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Note

Alkylation of 2-vinylpyridine and crystal structure of bis{(acetylacetonate)(1-pyridylbutyl)nickel(II)} complex

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Abstract

The alkylation of 2-vinylpyridine (2-vpy) was produced by the reaction of $[Ni(acac)_2]$ (acac = acetylacetone), 2-vpy and $AlEt_3$ to isolate the dinickel(II) complexes with 1-pyridylbutanate (L). Two nickel atoms are bridged by the N atom and carbonate atom of L to form the binuclear complex. Each Ni atom is also coordinated by two O atoms of acetylacetonate, providing the square-planar geometry. The bridging mode of L is head-to-tail coordination, and the eight-membered ring $Ni_2N_2C_4$ framework has a rare staggered conformation.

Keywords: Crystal structures; Nickel complexes; Alkylation; Acetylacetonate complexes; Insertion reactions

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1. Introduction

Various organic compounds have been produced so far using organometallic compounds such as those of Ni, Pd and Pt. In particular, the characterization of [Ni(acac)(alkyl)(L)] compound (acac = acetylacetone) is important in order to determine the intermediates in the reduction of Ni acac complexes by $AlEt_3$ [1–4], with respect to the insertion reaction of alkyls to alkynes and alkenes. However, only a few alkylnickel compounds have been characterized crystallographically [1–3], as these compounds are difficult to isolate and crystallize owing to their instability. In this study we prepared a binuclear alkylnickel complex with 1-pyridylbutanate (L), which was produced by alkylation of 2-vinylpyridine and characterized crystallographically.

2. Experimental

2.1. Synthesis of bis{(acetylacetonate)(1-pyridylbutyl)-nickel(II)} (1)

$[Ni(acac)_2]$ (77.1 mg, 3×10^{-4} mol) and 2-vinylpyridine (63.2 mg, 6×10^{-4} mol) were mixed in ether (10 ml). A 0.33 ml hexane solution of $AlEt_3$ (~15%) was added to the yellowish-green solution at 23 °C under Ar. The resultant blackish-brown suspension was filtered, and the filtrate was sealed in a 5 mm diameter glass tube. The glass tube was allowed to stand for one month at 23 °C and orange–brown crystals were collected. Yield 1.8 mg (0.5%).

2.2. X-ray crystallography of 1

An orange–brown crystal of **1** was attached to the end of a glass fiber and mounted on a Rigaku AFC-5R automated diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71079$ Å). The conditions for the data collection and the crystal data for **1** are listed in Table 1. Intensity data were measured by ω–2θ scans at 23 °C and were corrected for Lorentz and polarization effects. Empirical absorption corrections were carried out. A total of 2235 independent reflections having $I > 3\sigma(I_o)$ was used. The structure was solved by a direct method (MITHRIL) [5] and refined by full-matrix least-squares calculations with anisotropic thermal parameters, including isotropic hydrogen atoms located by difference Fourier synthesis. Reliability factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2}$, where $w = 4F_o{}^2/$

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Table 1
Crystal data and measurement conditions for **1**

Formula	$Ni_2O_4N_2C_{28}H_{38}$
Formula weight	584.02
Crystal system	monoclinic
Space group	$P2_1/a$
a (Å)	14.164(3)
b (Å)	11.625(4)
c (Å)	8.876(2)
β (°)	103.78(2)
V (Å^3)	1419(1)
Z	2
D_{calc} (g cm^{-3})	1.366
$F(000)$	308
λ (Mo Kα) (Å)	0.71069
μ (Mo Kα) (cm^{-1})	13.65
Scan type	ω–2θ
Scan rate (° min^{-1})	8.0
Scan width (°)	$1.63+0.30\theta$
$2\theta_{max}$ (°)	55.0
No. reflections measured	3639 (total), 3428 (unique)
No. observed reflections	2235 ($I>3\sigma(I_o)$)
R [a]	0.037
R_w [b]	0.044

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$, where $w=4F_o^2/\sigma^2(F_o^2)$.

Table 2
Positional and equivalent isotropic parameters for **1**

Atoms	x	y	z	B_{eq} [a] (Å^2)
Ni(1)	0.44161(3)	0.39845(4)	0.63282(4)	2.52(2)
O(1)	0.3715(2)	0.4467(2)	0.7829(2)	3.4(1)
O(2)	0.5151(2)	0.2914(2)	0.7649(2)	3.5(1)
N(1)	0.3596(2)	0.4992(2)	0.4919(3)	2.6(1)
C(1)	0.2679(3)	0.4626(3)	0.4307(4)	3.5(1)
C(2)	0.1986(3)	0.5287(4)	0.3374(4)	4.2(2)
C(3)	0.2225(3)	0.6388(4)	0.3042(4)	4.0(2)
C(4)	0.3146(3)	0.6776(3)	0.3651(4)	3.4(1)
C(5)	0.3851(2)	0.6075(3)	0.4594(3)	2.6(1)
C(6)	0.4863(2)	0.6440(3)	0.5246(3)	2.7(1)
C(7)	0.5003(3)	0.7708(3)	0.5664(4)	3.5(1)
C(8)	0.6030(3)	0.8044(4)	0.6393(4)	4.4(2)
C(9)	0.6127(4)	0.9275(4)	0.6974(6)	6.9(3)
C(10)	0.3341(3)	0.4757(4)	1.0254(4)	4.7(2)
C(11)	0.3920(2)	0.4171(3)	0.9254(4)	3.3(1)
C(12)	0.4618(3)	0.3367(4)	0.9899(4)	3.9(2)
C(13)	0.5174(3)	0.2778(3)	0.9085(4)	3.9(2)
C(14)	0.5896(4)	0.1901(5)	0.9900(5)	7.3(3)

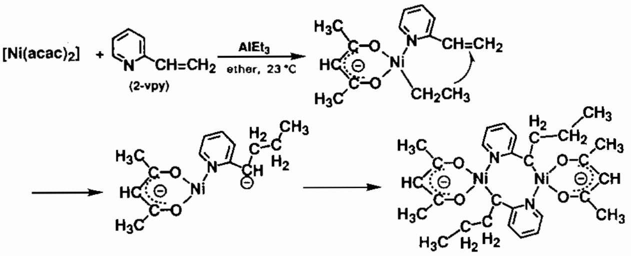
[a] $B_{eq}=(4/3)\Sigma_i\Sigma_j\beta_{ij}a_i\cdot a_j$.

$\sigma^2(F_o^2)$. Atomic scattering factors and anomalous dispersion terms were taken from Ref. [6]. All calculations were performed using the TEXSAN crystallographic software package [7]. The final R and R_w values were 0.037 and 0.044, respectively. Positional and equivalent isotropic parameters for **1** are given in Table 2.

3. Results and discussion

The alkylation of 2-vinylpyridine was effected by the reaction of $[Ni(acac)_2]$, 2-vpy and $AlEt_3$ to produce the compound 1-pyridylbutanate (L). Single crystals of the phdinickel(II) complex (**1**) with L were isolated (see Scheme 1). The molecular structure of **1** is shown in Fig. 1, and selected bond distances and angles are listed in Table 3. Complex **1** has crystallographic $P2_1/a$ symmetry. Two nickel atoms are bridged by the N atom and the carbonate atom of L to form a binuclear structure. Each Ni atom is also coordinated by the two O atoms of acetylacetonate, providing the square-planar geometry. The bridging mode of L is head-to-tail coordination [8], and the eight-membered-ring $Ni_2N_2C_4$ framework has a staggered conformation [8,9]. This is a unique binuclear alkylnickel complex, because only a few binuclear complexes have a staggered conformation [8,9], and furthermore the reported alkylnickel complexes are almost all mononuclear [1–4,10].

The Ni–N distance of 1.896(3) Å is close to that found in the usual nickel(II) complexes with square-



Scheme 1.

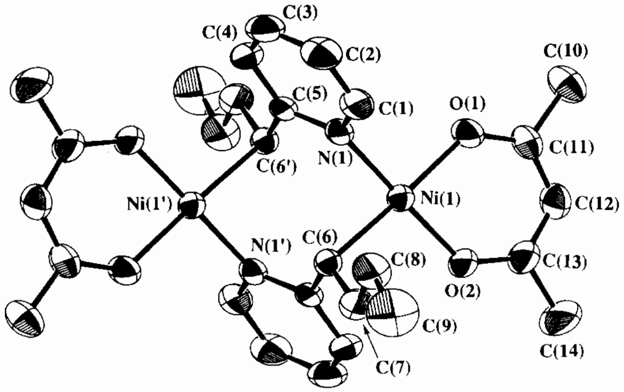


Fig. 1. Crystal structure of **1** and the atom labeling scheme.

Table 3
Selected bond distances (Å) and bond angles (°) for **1**

Ni(1)···Ni(1')	3.966(1)	Ni(1)–N(1)	1.896(3)
Ni(1)–C(6)	1.979(3)	Ni(1)–O(1)	1.925(2)
Ni(1)–O(2)	1.851(2)		
N(1)–Ni(1)–C(6)	91.5(1)	N(1)–Ni(1)–O(1)	86.6(1)
C(6)–Ni(1)–O(2)	88.4(1)	O(1)–Ni(1)–O(2)	93.6(1)

planar geometry (~1.90 Å) [11]. The Ni–C(σ) distance of 1.979(3) Å is rather longer than that of [Ni(acac)(PPh_3){(Ph)C=C(Ph)(CH_3)}] (1.897 Å) [3], but is similar to those of other alkylnickel complexes with acac (1.944–2.03 Å) [1,2,10]. The two Ni–O distances (1.851(2) and 1.925(2) Å) are very different. The Ni–O distance *trans* to the Ni–C(σ) bond shows considerable lengthening (0.074 Å) owing to the *trans* effect. This lengthening is the largest among the values (0.004–0.05 Å) reported for alkylnickel complexes with acac [1–3,10].

4. Supplementary material

Tables of fractional atomic coordinates, thermal parameters, and interatomic bond distances and angles are available on request from Professor M. Munakata.

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