± 1 °C.

^1H spectra were recorded at a frequency of 90 MHz (D₂O lock). Chemical shifts were given in relation to Me₄Si, with the use of acetone ($\delta = 2.14$ Me₄Si) as the internal standard.

^{13}C spectra were recorded at a frequency of 22.63 MHz (D₂O lock) in the proton noise decoupled mode. Chemical shifts were presented in relation to Me₄Si by using dioxane ($\delta = 67.4$ Me₄Si) as the internal standard.

^{59}Co spectra were recorded at a frequency of 21.5 MHz (external ^1H lock). Here, chemical shifts were given in relation to $[\text{Co}(\text{N}$

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Table I. ^{13}C and ^1H Chemical Shifts (and Calculated Cobalt(III) Magnetic Anisotropy Influence) of Glycinato Ligand Methylene Proton (H_α), Methylene Carbon (C_α), and Carboxylato Carbon (C_{OO}), as well as ^{59}Co Chemical Shifts, in the Series of $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ Complexes

no.	complex	ref	$\delta(^1\text{H}_\alpha)^a$	$\delta(^{13}\text{C}_\alpha)^a$	$\delta(^{13}\text{C}_{\text{OO}})^a$	$\delta(^{59}\text{Co})^b$
1	$[\text{Co}(\text{en})_3]\text{Cl}_3$	21				-1030
2	$[\text{Co}(\text{gly})(\text{en})_2]\text{Cl}_2$	18	3.60 (-0.06)	46.6 (-0.07)	185.8 (0.92)	-300
3	<i>trans</i> (O)- $[\text{Co}(\text{gly})_2(\text{en})]\text{Cl}$	18	3.59 (-0.11)	45.7 (-0.14)	186.6 (1.85)	800
4	<i>cis</i> (O)- C_2 - $[\text{Co}(\text{gly})_2(\text{en})]\text{Cl}$	18	3.65 (-0.16)	47.0 (-0.36)	186.4 (0.30)	550
5	<i>cis</i> (O)- C_1 - $[\text{Co}(\text{gly})_2(\text{en})]\text{Cl}$	18	3.60 (-0.16)	46.7 (-0.36)	186.4 (0.30)	550
6	<i>mer</i> - $[\text{Co}(\text{gly})_3]$	22	3.40 (0.11)	46.9 (0.29)	185.1 (0.62)	1740
			3.60 (-0.22)	46.4 (-0.42)	187.0 (0.69)	
			3.34 (0.05)	47.7 (0.21)	187.0 (-1.18)	
			3.60 (-0.28)	46.7 (-0.65)	185.7 (0.87)	
7	<i>fac</i> - $[\text{Co}(\text{gly})_3]$	22	3.40 (0)	47.8 (0)	186.3 (0)	1410
8	<i>cis</i> (N)- C_1 - $\text{K}[\text{Co}(\text{ox})(\text{gly})_2]$	18	3.58 (-0.11)	48.2 (-0.29)	185.9 (-0.62)	2420
			3.43 (-0.06)	46.8 (-0.07)	186.2 (0.92)	
9	<i>cis</i> (N)- C_2 - $\text{K}[\text{Co}(\text{ox})(\text{gly})_2]$	18	3.58 (-0.06)	47.6 (-0.07)	186.0 (0.92)	2470
10	<i>trans</i> (N)- $\text{K}[\text{Co}(\text{ox})(\text{gly})_2]$	18	3.70 (-0.33)	47.0 (-0.71)	187.0 (0.60)	2920
11	$\text{K}_2[\text{Co}(\text{ox})_2(\text{gly})]$	18	3.52 (-0.16)	47.7 (-0.36)	186.9 (0.30)	3680
12	$\text{K}_3[\text{Co}(\text{ox})_3]$	18				4800

^a In ppm. ^b In ppm to $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

$\text{H}_3)_6]\text{Cl}_3$ aqueous solution as the external standard.

The results obtained are given in Table I. The proton chemical shifts are in agreement with those already reported,^{8,16} within the limits of the experimental error. The obtained ^{13}C chemical shifts correspond well to those known so far,^{10,12} with the exception of data published by Ama and Yasui.²⁰ In the latter case there is a systematic deviation of about +1 ppm for methylene carbon shifts and of about -1 ppm for carboxylato carbon shifts. This is probably due to the fact that the authors determined chemical shifts by using an external standard.

Results and Discussion

While considering ^{59}Co chemical shifts, we have recently shown¹⁷ that magnetic anisotropy in complexes from the $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ series may be successfully explained on the basis of ligand field theory. Here, the magnitude of the anisotropy depends not only on the difference of d-electron excitation energies along the principal axes of the complexes but also upon the orbital reduction factor of the d orbitals. Ignoring reduction of the orbital moment may lead to greater deviations of computed from real anisotropy values.⁷ Correlation on ^{59}Co chemical shifts with first excitation energies of the d electrons enables the determination of that factor.²³⁻²⁵ The correlation for the given complex series is given by the expression¹⁷

$$\sigma^p(^{59}\text{Co}) = -(32/3)\beta^2\langle r^{-3} \rangle k'^2(\Delta_{xx}^{-1} + \Delta_{yy}^{-1} + \Delta_{zz}^{-1}) \quad (1)$$

where β stands for the Bohr magneton, r is the distance of the d electron from the cobalt nucleus, k' represents the orbital reduction factor of the d orbital, and Δ_{ii} are first excitation energies along the principal axes of the complex. These excitation energies may be determined from the partly resolved first absorption band.¹⁷ However, for complexes from this series it was shown that excitation energies along the principal axes may be well predicted on the basis of the ligand field theory;¹⁸ hence those values have been used in the present study.

Upon correlation of ^{59}Co chemical shifts with transition energies according to expression 1, it is derived from the slope (Figure 1) that

$$B = 32\beta^2\langle r^{-3} \rangle k'^2 = 4.30 \times 10^{-5} \text{ nm}^{-1} \quad (2)$$

The above value, which takes into account the contribution made by the orbital reduction factor, was used later in analysis of the influence of magnetic anisotropy of the cobalt(III) ion upon ^1H and ^{13}C chemical shifts of the glycinato ligand.

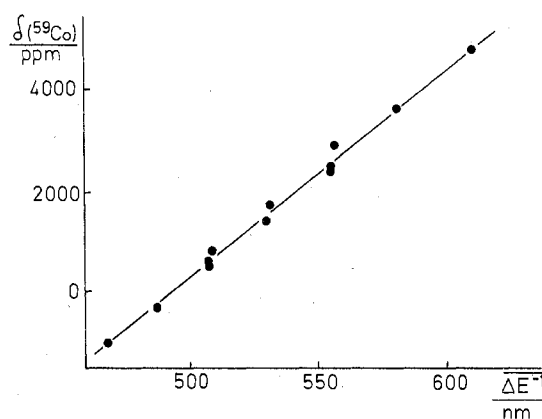


Figure 1. Correlation of ^{59}Co chemical shifts with mean value of reciprocal d-electron transition energies for the examined $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ complex series.

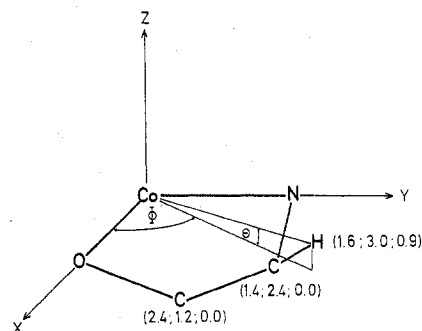


Figure 2. Typical geometry of chelated glycinato ligand in cobalt(III) complexes.

Nakashima, Sakaguchi, and Yoneda⁹ set up the theoretical relation between ^{59}Co paramagnetic shielding and shieldings on nuclei included in ligands (N), namely

$$\sigma^p(\text{N}) = -\left(\frac{1}{R^3} - \frac{3\vec{R}\cdot\vec{R}}{R^5}\right) \frac{1}{2\langle r^{-3} \rangle} \sigma^p(^{59}\text{Co}) \quad (3)$$

Here, R is the distance from cobalt to the N nucleus, while r is the distance of the d electron from the cobalt nucleus. This relation, combined with expression 1, gives the influence exerted by magnetic anisotropy of the cobalt nucleus on the shielding of ligands' nuclei in a form suitable for calculation:

$$\sigma^p(\text{N}) = B \frac{R^{-3}}{6\langle r^{-3} \rangle} |(1 - 3 \cos^2 \phi \cos^2 \theta) \Delta_{xx}^{-1} + (1 - 3 \sin^2 \phi \cos^2 \theta) \Delta_{yy}^{-1} + (1 - 3 \sin^2 \theta) \Delta_{zz}^{-1}| \quad (4)$$

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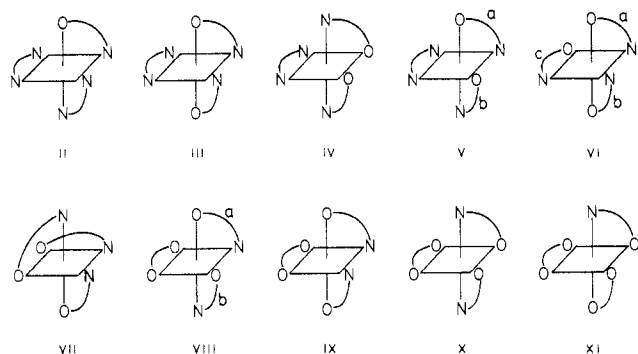


Figure 3. Glycinato ligand positions in the examined $[\text{Co}(\text{ox})_x(\text{gly})_y(\text{en})_z]$ complex series.

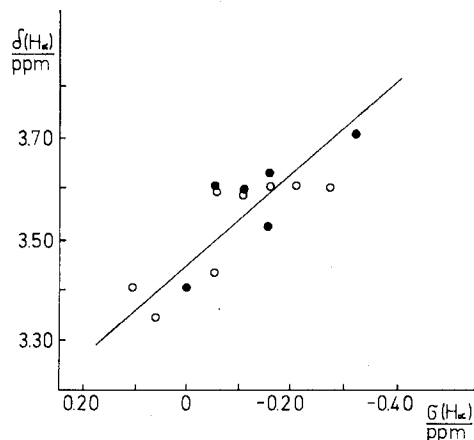


Figure 4. Correlation between methylene proton chemical shifts and computed cobalt(III) magnetic anisotropy influence. Correlation is unambiguous for values marked by solid circles.

On the basis of the above expression and typical geometry of the glycinato ligand²⁶ (Figure 2), the expressions (5) for the influence of d-electron magnetic anisotropy on methylene proton (H_α), methylene carbon (C_α), and carboxylato carbon (C_{oo}) are obtained, where the value of $\langle r^{-3} \rangle = 5.77$ au was used.^{9,10}

$$\begin{aligned} \sigma^p(H_\alpha) &= 3.85 \times 10^{-9}(0.41\Delta_{xx}^{-1} - 1.22\Delta_{yy}^{-1} + 0.81\Delta_{zz}^{-1}) \\ \sigma^p(C_\alpha) &= 8.25 \times 10^{-9}(0.24\Delta_{xx}^{-1} - 1.24\Delta_{yy}^{-1} + 1.00\Delta_{zz}^{-1}) \\ \sigma^p(C_{\text{oo}}) &= -17.8 \times 10^{-9}(1.48\Delta_{xx}^{-1} - 0.48\Delta_{yy}^{-1} + 1.00\Delta_{zz}^{-1}) \end{aligned} \quad (5)$$

The results of computation of magnetic anisotropy for all glycinato ligand positions in the series of complexes examined (Figure 3) are given in Table I. As may be seen from the table, the strongest influence of magnetic anisotropy is displayed at the carboxylato carbon, while for H_α and C_α the influence is less pronounced. However, this influence on proton shielding is sufficiently strong for one to suspect it to be the dominating factor determining differences in methylene proton shielding in the complexes examined. Proof of this follows from the correlation of measured proton shifts with computed magnetic anisotropy influence (Figure 4). Satisfactory correlation and the unit slope provide undoubted proof that proton chemical shifts are mainly given by relation 5. It should be noted that, for complexes which contain only one glycinato ligand and two or three geometrically equivalent glycinato ligands, respectively, the correlation between computed magnetic anisotropy values and found chemical shifts is unambiguous (Figure 3:

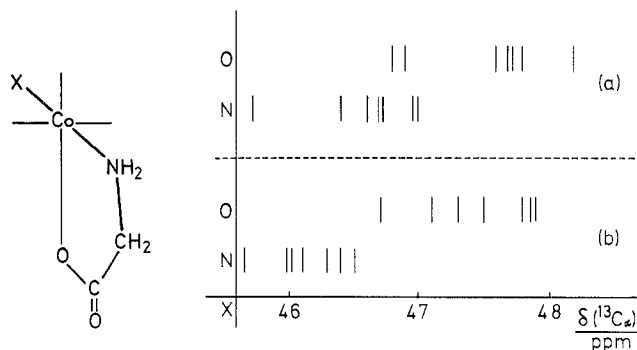


Figure 5. The influence of ligand in trans position to the NH_2 group on methylene carbon chemical shifts. ^{13}C chemical shifts before (a) and after (b) correction for the contribution from d-electron magnetic anisotropy.

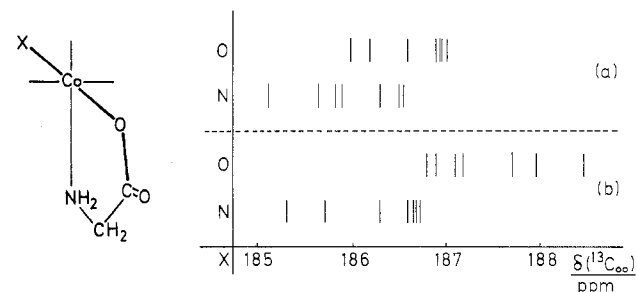


Figure 6. The influence of ligand in trans position to the carboxylato group on carboxylato carbon chemical shifts. ^{13}C chemical shifts before (a) and after (b) correction for the contribution from d-electron magnetic anisotropy.

<u>46.4</u> <u>186.7</u>	<u>45.6</u> <u>188.4</u>	<u>47.8</u> <u>186.3</u>	<u>47.3</u> <u>187.2</u>
<u>46.5</u> <u>186.7</u>	<u>46.0</u> <u>188.0</u>	<u>47.9</u> <u>185.3</u>	<u>47.5</u> <u>186.9</u>
<u>46.3</u> <u>186.7</u>	<u>46.0</u> <u>187.7</u>	<u>47.1</u> <u>185.7</u>	<u>47.9</u> <u>186.8</u>
46.1 186.6			46.7 187.1

Figure 7. ^{13}C chemical shifts (ppm) of chelated glycinato ligand, corrected for the magnetic anisotropy influence and systematized according to trans ligands. Underlined values are those for which application of formula 5 is unambiguous. Relative changes of electronic charge on carbon nuclei are indicated in such a way that δ_\pm corresponds to about ± 0.3 ppm shift change.

I–IV, VI, IX–XI). On the contrary, when two or three signals appear, due to the nonequivalence of ligands, the correlation is tentative. The reasons for the observed deviation from the ideal correlation may be manifold, for example, deviation from the assumed glycinato ligand geometry, deviation from the computed electronic transition energies, and the existence of other factors (electric field, inductive and/or steric influences, etc.).

For methylene carbons, the d-electron magnetic anisotropy exerts a relatively weak influence with respect to the perceived ^{13}C chemical shift span. In this case, as it has been already reported,¹² the influence of ligand in the trans position to the NH_2 group is clearly manifested. Namely, when nitrogen is in the trans position to the NH_2 group, the chemical shifts of the majority of investigated complexes are moved toward a lower field in relation to the field when oxygen is in the trans position (Figure 5a). However, this is partly obscured by magnetic anisotropy influence. Namely, when correction of methylene carbon chemical shifts for the contribution from magnetic anisotropy is made, the above mentioned regularity

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is observed for all investigated complexes (Figure 5b). Analogous regularity with carboxylato carbon chemical shifts has been also established (Figure 6). However, in the latter case the d-electron magnetic anisotropy has a stronger influence.

^{13}C chemical shifts of the glycinato ligand, so obtained, systematized according to trans ligators, are presented in Figure 7. It is interesting to note that trans influence on chemical shifts is more pronounced when different ligators are facing the glycinato ligand. This fact signifies that apart from the influence exerted on the closer carbon, there is a smaller opposite influence upon carbon which is further away.

The corrected ^{13}C chemical shifts most probably are determined by the value of paramagnetic shielding term on carbon nuclei, since this term has the greatest bearing on the ^{13}C chemical shift.²⁷ In this way, trans-ligand influence should change the paramagnetic shielding term. This term depends upon electron density on carbon nuclei, electron excitation energy, and bond order,²⁷ and it is questionable which of these properties is the most affected by trans ligator. This problem may be approached by considering the changes in ^1H and ^{13}C chemical shifts of the glycinato ligand when bonding with cobalt. Namely, one should expect cobalt to transmit part of its positive electric charge onto the ligands,²⁸ thus decreasing ligand electron density. Consequently a smaller proton shielding due to the lowering of the diamagnetic shielding term, as well as a lesser shielding of carbon nucleus because of a paramagnetic shielding term increase might be expected. For the glycinato anion both the ^{13}C chemical shifts²⁸ [$\delta(^{13}\text{C}_\alpha) = 45.4$ and $\delta(^{13}\text{C}_\infty) = 183.5$] and the proton chemical shifts²⁹ [$\delta(^1\text{H}_\alpha) = 3.1$] have been reported. These values should be compared with the shifts in the *fac*-[Co(gly)₃] complex in which there is no contribution of magnetic anisotropy to the glycinato nuclei chemical shielding (Table I). As it may be seen, proton and ^{13}C chemical shifts move to lower field after complex formation. This fact signifies that changes in electron density may be used to determine chemical shifts of the nuclei under consideration. (On the basis of ^{14}N chemical shifts it was shown⁵ that the glycine nitrogen shielding is determined by changes in the excitation energy and that after bonding to cobalt(III) a shift toward a higher

field is observed. Such a difference is not surprising, since the nitrogen σ orbital directly participates in the metal-ligand bond, whereas carbon orbitals probably do not partake significantly in these molecular orbitals.) Consequently, trans-ligand influence on ^{13}C chemical shifts of the glycinato ligand probably operates through an inductive change of carbon electron density. In line with this, Figure 7 shows the relative change of charge densities on glycinato carbons when δ represents a charge which corresponds to a ~ 0.3 ppm shift change. From the scheme on Figure 7, it may be concluded that nitrogen in the trans position increases the relative density on the closest carbon, while oxygen performs an opposite influence. Such a finding is consistent with the perceived trans-ligand influence on the rate of the amine proton isotope exchange.³⁰ Research carried out by other authors^{14,15} regarding the influence of trans ligands on the chemical shift of various nuclei speaks in favor of the proposed explanation.

Finally, we have studied the possible influence of the complex ion electric field on ^1H and ^{13}C chemical shifts, the reason being that this effect had been used in explaining the corresponding amino acid chemical shifts.²⁹ One of the basic phenomena caused by the electric field is the polarization of C-H bonds, which causes ^1H and ^{13}C chemical shifts to move in opposite directions.^{11,29} However, the latter phenomenon has not been observed in complexes examined, neither before nor after making corrections of chemical shifts for the influence of magnetic anisotropy. No shift dependence on complex ion charge had been found, as well. Hence, the electric field influence is relatively weak in the investigated complexes.

A general conclusion which presents itself on the basis of the results obtained in this study is the necessity of performing a correction of chemical shifts of the nuclei of the ligands for the contribution from the magnetic anisotropy of the central ion in the complex. This task should be carried out before approaching the study of other influences.

Registry No. [Co(en)₃]Cl₃, 13408-73-6; [Co(gly)(en)₂]Cl₂, 14408-57-2; *trans*(O)-[Co(gly)₂(en)]Cl, 57298-57-4; *cis*(O)-C₂-[Co(gly)₂(en)]Cl, 57298-58-5; *cis*(O)-C₁-[Co(gly)₂(en)]Cl, 57335-06-5; *mer*-[Co(gly)₃], 30364-77-3; *fac*-[Co(gly)₃], 21520-57-0; *cis*(N)-C₁-K[Co(ox)(gly)₂], 65816-56-0; *cis*(N)-C₂-K[Co(ox)(gly)₂], 65816-57-1; *trans*(N)-K[Co(ox)(gly)₂], 16986-03-1; K₂[Co(ox)₂(gly)], 46846-80-4; K₃[Co(ox)₃], 14239-07-7.

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Coordination Complexes of Tetrakis(trifluoroacetato)dimolybdenum. A Solution ^1H , ^{19}F , and ^{31}P Nuclear Magnetic Resonance and Infrared Spectroscopic Study

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New coordination complexes of the type $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4(\text{L})_2$ where L is Me_3P , Me_2PhP , MePh_2P , Ph_3P , Et_3P , $(\text{c-Hx})_3\text{P}$ (c-Hx = cyclohexyl), $(t\text{-Bu})_3\text{P}$, $(\text{Me}_3\text{Si})_3\text{P}$, Me_3PO , and quinuclidine have been prepared. These complexes fall into two classes, viz., class I or class II. Class I complexes are formed with MePh_2P , Ph_3P , $(\text{c-Hx})_3\text{P}$, $(t\text{-Bu})_3\text{P}$, $(\text{Me}_3\text{Si})_3\text{P}$, Me_3PO , and quinuclidine. Solution infrared and ^{19}F NMR studies show that these complexes are of the classical type (axial coordination) as shown by X-ray crystallography for L = pyridine, some years ago. Solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy of these phosphine adducts indicates that they are extensively dissociated in CDCl_3 . Class II complexes (L = Me_3P , Me_2PhP , or Et_3P) exist in solution (CDCl_3) with bidentate and monodentate trifluoroacetate groups as determined by infrared and ^{19}F NMR spectroscopy. At least two isomers are present as shown by $^{31}\text{P}\{^1\text{H}\}$ and $^1\text{H}\{^{31}\text{P}\}$ NMR spectroscopy. Some bidentate phosphine complexes are also described.

Base-free molybdenum(II) carboxylates, $\text{Mo}_2(\text{O}_2\text{CR})_4$, where R = H,¹ Me,^{2,3} CF_3 ,⁴ Ph,⁵ *t*-Bu,⁵ or CH_2NH_3^+ ,⁶ have

been shown to be of structure A by X-ray crystallography. A number of other carboxylates have been prepared, and these