BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (12), 3647—3648 (1978)

Nitric Acid Oxidation of 3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) Perchlorate

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(Received June 21, 1978)

Synopsis. Oxidative dehydrogenation of three kinds of the title compounds, *meso*[1*R*(*S*), 3*S*(*R*), 8*S*(*R*), 10*R*(*S*)]-, *rac*[1*S*(*R*), 3*R*(*S*), 8*S*(*R*), 10*R*(*S*)]-, and optically active[1*S*, 3*R*, 8*S*, 10*R*]-forms produced the complexes with four isolated imine groups. Some spectroscopic data of the tetraimine complexes are presented.

It has been found that some nickel(II) complexes of cyclic ligand containing secondary amine donors are chemically oxidized to forms containing a higher unsaturation in the ligand.[1–4] The *meso*-, *rac*-, and optically active-forms of the title complex **1**[5] underwent oxidative dehydrogenation of the ligand in concentrated nitric acid to give the respective tetraimine complexes **2**. The elemental analyses of each oxidation product indicated the presence of two additional sites of unsaturation. The IR spectra of the oxidation products showed no absorption for N–H stretching modes (≈3200 cm^{-1}). These two results lead to the isolated tetraimine structure **2**.

The proton noise decoupling ^{13}C NMR spectra of the *meso*- and *rac*-complexes show nine resonance lines, respectively, indicating that each carbon atom within each isomer is pairwise equivalent. The *meso*- and *rac*-complexes have C_i and C_2 symmetry, respectively. The off-resonance spectrum of each isomer consists of four quartets, one triplet, two doublets, and two singlets. This spectral pattern is as expected from the structure **2**. The resonance lines were assigned in the way similar to that for the complex **1**.[6] The ^{1}H NMR spectra of the products also support the structure. The ^{1}H and ^{13}C NMR spectral data are listed in Tables 1 and 2, respectively.

Table 1. ^{1}H NMR spectral data for tetraimine complexes[a)]

Assignments[b)]	Signal shape[c)]	Rel. intens.	Chem. shift, ppm *vs.* TMS	
			rac-isomer	*meso*-isomer
CH_3(a)[d)]	s	3	1.38	1.40
CH_3(b)[e)]	s	3	1.16	1.20
CH_3(c)	s	(3)	(2.33)	(2.32)
CH_3(d)	d	3	1.53	1.56
H_a H_b	AB-q	(2)	(2.93)	(2.94)
H_c	q of d	1	5.02	4.98
H_d	d	1	7.98	7.88

a) Data for the perchlorate salts in DMSO-d_6 solutions. The signals, whose chemical shifts are given in parentheses, disappear upon d_{10}-deuteration. b) See the structure **2** for numbering. c) The abbreviations, s, d, AB-q, and q of d, denote singlet, doublet, AB-quartet, and quartet of doublet, respectively. d) Axial. e) Equatorial.

Table 2. ^{13}C NMR spectral data for the *rac*- and *meso*-tetraimine complexes[a)]

Assignments[b)]	Chemical shift, ppm *vs.* TMS	
	rac-isomer	*meso*-isomer
C_1[c)]	24.7 q	24.5 q
C_2[d)]	25.7 q	25.5 q
C_3	(23.6) q	(23.8) q
C_4	15.9 q	16.3 q
C_5	56.9 s	57.2 s
C_6	(50.9) t	(50.1) t
C_7	185.1 s	185.2 s
C_8	69.1 d	69.2 d
C_9	177.4 d	175.6 d

a) Data for the perchlorate salts in DMSO-d_6. The signals, whose chemical shifts are given in parentheses, disappear substantially upon d_{10}-deuteration. The abbreviations, q, t, d, and s, denote quartet, triplet, doublet, and singlet, respectively, which are signal shape upon off-resonance decoupling. b) See the structure **2** for numbering. c) Axial. d) Equatorial.

The perchlorate salts of the tetraimine complexes are square planar and diamagnetic in most solvents (H_2O, MeOH, DMSO, CH_3CN, Py) as revealed by the ligand field spectra. The optically active isomer in H_2O has a d-d electronic absorption band at 23000 cm^{-1} with an ε_{max} of 86 and an absorption at 34100 cm^{-1} (ε_{max}= 5580) associated with the isolated imine functions. The corresponding CD peaks appear at 20800 ($\Delta\varepsilon$= −0.29) and 24300 ($\Delta\varepsilon$=+2.62), and 33800 cm^{-1} ($\Delta\varepsilon$=−5.75). The *meso*-isomer shows a similar electronic spectrum; $\tilde{\nu}_{max}(\varepsilon_{max})$=23400 (58), 34400 cm^{-1} (5860).[7] These features of the electronic spectra and the circular dichroism spectrum demonstrate a square planar structure for these complexes in water.[1]

The tetraimine complexes are stable in neutral or acidic solutions but decompose in basic solutions.

It is well known for analogous marcrocyclic nickel(II) complexes that the protons α to the imine carbon atom can be exchanged for deuterium atoms in basic D_2O solution.[3–5,8] Recrystallization of **1** from basic D_2O deuterates selectively the methylene protons of the six-membered chelate rings and the protons of the imine methyl groups (CH_3(c)), giving the d_{12}-derivative **4**.[5] Oxidation of the d_{12}-derivatives **4** of the *rac*- and the *meso*-diene complexes with nitric acid produced the d_{10}-derivative of their respective tetraimine complexes **5**. The ^{1}H and ^{13}C NMR spectra of the deuterated,

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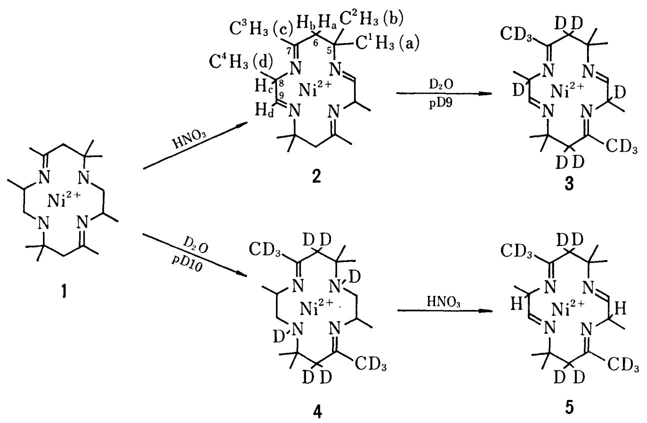

oxidized species indicate the deuterated sites remain intact upon oxidation.

Attempts to prepare d_{12}-derivatives **3** by recrystallization of **2** from basic D_2O solution were partly successful. The ^1H and ^{13}C NMR spectra of the *meso*-tetraimine complex recrystallized from weakly basic D_2O solution indicated that the desired deuteration accomplished. However, the resonance lines of the ^1H and ^{13}C NMR spectra were broad, indicating the presence of the paramagnetic species. All attempts to prepare the d_{12}-derivative **3** of the *rac*-tetraimine complexes in the same way were unsuccessful. As was mentioned before, the tetraimine complexes are unstable in basic solutions as compared with the parent diene complexes.

Experimental

Materials. meso[*1*R(S), *3*S(R), *8*S(R), *10*R(S)]-, rac-[*1*S(R), *3*R(S), *8*S(R), *10*R(S)]-, *and Optically Active*[*1*S, *3*R, *8*S, *10*R]*-form of 3,5,7,7,10,12,14,14-Octamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(II) Perchlorates (1)*: These complexes were prepared as reported in the previous papers.[5,6]

Oxidation of 1: Ten grams of the *meso*-diene complex was dissolved in 30 ml of concentrated nitric acid. Dissolution was immediate and a deep orange solution was produced. This solution was heated on a water bath (80 °C) for 2 h. After cooling, 150 ml of cold acetone was added. A yellow product precipitated. This material was removed by filtration and recrystallized from hot water; yield 6.4 g. This was identified as the *meso*-isomer of **2** (see text). The *rac*- and optically active tetraimine complexes were prepared in a similar way. However, since these isomers were more soluble than the *meso*-isomer, an acetone–diethyl ether mixture (1:2 (v/v)) was used instead of acetone to obtain the precipitates. Found for the *meso*-isomer: C, 38.44; H, 5.70; N, 10.03%. Found for the *rac*-isomer: C, 38.77; H, 5.64; N, 10.17%. Found for the optically active isomer: C, 38.41; H, 5.98; N, 10.21%. Calcd for $NiC_{18}H_{32}N_4Cl_2O_8$: C, 38.46; H, 5.74; N, 9.97%.

The d_{10}-Derivatives 5: The d_{12}-derivatives **4** of the *meso*-, *rac*-, and optically active dienes[5,6] were used as strating materials and oxidized with concentrated nitric acid in the same way.

Measurements. Instruments used for the spectral measurements were as follows: ^{13}C NMR spectra, a JEOL NMR Spectrometer, Model JNM-PFT-60, operating at 15.09 MHz; ^1H NMR spectra, a JEOL NMR Spectrometer, Model PS-100; Electronic spectra, a Hitachi EPS-3T Recording Spectrophotometer; Circular dichroism spectra, a JASCO ORD/UV-5 Spectrometer with CD attachment; Infrared spectra, a JASCO IR-G Spectrophotometer.

References

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7) Because of the low solubility, the electronic absorption spectra for the *meso*-isomer were measured in 0.1 M HNO_3 for UV region and in *ca.* 2 M HNO_3 for visible region.

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