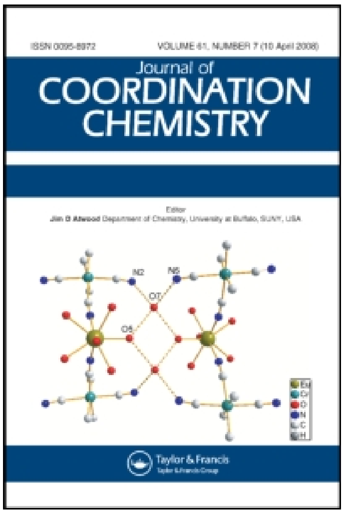

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

# A $^{59}$Co NMR STUDY OF Co(III) COMPLEXES CONTAINING AMINOCARBOXYLATO LIGANDS

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**To cite this Article** Juranić, N. , Ćelap, M. B. , Vučelič, D. , Malinar, M. J. and Radivojša, P. N.(1979) 'A $^{59}$Co NMR STUDY OF Co(III) COMPLEXES CONTAINING AMINOCARBOXYLATO LIGANDS', Journal of Coordination Chemistry, 9: 2, 117 — 123

**To link to this Article: DOI:** 10.1080/00958977908076515

**URL:** http://dx.doi.org/10.1080/00958977908076515

*J. Coord. Chem.*
1979, Vol. 9, pp. 117–123

# A $^{59}$Co NMR STUDY OF Co(III) COMPLEXES CONTAINING AMINOCARBOXYLATO LIGANDS

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*(Received July 7, 1978; in final form October 17, 1978)*

The chemical shifts and line widths in the $^{59}$Co spectra of 49Co(III) complexes with different aminocarboxylato ligands were determined. The effect of increase of chelate ring size and of the kind of ligand side chain on chemical shift was examined. In addition, the order of the investigated aminocarboxylato ligands according to the magnitude of shielding of cobalt nucleus was found.

The effect of the chelate ring size and the nature of side chain on the ligand field strength of coordinated aminocarboxylato ligand was considered in the *cis*($NO_2$)-*trans*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$]* complex on the basis of $^{59}$Co and $^{13}$C NMR spectra and electronic absorption spectra in the visible region.

## INTRODUCTION

Although $^{59}$Co spectroscopic data of a rather large number of Co(III) complexes[1–6] have been published, until now there are no such data for complexes with amino acids, except those recently reported by us for complexes with glycine[7].

The $^{59}$Co chemical shifts in Co(III) complexes may be well correlated with the position of the first absorption maximum in the visible region of the spectrum[1,8]. Therefore data obtained by $^{59}$Co spectroscopy are supplementary to those obtained from electronic spectra. However, chemical shifts of Co(III) complexes are distributed over a wide region, hence $^{59}$Co spectroscopy is more sensitive to changes in a complex and is therefore more suitable for a detailed study of such complexes.

So far the effects of geometric isomerism and the replacement of ligands on chemical shifts in $^{59}$Co spectra of Co(III) complexes have been investigated[3,5]. However, the effects of minor changes in ligand composition and structure, which occur, for instance, when one aminocarboxylato ligand is replaced by another, have not been investigated. When the $NH_2$-group in an aminocarboxylato ligand is moved from α- to β-position a substantial change in chemical shift can be expected due to the increase of chelate ring, since in such cases it was found that there are considerable differences in electronic absorption spectra.[9,10] It is less certain whether a change in the side chain of a coordinated amino-acid and a change in the optical isomerism of the complex can be detected using this method. Therefore, in this work we undertook to investigate all the above mentioned effects and to establish subsequent regularities. For this purpose use was made of 49 mixed complexes of Co(III) with amino acids. In order to compare diamine with amino acid chelates, 5 more mixed Co(III) complexes with diamine chelate rings were investigated.

## EXPERIMENTAL

The synthesis of the investigated complexes has been described in earlier works (for references see Table 1).

### $^{59}$*Co Spectra*

Spectra were recorded by a Bruker Pulse SXP-100 FFT spectrometer in a field of 2.222 T. The chemical shifts of complexes dissolved in water are given relative to the external standard $[Co(NH_3)_6]Cl_3$ (capillary) using the δ-scale convention. Line widths are measured at half-height of the absorption line. For lines whose widths are below $5 \times 10^{-4}$ T, from $5 \times 10^{-4}$ to $10 \times 10^{-4}$ T and from $10 \times 10^{-4}$ to $15 \times 10^{-4}$ T chemical shift is determined with an accuracy of within ±5 ppm, ±10 ppm and ±15 ppm,

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*AmH denotes amino acid.

TABLE I
$^{59}$Co spectroscopic data on the investigated Co(III) complexes

| No. | Complex[a] | Ref. | $\delta_{^{59}\text{Co}}$ ppm $[\text{Co(NH}_3)_6]\text{Cl}_3$ | Line width $\times 10^4$ T |
|---|---|---|---|---|
| | *mer-* | | | |
| 1 | -[Co(gly)$_3$] | 27 | 1730 | 6.0 |
| 2 | (L-ala)$_3$ | 29 | 1460 | 6.5 |
| 3 | ($\beta$-ala)$_3$ | 9 | 2550 | 8.0 |
| 4 | (L-nva)$_3$ | 30 | 1600 | 7.0 |
| | *cis*(NO$_2$)-*trans*(NH$_2$)- | | | |
| 5 | -K[Co(gly)$_2$(NO$_2$)$_2$] | 16 | −170 | 3.5 |
| 6 | (L-ala)$_2$ | 16 | −275 | 4.0 |
| 7 | gly($\beta$-ala) | 17 | 155 | 5.0 |
| 8 | ($\beta$-ala)$_2$ | 16 | 380 | 6.0 |
| 9 | (L-abu)$_2$ | 18 | −240 | 10 |
| 10 | ($\beta$-abu)$_2$ | 18 | 297 | 12 |
| 11 | (aibu)$_2$ | 18 | −243 | 10 |
| 12 | ($\beta$-aibu)$_2$ | 18 | 298 | 12 |
| 13 | (L-nva)$_2$ | 19 | −225 | 10 |
| 14 | (L-val)$_2$ | 19 | −248 | 11 |
| 15 | (L-nle)$_2$ | 19 | −180 | 14 |
| 16 | (L-leu)$_2$ | 19 | −232 | 13 |
| 17 | (L-ile)$_2$ | 19 | −220 | 14 |
| | *trans-trans-trans-* | | | |
| 18 | -K[Co(gly)$_2$(NO$_2$)$_2$] | 20 | 257 | 6.0 |
| 19 | (L-ala)$_2$ | 20 | 150 | 6.5 |
| 20 | ($\beta$-ala)$_2$ | 20 | 896 | 9.0 |
| 21 | ($\beta$-aibu)$_2$ | 20 | 810 | 10 |
| | *trans*(NO$_2$)-*cis*(NH$_2$)- | | | |
| 22 | -K[Co(gly)$_2$(NO$_2$)$_2$] | 20 | 177 | 0.7 |
| 23 | (L-ala)$_2$ | 20 | 60 | 1.0 |
| | *cis*(O)-*trans*(NH$_2$)- | | | |
| 24 | -[Co(NH$_3$)(gly)$_2$(NO$_2$)] | 22 | 283 | 3.0 |
| 25 | (L-ala)$_2$ | 22 | 207 | 7.0 |
| 26 | ($\beta$-ala)$_2$ | 22 | 830 | 9.0 |
| 27 | (L-abu)$_2$ | 21 | 218 | 8.0 |
| 28 | (L-nva)$_2$ | 21 | 220 | 10 |
| 29 | (L-nle)$_2$ | 21 | 224 | 12 |
| 30 | (L-ile)$_2$ | 21 | 280 | 10 |
| | *cis-cis-cis-* | | | |
| 31 | -K[Co(gly)$_2$(NO$_2$)$_2$] | 20 | 74 | 1.0 |
| 32 | (L-ala)$_2$ | 20 | −30 | 1.2 |
| | *cis*(NO$_2$)-*trans*(NH$_2$,NH$_3$)- | | | |
| 33 | -[Co(NH$_3$)$_2$gly(NO$_2$)$_2$] | 22 | −455 | 3.6 |
| 34 | L-ala | 22 | −515 | 3.0 |
| 35 | L-abu | 21 | −510 | 3.2 |
| | *trans*(NO$_2$)-*cis*(NH$_2$,NH$_3$)- | | | |
| 36 | -[Co(NH$_3$)$_2$gly(NO$_2$)$_2$] | 22 | −385 | 4.2 |
| 37 | L-ala | 22 | −440 | 3.0 |
| 38 | L-abu | 22 | −410 | 3.3 |
| | *cis*(NO$_2$)-*trans*(NH$_2$)- | | | |
| 39 | -[Co tn gly(NO$_2$)$_2$] | 17 | −720 | 7.0 |
| 40 | $\beta$-ala | 17 | −380 | 15 |
| | *cis*(NO$_2$)-*trans*(NH$_2$)- | | | |
| 41 | -[Co en gly(NO$_2$)$_2$] | 17 | −900 | 7.0 |
| 42 | $\beta$-ala | 17 | −690 | 8.0 |
| | *mer-* | | | |
| 43 | -K[Co(NH$_3$)gly(NO$_2$)$_3$] | 23 | −760 | 3.3 |
| 44 | L-ala | 23 | −825 | 3.4 |
| 45 | L-abu | 23 | −820 | 4.2 |
| 46 | L-nva | 23 | −790 | 5.4 |
| 47 | L-val | 28 | −780 | 5.0 |
| 48 | Ba[Co gly(NO$_2$)$_4$] | 24 | −580 | 1.6 |
| 49 | $\beta$-ala | 24 | −230 | 3.0 |
| | *cis-* | | | |
| 50 | -[Co(en)$_2$(NO$_2$)$_2$]Cl | 25 | −930 | 1.2 |
| 51 | (tn)$_2$ | 26 | −1010 | 1.5 |
| | *trans-* | | | |
| 52 | -[Co(en)$_2$(NO$_2$)$_2$]Cl | 25 | −1510 | 1.7 |
| 53 | (en)tn | 17 | −1400 | 1.4 |
| 54 | (tn)$_2$ | 26 | −1140 | 1.2 |

[a] Abbreviations:
glyH = glycine
L-alaH = L-alanine
$\beta$-alaH = $\beta$-alanine
L-nvaH = L-n-valine
en = ethylenediamine
tn = 1,3-diaminopropane
L-abuH = L-aminobutyric acid
$\beta$-abuH = $\beta$-aminobutyric acid
aibuH = aminoisobutyric acid
$\beta$-aibuH = $\beta$-aminoisobutyric acid
L-valH = L-valine
L-nleH = L-n-leucine
L-leuH = L-leucine
L-ileH = L-isoleucine

respectively. Data are taken at a temperature of 310 ±1 K.

### $^{13}$C *Spectra*

Spectra were recorded by the same spectrometer in a field of 2.114 T (D$_2$O lock) in a Fourier transform proton noise decoupled (or undecoupled) mode at room temperature. The chemical shifts of complexes dissolved in D$_2$O are given relative to TMS using dioxane as the internal standard.

### *Electronic Absorption Spectra*

Spectra were obtained by means of a Varian Super Scan 3 spectrophotometer. The position of the first absorption maximum was determined with an accuracy of ±0.3 nm.

## RESULTS

Values of chemical shifts and line widths in the $^{59}$Co spectra of the investigated complexes are given in Table I. As seen in the table, line widths as a rule increase, the greater number of carbon atoms in the acid molecule which forms a five-membered ring. Enlargement of a five-membered to a six-membered chelate ring leads to an even greater broadening of the line. For this reason it is relatively difficult to detect $^{59}$Co resonance in complexes with amino acids containing either a larger number of carbon atoms in a molecule or six-membered aminocarboxylato rings.

Further, it can be seen from the table that differences in chemical shift also appear when an amino acid is replaced by another acid in the same complex. Thus, for example, for thirteen investigated aminocarboxylato *cis*($NO_2$)-*trans*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$] complexes the chemical shifts are distributed over a region of ~650 ppm. For easier comparison of the effects which take place upon replacement of amino acids in different complexes, in Table II we give values of change in chemical shift when the coordinated glycinato ligand is replaced by other aminocarboxylato ligands for all kinds of investigated complexes. It may be noticed that the larger the number of replaced amino acids, the larger the change in chemical shift. This is observed in a gradual replacement of amino acids in the same complex (e.g. in Table I, complexes 5, 7 and 8) as well as in comparing complexes containing one, two or three amino acids (Table II). In this way a certain additivity of the effects of replacement of amino acids may be noted. Furthermore, comparing the changes in chemical shifts upon replacement of an amino acid by another within the same kind of complex (Table II) the investigated amino acids might be arranged in the following sequence according to the shielding magnitude of the cobalt nucleus:

β-ala < (β-abu, β-aibu) $\leqslant$ gly < L-ala < (L-abu, aibu, L-val, L-nva, L-leu, L-nle, L-ile).

As expected, the largest differences in chemical shift were observed when a five-membered chelate ring was replaced by a six-membered one. Table III shows values of the change in chemical shift when glycine is replaced by β-alanine and when L-alanine is replaced by β-aminoisobutyric acid or β-aminobutyric acid. The changes range from 210 to 350 ppm per ring and do not differ much from the ones which appear when five-membered diamine chelates are replaced by a six-membered ones (ranging from 100 to 310 ppm per ring).

The effect of replacement of the chelate ring $CH_2$-group hydrogen atom by a $CH_3$-group is also pronounced. As seen in Table IV, on replacement of glycine by L-alanine the change is between 38 to 90 ppm per amino acid, whereas on replacement of β-alanine by β-aminoisobutyric acid or β-aminobutyric acid it amounts to about 40 ppm. The replacement of a hydrogen atom by a larger group somewhat weakens this effect, and there is no large difference in effect when hydrogen is replaced by different alkyls.

Finally, no difference in chemical shift was observed for diastereoisomers of the investigated complexes.

In order to gain a deeper insight into the nature of the effect of increase in chelate ring size and replacement of hydrogen atom of the $CH_2$-group of the ring by aliphatic group, for the series of (+)-*cis*($NO_2$)-*trans*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$] complexes, in addition to $^{59}$Co NMR spectra we also recorded electronic absorption spectra and $^{13}$C NMR spectra. Obtained results are shown in

TABLE II

Differences in $^{59}$Co chemical shifts due to the replacement of glycine in the complex by another amino acid

| | $\Delta_{^{59}Co}$ (ppm) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Complex | β-ala | β-aibu | β-abu | L-ala | aibu | L-abu | L-val | L-nva | L-ile | L-leu | L-nle |
| *mer*-[Co(Am)$_3$] | 820 | | | −270 | | | | −130 | | | |
| *cis*($NO_2$)-*trans*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$] | 550 | 468 | 467 | −105 | −73 | −70 | −78 | −55 | −50 | −62 | −10 |
| *trans*($NO_2$)-*cis*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$] | | | | −117 | | | | | | | |
| *cis-cis-cis*-K[Co(Am)$_2$($NO_2$)$_2$] | | | | −104 | | | | | | | |
| *trans-trans-trans*-K[Co(Am)$_2$($NO_2$)$_2$] | 639 | 553 | | −105 | | | | | | | |
| *cis*(O)-*trans*($NH_2$)-[Co($NH_3$)(Am)$_2$($NO_2$)] | 547 | | | −76 | | −65 | | −63 | −3 | | −59 |
| *mer*-K[Co($NH_3$)(Am)($NO_2$)$_3$] | | | | −65 | | −60 | −20 | −30 | | | |
| *cis*($NO_2$)-*trans*($NH_2$,$NH_3$)-[Co($NH_3$)$_2$(Am)($NO_2$)$_2$] | | | | −60 | | −55 | | | | | |
| *trans*($NO_2$)-*cis*($NH_2$,$NH_3$)-[Co($NH_3$)$_2$(Am)($NO_2$)$_2$] | | | | −55 | | −25 | | | | | |
| *cis*($NO_2$)-*trans*($NH_2$)-[Co(tn)(Am)($NO_2$)$_2$] | 340 | | | | | | | | | | |
| *cis*($NO_2$)-*trans*($NH_2$)-[Co(en)(Am)($NO_2$)$_2$] | 210 | | | | | | | | | | |
| Ba[Co(Am)($NO_2$)$_4$] | 350 | | | | | | | | | | |

TABLE III

Effect of the increase of chelate ring from a five-membered to a six-membered one on $^{59}Co$ chemical shift in the investigated complexes

| Compared complexes[a] | $\Delta_{^{59}Co}$ (ppm per ring) |
|---|---|
| 5 – 7 | 305 |
| 5 – 8 | 265 |
| 18 – 20 | 320 |
| 24 – 26 | 275 |
| 39 – 40 | 340 |
| 41 – 42 | 210 |
| 48 – 49 | 350 |
| 6 – 12 | 285 |
| 18 – 21 | 330 |
| 6 – 10 | 285 |
| 52 – 53 | 110 |
| 53 – 54 | 260 |
| 39 – 41 | 180 |
| 40 – 42 | 310 |
| 50 – 51 | 250 |
| 52 – 54 | 225 |

[a]Complexes are represented by their ordinal numbers in Table I.

TABLE IV

Effect of replacement of the chelate ring $CH_2$-group hydrogen atom by a $CH_3$-group on $^{59}Co$ chemical shift

| Compared complexes[a] | $\Delta_{^{59}Co}$ (ppm per ring) |
|---|---|
| 1 – 2 | −90 |
| 5 – 6 | −53 |
| 18 – 19 | −53 |
| 22 – 23 | −59 |
| 24 – 25 | −38 |
| 31 – 32 | −52 |
| 33 – 34 | −60 |
| 36 – 37 | −55 |
| 43 – 44 | −65 |
| 8 – 12 | −41 |
| 20 – 21 | −43 |
| 8 – 10 | −42 |

[a]Complexes are represented by their ordinal numbers in Table I.

TABLE V

Spectroscopic data on (+)-*cis*($NO_2$)-*trans*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$] complexes

| | | | $\delta_{^{13}C}$ (ppm TMS) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Am | λ (nm) | $\delta_{^{59}Co}$ (ppm) | $C_{carb.}$ | $C_\alpha$ | $C_\beta$ | $C_R^*$ | | | | $J_{C_\alpha-H}$ (Hz) |
| gly | 468.5 | −170 | 187.0 | 46.2 | | | | | | 141.6 |
| L-ala | 465.5 | −275 | 188.1 | 53.5 | | 19.4 | | | | |
| β-ala | 477.0 | 380 | 183.4 | 34.5 | 39.0 | | | | | 142.8 |
| L-abu | 467.0 | −240 | 187.2 | 59.0 | | 26.4 | 9.5 | | | |
| β-abu | 474.5 | 297 | 184.0 | 41.4 | 47.0 | 22.7 | | | | |
| aibu | 467.0 | −243 | 186.5 | 60.1 | | 27.9 | 27.5 | | | |
| β-aibu | 475.0 | 298 | 186.2<br>185.0 | 39.4<br>38.8 | 45.6 | 15.0<br>14.8 | | | | |
| L-nva | 466.0 | −255 | 187.5 | 57.4 | | 35.5 | 18.8 | 13.8 | | |
| L-val | 467.5 | −248 | 187.7 | 63.2<br>62.9 | | 30.8 | 19.0 | 16.5<br>16.2 | | |
| L-nle | 467.5 | −180 | 187.4 | 57.8<br>57.7 | | 33.0 | 27.8<br>27.5 | 22.6 | 13.9 | |
| L-leu | 466.5 | −232 | 188.9<br>188.1 | 56.2 | | 43.1<br>42.7 | 24.8 | 23.3 | 21.2 | |
| L-ile | 467.0 | −220 | 186.6 | 62.8 | | 38.0 | 24.5 | 15.9 | 21.4 | |

*Side chain carbons

Table V. In the electronic absorption spectra aforementioned differences in position of the first absorption maximum between complexes containing α- and β-amino acids (7.5–11.5 nm) are distinctly noticed. The difference between complexes with glycine and L-alanine (3 nm) is also noticeable.

Finally, it is interesting that on the basis of $^{13}C$ spectra it can be concluded that in some cases two amino acids in the complex are not in the same environment, although one expects a complex of $C_2$-symmetry.

## DISCUSSION

As is well known,[1] the chemical shielding of $^{59}$Co is determined by a diamagnetic and a paramagnetic term; in Co(III) complexes the large changes in the paramagnetic term upon replacement of ligands lead to large changes in chemical shifts. For complexes of octahedral ligand field symmetry the paramagnetic term is given on the basis of ligand field theory, by the expression:

$$\sigma^{p}_{zz} = -32\,\beta^2 \left\langle \frac{1}{r^3} \right\rangle \frac{k'^2}{E_{{}^1A_{1g}\rightarrow {}^1T_{1g}}} \qquad (1)$$

where $\beta$ is the Bohr magneton, $k'$ is the orbital reduction factor, $r$ is the distance of d-electron from the nucleus, and $E$ is the energy of the d-d electronic transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ which corresponds to the first absorption maximum in the visible region of the spectrum. On the basis of this expression, an increase in ligand field strength leads to an increase in shielding of the cobalt nucleus, i.e. to a decrease in chemical shift. If the orbital reduction factor does not change, the decrease in $^{59}$Co chemical shift may be interpreted as an increase of ligand field strength in complexes of octahedral symmetry. Ligand field symmetry in all complexes in Table I is lower than octahedral, hence expression (1) is not quite applicable to the consideration of their chemical shifts. However, since there is no considerable change in ligand field symmetry on replacement of an amino acid by another, by applying the appropriate expression for the given symmetry,[11] a linear dependence of $^{59}$Co chemical shifts on the wavelength of the first absorption maximum can be expected. Figure 1 shows that for *cis*($NO_2$)-*trans*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$] such a dependence actually exists. From this it may be concluded that the increase in $^{59}$Co chemical shift on replacement of an amino acid with another in the complex ion is due to an increase in ligand field

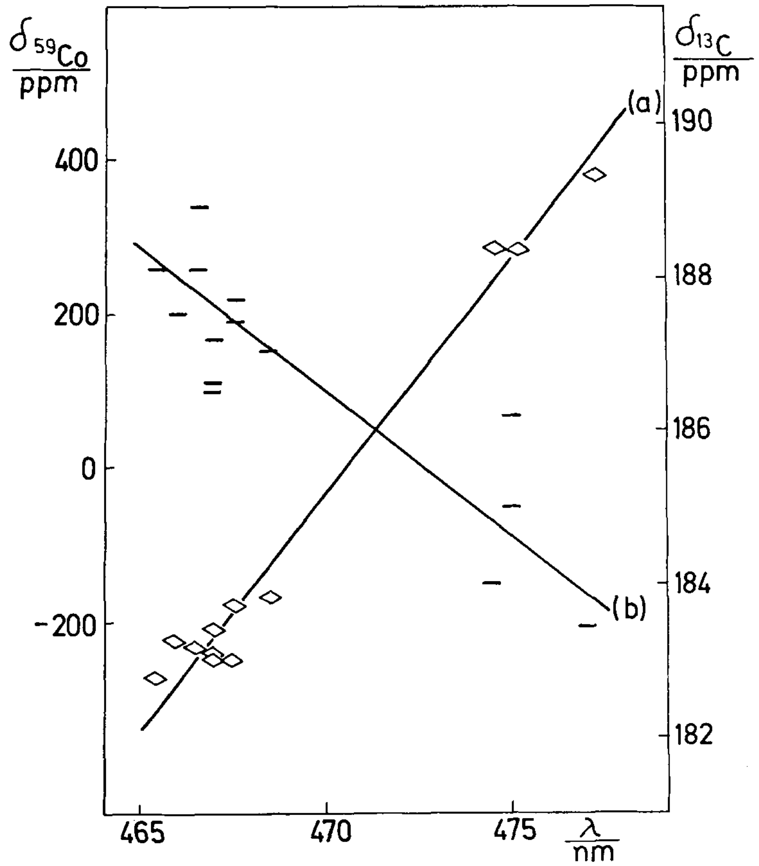

FIGURE 1 Correlation of $^{59}$Co chemical shifts (a) and $^{13}$C chemical shifts (b) with ligand field strength in *cis*($NO_2$)-*trans*($NH_2$)-K[Co(Am)$_2$($NO_2$)$_2$] complexes.

strength, and *vice versa.* In this sense the above sequence of amino acids given according to the magnitude of shielding of the cobalt nucleus corresponds to the spectrochemical series. In this way the earlier series is supplemented by new members.

The two well pronounced effects – the increase of ligand field strength upon replacement of hydrogen of the $CH_2$-group in the ring by a $CH_3$-group and the decrease of ligand field strength with the increase of the ring size – require an explanation. The first effect could be attributed probably to the inductive effect of the $CH_3$-group, which should lead to an increase of electronic density on ligators. However, this effect somewhat diminishes on replacement of a hydrogen atom by more voluminous alkyl groups, which might be due to a change in conformation of chelate rings induced by steric effects.

In connection with the weakening of ligand field strength of six-membered rings relative to five-membered ones it is important to note that β-alanine is a weaker acid and a stronger base than glycine. On the basis of this if ligand field strength depended primarily on electronic density on ligators of amino acid before coordination it should be expected that β-alanine has a stronger ligand field. However, as we have already mentioned, just the opposite was found. This indicates that during formation of chelate rings of glycine and β-alanine a significant redistribution of electronic density in the ligand occurs in such a way that glycine produces a stronger ligand field. Confirmation that such redistribution occurs and that it differs considerably in five-membered rings relative to six-membered ones is given by the $^{13}C$ spectra of Co(III) complexes in which amino acid is coordinated as a unidentate ligand (through the carboxylic group), and of those in which it is coordinated as a bidentate ligand.[12] Namely, on closing a chelate ring through an amino group in α-amino acid the resonant signal of carboxylic carbon shifts considerably to a higher frequency (7–9 ppm). Contrary to this, in β-alanine a small shift to a lower frequency (2 ppm) is observed. In addition, we also noticed that there is a correlation between $^{13}C$ chemical shifts of carboxylic carbon and ligand field strength in *cis*($NO_2$)-*trans*($NH_2$)-K[$CoAm_2(NO_2)_2$] complexes (Figure 1). A larger chemical shift corresponds to a stronger ligand field, which indicates that the increase of ligand field strength is related to departure of electronic density from the amino acid ligand.

The results of the X-ray analysis of mixed Co(III) complexes containing glycine and β-alanine[13,14] show that as the ring increases ring valence angles of ligators, carboxylic carbon and cobalt increase considerably. In methylene carbon angles undergo practically no change which is also confirmed by the coupling constants $J_{C-H}$ (Table V). As a result of this the angles of ligators and carboxylic carbon in a five-membered ring correspond closer to $sp^3$-hybridization, while in a six-membered ring to angles of $sp^2$-hybridization. Since four-covalent nitrogen, and two-covalent oxygen tend to be $sp^3$ hybridized,[15] a better overlap of orbitals of ligators on the $e_g$ set of d-orbitals of central ion can be expected in five-membered rings. Consequently, an increase in ligand field strength and shifting of electron density toward the central ion is to be expected in five-membered rings.

Such an interpretation where the ligand field strength of chelates is correlated with valence angles formed by them in a complex is also acceptable for explanation of the difference in ligand field strength in five-membered and six-membered diamine chelates.

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