Adducts of nickel(II) acetylacetonate chelating with heterocyclic bases: 3-cyanopyridine and 4-cyanopyridine

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In both title compounds, (acetylacetonato-O,O')bis(3-cyano-pyridine-N)nickel(II), (I), and (acetylacetonato-O,O')bis-(4-cyanopyridine-N)nickel(II), (II), both [Ni($C_5H_7O_2$)$_2$-($C_6H_4N_2$)$_2$], the Ni^{II} atom, which is situated on a centre of symmetry, is octahedrally coordinated. Distances and angles for (I) and (II), respectively, are: Ni—O 2.009 (2)/2.016 (2) and 2.0110 (16)/2.0238 (18) Å, Ni—N 2.116 (3) and 2.179 (2) Å, O—Ni—O 91.86 (10) and 90.19 (7)°, and O—Ni—N 91.27 (11)/90.19 (11) and 89.65 (8)/90.79 (7)°.

Comment

Adducts of Ni^{II} acetylacetonate (AcAc) chelating with heterocyclic bases have been synthesized with the aim of establishing correlations between the bond energies and other thermochemical parameters (Dunstan, 1998). Among these compounds of general formula [Ni(AcAc)$_2$·2L] were those with L = 3-cyanopyridine, (I), and 4-cyanopyridine, (II). Based on the $\Delta_r H^{\theta}$ (standard enthalpy of the acid/base reaction) values of these adducts, Dunstan (1998) ascertained that the basicity order was 4-cyanopyridine > 3-cyanopyridine, instead

(I)   (II)
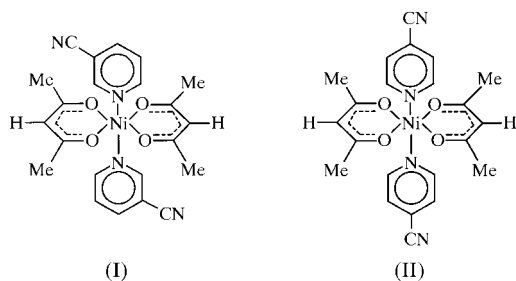
of the expected reverse order. It was then postulated that this could be due to the contribution of another kind of interaction, such as hydrogen bonding, between the N atom of the cyano group and the C atoms of the AcAc moiety. In order to
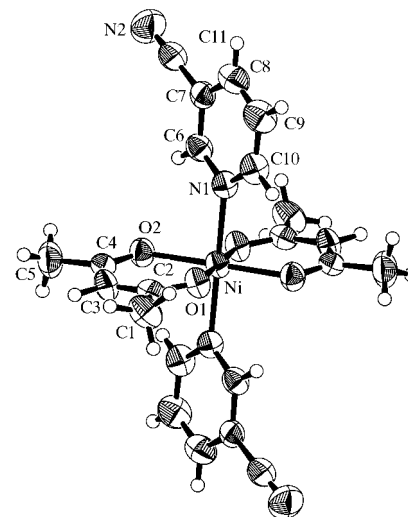

Figure 1
The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

study this possibility, crystal structure determinations of (I) and (II) were undertaken.

In both compounds, the AcAc moiety is planar to within experimental accuracy, the r.m.s. deviation of the seven atoms being 0.012 and 0.016 Å for (I) and (II), respectively. The Ni^{II} atom does not lie in the plane of the AcAc residue but 0.247 (4) and 0.139 (3) Å from it for (I) and (II), respectively. The Ni^{II} atom is situated on a centre of symmetry and is octahedrally bonded to two equatorial AcAc groups and two 3-cyanopyridine [for (I)] and two 4-cyanopyridine [for (II)] groups, which are axially coordinated in a *trans* configuration. The Ni—O$_{AcAc}$ distances in (II) of 2.0110 (16) and 2.0238 (18) Å give rise to tetragonal distortion; this is less important in (I), for which the Ni—O$_{AcAc}$ distances are 2.009 (2) and 2.016 (2) Å.
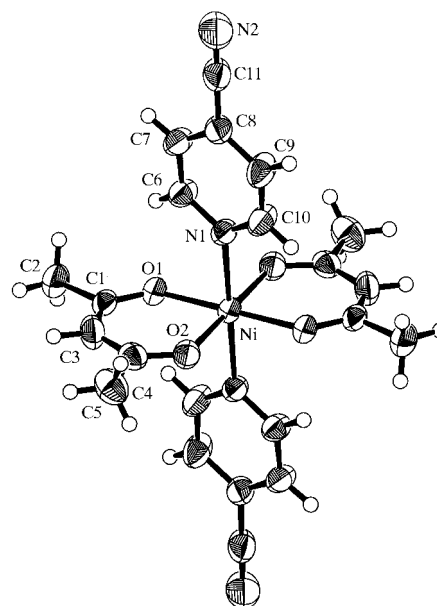

Figure 2
The molecular structure of (II) showing the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

In the solid state, no short intramolecular distances were found. The shortest intermolecular contacts found for the N atom of the cyano group and the C atoms of the AcAc moiety have the geometry N2···H1A^{i} = 2.90, N2···C1^{i} = 3.832 (6) Å and N2···H1A^{i}—C1^{i} = 164° for (I), and N2···H5C^{ii} = 2.65, N2···C5^{ii} = 3.533 (4) Å and N2···H5C^{ii}—C5^{ii} = 153° for (II). Moreover, there is an additional interaction in (I) involving a phenyl H atom; N2···H9^{iii} = 2.79, N2···C9^{iii} = 3.503 (6) Å and N2···C9^{iii}—H9^{iii} = 134° [symmetry codes: (i) $-\frac{3}{2} - x, -\frac{1}{2} + y, 1 - z$; (ii) $1 - x, -1 - y, 1 - z$; (iii) $-\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$].

Whether these interactions are true hydrogen bonds is difficult to assert because, as pointed out by Cotton *et al.* (1997), 'the field is getting muddier and muddier as the definition of a hydrogen bond is relaxed'. In any case, in (II), the N···H distance is marginally shorter than the sum of the van der Waals radii of H and N (2.7 Å).

Experimental

Crystals of both compounds were obtained by slow evaporation from ethanol at 277 K.

Compound (I)

Crystal data

[Ni(C$_5$H$_7$O$_2$)$_2$(C$_6$H$_4$N$_2$)$_2$]	D_x = 1.398 Mg m^{-3}
M_r = 465.14	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 25
a = 7.8295 (6) Å	reflections
b = 19.3334 (18) Å	θ = 8.89–12.93°
c = 8.1244 (10) Å	μ = 0.913 mm^{-1}
β = 116.019 (8)°	T = 293 K
V = 1105.16 (19) Å^3	Irregular, blue
Z = 2	0.20 × 0.18 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.022
$\omega/2\theta$ scans	θ_{max} = 27.47°
Absorption correction: ψ scan	$h = -10 \to 0$
(North *et al.*, 1968)	$k = 0 \to 25$
T_{min} = 0.839, T_{max} = 0.956	$l = -9 \to 10$
2737 measured reflections	3 standard reflections
2529 independent reflections	frequency: 30 min
1131 reflections with $F^2 > 2\sigma F^2$	intensity decay: 0.8%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.045	$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$
$wR(F^2)$ = 0.115	where $P = (F_o^2 + 2F_c^2)/3$
S = 0.953	$(\Delta/\sigma)_{max} < 0.001$
2529 reflections	$\Delta\rho_{max}$ = 0.27 e Å^{-3}
144 parameters	$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Ni—O1	2.009 (2)	N2—C11	1.135 (5)
Ni—O2	2.016 (2)	O1—C2	1.260 (4)
Ni—N1	2.116 (3)	O2—C4	1.258 (4)
O1—Ni—O2	91.86 (10)	O1—C2—C3	125.6 (4)
O1—Ni—N1	91.27 (11)	O1—C2—C1	115.7 (3)
O2—Ni—N1	90.19 (11)	O2—C4—C3	125.1 (4)
C2—O1—Ni	124.3 (2)	O2—C4—C5	116.1 (4)
C4—O2—Ni	124.5 (3)	N2—C11—C7	178.5 (5)

Compound (II)

Crystal data

[Ni(C$_5$H$_7$O$_2$)$_2$(C$_6$H$_4$N$_2$)$_2$]	Z = 1
M_r = 465.14	D_x = 1.379 Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
a = 6.2795 (6) Å	Cell parameters from 25
b = 9.912 (1) Å	reflections
c = 10.392 (1) Å	θ = 8.16–13.87°
α = 64.96 (1)°	μ = 0.901 mm^{-1}
β = 86.441 (8)°	T = 293 (2) K
γ = 73.333 (9)°	Irregular, blue
V = 560.10 (9) Å^3	0.22 × 0.18 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.022
$\omega/2\theta$ scans	θ_{max} = 25.48°
Absorption correction: ψ scan	$h = -7 \to 7$
(North *et al.*, 1968)	$k = -11 \to 10$
T_{min} = 0.855, T_{max} = 0.961	$l = -12 \to 0$
2180 measured reflections	3 standard reflections
2059 independent reflections	frequency: 60 min
1605 reflections with $I > 2\sigma(I)$	intensity decay: 1.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.029P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.035	+ 0.1589P]
$wR(F^2)$ = 0.084	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.055	$(\Delta/\sigma)_{max} < 0.001$
2059 reflections	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
144 parameters	$\Delta\rho_{min}$ = −0.26 e Å^{-3}
H-atom parameters constrained	

Table 2
Selected geometric parameters (Å, °) for (II).

Ni—O1	2.0110 (16)	O1—C1	1.264 (3)
Ni—O2	2.0238 (18)	O2—C4	1.255 (3)
Ni—N1	2.179 (2)		
O1—Ni—O2	90.19 (7)	C4—O2—Ni	125.94 (18)
O1—Ni—N1	90.79 (7)	C10—N1—Ni	121.98 (17)
O2—Ni—N1	89.65 (8)	C6—N1—Ni	121.26 (18)
C1—O1—Ni	126.17 (18)	N2—C11—C8	177.7 (4)

H atoms were located on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they were attached.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1082). Services for accessing these data are described at the back of the journal.

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