

transition-state geometries featuring "inside" alkoxy groups are retained in the new proposal, and an X-ray structure reveals similar geometry in the product. Comparison of product X-ray structures with relatively advanced cycloaddition transition states may also prove informative in osmylations, but suitable crystals have not been obtained to date.

Results from several epoxidations are included (Table I)^{13a} to underscore the unique nature of interactions observed in the osmylations. The selectivity in epoxidation vs. osmylation is reversed in each of the *E* alkenes! This requires that osmium ligand effects are important and that they can be quite different in *E* vs. *Z* alkenes. Selectivities for epoxidations are rationalized elsewhere,^{7b,9,15} but the similarity of our sulfone and silane examples suggests that σ -donor effects may have been overemphasized in the previous discussions of silanes.^{7b,15} Caution is appropriate because simple steric effects would favor the same product as σ -donor effects for those allyl silanes studied so far.

In summary, our results do not support a hyperconjugative model for osmylations. Our transition state models are somewhat different and more product-like than Kishi's, but qualitative predictions follow a similar pattern. Since the directive effects in osmylations (and probably, in many other cycloadditions) are mostly steric, one should not expect that olefin conformational and electronic effects will consistently result in the same transition-state geometry regardless of the electrophilic reactant. Empirical correlations may appear to support such models in many cases, but caution is appropriate since only two results are possible.

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Isotopic Multiplets¹ in the ¹³C NMR Spectra of Cobalt(III) Complexes with Partially Deuterated Coordinated NH₂ or NH Groups. Dihedral Angular Dependence of the Three-Bond Isotope Effects

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Recent reports have demonstrated that isotopic multiplets¹ observed in the ¹³C NMR spectra of amides,² carbohydrates,³ or amines⁴ with partially deuterated NH or OH groups can be very helpful in spectral assignments. These multiplets are due to upfield deuterium isotope effects on the ¹³C chemical shifts⁵ and can be observed in the slow hydrogen exchange conditions. The magnitudes of the reported isotope shifts for the two-bond effects are about in the range 120–90 ppb, while those for the three-bond effects are about in the range 70–0 ppb. Although understanding

(1) This expression is often used in the literature,^{3d} since there is a similarity between these phenomena and the multiplets due to spin-spin couplings. It involves, in fact, a sum of the individual isotope effects on ¹³C chemical shifts of different isotopomers in the mixture.

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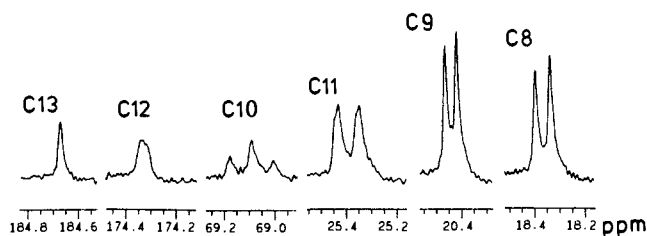


Figure 1. Isotopic multiplets¹ in the ¹³C resonances (at 100.53 MHz) of the α -amino- α -methylmalonato (AMM) moiety and of the methyl groups in the tetraamine moiety of Λ - β -₂-[Co(AMM)(5(*R*),7(*R*)-Me₂-2,3,2-tet¹¹)]⁺ (7) observed in a neutral ca. 1:1 H₂O/D₂O mixture. Carbon numbers are same to those of 7 in Table II.

of the factors that govern the magnitudes of these effects is incomplete, the magnitude of the three-bond effect seems to provide information concerning steric features of a molecule.^{3d,6} Therefore, elucidation of these factors should contribute significantly to the progress of this technique. This paper presents the first application of the isotopic multiplets¹ to the ¹³C NMR spectra of the coordination compounds, which can provide interesting examples of dihedral angular dependence of the three-bond isotope effects.⁷

Partial deuteration of the coordinated NH₂ or NH groups in the cobalt(III)-amine systems could be achieved in neutral H₂O/D₂O mixtures. Due to slow exchange between the isotopomers, the isotope effects on the ¹³C resonances of the α - and β -carbons could give rise to distinct ¹³C resonances for the individual isotopomers.^{8,9} Partial deuteration of a coordinated NH₂ group produces four species, NH₂, NHD, NDH, and ND₂, which cause ¹³C resonances of the α - and β -carbons to result in quartets or in triplets. The latter case is 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 cause ¹³C resonances of the α - and β -carbons to result in doublets. Therefore, the individual carbon gives a characteristic isotopic multiplet¹ according to the type of nitrogens on the observed and the neighboring carbons, which can be very helpful to assign the ¹³C resonances of coordinated polyamines. Examples of assignments of the ¹³CH₂ resonances in [Co(ox)(tetraamine)]⁺ are listed in Table I.¹⁰ It can be clearly seen that chemical shifts of the ¹³CH₂ resonances depend on the type of the nitrogens both on the observed and the neighboring carbons. They tend to shift to lower field with the order NR₂ > NHR > NH₂ > (CH₂).

A very important phenomenon concerning the magnitude of the three-bond isotope effect was observed with α -amino- α -methylmalonato (AMM) complexes. Figure 1 presents typical isotopic multiplets¹ in the ¹³C NMR spectrum of Λ - β -₂-[Co(AMM)(5(*R*),7(*R*)-Me₂-2,3,2-tet¹¹)]⁺ (7). C11, β to a coor-

(6) Majerski, Z.; Žuanič, M.; Metelko, B. *J. Am. Chem. Soc.* 1985, 107, 1721–1726 and the references cited therein.

(7) FT carbon-13 NMR spectra were obtained at 100.53 MHz with broad-band proton decoupling on a JEOL GX-400 spectrometer.

(8) The observation of the multiplets could be anticipated from the reported multiplets in the ⁵⁹Co NMR spectra of the cobalt(III)-amine systems with partially deuterated coordinated NH₂ or NH groups obtained in water. Sudmeier, J. L.; Blackmer, G. L.; Bradley, C. H.; Anet, F. A. L. *J. Am. Chem. Soc.* 1972, 94, 757–761. Au-Yeung, S. C. F.; Eaton, D. R. *J. Magn. Reson.* 1983, 52, 351–365. Russell, J. G.; Bryant, R. G. *Anal. Chim. Acta* 1983, 151, 227–229. Peterson, S. H.; Bryant, R. G.; Russell, J. G. *Ibid.* 1983, 154, 211–218.

(9) This sample preparation is remarkably easy compared with the reported cases of amines, which needed to acidify or to choose aprotic solvent such as Me₂SO. In a neutral H₂O/D₂O mixture, the uncoordinated NH₂ or NH group does not cause the isotopic multiplets. On the basis of the remarkable difference in the observable conditions of the isotopic multiplets, it may be possible to differentiate the coordinated nitrogens from the uncoordinated ones. Therefore, this technique can be applied, for example, to the direct determination of the coordinating position in a macromolecule-metal associating system.

(10) Different multiplicities due to the three-bond effects are observed between the pairs of diastereotopic carbons for compound 1. It should suggest that they are in different steric environment with regard to NH₂ or NH. Therefore, it is potentially possible to assign these pairs of carbons.

Table I. ^{13}C Chemical Shifts (in Ppm),^a Multiplicities,^b and Deuterium Isotope Effects^c (in Ppb/Deuteron) for Tetraamines in *cis*-Oxalatocobalt(III) Systems

complexes	C1; C1'	C2; C2'	C3; C3'	C4; C4'			
1. <i>cis</i> - β -[Co(ox)(NH ₂ CH ₂ ¹ CH ₂ ² NHCH ₂ ³ CH ₂ ⁴ NHCH ₂ ⁵ CH ₂ ⁶ NH ₂) ⁺	47.9; t, 125; d, 12;	43.3; t, 118; 0	52.9; d, 115; t, 18;	51.5; d, 121; q, 30, 18;	53.1; d, 115; d, 22;	50.3; d, 128; 0	
2. <i>cis</i> - β -[Co(ox)(NH ₂ CH ₂ ¹ CH ₂ ² NHCH ₂ ³ CH ₂ ⁴ NHCH ₂ ⁵ CH ₂ ⁶ NH ₂) ⁺	44.6; t, 125; d, 12;	43.7; t, 118; d, 12;	56.8; d, 121; t, 22;	51.5; d, 91; t, 15;	49.7; d, 115;	46.9; d, 109; d, d, 24, 12	
3. <i>cis</i> - β -[Co(ox)(NH ₂ CH ₂ ¹ CH ₂ ² CH ₂ ³ CH ₂ ⁴ NHCH ₂ ⁵ CH ₂ ⁶ NHCH ₂ ⁷ CH ₂ ⁸ NH ₂) ⁺	39.7; t, 112;	39.2; t, 121;	27.3; -	22.3; -	49.8; d, 115;	46.1; d, 115; d, 124; d, 21;	54.7; d, 109; 48.9; d, 24
4. <i>cis</i> -[Co(ox)(NH ₂ CH ₂ ¹ CH ₂ ² N(CH ₂ ³ CH ₂ ⁴ NH ₂) ₂) ⁺	45.0; t, 115;	-	61.3; b	-	63.2; b	45.6; t, 128;	-

^a Dioxane was used as an internal reference with a chemical shift of 67.8 ppm. Chemical shift values are for the protio form (low-field component).

^b Multiplicities due to the two-bond and the three-bond deuterium isotope effects are separately shown (two-bond, the second lines; three-bond, the third lines). q = quartet, t = triplet, d = doublet, b = a broad line, 0 = no isotope effect, - = theoretically no isotope effect. ^c All two-bond and three-bond effect magnitudes are negative (upfield shifts). Digital resolution is 3 ppb. ^d The most stable isomer; $\Delta(R,R)$ and its enantiomer.

Table II. Three-Bond Deuterium Isotope Effects (in Ppb)^a in the ^{13}C Resonances of the Methyl and the Carboxyl Carbons and the Related Dihedral Angles^b

complexes	methyl			carboxyl	
	C8	C9	C11	C12 ^c	C13
5, Δ - <i>cis</i> - β -[Co(ox)(5(R),7(R)-Me ₂ -2,3,2-tet ^d)] ⁺	64	46			
6, <i>cis</i> - β -[Co(AMM ^e)(2,3,2-tet ^f)] ⁺			85, <15	<20	0
7, Δ - <i>cis</i> - β -[Co(AMM ^e)(5(R),7(R)-Me ₂ -2,3,2-tet ^d)] ⁺	58	46	85, <15	<30	0

5

R = -H 6
-CH₃ 7

^a Digital resolution is 3 ppb. All three-bond effect magnitudes are negative (upfield shifts). ^b The Newman projections are viewed along the C-N bonds. Conformations concerning C8 and C9 are taken from the crystallographically established structures of **5**¹³ and **7**¹⁴ and from the strain energy minimized structure of **5**.¹⁵ The values from these three structures coincided well within a few degrees' deviations, thus their mean values are given. Conformation concerning the AMM moiety (C(10)-C(13)) is taken from the crystallographically established structure of **7**.¹⁴ All hydrogen atom positions were calculated by assuming the regular tetrahedral geometries. ^c The uncoordinated carboxyl group forms the intramolecular hydrogen bond to one of the secondary nitrogens of the tetraamine. Thus, an isotope effect through the hydrogen bond may be involved. ^d 5(R),7(R)-Me₂-2,3,2-tet = (4R,6R)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine. ^e AMM = α -amino- α -methylmalonate. ^f 2,3,2-tet = 3,7-diaza-1,9-nonanediamine.

minated NH₂ group, is a quartet with unequivalent two spacings. One of which is unusually large (85 ppb) compared with the reported values for the three-bond deuterium isotope effects,^{2-6,12} while the other is very small and can be observed as shoulders (less than 15 ppb). This observation indicates that one of the two ways of monodeuteration of the NH₂ group causes a large isotope effect on the C11 chemical shift, while the other causes only a small isotope effect. The crystallographically established structure of this complex¹⁴ indicates that the dihedral angles C11-C10-N-H_a and C11-C10-N-H_b are 11° and 109°, respectively. Thus, the dihedral angular dependence of the three-bond isotope effect should be strongly suggested. The unusually large isotope effect on C11 may be probably due to the deuterium substitution of H_a which is fixed in a small dihedral angle (11°).¹⁶ In contrast, the

isotope effects on C12 are much smaller (less than 30 ppb) than those on C11 although the dihedral angle C12-C10-N-H_b is small (14°), similar to the case of C11-C10-N-H_a. These observations indicate that the isotope effects on the $^{13}\text{COO}^-$ resonances are smaller than those on the $^{13}\text{CH}_3$ resonances.¹⁷ Typical values of the three-bond isotope effects are summarized in Table II. The results suggest an apparent dependence of the isotope effect on the dihedral angle C-C-N-H, both for the effects on the $^{13}\text{CH}_3$ resonances and for the effects on the $^{13}\text{COO}^-$ resonances.

In conclusion, the magnitude of the three-bond isotope effect seems to be governed both by the dihedral angle and by the type of the observed carbon. Thus, we believe that the three-bond isotope effect should provide useful information concerning a molecular geometry and concerning the position of an exchangeable proton such as a hydroxyl proton in a carbohydrate.

(11) The fully systematic name is (4R,6R)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine.

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(14) Yashiro, M.; Yano, S.; Ajioka, M.; Toriumi, K.; Ito, T.; Yoshikawa, S., unpublished results. The structure of the perchlorate salt (Δ -*cis*- β -[Co(AMM)(5(R),7(R)-Me₂-2,3,2-tet)]ClO₄·H₂O) was solved by the heavy-atom methods and refined by the block-diagonal least-squares procedures with anisotropic temperature factors for non-H atoms (hydrogen atoms isotropically), using 2374 unique reflections with $|F_o| \geq 3\sigma(F_o)$ (corrected for absorption, $\mu = 1.041 \text{ mm}^{-1}$) to final $R = 0.0432$ and $R_w = 0.0428$ ($1/w = \sigma^2 + (0.015|F_o|)^2$).

(15) Yashiro, M.; Yano, S.; Ajioka, M.; Yoshikawa, S. *Inorg. Chem.* **1985**, *24*, 3607-3610.

(16) Dihedral angular dependence of the three-bond isotope effects have been recently indicated in the selectively deuterated protoadamantane system.⁶ In this system, the deuterium isotope effect on the $^{13}\text{CH}_2$ resonance is maximal when the dihedral angle C-C-H is close to 0° and decreases gradually with an increase in this angle. Therefore, we assume in our case that the larger isotope effect on the $^{13}\text{CH}_3$ resonance is due to the deuterium substitution of H_a which is fixed in a small dihedral angle and the smaller isotope effect is due to the deuterium substitution of H_b which is fixed in a larger dihedral angle. The possibility of dihedral angular dependence of three-bond isotope effects have also been suggested in the third entry of ref 3d and in the references cited in ref 6.

(17) This observation is consistent with the suggestion in the ref 12 that the magnitude of the three-bond isotope effect depends on the degree of substitution on the observed carbons.