

Friedel–Crafts acetylation of a (NiC₃N₂)-quasi-aromatic ring in a nickel(II) complex, Nioyal

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(Received May 31, 1991; revised September 11, 1991)

Abstract

Electrophilic substitution of an acetyl group onto the quasi-aromatic ring of Nioyal, (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene)nickel(II) was accomplished at 70 °C utilizing acetyl bromide and aluminum chloride dissolved in tetrachloroethylene. ¹H and ¹³C NMR were used to establish the basic structure which results from substitution of the hydrogen by an acetyl group on the central carbon of the metal containing aromatic ring. The single crystal X-ray structure is presented which confirms the position of substitution and that the basic Nioyal structure is maintained. Ni₁O₃N₄Cl₁₅H₂₄, *M_r* = 367.1, orthorhombic, *Pbca*, *a* = 17.684(9), *b* = 10.244(4), *c* = 18.542(8) Å, *V* = 3359.0 Å³, *Z* = 8, *D_x* = 1.456(2) g cm⁻³, (Mo Kα) = 0.71073 Å, *μ* = 11.8 cm⁻¹, *F*(000) = 1560, *T* = 297 K, *R* = 0.031, *R_w* = 0.038, for 1246 observed reflections (of 4306 unique data). The IR absorption band ascribed to the carbonyl stretching frequency (1584 cm⁻¹) is much lower than expected for a free uncoordinated acetyl group. The bond distances and angles in the molecule are compared with the parent Nioyal in an attempt to understand the nature of the bonding of the acetyl group to the metal containing ring.

Introduction

Shortly after it was first reported [1], the neutral, planar macrocyclic nickel(II) complex, Nioyal, was shown to be susceptible to electrophilic substitution reactions at the central methine position [2]. Some of the electrophiles which have been successfully substituted under very mild conditions are the halogens (Cl, Br, I), NO and NO₂ as well as aldehydes in general.

Several reports have appeared concerning the reactivity of electrophiles toward macrocyclic metal complexes possessing aromatic character [3–6] but few have been shown to undergo as wide a variety of reactions as Nioyal or to do so in high yields. For instance the dimer Nioyal–Nioyal, linked through the central methine carbon was early prepared as well as the methane substituted derivatives (Nioyal)₂CH₂ and (Nioyal)₃CH. More recently aromatic diazonium salts were found to react quantitatively to give for example, Nioyal–N=N–(C₆H₄SO₃H) [7]. The scope of the area of interest increased dramatically with the discovery that analogous aromatic-like macrocycles of Cu(II), Pd(II), and Pt(II) are stable and undergo the same reactions [8].

In the continuing study of these unique, well behaved molecules which can serve as models of a wide variety of similar metal containing aromatic ring complexes, this paper reports the preparation and characterization of acetyl-Nioyal (Fig. 1) under rather harsh conditions

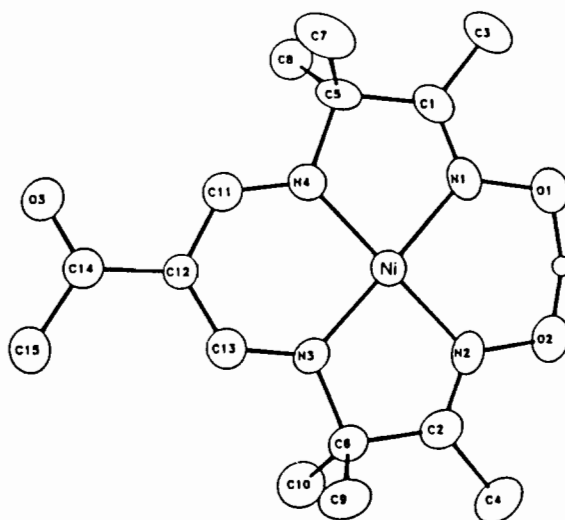


Fig. 1. Acetyl-Nioyal.

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where it was anticipated that other competing reactions, especially at the oxime-hydrogen bond, might occur more rapidly and prevent acetylation.

Experimental

NiOyl, [Ni(PnAO-6H)]^o

This was prepared from [Ni(PnAO)-H]Cl as previously described [1].

Acetyl-NiOyl

To a solution of 2.00 g (0.00165 mol) of NiOyl in 75 ml of tetrachloroethylene, was added 0.90 g (0.0068 mol) of anhydrous aluminum chloride. The mixture was gently warmed for 20 min after which 0.76 g (0.0061 mol) of acetyl bromide was slowly added. The mixture was brought to 70 °C and maintained there for 24 h. After cooling to room temperature the mixture was added to crushed ice and extracted with several portions of chloroform. The chloroform extracts were washed 3× with 10% NaOH solution and 3× with water and then dried overnight with anhydrous calcium chloride. After the solvent was removed by evaporation the impure product was dissolved in methanol and precipitated with water. The solid was then dissolved in the minimum quantity of ethyl acetate and n-hexane added until the solution appeared cloudy. After filtration the solution was allowed to evaporate and fine yellow crystals developed. These were collected and dried under vacuum at 60 °C for 1 h. Yield 30% of theory. Recrystallization for X-ray quality crystals was made from acetonitrile by slow cooling of a saturated solution. *Anal.* Calc. for C₁₅H₂₄O₃N₄Ni: C, 49.08; H, 6.59; N, 15.26. Found: C, 49.38; H, 6.65; N, 14.95%. ϵ_{\max} (95% ethanol): 206 nm, 1.99×10^4 ; 262 nm, 1.24×10^4 ; 308 nm, 6.46×10^3 ; 378 nm, 3.66×10^3 ; 402 nm, 3.40×10^3 .

All chemicals were reagent grade. UV-Vis spectral measurements were made in a Hewlett-Packard 8452A diode array spectrophotometer. The IR spectrum was obtained on a Perkin-Elmer 1600 FTIR in CDCl₃ solution. Proton and ¹³C NMR spectra were observed on a General Electric Omega 300 using deuterated chloroform at room temperature (20 °C) with TMS as the internal standard.

X-ray data collection

Crystals were well formed yellow plates and were stable indefinitely in air. The one selected had dimensions of 0.2×0.15×0.24 mm. An Enraf-Nonius CAD-4 diffractometer was used to collect and center 25 standard reflections having $8 < \theta < 14^\circ$ using Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$. These were used to determine the unit cell and refine the cell constants. Systematic absences were $0kl, k = 2n; h0l, l = 2n; hk0, h = 2n$. The

θ - 2θ scan method was employed to obtain 3% counting statistics to a maximum scan time of 50 s. The range of reflections measured was $+h+k \pm l: 1-20^\circ, +h+k+l: 20-22^\circ$ in θ . From three psi-scans it was determined that absorption was small (max.-min. <5%), but the empirical corrections were made. Decay, over the period of data collection, based on three standards measured every 6000 s, was less than 0.5% and no correction was made for it. Of 4306 reflections measured, 3558 were present and 1246 were unique and not systematically absent ($I > 2\sigma(I)$). The intensities of equivalent reflections (534) were averaged giving an agreement factor of 2% based on intensity. The structure was solved by MULTAN [9] with the function minimized during refinement being $\sum w(|F_o - F_c|)^2$ with $w^{-1} = \sigma^2_{\text{counting}} + (0.04F_o^2)^2/4F_o^2$. All heavy atoms were found from difference Fourier maps and were refined with anisotropic thermal parameters. All hydrogens were located from difference Fourier maps and their positions optimized by calculation. They were entered into the calculations with fixed positional parameters and isotropic temperature factors. The extinction coefficient was insignificant and was not used. A total of 208 parameters was refined with 1246 data giving $R = 0.031, R_w = 0.038, S = 1.17$ and $(\Delta/\sigma)_{\max}$ in final cycle 0.01. In the final difference Fourier the highest peak height = 0.35 e \AA^{-3} with an estimated error of 0.11. Atomic scattering factors and anomalous-dispersion corrections were from the International Tables for X-ray Crystallography, 1974. The structure was refined in full-matrix least-squares with SDP [10]. See also 'Supplementary material'.

Results and discussion

The unit cell contains one independent neutral molecule which is nearly planar except for geminal methyl groups and has the acetyl group attached at the C12 position. Final positional parameters are given in Table 1. Intramolecular bond distances and angles are listed in Tables 2 and 3, respectively. Figure 1 shows an ORTEP [11] drawing of the molecule and the numbering scheme used. Table 4 gives the least-squares planes through the main molecule and that formed by the acetyl group. It is clear that the molecule is essentially planar except for the *gem*-dimethyl groups which are on either side of the plane.

Acetyl-NiOyl is soluble in methanol, acetonitrile and chloroform but only slightly soluble in carbon tetrachloride and water. A 0.004 M solution in 1/1 methanol water was essentially non-conducting electrically showing it to be non-ionic. The sharp ¹H NMR signals which are observed establish the diamagnetic nature of the d⁸-Ni(II) planar complex. The ¹H and ¹³C NMR spectra are summarized in Table 5.

TABLE 1

Positional parameters and their e.s.d.s

Atom	x	y	z	B(Å ²)
Ni	0.42245(3)	0.23564(5)	0.58550(3)	2.59(1)
O1	0.4734(2)	0.1648(3)	0.4460(2)	3.98(8)
O2	0.5440(2)	0.3368(3)	0.5025(2)	4.01(8)
O3	0.2199(2)	0.1108(4)	0.7897(2)	5.3(1)
N1	0.4261(2)	0.1366(4)	0.5014(2)	2.89(8)
N2	0.5027(2)	0.3463(4)	0.5636(2)	2.95(9)
N3	0.4177(2)	0.3331(4)	0.6687(2)	2.66(8)
N4	0.3464(2)	0.1216(3)	0.6094(2)	2.55(8)
C1	0.3843(3)	0.0354(5)	0.4958(3)	2.8(1)
C2	0.5220(3)	0.4324(5)	0.6097(3)	2.9(1)
C3	0.3877(3)	-0.0533(5)	0.4326(3)	4.1(1)
C4	0.5888(3)	0.5194(5)	0.5990(3)	4.1(1)
C5	0.3312(3)	0.0136(5)	0.5582(3)	2.9(1)
C6	0.4743(3)	0.4402(5)	0.6761(3)	3.0(1)
C7	0.2493(4)	0.0196(6)	0.5311(3)	5.0(1)
C8	0.3472(3)	-0.1179(5)	0.5940(3)	4.0(1)
C9	0.4335(3)	0.5718(5)	0.6774(3)	4.6(1)
C10	0.5227(3)	0.4208(6)	0.74.25(3)	5.2(1)
C11	0.3061(3)	0.1246(5)	0.6692(3)	3.0(1)
C12	0.3147(3)	0.2165(4)	0.7243(2)	2.7(1)
C13	0.3692(3)	0.3163(5)	0.7218(3)	3.0(1)
C14	0.2652(3)	0.2006(5)	0.7865(3)	3.3(1)
C15	0.2701(4)	0.2935(5)	0.8484(3)	5.0(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

TABLE 2

Bond distances

Distances (Å)			
Ni-N1	1.861(4)	C1-C3	1.483(7)
Ni-N2	1.861(4)	C1-C5	1.507(7)
Ni-N3	1.840(4)	C2-C4	1.493(7)
Ni-N4	1.836(4)	C2-C6	1.495(7)
O1-N1	1.356(5)	C5-C7	1.535(7)
O2-N2	1.352(5)	C5-C8	1.528(7)
O3-C14	1.220(6)	C6-C9	1.529(7)
N1-C1	1.278(6)	C6-C10	1.514(8)
N2-C2	1.275(6)	C11-C12	1.397(6)
N3-C6	1.492(6)	C12-C13	1.405(7)
N3-C13	1.316(6)	C12-C14	1.457(6)
N4-C5	1.482(6)	C14-C15	1.494(7)
N4-C11	1.319(6)		

Numbers in parentheses are e.s.d.s in the least significant digits.

The proton NMR spectrum for Nieryl is consistent with the assignment to the C_{2v} point group as previously reported [2]. There are two sets of four and two equivalent methyl groups (singlet), at 1.32 and 1.97 ppm, respectively, a C12 proton (triplet) at 5.07 ppm, a C11 proton (doublet) at 7.03 and the hydrogen bond hydrogen at 19.02 ppm downfield. In the spectrum of acetyl-Nieryl the two sets of methyl groups are slightly

TABLE 3

Bond angles

Angles (°)			
N1-Ni-N2	97.1(2)	N2-C2-C6	116.0(4)
N1-Ni-N3	179.3(2)	C4-C2-C6	121.6(5)
N1-Ni-N4	83.1(2)	N4-C5-C1	105.5(4)
N2-Ni-N3	83.5(2)	N4-C5-C7	110.5(4)
N2-Ni-N4	177.3(2)	N4-C5-C8	110.3(4)
N3-Ni-N4	96.3(2)	C1-C5-C7	109.3(4)
Ni-N1-O1	122.7(3)	C1-C5-C8	110.4(4)
Ni-N1-C1	119.4(3)	C7-C5-C8	110.7(5)
O1-N1-C1	117.9(4)	N3-C6-C2	105.3(4)
Ni-N2-O2	123.4(3)	N3-C6-C9	109.5(4)
Ni-N2-C2	118.7(4)	N3-C6-C10	111.0(4)
O2-N2-C2	117.9(4)	C2-C6-C9	109.1(4)
Ni-N3-C6	116.5(3)	C2-C6-C10	110.1(5)
Ni-N3-C13	125.8(3)	C9-C6-C10	111.7(5)
C6-N3-C13	117.7(4)	N4-C11-C12	124.8(5)
Ni-N4-C5	117.0(3)	C11-C12-C13	122.7(4)
Ni-N4-C11	125.7(3)	C11-C12-C14	115.9(4)
C5-N4-C11	117.2(4)	C13-C12-C14	121.3(4)
N1-C1-C3	122.5(5)	N3-C13-C12	124.5(4)
N1-C1-C5	114.7(4)	O3-C14-C12	121.2(5)
C3-C1-C5	122.8(5)	O3-C14-C15	118.7(5)
N2-C2-C4	122.4(5)	C12-C14-C15	120.1(5)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 4

Least-squares planes through the molecule

The equation of the plane is $A^*x + B^*y + C^*z - D = 0$ where x , y , z are orthogonalized coordinates and A , B , C , and D are constants

Plane 1* $A = -0.6496$, $B = 0.6181$, $C = -0.4426$, $D = -8.2255$
 Ni (0.059), N1 (0.082), N2 (0.018), N3 (0.050), N4 (0.012), O1 (0.170), O2 (-0.016), C1 (-0.035), C2 (0.037), C3 (0.121), C4 (0.162), C5 (0.069), C6 (0.014), C11 (0.005), C12 (0.034), C13 (0.063), C15 (-0.009), C15 (0.022), O3 (-0.082) (atom deviation from plane, Å) e.s.d. av. 0.004

Other atoms: C7 (1.124), C8 (-1.391), C9 (1.306), C10 (-1.215)

Plane 2* $A = -0.6928$, $B = 0.5770$, $C = -0.4325$, $D = -8.2255$
 C14 (0), C15 (0), O3 (0)

Dihedral angle, plane 1/plane 2 $3.5 \pm 4.1^\circ$

shifted downfield (singlets) and the triplet at 5.07 ppm is missing. The two equivalent C11 protons are now deshielded by the carbonyl group and appear at 7.98 ppm as a singlet. The new resonance at 2.31 ppm is easily assigned to the acetyl-methyl group hydrogens (C15).

The proton decoupled ¹³C NMR spectrum of Nieryl shows the six magnetically different carbon atom signals expected and previously assigned [12]. The analogous spectra for acetyl-Nieryl show eight magnetically different carbon atom signals, six of which are analogous to those in Nieryl and slightly shifted downfield due to the increased shielding caused by the carbonyl group. The

TABLE 5
NMR spectra of Nioyl and acetyl-Nioyl in CDCl₃ (TMS)

¹ H NMR (ppm (no. of H atoms))		¹³ C NMR (ppm (carbon atom, see Fig. 1))	
Nioyl	Acetyl-Nioyl	Nioyl	Acetyl-Nioyl
1.32(12)	1.41(12)	11.83(3)	12.08(3)
1.97(6)	2.01(6)		26.14(15)
	2.31(3)	26.72(7,8)	26.88(7,8)
5.07 ^a (1)		69.01(5)	70.05(5)
7.03 ^b (2)	7.98(2)	92.50(12)	112.18(12)
19.02(1)	18.98(1)	146.75(11)	151.92(11)
		161.42(1)	161.77(1)
			193.40(14)

^aTriplet. ^bDoublet.

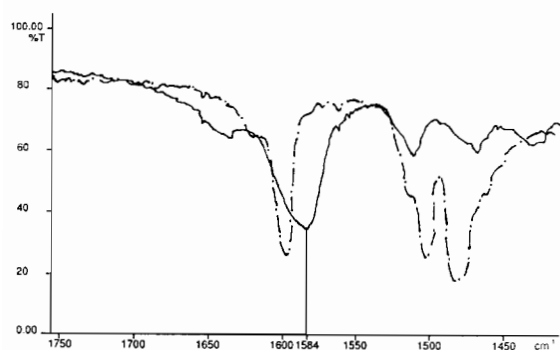


Fig. 2. Expanded FT-IR spectra of Nioyl (---) and acetyl-Nioyl (—) in CDCl₃. The absorption bands for Nioyl (C=N) and acetyl-Nioyl (C=O) occur at 1598 and 1584 cm⁻¹, respectively.

two new resonances are assigned to the acetyl-methyl carbon (C15) at 26.14 ppm and the farthest downfield at 193.40 ppm to the carbonyl carbon atom (C14). Thus the NMR spectra are completely consistent with the assigned structure assuming rapid rotation about the acyl-to-ring bond.

The IR spectrum of Nioyl shows a strong band centered at 1598 cm⁻¹ which is assigned to the carbon-nitrogen double bond stretching frequency [13]. The intramolecular OHO bond gives rise to the broad signal at 1792 cm⁻¹ [14]. With acetyl-Nioyl the intramolecular OHO bond absorption is at 1792 cm⁻¹, unshifted. The strong band at 1584 cm⁻¹ is attributed to the carbonyl stretching vibration. A shoulder exists on it at 1598 cm⁻¹ which we ascribe to the carbon-nitrogen double bond that is present in both complexes. Figure 2 shows the two spectra in the region of interest. The carbonyl band position occurs at an unusually low wavelength (1584 cm⁻¹) for a free uncoordinated acetyl group. Saturated aliphatic ketones show bands in the vicinity of 1715 cm⁻¹ whereas conjugation with olefinic or phenyl groups results in a lowering to 1685–1666 cm⁻¹ [13]. The quasi-aromatic acetylated chromium(III) and cobalt(III) acetylaceton-

ates exhibit absorption at about 1680 cm⁻¹ [6]. The unsubstituted acetylacetonates of Cr(III) and Co(III) show similar proton-NMR behavior of the hydrogen which is substituted by the acetyl group: Nioyl 5.07, acacs 5.36 ppm. The significantly greater bathochromic shift that occurs in acetyl-Nioyl may be attributed to interaction between the ring protons and the carbonyl oxygen atom which cannot occur in the acetylated acetylacetonates because of the adjacent methyl groups. Alternatively there may be greater charge transfer due to conjugation to the quasi-aromatic ring because of the planarity allowed only in the Nioyl system. These possibilities will be discussed later utilizing the bond distances and angles found with the X-ray study.

A comparison of the bond distances in Nioyl [7] and acetyl-Nioyl (Table 2) reveals practically no significant differences in the amine-oxime chelate ring outside of the 2σ estimated to be a reasonable error in the bond length. (Note that since the molecule does not have a mirror plane, in the X-ray description of the molecule there are more atoms in than in the NMR assignment.) The distance between O1 and O2 is exactly the same, 2.40(1) Å, in the two structures but there appears to be a slight shifting of O1 out of the plane of the acetyl-Nioyl molecule. The position of the hydrogen in the intramolecular hydrogen bond is about normal with distances of 1.23 and 1.20 Å to O1 and O2 and an angle of 160°. The acetyl-Nioyl molecule is extremely planar with all heavy atoms nearly in a single plane except for the *gem*-dimethyl groups, and they are nearly symmetrically disposed on either side of the plane. The plane of the acetyl group makes a dihedral angle with the main complex ion of 3.5 ± 4.1° or zero within the estimated error. One would anticipate that one side of the quasi-aromatic ring would have significantly different bond distances than the other if there were significant electronic interaction between the acetyl group and the aromatic ring. This does not seem to be the case however since C12–C11 = 1.397(6), C12–C13 = 1.405(7) and N4–C11 = 1.319(6), N3–C13 = 1.316(6) and Ni–N4 = 1.836(4), Ni–N3 = 1.840(4) Å are all equal in pairs within the estimated errors. The possibility that the C11 proton, HC11, interacts with the carbonyl group was tested by calculating the distances and angles between those atoms. The C11–HC11–O3 bond angle is 105.9° and the bond distance between HC11 and O3 is 2.248 Å. Thus there appears to be a significant interaction between the C11–hydrogen and the carbonyl oxygen and this may result in or certainly contribute to, the acetyl group being coplanar with the Nioyl ring. This agrees with one interpretation of the low IR stretching frequency for the carbonyl group and suggests that the hydrogen bonding is sufficiently strong that it is retained to a significant degree in solution during

the IR measurements. It has been shown that C11 has a positive charge of about 0.12 compared to the negative C12 of -0.24 which would provide for strong hydrogen bonding of this sort. There does not appear to be any evidence from this work to indicate significant conjugation of the acetyl group to the pseudoaromatic ring.

Supplementary material

Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom *xyz* coordinates and isotropic temperature factors, and bond distances and angles for hydrogen atoms have been deposited with the British Library Document Supply Center. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, UK.

Acknowledgements

We thank the University of Western Carolina for providing a Research Assistantship (S.C.) and the University of Missouri Research Council for partial support.

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