Inorganica Chimica Acta, 25 (1977) 229–232

The ^{13}C and ^{59}Co Nuclear Magnetic Resonance Study of Mixed Co(III) Complexes Containing Glycinato Ligand

N. JURANIĆ, M. B. ĆELAP, D. VUĆELIĆ, M. J. MALINAR and P. N. RADIVOJŠA
Department of Chemistry and Physical Chemistry, University of Beograd, Beograd, Yugoslavia
Received April 19, 1977

The carbon-13 chemical shifts of coordinated bidentate glycinato ligand were measured in a series of seventeen mixed Co(III) complexes. A characteristic effect of trans-*ligand on the* ^{13}*C chemical shifts of the methylene carbon of glycine was observed. The results obtained enable one to distinguish easily between the investigated geometric isomers by means of* ^{13}*C spectra. On the basis of* ^{13}*C and* ^{59}*Co chemical shifts it was established that the chemical shifts of the Co(III) complexes are affected by both electric field and neighbouring anisotropy effect.*

Introduction

Carbon-13 nuclear magnetic resonance spectroscopy has only recently started to be applied to the study of Co(III) complexes, hence a small number of paper dealing with this research area have been published so far. Complexes containing amino acids have been studied most fully [1–4]. The changes in ^{13}C chemical shifts in amino acids on their coordination to Co(III) as unidentate and bidentate ligands have been investigated systematically [3]. The coordination to cobalt as unidentate ligand *via* the carboxyl group was found to affect the ^{13}C chemical shifts of amino acid much less than does the coordination as bidentate ligand. In both cases a downfield shift relative to NH_3^+–R–COOH was found.

To our knowledge, so far it has not been examined how various ligands affect the ^{13}C chemical shifts of the amino acid coordinated as a bidentate ligand when they are contained in the same complex compound. However, PMR investigations of α-aminocarboxylato Co(III) complexes, as well as PMR and ^{15}N NMR studies of corresponding ammine complexes [5, 6], have shown that a greater effect on the chemical shift of the nuclei under consideration occurs upon substitution of a ligand *trans* to the nucleus than upon substitution of a *cis*-ligand. Therefore it may be expected that similar effects will be observed also in ^{13}C chemical shifts. In that case the different sensitivity of ^{13}C in comparison with ^{1}H nuclei to the types of interaction inducing chemical shifts may be helpful in explaining the effects.

For this purpose in the present work seventeen Co(III) complex compounds have been studied which contained, in addition to glycine, some of the following ligands: NH_3, 1,3-diaminopropane, NO_2^-, $C_2O_2^{4-}$ and Co_2^{3-}. Beside an analysis of the effect of these ligands on the ^{13}C chemical shift of glycine in the complexes, the influence of their arrangement, *i.e.* of the geometric configuration of the complex, has been investigated. Furthermore, the ^{59}Co resonance frequencies of the complex compounds have been measured, which have not been determined up to now, because it has formerly been shown [5, 7] that the chemical shifts of protons in Co(III) complexes are related to that of the ^{59}Co nucleus.

Experimental

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

^{13}*C Spectra*

Measurements were made on a Bruker SXP-100 spectrometer in Fourier transform/proton noise decoupled mode at a frequency of 22.63 MHz and at a temperature of 25 °C. The complexes were dissolved in D_2O in concentrations of 5–20 mg per cm^3, depending on the solubility and available quantity of the complex compound. Chemical shifts are given relative to TMS using dioxane as internal standard.

^{59}*Co spectra*

The spectra were recorded on the same spectrometer and with the same samples at 21.5 MHz and 25 °C. Chemical shifts are given relative to $Na_3[Co(NO_2)_6]$ as external standard (the $Na_3[Co(NO_2)_6]$ compound in aqueous solution gives, in addition to an intense line, another line of an intensity lower by a factor of about 16). The position of the intense line, relative to which the chemical shifts are given, was determined through proton as external standard. In a field of 21.14 kG (proton resonance at 90.000 MHz) its central resonant frequency is at 21.51 MHz.

TABLE I. The ^{13}C chemical shifts of the methylene (C_m) and carboxyl (C_c) carbons of glycinato ligand, and ^{59}Co chemical shifts in the mixed Co(III) complexes investigated.

No	Complex[a]	Ref.	C_m (ppm TMS)	C_c (ppm TMS)	^{59}Co (ppm $Na_3[Co(NO_2)_6]$
	$[Cotngly(NO_2)_2]$				
1	*cis* NO_2–*trans* NH_2	12	45,7	185,7	−9,3
2	$Na_2[Cogly(NO_2)_4]$	13	46,7	?	130
	$[Co(NH_3)_2gly(NO_2)_2]$				
3	*cis* NO_2–*trans*(NH_2, NH_3)	14	45,8	?	223
	$K_2[Cogly_2(NO_2)_2]$				
4	*cis* NO_2–*trans* N	15	46,2	186,8	455
5	*cis–cis–cis*	15	46,3; 47,7	185,9; 184,2	781
6	*trans* NO_2–*cis* N	15	48,4	?	872
7	*trans–trans–trans*	15	46,0	?	967
	$[Cotngly_2]Cl$				
8	*cis* O–C_2	19	46,2	185,4	1060
9	*cis* O–C_1	19	46,6; 46,9	184,9; 186,1	1525
10	*trans* O	19	45,5	186,1	1664
	$K[Cogly_2CO_3]$				
11	*cis* N–C_1	16	47,1; 47.9	186,3; 187,0	3472
12	*cis* N–C_2	17	47,2	187,6	3495
	$K[Cooxgly_2]$				
13	*cis* N–C_1	18	46,8; 48,2	185,9; 186,2	3128
14	*cis* N–C_2	18	47,6	?	3181
15	*trans* N–C_2	18	46,9	187,3	3600
	$[Cogly_3]$				
16	*mer*	20	46,4; 47,7	185,6; 186,9	2450
17	*fac*	20	48,4	186,7	2157

[a] tn = 1,3-diaminopropane. glyH = glycine. H_2ox = oxalic acid.

Results

The observed ^{13}C and ^{59}Co chemical shifts of the complexes under study are given in Table I. The ^{13}C resonance line of the carboxyl carbon (C_c) is in many cases of a considerable lower intensity, so that in some complexes we have not managed to detect it.

Considering the chemical shifts of the methylene carbon (C_m), which are given in Table I, we arrive at the conclusion that they are primarily affected by the ligand in the *trans*-NH_2 position. For example, in bisglycinato complexes with the *trans*-NH_2 arrangement of glycine ligands the chemical shifts of the methylene carbons remain within the limits of 46.0–46.9 ppm irrespective of the nature of other ligands in the complex (complexes 4, 8, 15 and 16) or the geometric isomerism of the complex compound (complexes 4 and 7). On the contrary, if the ligand in *trans*-NH_2 position is varied, *e.g.* in the bisglycinato *cis*-NH_2 complexes of C_2 symmetry, or in *mer*-trisglycinato complex*, considerably greater changes in chemical shifts (from 45.5 to 47.7) occur, depending on the ligand (complexes 10, 12, 13 and 16).

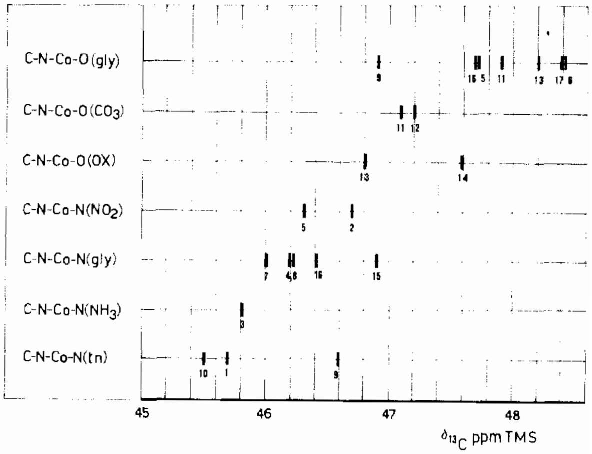

Figure 1. Classification of the ^{13}C chemical shifts of methylene (C_m) in a C–N–Co–X fragment according to the ligand in the position of X in the Co(III) complexes investigated.

On the basis of this it is most convenient to classify C_m chemical shifts according to the ligand in *trans*-N–H_2 position. Such a classification is presented by a

---

*We did not observe three lines as has been reported in ref. 5 for spectra obtained from very acidic solutions (complex dissolved in 1:1 D_2SO_4–D_2O).

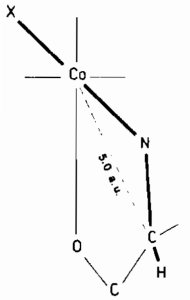

Figure 2. Geometry of a H–C–N–Co–X fragment in mixed Co(III) complexes containing glycinato ligand.

diagram (Fig. 1)* where the chemical shifts of C_m carbons from a C_m–N–Co–X fragment are plotted. It is evident that the observed C_m shifts may be divided, according to the ligator in *trans*-NH_2 position, into two large groups, which do not overlap: if in *trans*-position the ligator is oxygen, the C_m chemical shifts are displaced to lower fields than when in *trans*-position the ligator is nitrogen. According to the magnitude of the downfield shift of C_m chemical shifts in the cases studied, the *trans*-ligands might be arranged in the following order:

$$\mathrm{tn} < NH_3 < NH_2(\mathrm{gly})^- < NO_2^- < OX^{2-} \sim CO_3^{2-} < O(\mathrm{gly})^-$$

Owing to the observed effect of replacement of the ligand in *trans*-NH_2 position on the chemical shift of the methylene carbon (C_m), one may easily distinguish between the geometric isomers being investigated, as is seen in Table I on the example of four geometric isomers of K[Co $gly_2(NO_2)_2$] as well as on the example of the *fac*- and *mer*-[Co gly_3]. For the same reason all bisglycinato complexes of C_1 symmetry exhibit two different lines for C_m carbons.

The chemical shifts of the carboxyl carbon are less instructive, since they are almost equaly influenced through both ends of glycinato ligand. This is in accordance with the observed changes in ^{13}C chemical shift on glycine coordination as unidentate and bidentate ligand [3].

The ^{59}Co chemical shifts given in Table I are, as was to be expected [8], mainly proportional to the wavelength of the absorption maximum which corresponds to the lowest-energy electron transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) of the complex compound. From the results obtained it may be noticed that the rule of additivity of effects of different ligands on ^{59}Co chemical shifts [7] can hardly be applied to the complexes under consideration, because different geometric isomers of the same complex compound, *e.g.* K[Co $gly_2(NO_2)_2$], which contain the same ligands, have very different values of chemical shifts.

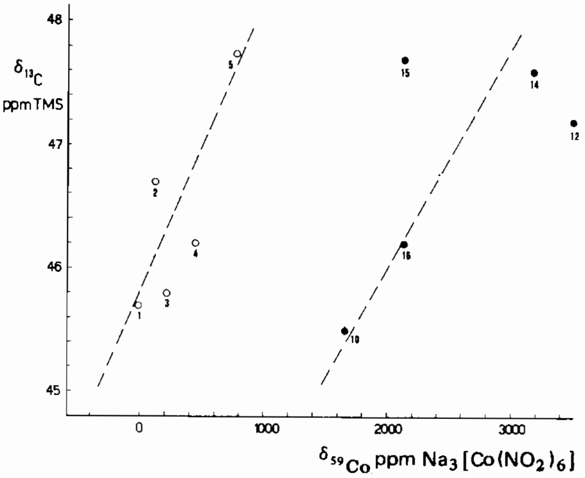

Figure 3. Correlation of the ^{13}C chemical shifts of methylene carbon with ^{59}Co chemical shifts in a series of mixed complex compounds with one (open circles) and two (solid circles) glycinato ligands, where the ligands in *trans*-NH_2 position are varied.

Discussion

The results obtained are of double interest. First, ^{13}C chemical shifts make it possible to distinguish easily between geometric isomers on the basis of the observed "*trans*" effect; second, they may contribute to a better understanding of the effect of cobalt(III) on the NMR chemical shifts of nuclei contained in ligands.

We have found that in a H–C–N–Co–X fragment (Fig. 2) the ^{13}C nucleus resonates at a higher resonance field if X is nitrogen, whereas Watabe [5] has established just the opposite for methylene protons, *i.e.* he has observed that the proton resonates at a higher field if X is oxygen. This may be compared with the results obtained by Lehman and Fung [6], who have found for pentaammine Co(III) complexes that the replacement of nitrogen by oxygen induces a downfield shift of the resonance of nitrogen in *trans*-position, while the proton resonance is shifted upfield. Whence it follows that the carbon and nitrogen nuclei behave similarly to each other and oppositely to proton.

The chemical shifts of the protons contained in ligands of Co(III) complexes have been explained, first of all, by the effect of Co(III) paramagnetism [7, 9, 10]. Changes in paramagnetic susceptibility of Co(III) may influence adjacent nuclei by neighbouring anisotropy effect. It has been shown [5, 7] that on the basis of this effect the shielding of ligand

---

*In the case of bisglycinato complexes of C_1 symmetry, where two lines appear due to two different *trans*-ligands, the assignment of ^{13}C shifts was made on the basis of a comparison of their values with those obtained for corresponding complexes of C_2 symmetry.

nucleus (σ_N) may be related to that of the cobalt-59 nucleus (σ_{Co}) by the expression:

$$\sigma_N = \frac{-(1 - 3\cos\theta)}{2R^{-3}\langle r^{-3}\rangle}\,\sigma_{^{59}Co} \qquad (1)$$

where $\langle r^{-3}\rangle$ is the mean value of r^{-3} for 3d-orbitals, R is the cobalt-to-nucleus distance, and θ is the angle between the vector $\bar{R}$ and the principal axis of the Co(III) magnetic susceptibility tensor.

On inspecting the correlation between the chemical shifts of the ^{13}C nucleus and those of the ^{59}Co nucleus which is presented in Fig. 3 for a series of mixed complexes with one or two glycinato ligands where ligands in *trans*-NH_2 position are varied, we may conclude that, in spite of the wide spread of points, there is a distinct direct proportionality between the ^{13}C and ^{59}Co chemical shifts. Substituting into equation (1) the following numerical values of parameters: $r^{-3} = 5.77$ a.u. [10] and R = 5.0 a.u. (Fig. 2), we find the ratio of chemical shifts of the two nuclei to be:

$$\frac{\delta_{^{13}C}}{\delta_{^{59}Co}} = \frac{-(1 - 3\cos\theta)}{1600}$$

while from Fig. 2 it may be estimated that $\delta_{^{13}C}/\delta_{^{59}Co} \sim 1/800$, so that by an appropriate choice of the value of angle θ the prediction of expression (1) turns out to be even a quantitative one. However, it cannot be explained why the signs of displacement of the chemical shifts of the proton and ^{13}C in methylene group are opposite to each other. Although expression (1) allows for the appearance of different sign of shift, depending on the angle θ, the change of angle between C and H in the CH_2 group (Fig. 2) is small and no change in sign can occur. Hence it may be concluded that the effect of Co(III) paramagnetic anisotropy is insufficient to explain the NMR chemical shifts of nuclei contained in ligands.

The opposit trend of displacement of the proton and ^{13}C chemical shifts is not a phenomenon occurring exclusively in Co(III) complexes with amino acids, since it was observed a long time on protonation of amino acids. Horsley and Sternlicht [11] have explained this phenomenon by electric field effect. Namely, the constant electric field produced by protonation polarizes other C–H bonds, inducing a dipole moment; the charge separation along the C–H bond displaces the ^{13}C and ^1H chemical shifts in opposite directions.

Coordination of amino acids to cobalt, which is formally a triply positive ion, certainly brings about the same effect. The polarity of the Co–N bond produces a primary induced field. The replacement of ligand in *trans*-N position may effect the polarity of the bond and thereby a through-bond and through-space inductive effect is exerted on the ^{13}C and ^1H chemical shifts.

It is most likely that both effects, *i.e.* neighbouring anisotropy effect (correlation between the ^{13}C and ^{59}Co chemical shifts) and electric field effects (opposite displacement of the ^{13}C and ^1H chemical shifts) determine the observed chemical shifts. However, additional experimental data are needed to define their individual contributions.

References

1 T. Ama and T. Yasui, *Bull. Chem. Soc. Japan, 49,* 472 (1976).
2 *ibid., 48,* 3171 (1975).
3 T. Ama and T. Yasui, *Chem. Lett. Chem. Soc. Japan,* 1295 (1974).
4 H. Gerlach and K. Mülen, *Helv. Chim. Acta, 57,* 2234 (1974).
5 H. Yoneda, U. Sakaguchi and Y. Nakashima, *Bull. Chem. Soc. Japan, 48,* 209 (1975).
6 J. W. Lehman and B. M. Fung, *Inorg. Chem., 11,* 214 (1972).
7 Y. Nakashima, U. Sakaguchi and H. Yoneda, *Bull. Chem. Soc. Japan, 48,* 762 (1975).
8 R. Freeman, G. R. Murray and R. E. Richards, *Proc. Roy. Soc., A242,* 455 (1957).
9 B. M. Fung, *J. Phys. Chem., 72,* 4709 (1968).
10 Y. Nakashima, *Bull. Chem. Soc. Japan, 48,* 766 (1975).
11 W. Horsley and H. Sternlicht, *J. Am. Chem. Soc., 90,* 3738 (1968).
12 M. B. Ćelap, M. J. Malinar and T. J. Janjić, *Rev. Chim. Min., 13,* 269 (1976).
13 M. B. Ćelap, T. J. Janjić and P. M. Radivojša, *Rev. Chim. Min., 10,* 607 (1973).
14 M. B. Ćelap, M. J. Malinar and T. J. Janjić, *Rev. Chim. Min., 13,* 175 (1976).
15 M. B. Ćelap, S. M. Nešić, M. J. Malinar, T. J. Janjić and P. N. Radivojša, *Glasnik Hem. društva Beograd, 39,* 559 (1974).
16 M. Shibata, H. Nishikava and Y. Nishida, *Inorg. Chem., 7,* 9 (1968).
17 M. B. Ćelap, M. J. Malinar, P. N. Radivojša and R. Marković, *"Proceedings* of 6th Yugoslav Conference on General and Applied Spectroscopy", Bled (1976), IR-16.
18 N. Matsuaka, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan, 40,* 1868 (1967).
19 M. B. Ćelap, M. J. Malinar and P. N. Radivojša, to be published.
20 H. Ley and H. Winhler, *Ber., 42,* 3894 (1909).