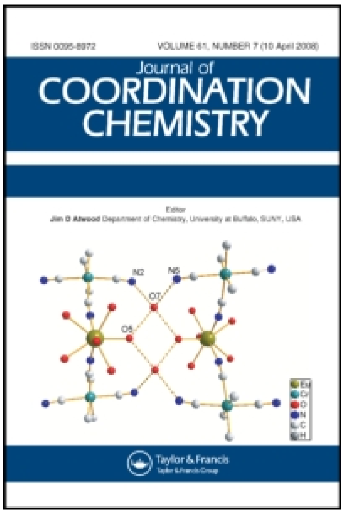

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Evidence for the C-N Bond Formation Between An Aldose and Ethylenediamine on Cobalt(III) Complexes. Deuterium Isotope Effects on Carbon-13 NMR Chemical Shifts

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To cite this Article Ishida, Katsuaki , Yano, Shigenobu , Hidai, Masanobu , Yashiro, Morio and Yoshikawa, Sadao(1988) 'Evidence for the C-N Bond Formation Between An Aldose and Ethylenediamine on Cobalt(III) Complexes. Deuterium Isotope Effects on Carbon-13 NMR Chemical Shifts', Journal of Coordination Chemistry, 18: 1, 197 — 200

To link to this Article: DOI: 10.1080/00958978808080709

URL: http://dx.doi.org/10.1080/00958978808080709

J. Coord. Chem. 1988, Vol. 18, pp. 197–200
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EVIDENCE FOR THE C-N BOND FORMATION BETWEEN AN ALDOSE AND ETHYLENEDIAMINE ON COBALT(III) COMPLEXES. DEUTERIUM ISOTOPE EFFECTS ON CARBON-13 NMR CHEMICAL SHIFTS.

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(Received April 18, 1988)

Keywords: C-N Bonds, deuterium isotope effects

We have already reported the synthesis and characterization of Co(III) complexes containing an N-glycoside derived from ethylenediamine (en) and an aldose.[1] In the report, the formation of a new C-N bond has been presumed according to the chemical shifts of the ^{13}C signals originated from the en units in their ^{13}C NMR spectra: one of the signals assigned to the en carbon atoms, which is presumably corresponding to the carbon atom adjacent to the glycosidic nitrogen, appears at 7-8 ppm downfield from the other three.

Deuterium isotope effects on ^{13}C NMR chemical shifts are very helpful in spectral assignments and molecular structure determination. Partial deuteration of exchangeable amino protons in amines leads to isotopic multiplets in ^{13}C NMR spectra observed under slow exchange conditions.[2,3] In the spectra of the Co(III)-amine complexes, indeed, isotopic multiplets corresponding to isotopomers of coordinated amino groups were observed in neutral H_2O-D_2O mixtures.[2] We applied this technique to the Co(III)-N-glycoside complexes in order to obtain the direct evidence of the C-N bond formation.

$[Co(D\text{-}Rib\text{-}en)(en)]ClO_4\cdot 2H_2O$ (1) and $[Co(L\text{-}Rha\text{-}en)(en)]Br\cdot H_2O$

(2) (D-Rib-en = 1-[(2-aminoethyl)amino]-1-deoxy-D-ribose, L-Rha-en = 1-[(2-aminoethyl)amino]-1,6-dideoxy-L-mannose) were prepared by the methods of ref. 1. Solutions of ca. 10 % w/v in ca. 1:1 H_2O-D_2O were prepared and allowed to stand for 10 days at ambient temperatures. Using these samples, 100MHz ^{13}C NMR spectra of (1) and (2) were obtained at ambient temperatures under low-power broad-band proton decoupled conditions. Partial deuteration of the coordinated NH_2 or NH groups in (1) and (2) was easily achieved in the neutral H_2O-D_2O mixtures.

Generally hydrogen exchange of coordinated amino groups in aqueous solutions is expected to be slow on the NMR time scale. As a result, the isotope effects on the ^{13}C resonance of the α- (two-bond isotope effect: $^2\Delta$) and β- (three-bond isotope effect: $^3\Delta$) carbons to the coordinated nitrogen atoms should give rise to distinct ^{13}C resonances for the individual isotopomers. Partial deuteration of a coordinated NH_2 group produces four species, NHH, NHD, NDH, and NDD, which results in quartet or triplet ^{13}C resonance of α- and β-carbons. The latter cases are commonly observed, because, in many cases, isotope effects corresponding to the two ways of monodeuteration are almost equivalent. Partial deuteration of a coordinated NH group produces two species, NH and ND, which gives ^{13}C resonance of α- and β-carbons doublet. The magnitudes of two-bond isotope effects (55-128 ppb/deuteron) is usually greater than those of three-bond isotope effects (0-85 ppb/deuteron),[2,3] and those of four-bond isotope effects are commonly too small to be observed. The resonance of carbon atoms with two possible isotope effects exhibit multiplicities analogous to those due to spin-spin couplings. Thus, the individual carbon gives characteristic multiplets depending on the bonding geometry around the nitrogen atom.

The isotopic multiplet patterns in the ^{13}C NMR spectrum of (1) are expected as follows on the basis of these empirical rules.

Each ^{13}C signal from the bidentate en may be observed as a triplet of triplets corresponding to the two-bond effect by one NH_2 group and the three-bond effect by the other NH_2 group. On the other hand, as to the two coordinated amino groups of the tetradentate N-glycoside ligand, one is an NH_2 group and the other is an NH group, which can give fingerprints of the formation of the N-glycoside bond. The carbon adjacent to the NH_2 group of the en unit may appear as a triplet of doublets corresponding to the two-bond effect by the NH_2 group and the three-bond effect by the NH_2 group. The carbon adjacent to the NH group of the en unit may appear as a doublet of triplets due to the two-bond effect by the NH group and the three-bond effect by the NH_2 group. C1 of the sugar unit may be observed as a doublet corresponding to the two-bond effect by the NH group, and C2 as a doublet due to the three-bond effect by the NH group. The possible two- and three-bond isotope effects for the carbon atoms and the expected isotopic multiplet patterns for (1) are summarized in FIGURE 1, and those for (2) are expected to be in the same manner.

All the ^{13}C NMR signals from the sugar units of (1) and (2) in D_2O were previously assigned completely by 2D-NMR spectroscopies based on the ^{1}H-^{1}H and ^{13}C-^{1}H shift correlation. Assign-

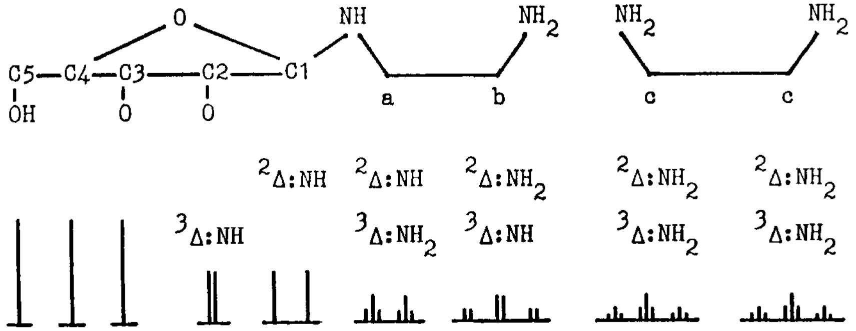

FIGURE 1. Possible Two- and Three-bond Isotope Effects and Expected Multiplet Patterns of (1).

TABLE I ^{13}C Chemical Shifts[a] (in ppm), Multiplicities,[b] and Deuterium Isotope Effects[c] (in ppb/deuteron).

complex	C1	C2	C3	C4	C5	C6
(1)	97.83	87.40	77.00	91.20	63.96	
	d 67	-	-	d 12	-	
(2)	97.65	88.68	76.12	87.27	69.24	21.70
	d 70	-	-	-	-	-

complex	en (a)	en (b)	en (c)	
(1)	53.92	46.20	46.70	45.74
	d 106	t 121	t 119	t 121
	t 15	d 27	t 21	t 15
(2)	53.67	46.38	46.88	45.57
	d 106	t 119	t 119	t 121
	t 20	d 24	t 18	t 15

a) ^{t}BuOH as an internal reference at 31.9 ppm. b) d: doublet, t: triplet. c) Upfield shifts, digital resolution is 3 ppb.

ments of observed isotopic multiplets of (1) and (2) are listed in Table I. The resonances of C1 of the sugar unit and the carbons of the en unit of the N-glycoside ligand exhibit multiplet patterns originated from the presence of the glycosidic NH group as expected. These results reveal evidence for the presence of the structure of C1-NH-C-C-NH_2. Thus the C-N bond formation on the Co(III) complexes could be unambiguously proved by the application of the isotopic multiplets in the ^{13}C NMR spectra. The C4 signal of (1) exhibits an extra split (12 ppb) corresponding to the four-bond isotope effect by the NH group, although the C2 and C3 signals show no significant split. This extra isotope effect indicates that the sugar ring of (1) takes the furanose form.

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