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Inorganica Chimica Acta 227 (1994) 137–143

Inorganica Chimica Acta

Note

Synthesis, crystal structure and characterization of nickel(0) acrylonitrile complexes with a bidentate N-donor ligand

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Received 21 January 1994; revised 20 April 1994

Abstract

Three nickel(0) acrylonitrile complexes with a bidentate N-donor ligand, [Ni(biL)(AN)$_2$] (biL = 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy); **1**, 2,2′-dipyridylamine (dpa); **2**, 2,2′-pyridylbenzimidazole (pbi); **3**, AN = acrylonitrile), have been prepared and characterized. The crystal structures have been determined by X-ray single-crystal diffraction. Complex **1** is triclinic, space group $P\bar{1}$, with $a = 10.279(2)$, $b = 11.071(1)$, $c = 7.5409(9)$ Å, $\alpha = 95.68(1)$, $\beta = 99.26(1)$, $\gamma = 85.03(1)°$, $U = 840.6(2)$ Å^3, $Z = 2$, $R = 0.032$ and $R_w = 0.038$. The nickel atom of **1** is coordinated by two N atoms of Me$_2$bpy and the C=C moiety of two AN molecules, providing a distorted tetrahedral geometry. Complexes **2** and **3** have the following crystal data: **2**, monoclinic space group $P2_1/n$, $a = 8.755(4)$, $b = 13.713(2)$, $c = 12.740(2)$ Å, $\beta = 92.94(2)°$, $U = 1527.5(8)$ Å^3, $Z = 4$, $R = 0.038$ and $R_w = 0.039$; **3**, monoclinic space group $P2_1/n$, $a = 12.829(3)$, $b = 8.068(1)$, $c = 17.024(2)$ Å, $\beta = 107.62(1)°$, $U = 1679.5(5)$ Å^3, $Z = 4$, $R = 0.033$ and $R_w = 0.036$. The geometries of **2** and **3** are similar to that of **1** except for the dihedral angles. The average Ni–N distance is 2.004, 2.034 and 2.045 Å for **1**, **2** and **3**, respectively. The average C=C distance of AN is 1.402(2), 1.403(6) and 1.409(4) Å for **1**, **2** and **3**, respectively. These C=C distances are rather longer than that of free AN (1.343 Å), indicating contribution from a large π back-donation. The IR and ^{1}H NMR results also support the presence of π back-donation.

Keywords: Nickel complexes; Acrylonitrile complexes; Crystal structures; Bidentate ligand complexes; Amine complexes

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1. Introduction

Since Zeise's salts were prepared for the first time in 1825 [1,2], many organometallic compounds have been synthesized and characterized. In particular, there has been considerable interest in the chemistry of small gaseous molecules linked to a transition metal. Nickel(0) [3,4] is capable of bonding to small gaseous molecules such as alkenes [5,6], alkynes [7], carbon monoxide [8–11], carbon dioxide [12], oxygen [13], nitrogen [14] and so on, although these nickel(0) complexes are generally unstable against moisture, O$_2$ and temperature and their isolation and crystallization are very difficult. Many of the isolated nickel(0) complexes are coordinated by one olefin molecule and phosphorus atoms to give a three-coordinate structure with a distorted trigonal geometry [6,15–17]. Studies of such three-coordinate nickel(0) complexes have already been performed both experimentally and theoretically [3,4]. On the other hand, four-coordinate nickel(0) complexes with two olefin molecules are extremely rare [3,4]. The properties and crystal structures of four-coordinate nickel(0) complexes are not at all obvious. In this study, we have prepared three four-coordinate nickel(0) olefin complexes with a bidentate N-donor ligand and two acrylonitrile molecules. The structures were determined crystallographically, and the properties were characterized using IR and NMR spectroscopy.

2. Experimental

2.1. Starting materials

[Ni(cod)$_2$] (cod = 1,5-cyclooctadiene), 4,4′-dimethyl-2,2′-bipyridine (Me$_2$bpy), 2,2′-dipyridylamine (dpa),

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SSDI 0020-1693(94)04112-9

2,2′-pyridylbenzimidazole (pbi) and acrylonitrile (AN) were purchased commercially. All reagents were used without further purification. All organic solvents were dried and distilled before use. All operations were carried out under an argon atmosphere using standard Schlenk and vacuum-line techniques.

2.2. *[Ni(Me$_2$bpy)(AN)$_2$] (1)*

[Ni(cod)$_2$] (82.5 mg, 0.3 mmol) and Me$_2$bpy (55.3 mg, 0.3 mmol) were mixed in toluene (10 ml) at −30 °C. AN (1.0 ml) ligand was added to a yellow suspension after a few minutes. The resultant red solution was filtered and the filtrate was sealed in a 5-mm-diameter glass tube. The glass tube was allowed to stand for 2 months at −10 °C, and red prism crystals were collected; yield 5 mg (5%). IR data (KBr), cm^{-1}: 2175 (ν(C≡N)).

2.3. *[Ni(dpa)(AN)$_2$] (2)*

[Ni(cod)$_2$] (82.5 mg, 0.3 mmol) and dpa (51.4 mg, 0.3 mmol) were mixed in tetrahydrofuran (10 ml) at −30 °C. AN (0.5 ml) ligand was added to the brown solution. The resultant brown solution was filtered and the filtrate was sealed in a 5-mm-diameter glass tube. The glass tube was allowed to stand for three days at ambient temperature, and orange prism crystals were collected; yield 42 mg (42%). IR data (KBr), cm^{-1}: 2174 (ν(C≡N)).

2.4. *[Ni(pbi)(AN)$_2$] (3)*

The synthesis of **3** was performed in tetrahydrofuran, using pbi (58.6 mg, 0.3 mmol). The resultant dark red solution was allowed to stand for three days at ambient temperature, and red needle crystals were collected; yield 38 mg (36%). IR data (KBr), cm^{-1}: 2178 (ν(C≡N)).

2.5. *X-ray crystallography*

The crystals of **1**, **2** and **3** are stable *in air* for only several minutes at room temperature. When the crystals were taken out of the sealed glass tube, they were quickly covered with liquid paraffin to protect them from O$_2$ and moisture. Each crystal was attached to the end of a glass fiber using Araldite bonding agent and mounted on a Rigaku AFC-5R automated diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). The 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. The structure was solved using a direct method (MITHRIL) [18] and refined by full-matrix least squares calculations with anisotropic

Table 1
Crystal data and measurement conditions for [Ni(Me$_2$bpy)(AN)$_2$] (**1**), [Ni(dpa)(AN)$_2$] (**2**) and [Ni(pbi)(AN)$_2$] (**3**)

Complex	**1**	**2**	**3**
Formula	$C_{18}H_{18}NiN_4$	$C_{16}H_{14}NiN_5$	$C_{18}H_{15}NiN_5$
M	349.07	335.02	360.05
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	10.279(2)	8.755(4)	12.829(3)
b (Å)	11.071(1)	13.713(2)	8.068(1)
c (Å)	7.5409(9)	12.740(2)	17.024(2)
α (°)	95.68(1)	90.0	90.0
β (°)	99.26(1)	92.94(2)	107.62(1)
γ (°)	85.03(1)	90.0	90.0
U (Å^3)	840.6(2)	1527.5(8)	1679.5(5)
Z	2	4	4
D_{calc} (g cm^{-3})	1.379	1.457	1.424
λ (Mo Kα) (Å)	0.71069	0.71069	0.71069
μ (Mo Kα) (cm^{-1})	11.61	12.77	11.66
Scan type	ω–2θ	ω–2θ	ω–2θ
Scan rate (° min^{-1})	8.0	8.0	8.0
Scan width (°)	$1.57+0.30 \tan \theta$	$1.42+0.30 \tan \theta$	$1.57+0.30 \tan \theta$
$2\theta_{max}$ (°)	55.0	55.0	55.0
Reflections measured	4085	3911	4325
Reflections measured with $I > 3\sigma(I_o)$	2937	1905	2588
F(000)	364	692	744
R[a]	0.032	0.038	0.033
R_w[b]	0.038	0.039	0.036

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

thermal parameters including isotropic hydrogen atoms located on Fourier difference synthesis. Reliability factors are defined as $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, $w=4F_o^2/\sigma^2F_o^2$. Atomic scattering factors and anomalous dispersion terms were taken from Ref. [19]. All calculations were performed using the TEXSAN crystallographic software package [20]. The crystal data and measurement conditions are given in Table 1. Atomic positional parameters for nonhydrogen atoms are listed in Tables 2, 3 and 4 for

Table 2
Atomic positional parameters for nonhydrogen atoms and B_{eq}[a] for [Ni(Me$_2$bpy)(AN)$_2$] (**1**)

Atom	x	y	z	B_{eq} (Å^2)
Ni(1)	0.30521(3)	0.23061(3)	0.87478(4)	2.98(1)
N(1)	0.1210(2)	0.2704(2)	0.7552(2)	2.93(7)
N(2)	0.2270(2)	0.0731(2)	0.8950(2)	2.95(8)
N(3)	0.2822(3)	0.0705(3)	0.4095(4)	6.4(1)
N(4)	0.3057(3)	0.5557(3)	1.0435(4)	6.5(1)
C(1)	0.0659(3)	0.3796(2)	0.7093(3)	3.6(1)
C(2)	−0.0630(3)	0.3987(2)	0.6330(3)	3.7(1)
C(3)	−0.1440(2)	0.3025(2)	0.5974(3)	3.5(1)
C(4)	−0.0887(2)	0.1897(2)	0.6450(3)	3.2(1)
C(5)	0.0414(2)	0.1764(2)	0.7271(3)	2.84(9)
C(6)	0.1045(2)	0.0630(2)	0.7996(3)	2.75(9)
C(7)	0.0418(2)	−0.0447(2)	0.7812(3)	3.2(1)
C(8)	0.1033(2)	−0.1454(2)	0.8608(3)	3.2(1)
C(9)	0.2276(3)	−0.1347(3)	0.9603(4)	3.7(1)
C(10)	0.2856(2)	−0.0253(2)	0.9725(3)	3.6(1)
C(11)	−0.2846(3)	0.3190(3)	0.5031(4)	5.1(1)
C(12)	0.0357(3)	−0.2623(2)	0.8416(4)	4.4(1)
C(13)	0.3994(3)	0.3118(2)	0.7178(4)	4.1(1)
C(14)	0.4189(2)	0.1861(2)	0.6777(3)	3.6(1)
C(15)	0.3432(3)	0.1228(3)	0.5271(4)	4.1(1)
C(16)	0.4344(3)	0.2545(3)	1.0980(3)	4.1(1)
C(17)	0.3205(3)	0.3320(3)	1.1146(3)	4.0(1)
C(18)	0.3130(3)	0.4560(3)	1.0779(4)	4.5(1)

[a] $B_{eq}=(4/3)(\Sigma_i\Sigma_{ij}B_{ij}\mathbf{a}_i\cdot\mathbf{a}_j)$.

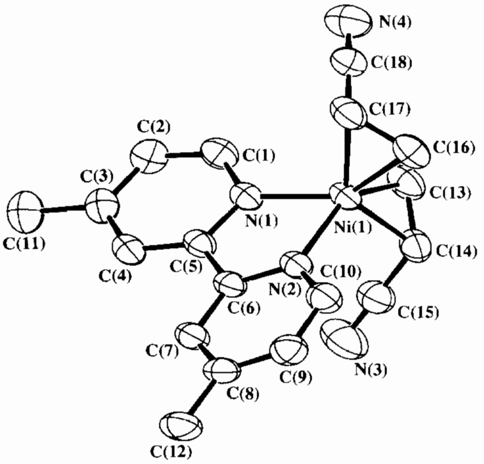

Fig. 1. Molecular structure of [Ni(Me$_2$bpy)(AN)$_2$] (**1**) and the atomic labeling scheme.

Table 3
Atomic positional parameters for nonhydrogen atoms and B_{eq} for [Ni(dpa)(AN)$_2$] (**2**)

Atom	x	y	z	B_{eq} (Å^2)
Ni(1)	0.22316(6)	0.47819(4)	0.21708(4)	2.64(2)
N(1)	0.2659(3)	0.5003(2)	0.3730(2)	2.8(2)
N(2)	0.3847(4)	0.3464(2)	0.3977(2)	3.1(2)
N(3)	0.3998(3)	0.3811(2)	0.2146(2)	2.8(1)
N(4)	0.0142(5)	0.2789(3)	0.0657(3)	5.6(2)
N(5)	0.5949(5)	0.6091(4)	0.1635(4)	6.7(3)
C(1)	0.2145(5)	0.5829(3)	0.4178(4)	3.9(2)
C(2)	0.2182(5)	0.5994(4)	0.5237(4)	4.2(2)
C(3)	0.2811(5)	0.5271(4)	0.5891(3)	4.0(2)
C(4)	0.3362(5)	0.4444(3)	0.5469(3)	3.5(2)
C(5)	0.3285(4)	0.4323(3)	0.4365(3)	2.8(2)
C(6)	0.4467(4)	0.3304(3)	0.3003(3)	2.5(2)
C(7)	0.5581(5)	0.2571(3)	0.2980(3)	3.4(2)
C(8)	0.6259(5)	0.2377(3)	0.2060(4)	4.1(2)
C(9)	0.5798(6)	0.2903(4)	0.1176(4)	4.6(2)
C(10)	0.4693(5)	0.3600(4)	0.1248(3)	4.2(2)
C(11)	−0.0008(4)	0.4864(4)	0.2259(4)	3.9(2)
C(12)	0.0426(5)	0.3878(3)	0.2299(3)	3.3(2)
C(13)	0.0256(5)	0.3268(3)	0.1388(4)	3.7(2)
C(14)	0.2244(5)	0.5385(4)	0.0767(3)	4.1(2)
C(15)	0.3017(5)	0.5989(3)	0.1504(3)	3.7(2)
C(16)	0.4663(6)	0.6055(4)	0.1582(4)	4.3(2)

[a] $B_{eq}=(4/3)(\Sigma_i\Sigma_{ij}B_{ij}\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table 4
Atomic positional parameters for nonhydrogen atoms and B_{eq} for [Ni(pbi)(AN)$_2$] (**3**)

Atom	x	y	z	B_{eq} (Å^2)
Ni(1)	0.80575(3)	0.22360(4)	0.54986(2)	3.14(1)
N(1)	0.6576(2)	0.2934(3)	0.5637(1)	3.20(8)
N(2)	0.7037(2)	0.1003(3)	0.4553(1)	3.25(8)
N(3)	0.5319(2)	0.0724(3)	0.3722(1)	3.58(9)
N(4)	0.7007(2)	−0.0678(4)	0.6751(2)	4.9(1)
N(5)	0.8578(3)	0.6750(4)	0.5780(2)	6.7(2)
C(1)	0.6389(2)	0.3860(4)	0.6234(2)	4.0(1)
C(2)	0.5358(3)	0.4192(4)	0.6281(2)	4.4(1)
C(3)	0.4462(2)	0.3567(4)	0.5682(2)	4.3(1)
C(4)	0.4633(2)	0.2636(3)	0.5050(2)	3.7(1)
C(5)	0.5692(2)	0.2347(3)	0.5046(1)	3.1(1)
C(6)	0.5999(2)	0.1370(3)	0.4433(2)	3.1(1)
C(7)	0.5964(2)	−0.0139(3)	0.3344(2)	3.6(1)
C(8)	0.7043(2)	0.0027(3)	0.3863(2)	3.6(1)
C(9)	0.7895(2)	−0.0782(4)	0.3675(2)	4.8(1)
C(10)	0.7631(3)	−0.1713(5)	0.2972(2)	6.2(2)
C(11)	0.6558(4)	−0.1849(5)	0.2454(2)	6.2(2)
C(12)	0.5707(30	−0.1083(4)	0.2631(2)	5.0(1)
C(13)	0.7752(2)	−0.0145(4)	0.6606(2)	3.7(1)
C(14)	0.8655(2)	0.0584(3)	0.6418(2)	3.5(1)
C(15)	0.8964(2)	0.2239(4)	0.6655(2)	3.9(1)
C(16)	0.9236(2)	0.2925(4)	0.5047(2)	4.4(1)
C(17)	0.8428(2)	0.4157(4)	0.4881(2)	3.9(1)
C(18)	0.8523(2)	0.5600(4)	0.5375(2)	4.5(1)

[a] $B_{eq}=(4/3)(\Sigma_i\Sigma_{ij}B_{ij}\mathbf{a}_i\cdot\mathbf{a}_j)$.

1, **2** and **3**. The final R and R_w values were 0.032 and 0.038 for **1**, 0.038 and 0.039 for **2**, and 0.033 and 0.036 for **3**, respectively.

2.6. Physical measurements

IR spectra were measured using a JASCO 8000 FT-IR spectrometer in the region 4600–400 cm^{-1}, using a KBr pellet. ^1H NMR spectra were obtained with a JEOL GSX-270 FT-NMR spectrometer at 23 °C. Tetramethylsilane was used as an internal reference.

3. Results and discussion

3.1. Molecular structure of $[Ni(Me_2bpy)(AN)_2]$ (1)

The analogous nickel(0) acrylonitrile complex $[Ni(bpy)(AN)_2]$ [21], which was prepared by another procedure, has already been reported, but the crystal structure is still unknown. The molecular structure of **1** is shown in Fig. 1. Selected bond distances and angles are shown in Table 5. The Ni atom is coordinated by two nitrogen atoms of Me_2bpy and the C=C bond moiety of two AN molecules, providing a distorted tetrahedral geometry. The C≡N group of each AN molecule is not coordinated to the Ni atom. Most of the reported nickel(0) olefin complexes are three-coordinate [6,15–17], with one olefin molecule in a distorted trigonal geometry. To the best of our knowledge, this crystal structure is the first example of a four-coordinate nickel(0) olefin complex with two mono-olefin molecules.

The C=C bond distances of the coordinating AN molecules are 1.399(4) and 1.405(4) Å, respectively. The average distance of 1.402(4) Å is longer than that (1.343 Å) of free AN. According to the Dewar–Chatt–Duncanson model [22,23] the metal–olefin bond consists of a σ donation bond and a π back-donation bond. When π back-donation is dominant, the C=C distance is longer than that in free olefin. In addition, the ^1H NMR signal of the olefin shifts upfield, and the $\nu(C=C)$ frequency of the olefin molecule shifts to lower frequency. The coordination shift ($\Delta_{C=C} = (C=C)_{complex} - (C=C)_{free}$) of 0.059 Å indicates that there is a contribution of a large π back-donation from the nickel(0) atom to the AN molecule. The C=C bond distances of nickel(0) olefin complexes are summarized in Table 6. The $\Delta_{C=C}$ distance is shorter than that ($\Delta_{C=C} = 0.117$ Å) of the three-coordinate nickel(0) acrylonitrile complex $[Ni\{P(O\text{-}o\text{-}tolyl)_3\}_2(CH_2=CHCN)]$ [24] and those (0.066–0.125 Å) of three-coordinate nickel(0) ethylene complexes [5,6,16,24–26]. The $\Delta_{C=C}$ distance is within those (0.016–0.069 Å) of nickel(0) cod complexes [27]. It is therefore suggested that the nickel(0)–olefin bond of four-coordinate nickel(0) acrylonitrile complexes is weaker than those of three-coordinate nickel(0) olefin complexes. The $\Delta_{C=C}$ distance is also longer than those (0.01–0.03 Å) of Cu(I) complexes [28] with ethylene and cod, and that (0.035 Å) of Zeise's salt [29]. On the other hand, the $\Delta_{C=C}$ distance is shorter than those of Rh ($\Delta_{C=C} = 0.075$ Å) [30] and Pt ($\Delta_{C=C} = 0.095$ Å) [5,26,31] ethylene complexes and that ($\Delta_{C=C} = 0.065$ Å) [32] of Fe acrylonitrile complex.

Table 5
Selected bond distances (Å) and angles (°) for $[Ni(Me_2bpy)(AN)_2]$ (**1**)

Ni(1)–N(1)	1.995(2)	Ni(1)–N(2)	2.012(2)
Ni(1)–C(13)	1.969(2)	Ni(1)–C(14)	2.033(3)
Ni(1)–C(16)	1.980(2)	Ni(1)–C(17)	2.023(3)
C(13)–C(14)	1.399(4)	C(16)–C(17)	1.405(4)
C(14)–C(15)	1.428(3)	C(15)–N(3)	1.139(3)
C(17)–C(18)	1.420(4)	C(18)–N(4)	1.151(4)
N(1)–Ni(1)–N(2)	80.81(8)	N(1)–Ni(1)–C(13)	98.4(1)
N(1)–Ni(1)–C(14)	107.63(9)	N(1)–Ni(1)–C(16)	145.5(1)
Ni(1)–Ni(1)–C(17)	104.6(1)	N(2)–Ni(1)–C(13)	142.2(1)
N(2)–Ni(1)–C(14)	102.97(9)	N(2)–Ni(1)–C(16)	104.8(1)
Ni(2)–Ni(1)–C(17)	109.92(9)	C(13)–Ni(1)–C(14)	40.9(1)
C(13)–Ni(1)–C(16)	96.9(1)	C(13)–Ni(1)–C(17)	106.8(1)
C(14)–Ni(1)–C(16)	104.2(1)	C(14)–Ni(1)–C(17)	136.8(1)
C(16)–Ni(1)–C(17)	41.1(1)	C(13)–C(14)–C(15)	122.2(2)
C(14)–C(15)–N(3)	178.4(3)	C(16)–C(17)–C(18)	121.6(2)
C(17)–C(18)–N(4)	178.2(3)	Ni(1)–C(14)–C(15)	109.2(2)
Ni(1)–C(17)–C(18)	107.3(2)		

The Ni–N distances of 1.995(2) and 2.012(2) Å are similar to those (1.90(1)–2.016(5) Å) of four-coordinate nickel(0) complexes with bpy [27]. The average Ni–C distance of 2.001(3) Å is also within the values (1.964(1)–2.02(2) Å) for other nickel(0) olefin complexes [5,6,16,24–26,33,34]. It is interesting that the Ni–C distance of the side with the C≡N group is slightly longer than that of the other side[1].

The N–Ni–N angle of 80.81(8)° is smaller than those (81.5–84.1°) of nickel(0) complexes with bpy [27]. The C(13)–C(14)–C(15) angle of 122.2(2)° and the C(16)–C(17)–C(18) angle of 121.6(2)° are similar to that (121.7°) of free AN. The dihedral angles between the planes defined by {Ni(1), N(1) and N(2)} and {Ni(1), C(13) and C(14)}}, {Ni(1), N(1) and N(2)} and {Ni(1), C(16), C(17)}, and {Ni(1), C(13) and C(14)} and {Ni(1), C(16) and C(17)} are 108.65, 70.54, and 87.73°, respectively. Thus, one of the dihedral angles (108.65°) is much larger than the other two.

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[1] On the two coordinating AN ligands, the Ni–C(16) and Ni–C(17) distances are 1.980(2) and 2.023(3) Å, and the Ni–C(13) and Ni–C(14) distances are 1.969(2) and 2.033(3) Å.

Table 6
C=C, Ni–C and Ni–N bond distances of nickel(0) olefin complexes

Complex	C=C (Å), (Δ_{C-C} (Å))^a	Ni–C (Å)	Ni–N (Å)	Ref.
[Ni(4,4′-Me$_2$bpy)(CH$_2$=CHCN)$_2$]	1.402(4), (0.059)	2.001(3)	2.004(2)	this work
[Ni(dpa)(CH$_2$=CHCN)$_2$]	1.403(6), (0.060)	1.991(4)	2.034(3)	this work
[Ni(pbi)(CH$_2$=CHCN)$_2$]	1.409(4), (0.066)	1.991(3)	2.045(3)	this work
[Ni(bpy)(cod)]	1.382(8), (0.041)	2.052(5)	1.938(4)	[27]
[Ni{P(O-*o*-tolyl)$_3$}$_2$(CH$_2$=CHCN)]	1.46(2), (0.117)	1.964(11)		[24]
[Ni(Pcy$_3$)(CH$_2$=CH$_2$)$_2$]	1.401(14), (0.066)	2.014(10)		[16]
[Ni(PPh$_3$)$_2$(CH$_2$=CH$_2$)]	1.43(1), (0.095)	1.99(1)		[5,6,25,26]
[Ni{P(O-*o*-tolyl)$_3$}$_2$(CH$_2$=CH$_2$)]	1.46(2), (0.125)	2.02(2)		[24]
[Ni(Pcy$_2$)(CH$_2$=CH$_2$)]$_2$	1.388(8), (0.053)	1.969(5)		[33]
[Ni(CNBu^t)$_2${(CN)$_2$C=C(CN)$_2$}]	1.476(5)			[34]
[Ni{P(C$_6$H$_4$CH$_3$)$_3$}$_2$(PhHC=CHPh)]	1.471(19)	2.019(13)		[15]
[Ni(tcdp){(CH$_3$)$_2$C=C(CH$_3$)$_2$}]	1.421(3)	1.981(2)		[17]
Free CH$_2$=CH$_2$	1.335			
Free CH$_2$=CHCN	1.343			
Free cod	1.341			

^{a}The coordination shifts $\Delta_{C-C} = \Delta_{complex} - \Delta_{free}$.

3.2. Molecular structures of [Ni(dpa)(AN)$_2$] (2) and [Ni(pbi)(AN)$_2$] (3)

The molecular structures of **2** and **3** are shown in Figs. 2 and 3, and selected bond distances and angles are listed in Tables 7 and 8, respectively. Complexes **2** and **3** also have a distorted tetrahedral geometry, owing to the coordination of two N atoms of the bidentate ligand and two AN molecules. The dihedral angles[2] are {79.88, 83.01 and 85.01°} for **2** and {76.63, 83.23 and 84.90°} for **3**. The geometries of **2** and **3** are fairly similar, although these geometries are different from that {108.65, 70.54 and 87.73°} of **1**. It is interesting that the configuration of **3** is different from that of **1** and **2**: the configuration of **3** apparently provides an enantiomeric structure in relation to that of **1** and **2**. The exact reason is not obvious, but it probably depends on the steric effect of the benzene ring of pbi and structural molecular packing.

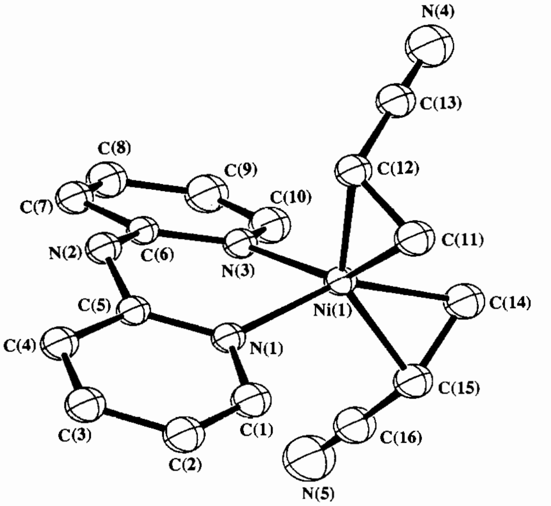

Fig. 2. Molecular structure of [Ni(dpa)(AN)$_2$] (2) and the atomic labeling scheme.

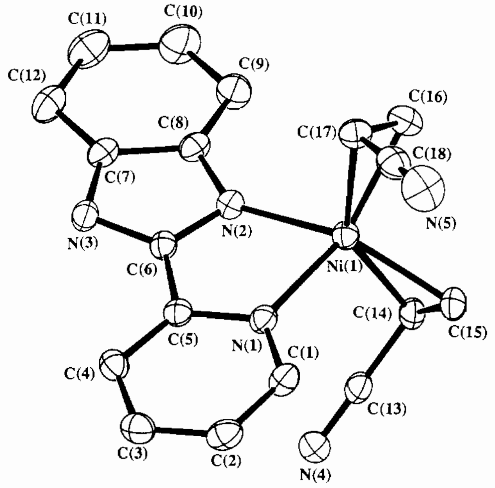

Fig. 3. Molecular structure of [Ni(pbi)(AN)$_2$] (3) and the atomic labeling scheme.

The average C=C bond distances of the AN molecules are 1.403(6) and 1.409(4) Å for **2** and **3**, respectively, and are longer than that (1.343 Å) of free AN. It is known that π back-donation is enhanced when the pK_a of the coordinated ligand increases [35]. However, the difference between the $\Delta_{C=C}$ values of **1**, **2** and **3** is within a standard deviation. It was indicated that these

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[2] For **2**, the dihedral angles between the planes defined by {Ni(1), N(1) and N(3)} and {Ni(1), C(14) and C(15)}, {Ni(1), N(1) and N(3)} and {Ni(1), C(11) and C(12)}, and {Ni(1), C(11) and C(12)} and {Ni(1), C(14) and C(15)} are 79.88, 83.01, and 85.01°, respectively. For **3**, the dihedral angles between the planes defined by {Ni(1), N(1) and N(2)} and {Ni(1), C(14) and C(15)}, {Ni(1), N(1) and N(2)} and {Ni(1), C(16) and C(17)}, and {Ni(1), C(14) and C(15)} and {Ni(1), C(16) and C(17)} are 76.63, 83.23, and 84.90°, respectively.

Table 7
Selected bond distances (Å) and angles (°) for $[\mathrm{Ni(dpa)(AN)_2}]$ (2)

Ni(1)–N(1)	2.026(3)	Ni(1)–N(3)	2.042(3)
Ni(1)–C(11)	1.973(4)	Ni(1)–C(12)	2.023(4)
Ni(1)–C(14)	1.970(4)	Ni(1)–C(15)	1.999(4)
C(11)–C(12)	1.406(6)	C(14)–C(15)	1.400(6)
C(12)–C(13)	1.432(6)	C(13)–N(4)	1.140(5)
C(15)–C(16)	1.443(7)	C(16)–N(5)	1.125(6)
N(1)–Ni(1)–N(3)	90.6(1)	N(1)–Ni(1)–C(11)	94.0(2)
N(1)–Ni(1)–C(12)	96.8(1)	N(1)–Ni(1)–C(14)	144.9(2)
N(1)–Ni(1)–C(15)	104.0(2)	N(3)–Ni(1)–C(11)	142.5(2)
N(3)–Ni(1)–C(12)	101.4(2)	N(3)–Ni(1)–C(14)	102.7(2)
N(3)–Ni(1)–C(15)	104.8(2)	C(11)–Ni(1)–C(12)	41.2(2)
C(11)–Ni(1)–C(14)	94.6(2)	C(11)–Ni(1)–C(15)	109.9(2)
C(12)–Ni(1)–C(14)	111.8(2)	C(12)–Ni(1)–C(15)	146.0(2)
C(14)–Ni(1)–C(15)	41.3(2)	C(11)–C(12)–C(13)	121.0(4)
C(12)–C(13)–N(4)	178.9(5)	C(14)–C(15)–C(16)	122.0(4)
C(15)–C(16)–N(5)	178.8(6)	Ni(1)–C(12)–C(13)	109.9(3)
Ni(1)–C(15)–C(16)	112.7(3)		

Table 8
Selected bond distances (Å) and angles (°) for $[\mathrm{Ni(pbi)(AN)_2}]$ (3)

Ni(1)–N(1)	2.063(2)	Ni(1)–N(2)	2.026(3)
Ni(1)–C(14)	2.022(3)	Ni(1)–C(15)	1.961(3)
Ni(1)–C(16)	1.972(3)	Ni(1)–C(17)	2.010(3)
C(14)–C(15)	1.416(4)	C(16)–C(17)	1.402(4)
C(13)–C(14)	1.419(4)	C(13)–N(4)	1.141(3)
C(17)–C(18)	1.420(4)	C(18)–N(5)	1.145(4)
N(1)–Ni(1)–N(2)	80.51(8)	N(1)–Ni(1)–C(14)	103.77(9)
N(1)–Ni(1)–C(15)	99.9(1)	N(1)–Ni(1)–C(16)	144.0(1)
N(1)–Ni(1)–C(17)	102.8(1)	N(2)–Ni(1)–C(14)	107.8(1)
N(2)–Ni(1)–C(15)	149.0(1)	C(2)–Ni(1)–C(16)	101.9(1)
N(2)–Ni(1)–C(17)	98.7(1)	C(14)–Ni(1)–C(15)	41.6(1)
C(14)–Ni(1)–C(16)	109.4(1)	C(14)–Ni(1)–C(17)	145.1(1)
C(15)–Ni(1)–C(16)	95.7(1)	C(15)–Ni(1)–C(17)	111.3(1)
C(16)–Ni(1)–C(17)	41.2(1)	C(13)–C(14)–C(15)	120.2(3)
C(14)–C(13)–N(4)	177.5(3)	C(16)–C(17)–C(18)	122.4(3)
C(17)–C(18)–N(5)	178.3(3)	Ni(1)–C(14)–C(13)	107.7(2)
Ni(1)–C(17)–C(18)	108.3(2)		

C=C distances are not sensitive to the pK_a of the N-donor ligands ($\mathrm{Me_2bpy}$ (5.32), pbi (≈5.5) and dpa (6.78)). The average Ni–N distances of 2.034(3) Å for **2** and 2.045(3) Å for **3** are similar to those (1.90(1)–2.016(5) Å) of the four-coordinate nickel(0) complexes [27] with bpy, although these distances are slightly longer than that (2.004(2) Å) of **1**. The average Ni–C(AN) distances of 1.991(4) Å for **2** and 1.991(3) Å for **3** are also shorter than that (2.001(3) Å) of **1**, although these distances are within the values (1.964(1)–2.02(2) Å) of other nickel(0) complexes [5,6,16,24–26,33,34].

The N(1)–Ni(1)–N(3) angle of 90.6(1)° for **2** is slightly larger than the values (81.5–84.1°) for nickel(0) complexes with bpy [27], and is also larger than those for **1** (80.81(8)°) and **3** (80.50°).

3.3. IR and ^{1}H NMR of nickel(0) acrylonitrile complexes

The IR spectra of **1–3** were measured by preparing samples *under Ar*. When the coordinating AN ligands were released in air, the absorptions of the AN ligands disappeared and the color changed from red to orange. The $\nu(\mathrm{C{\equiv}N})$ frequency was observed to be 2175, 2174 and 2178 $\mathrm{cm^{-1}}$ for **1**, **2** and **3**, respectively. The coordination shift values ($\Delta\nu = \nu_{\mathrm{complex}} - \nu_{\mathrm{free}}$) are −55, −56 and −52 $\mathrm{cm^{-1}}$, respectively, which are smaller than that (−61 $\mathrm{cm^{-1}}$) of the analogous nickel(0) complex $[\mathrm{Ni(bpy)(AN)_2}]$ [21]. However, the $\Delta\nu(\mathrm{C{\equiv}N})$ values are larger than that (10 $\mathrm{cm^{-1}}$) of two-coordinate nickel(0) acrylonitrile complex [36] and those (−32 to −50 $\mathrm{cm^{-1}}$) of three-coordinate nickel(0) acrylonitrile complexes [36,37]. It was found that the $\Delta\nu(\mathrm{C{\equiv}N})$ values become larger as the coordination number of nickel(0) increases. The $\Delta\nu(\mathrm{C{\equiv}N})$ values are also larger than those of other metal complexes with acrylonitrile, $[\mathrm{Mo(CH_2{=}CHCN)_3(CO)_3}]$ ($\Delta\nu(\mathrm{C{\equiv}N}) = 5\ \mathrm{cm^{-1}}$) and $[\mathrm{Cr(CH_2{=}CHCN)_3(CO)_3}]$ ($\Delta\nu(\mathrm{C{\equiv}N}) = -9\ \mathrm{cm^{-1}}$). The $\nu(\mathrm{C{=}C})$ absorptions of three nickel(0) acrylonitrile complexes could not be identified exactly, owing to overlapping of the absorptions of the bidentate ligands.

The ^{1}H NMR spectra of **1–3** were also measured. Complex **1** gave six ^{1}H NMR signals, at 8.73 (d, 6H), 8.42 (s, 3H), 7.53 (d, 5H) and 2.55 (s, $\mathrm{CH_3}$) ppm for $\mathrm{Me_2bpy}$, and 2.96 (m) and 2.72 (m) ppm for AN, in $\mathrm{(CD_3)_2CO}$ at 23 °C. The coordination shifts ($\Delta\delta = \delta_{\mathrm{complex}} - \delta_{\mathrm{free}}$) are from 0.12 to 0.31 ppm for $\mathrm{Me_2bpy}$, and −2.79 and −3.53 ppm for AN. The $\Delta\delta$ values for AN are within the values (−2.60 to −3.44 ppm) reported for nickel(0) olefin complexes [38], although the $\Delta\delta$ values are larger than those for ethylene complexes of Rh ($\Delta\delta = -2.28$ ppm) [38] and Cu ($\Delta\delta = -0.36$ and −0.66 ppm) [35], and are close to that ($\Delta\delta = -2.98$ ppm) of Pt ethylene complex [38]. It was indicated that π back-donation in the four-coordinate nickel(0) acrylonitrile bond is prominent. Complex **2** is insoluble in the usual organic solvents except for $\mathrm{(CH_3)_2SO}$, and gave two species of ^{1}H NMR signals in $\mathrm{(CD_3)_2SO}$ at 23 °C. The main species were resolved at 8.69 (d, 6H), 7.71 (t, 4H), 6.97 (d, 3H) and 6.71 (t, 5H) ppm for dpa, and 4.78 (broad) ppm for AN, and the other species were resolved at 7.19, 7.05, 6.49 and 6.07 ppm for dpa. It is considered that complex **2** is unstable compared with complex **1**. Complex **3** also shows six ^{1}H NMR signals of pbi at 8.95–7.41 ppm, and two broad ^{1}H NMR signals of AN at 4.55 and 3.61 ppm in $\mathrm{(CD_3)_2CO}$ at 23 °C.

4. Conclusions

In this study, four-coordinate nickel(0) olefin complexes with two mono-olefin molecules were synthesized and their structures were determined by X-ray single-crystal diffraction. It was found that the C=C distance in complexes **1–3** is rather longer than that of free AN and that the ^{1}H NMR signals shift upfield. From all these data, it is concluded that the four-coordinate nickel(0) π complexes are dominated by π back-donation. The $\Delta_{C=C}$ values of complexes **1–3** are smaller than those of three-coordinate nickel(0) olefin complexes with acrylonitrile [24] and ethylene [5,6,16,24,26]. This result indicates that the metal–olefin bond of four-coordinate nickel(0) olefin complexes is weaker than that of three-coordinate nickel(0) complexes.

5. Supplementary material

Complete listings of the atomic coordinates, bond distances, bond angles, hydrogen atomic coordinates, anisotropic thermal parameters, and a listing of observed and calculated structure factors are available from Professor M. Munakata on request.

Acknowledgements

We thank Mr Kazuyuki Kobayashi and Mr Shin-ichi Akiyama for their assistance. This work was partially supported by a Grant-in-Aid for Science Research (Nos. 06740517, 06269209 and 05453131) from the Ministry of Education, Science and Culture in Japan.

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