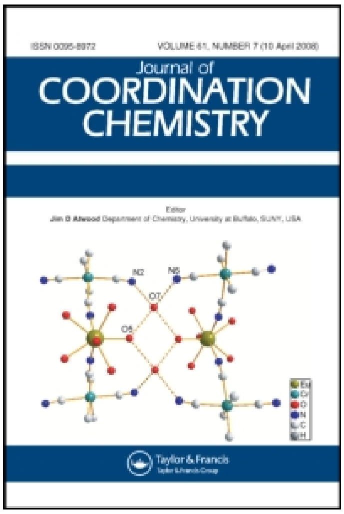

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Metal Ion Promoted Nucleophilic Substitution of Hydrogen in Chelated Macrocyclic α-Di-Imine

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METAL ION PROMOTED NUCLEOPHILIC SUBSTITUTION OF HYDROGEN IN CHELATED MACROCYCLIC α-DI-IMINE

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Base-catalyzed addition of nitromethane to the Ni(II) co-ordinated α-di-imine, followed by elimination of HNO_2 and rearrangement of the double bond formed, leads to the methyl substituted product, *i.e.* the nucleophilic substitution of the imine hydrogens occurred.

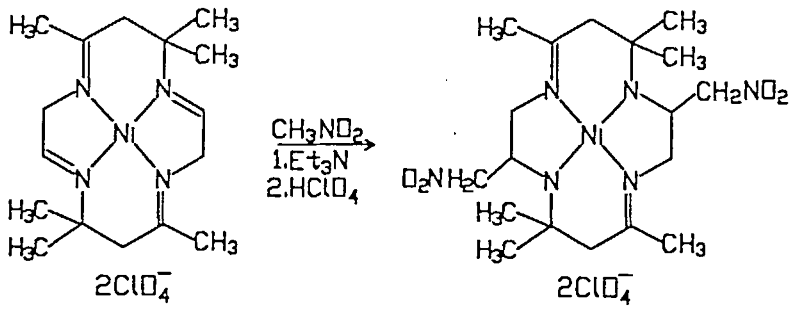
Keywords: Nickel(II), nitromethane, α-di-imine, tetraazamacrocycle, complexes, nucleophilic substitution of hydrogen

Nickel(II) co-ordinated macrocyclic nonconjugated di-imines in the presence of base add the nitromethane anion to the carbon atom of one of the C=N double bonds giving α-nitromethyl substituted amines.[1,2] Complexes of nonconjugated macrocyclic tetra-imines react by the similar way. Adding two nitromethane molecules to the less hindered C=N double bonds (Scheme 1).[3] On the other hand, the base-catalyzed elimination of nucleophile in β-substituted aminoacids is dramatically enhanced by Co(III) co-ordination.[4,5]

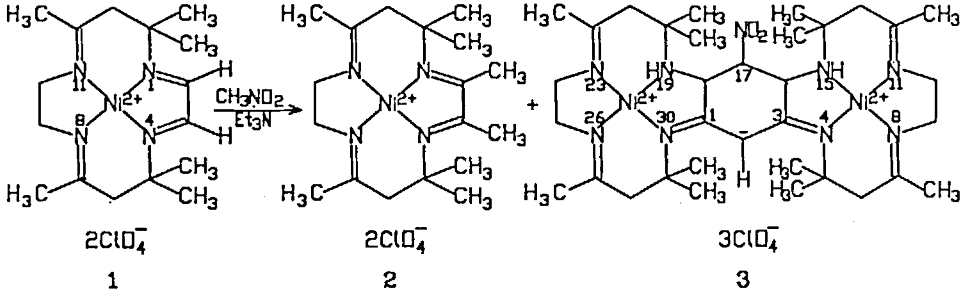
Here, we report the results of the base-catalyzed reaction of nitromethane with 5,5,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,7,11-tetraenenickel(II) diperchlorate (**1**),[6,7] possessing a chelated α-di-imine function (Scheme 2).

EXPERIMENTAL

Triethylamine (0.015 mol) was added to a vigorously stirred solution of complex **1** (0.005 mol) in nitromethane (10 mL). After 15 minutes the mixture was diluted with 50% methanol-water (100 mL), neutralized with 72% perchloric acid (1.2 mL), and absorbed on H^+ form Dowex 50WX2 cation exchange resin. The column was washed with water and 0.5 M HCl. The orange complex **2** was then eluted with 1.5 M HCl and this eluate taken to dryness under vacuum. The residue was dissolved in methanol and the product **2** crystallized upon addition of perchloric acid (yield *ca.* 60%). The column was then washed with 4 M HCl and a minor red band of dinuclear complex **3** was eluted with 5 M HCl. The eluate was evaporate to dryness under reduced pressure, dissolved in water and crystallized upon addition of a few drops of perchloric acid (yield *ca.* 3%). *Anal.* Calcd. for $C_{18}H_{32}N_4Cl_2O_8Ni$ (**2**): C, 38.5; H, 5.7; N, 10.0 Found: C, 38.3; H, 5.9; N, 10.2. Calcd. for $C_{34}H_{58}N_9O_{14}Cl_3Ni_2.(H_2O)$ (**3**): C, 38.6; H, 5.7; N, 11.9; Cl, 10.0. Found: C, 38.7; H, 5.7; N, 11.9; Cl, 10.0. ν_{max} (cm^{-1}, nujol): (**2**) 1670 and 1600 (C=N), 1090(ClO_4^-); (**3**) 3200(NH), 1665 and 1570(C=N), 1530(NO_2), 1100(ClO_4^-). $\lambda_{max}(\varepsilon)$ (nm, CH_3NO_2): (**2**) 420sh (1052); (**3**) 499 (3140).



Scheme 1



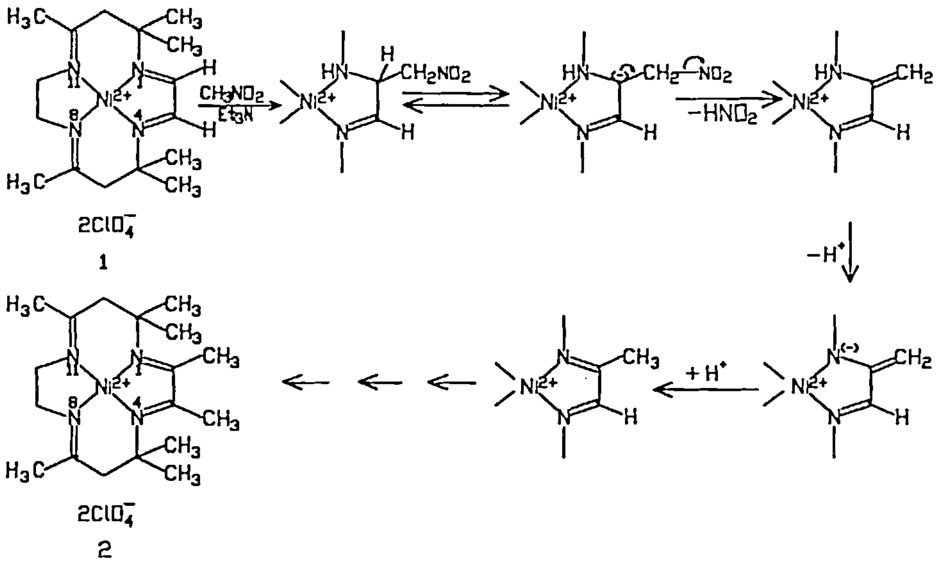
Scheme 2

RESULTS AND DISCUSSION

Complex **1** reacts with nitromethane in the presence of base, but all the evidence indicate the absence of expected nitromethyl pendant arms in the structure of isolated products **2** and **3**. Structures of compounds **2** and **3** were established on the basis of elemental analyses and spectroscopic, mainly ^1H and ^{13}C n.m.r.[8] evidence. The ^1H n.m.r. spectrum of complex **2** is nearly identical with that of complex **1**,[7] except, that the imine protons signal at δ 8.09 (2H) is substituted with the methyl groups singlet at δ 2.53 (6H). The ^1H n.m.r. spectrum of complex **3** indicates the presence of a plane of symmetry in the molecule and consists of signals characteristic for macrocyclic units, as well as, the 1 H singlet at δ 5.10 and the 1 H triplet at δ 5.28 originating from $=CH-$ and $>CH-NO_2$ linking groups respectively. These assignments were confirmed by 2D ^1H-^{13}C n.m.r. spectra.

Nucleophilic substitution of hydrogen in **1** (Scheme 3) is a multistep process consisting of nitromethane addition to $C{=}N$ double bond followed by HNO_2 elimination, and seems to be analogous to the vicarious nucleophilic substitution of hydrogen in nitroarenes.[9] Therefore, we intend to utilize this reaction for introduction of functionalized alkyl pendant arms into macrocyclic ring using another reagents, containing a leaving group at the carbanionic centre.

Complex **3** is probably formed from 2+2 dinitro adduct, which after oxidation by the nitric oxides present in the reaction mixture, eliminates one molecule of HNO_2.



Scheme 3

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8. (2,3,5,7,12,14,14-octamethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,7,11-tetraen-κ^4N)nickel(II) diperchlorate (2) ^{1}H n.m.r. (500 MHz, CD_3NO_2): 5,14-CH_3—1.48s,12H; 7,12-CH_3—2.39s,6H; 2,3-CH_3—2.53s,6H; 6,13-CH_2—3.21s,4H; 9,10-CH_2—3.82s,4H. ^{13}C n.m.r. (125 MHz, CD_3NO_2): CH_3—22.7, 24.7, 25.1; CH_2—55.0, 57.4; 5,14-C—60.8; 2,3-C—182.4; 7,12-C—187.5. (5,5,7,12,14,14,20,20,22,27,29,29-dodecamethyl-17-nitro-4,8,11,15,19,23,26,30-octa-azatricyclo[16,12,0,$0^{3,16}$]triaconta-1(30),3,7,11,22,26-hexaen-2-ato-κ^8N)dinickel(II) triperchlorate (3) ^{1}H n.m.r. (500 MHz, CD_3NO_2): CH_3—1.17s,6H, 1.39s,6H, 1,40s,6H, 2.15s,6H, 2.31s,6H, 2.37s,6H; 13,21-CH_2—2.86d, 3.02d,J=14.8Hz,4H; 6,28-CH_2—3.04d, 3.07d,J=20.0Hz,4H; 9,25 and 10,24-CH_2—3.39m,2H, 3.59m,2H, 3.79m,2H, 4.04m,2H; 15,19-NH—4.45d,J=6.8Hz,2H; 16,18-CH—4.61m,2H; 2CH—5.10s,1H; 17-CH—5.28t, J=1.6Hz,1H. ^{13}C n.m.r. (125 MHz, CD_3NO_2): CH_3—23.5, 23.7, 24.0, 25.7, 25.8, 26.3; 6,28-C—53.4; 13,21-C—59.1; 9,25 and 10,24-C—54.5 and 55.6; 5,29 and 14,20-C—56.0 and 58.6; 7.27 and 12,22-C—183.9 and 184.0; 1,3-C—169.8; 2-C—95.0; 17-C—85.0 p.p.m.
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