J. Serb. Chem. Soc. 51 (7—8)417—420(1986)
JSCS—1198

UDC 546.73:541.428.49
Original scientific paper

Influence of diamine ligands on the ^{59}Co NMR chemical shifts in cobalt(III) complexes

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(Received 13 May 1986)

The effect of diamine ligands on the ^{59}Co NMR chemical shift in 33 cobalt(III) complexes has been followed in a series of complexes containing 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane and 1,4-diaminobutane, respectively. It was established that ring enlargement and the introduction of a ring side CH_3-group causes, in all cases, a downfield shift due to weakening of the ligand field.

NMR spectroscopy of the central metal-ion in transition metal complexes has became a valuable analytical tool. General trends of the effects of complex compound composition and structure on the metal ion NMR chemical shift are now known, and to a considerable degree understood.[1,2] However, most of the data on the effect of minor changes of ligand composition and structure on the metal ion chemical shift is yet to be collected. Such data are of particular interest or determining metal coordination sites in biomacromolecules.

Cobalt(III) complexes are among the complexes most studied by metal-NMR spectroscopy. However, even for them only a few studies of the effect of the aforementioned changes on the metal chemical shift have appeared.[3–5] The only detailed study concerning chelate ligands is that on the effect of aminocarboxylato chelate ligand composition and structure on the ^{59}Co NMR chemical shift reported by us.[4] In that paper we established that increase of the chelate ring size from a five to a six-membered one is accompanied by a considerable increase in the ^{59}Co chemical shift (200—300 ppm) irrespective of the complex composition and geometrical configuration. Besides, in the all studied cases introduction of a chelate ring side CH_3-group caused a decrease of the ^{59}Co chemical shifts (by 40—90 ppm). Some data reported for ^{59}Co chemical shifts in cobalt(III) complexes containing diamine chelate ligands[4,6] suggested that the corresponding regularities may hold for these complexes as well. Therefore, in the present work we undertook the investigation of the effect of a diamine chelate ring enlargement and of the introduction of a side CH_3-group on ^{59}Co chemical shifts in a number of cobalt(III) complexes. Since cobalt(III) complexes containing seven-membered diamine chelate rings are available, the investigation of the effect of ring enlargement was extended to include enlargement to seven-membered rings.

EXPERIMENTAL

The following complexes were prepared according to methods from the literature: *cis*- and *trans*-bis(1,2-diaminopropane)dinitrocobalt(III) nitrate[7], *cis*- and *trans*-bis(1,4-diaminobutane)-dinitrocobalt(III) chloride[8], bis(1,3-diaminopropane)glycinatocobalt(III) chloride[8], *cis*(NO_2)-*trans*(NH_2)-(1,2-diaminopropane)diglycinatodinitrocobalt(III)[8] and *cis*(NO_2)-*trans*(NH_2)-(1,4-diamino butane)glycinatodinitrocobalt(III).[8]

Their ^{59}Co spectra were recorded by a Bruker Pulse SXP-100 FFT spectrometer operating at 21.5 MHz at room temperature. The chemical shifts of complexes dissolved in water were determined relative to the aqueous solution of hexaamminecobalt(III) chloride, used as the external standard (capillary), and reported relative to the aqueous solution of sodium hexacyanocobaltate(III) the conversion factor being +8170 ppm.

RESULTS AND DISCUSSION

The ^{59}Co chemical shifts of the investigated complexes are collected in Table I. For 9 complexes ^{59}Co chemical shifts are reported for the first time. For others, the literature values are used. For *cis*- and *trans*-bis(1,2-diaminoethane)dinitrocobalt(III) chloride we have previously reported erroneous values[10]; the correct value for the *trans*-isomer has been reported recently[11], and now we give the correct value for the *cis*-isomer. In complexes containing 1,2-diaminopropane there is a possibility of the existence of a number of geometrical and optical isomers, depending on the position and orientation of the CH_3-group. Usually in the synthesis a mixture of isomers is obtained and more than one ^{59}Co resonance is observed for the product. In these cases all the observed resonances are given in Table I, since all of them coluld be considered to represent the effect of introducing a side CH_3-group in the 1,2-diaminoethane chelate ring.

As seen from Table I, the effect of substitution of one diamine chelate by another was followed in *tris*-, *bis*- and *mono*(diamine)cobalt(III) complexes. In the eleven examples ring enlargement from a five to a six-membered ring was followed. In them, diamines were placed under the influence of various ligands, *i.e.*, CO_3^-, NO_2^-, CN^-, gly$^-$, β-ala$^-$ and diamines, respectively, and in a number of geometrical arrangements. Ring enlargement to the seven-membered ring or the introduction of a side CH_3-group was followed in four examples, again under the influence of various ligands and geometrical arrangements. In all cases a regularity in ^{59}Co chemical shifts was observed upon diamine chelate substitution. Enlargement of the five-membered 1,2-diaminoethane ring to a six-membered 1,3-diaminopropane ring has the most pronounced effect (160—400 ppm downfield). Introduction of a second CH_2-group, *i.e.*, enlargement to a seven-memebered 1,4-diaminobutane ring has a smaller impact (110—160 ppm downfield). The least pronounced effect was observed upon the introduction of a side CH_3-group into a five-membered 1,2-diaminoethane ring (20—100 ppm downfield). Hence, according to the increase of the ^{59}Co chemical shift the investigated diamines are ordered as follows: tmd>tn>pn>en.

TABLE I. ^{59}Co NMR chemical shifts of the investigated cobalt(III) complexes containing diamine ligands

Complex type[a]	dm			
	en	pn	tn	tmd
$[Co(dm)_3]^{3+}$	7130[b]	7200—7300[c,d]	8350[b]	8670[b]
cis-$[Co(NO_2)_2(dm)_2]^+$	6530	6580 6620	7180[e]	7410
trans-$[Co(NO_2)_2(dm)_2]^+$	6320[f]	6420	7040[e]	7140
cis-$[Co(CN)_2(dm)_2]^+$	4380[f]		5130	
trans-$[Co(CN)_2(dm)_2]^+$	4740[f]		5500	
$[Co(gly)(dm)_2]^{2+}$	7870[g]		8550	
$[Co(CO_3)(dm)_2]^+$	8900[h]		9400	
cis(NO_2)-*trans*(NH_2)-$[Co(NO_2)_2(gly)(dm)]$	7270[i]		7650	7800
cis(NO_2)-*trans*(NH_2)-$[Co(NO_2)_2(\beta\text{-ala})(dm)]$	7480[i]		7790[i]	
cis(O)-C_1-$[Co(gly)_2(dm)]^+$	8720[g]		8990[e]	
trans(O)-$[Co(gly)_2(dm)]^+$	8970[g]		9130[e]	

[a] Abreviations: en = 1,2-diaminoethane, pn = 1,2-diaminopropane, tn = 1,3-diaminopropane tmd = 1,3-diaminobutane, glyH = glycine, β-alaH = β-alanine. [b] Ref. 6. [c] Ref. 3, conversion factor +7140 ppm. [d] Ref. 9. [e] Ref. 10, conversion factor +8170. [f] Ref. 11. [g] Ref. 12, conversion factor +8170 ppm. [h] Ref. 13, conversion factor +8170 ppm. [i] Ref. 4, conversion factor +8170 ppm.

When these results are compared with those obtained for aminocarboxylato chelates,[4] it may be concluded that ring enlargement from a five to a six-membered one has a very similar influence in both kinds of chelates. Contrary to this, the introduction of a side CH_3-group into an aminocarboxylato ring causes an upfield shift, while in diamine chelates there is a downfield shift. In a rigid, almost planar aminocarboxylato ring, the effect of CH_3-group introduction was explained as an inductive effect.[4] In a diamine chelate, with a puckered, more flexible conformation, the introduction of a CH_3-group affects the ring conformation, and this seems to be of greater importance than the inductive effect. The presented comparison of the effect of the aminocarboxylato and diamine chelate composition and structure on ^{59}Co chemical shifts suggests that the regularity in the effect of ring enlargement is of wider importance, while the effect of the introduction of a ring side group critically depends on the kind of chelate considered.

The theory of ^{59}Co NMR chemical shifts in cobalt(III) complexes is well advanced[1,2] and chemical shift variations are properly ascribed to changes in the cobalt nucleus paramagnetic shielding term. This term is found to be proportional to the first d-d electronic transition wavelength and the nephelauxetic ratio.[6] In accordance with theory, the established deshielding of the cobalt nucleus upon ring enlargement from a five to a six-membered one follows the earlier established reqularity that the first d-d electronic transition is shifted toward longer wavelengths by 3 to 12 nm.[14] The same could be said for the enlargement of a six to a seven membered ring, where the less pronounceed deshielding of the cobalt nucleus parallels the smaller shift of the first d-d band toward longer wavelengths. The effect of the introduction of a ring side CH_3-group is hardly noticeable in the electronic absorption spectrum, but seems to be in acocrdance with changes in the ^{59}Co chemical shift. The nephelauxetic ratio, which could be determined only in *tris*(diamine)-cobalt(III) complexes, is almost the same for the studied diamines. Hence, it may be concluded that the observed changes in the ^{59}Co NMR chemical shift for different diamine chelates are mainly due to a change in the ligand field splitting magnitude.

There is no obvious reason why diamine chelates forming larger chelate rings produce smaller ligand field splitting. One may even expect the opposite behaviour. Namely, diamines with a larger aliphatic chain are stronger bases and thus more able to supply electrons to the metal-ligand bond. Besides, they are more flexible which may allow coordinated nitrogens to take the best position for coordination. However, conformational analyses of diamine chelate rings have shown that in a larger diamine chelate an additional strain is put on the metal-ligand bond,[15] which finally places the coordinated nitrogens in a position less suitable for bond formation. As a demonstration of this, we calculated the group overlap integral for σ-bonding ($G\sigma$) in *tris*(diamine)cobalt(III) complexes of 1,2-diaminoethane, 1,3-diaminopropane and 1,4-diaminobutane, relying on X-ray analysis data,[16-18] and obtained the following results:

$(G\sigma)_{en}:(G\sigma)_{tn}:(G\sigma)_{tmd}=1:0.968:0.910$, *i.e.*, in larger chelate rings metal-ligand σ-bond overlap is smaller.

ИЗВОД

УТИЦАЈ ДИАМИНСКИХ ЛИГАНАДА НА ^{59}Co NMR ХЕМИЈСКЕ ПОМАКЕ У КОБАЛТ(III)-КОМПЛЕКСИМА

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Утицај диаминских лиганада на ^{59}Co NMR хемијске помаке 33 кобалт(III)-комплекса проучен је код серије комплекса који су садржавали 1,2-диаминоетан, 1,2-диаминопропан, 1,3-диаминопропан или 1,4-диаминобутан. Утврђено је да проширење хелатног прстена, као и увођење бочне CH_3-групе у њега, узрокује у свим случајевима пораст хемијског помака, услед слабљења лигандног поља.

(Примљено 13. маја 1986

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