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THE CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE 1R(S),3S(R),8R(S),10S(R)- AND 1S(R),3R(S),8R(S),10S(R)-3,5,7,7,10,12,14,14-OCTAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECA-4,11-DIENENICKEL(II) COMPLEXES[1)]

Tasuku ITO,[*1,*2,*3] Kazuhiro SOMA,[*2] and Masanobu WATANABE[*2,*4]
*1 Department of Chemistry, Faculty of Science, Hokkaido University
Sapporo 060
and
*2 Department of Chemistry, Faculty of Education, Fukushima University
Fukushima 960

The carbon 13 nuclear magnetic resonance spectra of the title compounds were measured in aqueous solutions with Fourier-Transform NMR method. The resonance lines were assigned on the basis of off-resonance decoupling, selective proton decoupling, and comparison of the spectra with those of the stereospecifically deuterated derivatives.

Complexes of metal chelates that contain several chiral centers exhibit intricate stereochemistries and large numbers of possible isomers.[2)] Powerful techniques are required to deduce the detailed structures of individual isomer of such species in solution. A possible means for such purposes would be provided by carbon-13 nuclear magnetic resonance (cmr) spectroscopy.

We report here the assignments of the cmr spectra of the title compounds(I).[3-6)]

The perchlorate of the rac(1R(S),3S(R),8R(S),10S(R))-isomer was prepared by the template reaction,[4)] whereas the meso(1S(R),3R(S),8R(S),10S(R))-complex perchlorate was synthesized by the direct reaction of the free ligand salt with the nickel salt.[5)] The chlorides, which were prepared from the perchlorates by ion exchange (Dowex 1X8),[3)] were used for obtaining the cmr spectra. The stereospecifically deuterated derivatives (II)[3)] were also prepared for the present study.

All carbon-13 Fourier-Transform nuclear magnetic resonance spectra were obtained in D_2O solutions or H_2O solutions containing a small amount of D_2O, using a JEOL NMR spectrometer, Model JNM-PFT-60, operating at 15.09 MHz. Chemical shifts were measured relative to dioxane used as the internal standard. Addition of dioxane to the sample solutions was without effect on the electronic and cmr spectra of these complexes.

[*3] To whom correspondence should be addressed.

[*4] Present address: Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo, 158.

The proton noise decoupling spectra of the meso- and rac-complexes show nine resonance lines, respectively, indicating that each carbon atom within each isomer is pair-wise equivalent. Therefore, the meso- and rac-complexes have C_i and C_2 symmetry, respectively, which accord with the results of the pmr studies.3)

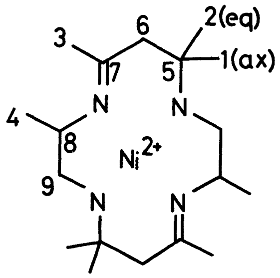
Spectral parameters are summarized in Table 1. Since the spectral analyses for the meso- and rac-complexes are quite similar, we present a detailed description only for the rac-isomer.

Spectra A and B in Fig. 1 show the normal and off-resonance spectra, in higher field region, of the rac-isomer. Spectra of the imine carbon region are not shown in Fig. 1 (vide infra). Off-resonance spectrum of this isomer consists of four quartets, two triplits, one doublet, and two singlets (see Table 1). This spectral pattern is as expected from the structure I, which has four methyl, two methylene, one methine, and one imine and one quarternary carbon atoms. Since an only one doublet has been observed, this singnal (-5.6 ppm) is unambiguously due to the methine carbon atom C_8. Out of two singlets observed in the off-resonance spectrum, the siglet at the lowest field (113.6 ppm) can be assigned to the imine carbon C_7 in view of the value of chemical shift.7) The other singlet (-12.9 ppm) is, therefore, due to the quarternary carbon C_5.

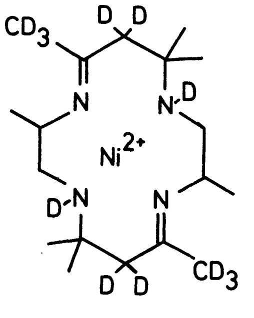
Spectrum C in Fig. 1 shows the off-resonance spectrum of the deuterated derivative (II) of this isomer. The triplet at -14.9 ppm and the quartet at -45.3 ppm of spectrum B essentially disappear upon deuteration. (The chemical shift values designated in parentheses in Table 1 are those of the disappeared signals upon deuteration.) The disappered triplet and quartet are unequivocally assigned to the methylene carbon of the six-membered ring C_6 and the imine methyl carbon C_3, respectively, since deuteration occurs on the carbon atoms adjacent to the imine carbon.3,8-10) Accordingly, out of two triplets, the undisappered triplet (-18.0 ppm) is due to the methylene carbon of the five-membered ring C_9.

To explain the resonance lines due to the three methyl carbons C_1, C_2 and C_3, which have not been assigned so far, selective proton decoupling experiments were carried out. When the C_4 methyl proton doublet (1.55 ppm vs. DSS)3) was selectively irradiated, the quartet at -48.7 ppm in spectrum B was converted into a singlet. Therefore this signal is assigned to the methyl carbon C_4. Specific assignments for the geminal dimethyl carbons C_1 and C_2 can be inferred from the results of the pmr studies for the present complexes3) and the analogous macrocyclic nickel (II) complexes.2,8,11) The location of the geminal carbon atom produces an axial and equatorial distinction between the two geminal methyl groups. In the pmr spectra of these complexes, the equatorial methyl proton resonance appears at higher field than the axial member.2,3,8,11) When the eqatorial methyl protons (1.18 ppm vs. DSS)3) were selectively decoupled, the quartet at -42.1 ppm in spectrum B was converted into a singlet. On the other hand, single frequency off-resonance decoupling of the axial methyl protons (2.20 ppm vs. DSS)3) converted the quartet at -43.2 ppm in spectrum B into a singlet, while it left the remaining signals essentially unchanged. Accordingly the signals at -42.1 and -43.2 ppm are assigned to the equatorial and axial methyl carbons, respectively. It should be noted that the equatorial methyl carbon resonance appears at lower field than the axial methyl carbon resonance, in contrast to the relative position in the pmr spectrum.

The analysis of the cmr spectrum for the meso-isomer was carried out in the same way. The spectral assignments are also listed in Table 1.



(I)



(II)

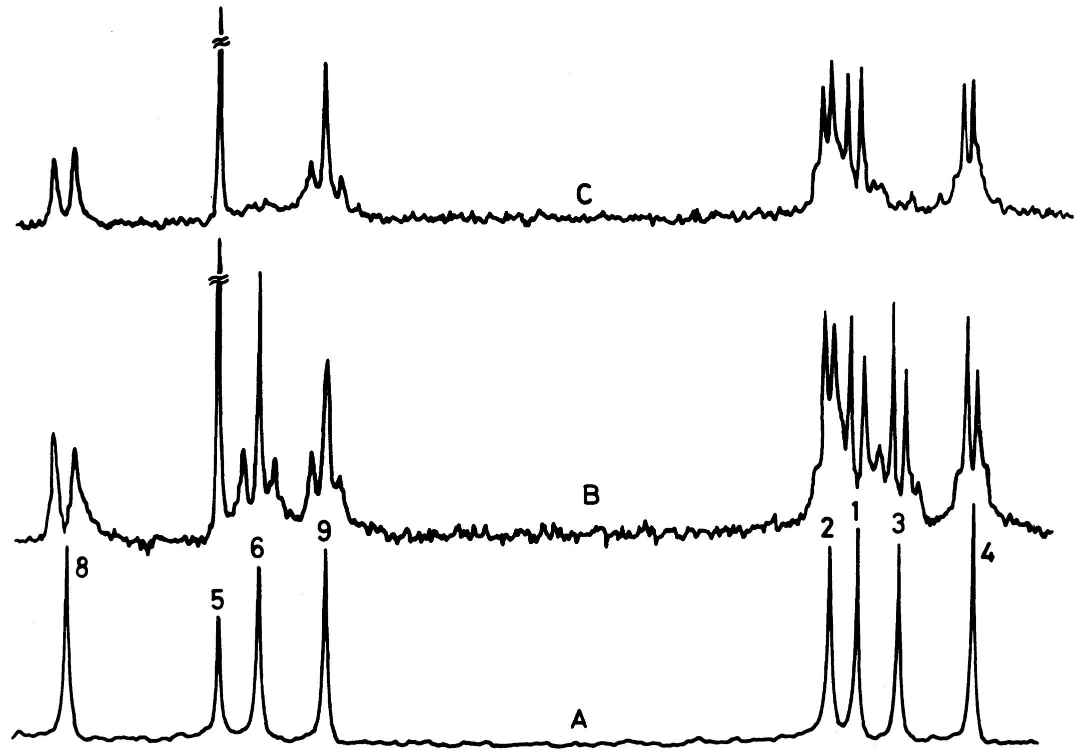


Fig. 1 The cmr spectra of the chloride salt of the rac-complex in D_2O.
(A) the proton noise decoupling spectrum, (B) the off-resonance spectrum, (C) the off-resonance spectrum of the deuterated complex. Chemical shifts are expressed downfield from the internal standard dioxane.

TABLE 1. Cmr spectral data for the rac- and meso-complexes.[a]

Assignments	rac isomer Chem. shift ppm	rac isomer Signal shape upon off-resonance decoupling	meso isomer Chem. shift ppm	meso isomer Signal shape upon off-resonance decoupling
1[b]	-43.2	quartet	-44.8	quartet
2[c]	-42.1	quartet	-42.2	quartet
3	(-45.3)	quartet	(-43.0)	quartet
4	-48.7	quartet	-48.5	quartet
5	-12.9	singlet	-13.3	singlet
6	(-14.9)	triplet	(-15.0)	triplet
7	113.6	singlet	116.7	singlet
8	-5.6	doublet	-7.2	doublet
9	-18.0	triplet	-17.1	triplet

a) Data for the chloride salts in D_2O. Chemical shifts are expressed downfield from the internal standard dioxane. The disappeared signals upon deuteration are given in parentheses. b) axial. c) equatorial.

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