A bis(1-phenyl-1,3-butanedionato)nickel(II) adduct with 3-aminopyridine

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In the adduct bis(1-phenyl-1,3-butanedionate)bis(3-amino-pyridine)nickel(II), $[Ni(C_{10}H_9O_2)_2(C_5H_6N_2)_2]$, the Ni^{II} atom lies on a crystallographic center of symmetry. The coordination geometry around the Ni^{II} atom is distorted octahedral. Four O atoms of two 1-phenyl-1,3-butanedionate ligands form the equatorial plane, with Ni—O distances in the range 2.0160 (14)–2.0338 (14) Å. The axial positions are occupied by N atoms of two 3-aminopyridine ligands. The adduct molecules translated by one unit along the a axis are linked by N—H···O hydrogen bonds, forming chains.

Comment

Metal chelates in which the metal ion is coordinatively unsaturated can act as electron acceptors, and yield adducts with neutral molecules as the electron donor. Adducts and their formation reactions have been found useful in a wide variety of applications. Numerous complexes of β-diketone chelates of divalent 3d-electron elements with several heterocyclic bases as electron donors have been reported in the literature. If an electron-donor molecule has a group which can form hydrogen bonds, then a coordination polymer can be formed. An effective strategy has been to arrange these binding units on a framework in such a way that multiple interactions can occur during binding (Decurtins *et al.*, 1999). However, there is a lack of information about structures with 1-phenyl-1,3-butanedionate (Bzac) as a bidentate ligand. We present here the structure of a 1:2 bis(1-phenyl-1,3-butanedionato)nickel(II) 3-aminopyridine adduct, (I).

(I)
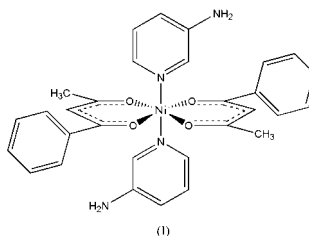
The asymmetric unit consists of one-half of the complex, with the other half being related by a crystallographic centre of symmetry at the Ni atom. The Ni atom is chelated by two Bzac anionic ligands in the equatorial plane. Two 3-amino-pyridine ligands, coordinated axially, complete the coordination environment of the Ni^{II} atom to *trans*-octahedral. The Ni—O bond lengths are in the range 2.0160 (14)–2.0338 (14) Å; the Ni—N distance of 2.1490 (16) Å is longer than the Ni—O distances. The chelate ring (O1—C2—C3—
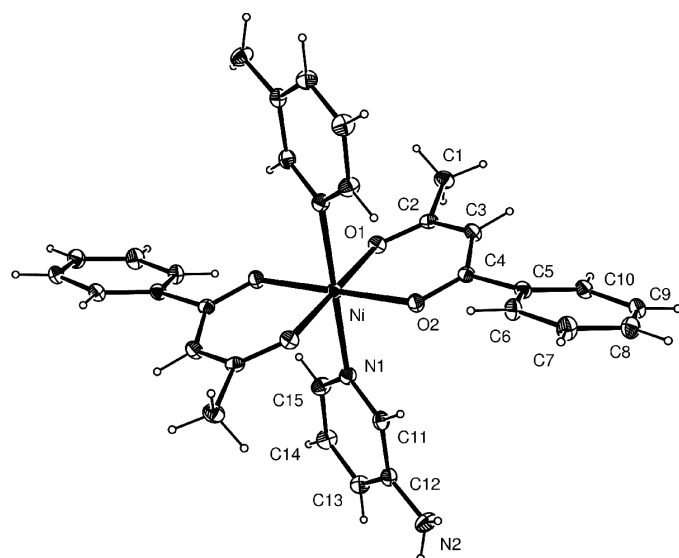
Figure 1
A view of bis(1-phenyl-1,3-butandionate)bis(3-aminopyridine)-nickel(II). Displacement ellipsoids are drawn at the 30% probability level.
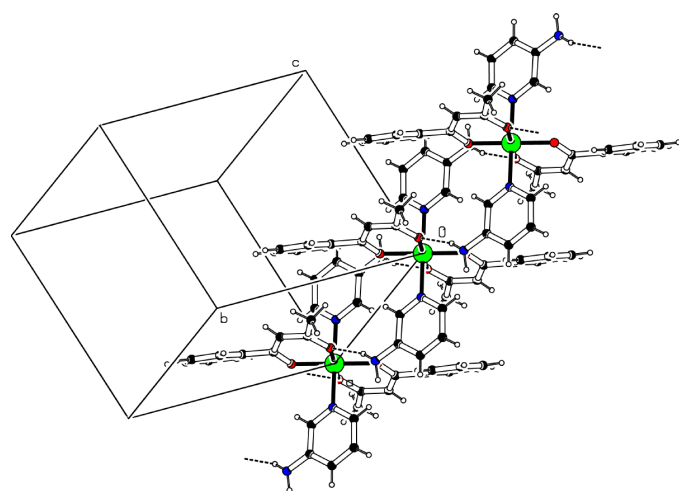

Figure 2
A fragment of the hydrogen-bonded network.

C4—O2—Ni) is distorted from planarity, the angle between the O1—C2—C3—C4—O2 and O1—Ni—O2 planes being 13.31 (5)°. The dihedral angle between the O1—C2—C3—C4—O2 plane and the phenyl ring is 31.61 (6)°. The O1···O2 bite distance of 2.880 (2) Å is in agreement with the value of 2.880 Å reported by Yoshida *et al.* (1999) for a Ni^{II} complex.

Molecules translated by a unit along the *a* axis are linked by N2—H1N···O1(1 + *x*, *y*, *z*) hydrogen bonds, forming chains (Fig. 2, Table 2). The other amino hydrogen, H2N, is not involved in hydrogen bonding.

Experimental

An aqueous ethanol solution of NiCl$_2$·6H$_2$O (0,475 g) and 1-phenyl-1,3- butanedione (0,645 g) was refluxed at 333 K for 5 h. The reaction

mixture was filtered. An ethanol solution (15 ml) of the green product, bis(1-phenyl-1,3-butandionate)nickel(II), and 3-amino-pyridine (0.377 g) was kept at 353 K for 10 min. The resulting dark green solution was filtered and allowed to evaporate very slowly. Single crystals were obtained after one week.

Crystal data

[Ni(C$_{10}$H$_9$O$_2$)$_2$(C$_5$H$_6$N$_2$)$_2$]	$D_x = 1.412$ Mg m^{-3}
$M_r = 569.29$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4673
$a = 7.546$ (2) Å	reflections
$b = 17.417$ (2) Å	$\theta = 2.2$–28.7°
$c = 10.342$ (2) Å	$\mu = 0.77$ mm^{-1}
$\beta = 99.87$ (1)°	$T = 100$ (1) K
$V = 1339.1$ (5) Å^3	Needle, green
$Z = 2$	0.60 × 0.20 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	3904 independent reflections
	3214 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.063$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$\theta_{max} = 30.1°$
	$h = -6 \rightarrow 10$
$T_{min} = 0.579$, $T_{max} = 0.862$	$k = -24 \rightarrow 24$
12114 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 0.987P]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
3904 reflections	$\Delta\rho_{max} = 0.79$ e Å^{-3}
186 parameters	$\Delta\rho_{min} = -0.50$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Ni—O2	2.0160 (14)	N2—C12	1.386 (2)
Ni—O1	2.0338 (14)	C1—C2	1.514 (2)
Ni—N1	2.1490 (16)	C13—C14	1.385 (3)
O2—C4	1.278 (2)	C13—C12	1.402 (3)
O1—C2	1.275 (2)	C15—C14	1.391 (3)
N1—C15	1.348 (3)	C3—C2	1.410 (3)
N1—C11	1.350 (2)	C6—C7	1.394 (3)
C11—C12	1.408 (3)	C6—C5	1.406 (3)
C4—C3	1.410 (2)	C8—C9	1.396 (3)
C4—C5	1.508 (2)	C8—C7	1.402 (3)
C10—C9	1.396 (3)	C14—H14	0.93
C10—C5	1.401 (3)		
O2—Ni—O1	90.63 (5)	N1—C15—C14	122.05 (17)
O2—Ni—N1	89.66 (6)	C4—C3—C2	124.99 (18)
O1—Ni—N1	93.01 (6)	N2—C12—C13	120.87 (17)
C4—O2—Ni	125.40 (11)	N2—C12—C11	121.44 (18)
C2—O1—Ni	124.45 (12)	C13—C12—C11	117.68 (17)
C15—N1—C11	118.49 (16)	O1—C2—C3	125.76 (17)
C15—N1—Ni	121.59 (12)	O1—C2—C1	115.60 (16)
C11—N1—Ni	119.78 (13)	C3—C2—C1	118.64 (17)
N1—C11—C12	122.91 (18)	C7—C6—C5	120.36 (18)
O2—C4—C3	125.91 (18)	C9—C8—C7	119.81 (18)
O2—C4—C5	114.63 (15)	C8—C9—C10	120.12 (18)
C3—C4—C5	119.46 (16)	C10—C5—C6	119.15 (17)
C9—C10—C5	120.47 (18)	C10—C5—C4	122.48 (16)
C12—N2—H1N	118.3 (16)	C6—C5—C4	118.28 (17)
C12—N2—H2N	116.2 (18)	C13—C14—C15	119.75 (18)
H1N—N2—H2N	118 (2)	C6—C7—C8	120.06 (19)
C14—C13—C12	119.12 (18)		

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1N$\cdots$O1[i]	0.94 (3)	2.04 (3)	2.951 (2)	164 (2)
C11—H11$\cdots$O2	0.93	2.49	3.020 (2)	117
C15—H15$\cdots$O2[ii]	0.93	2.55	3.055 (2)	114

Symmetry codes: (i) $1 + x, y, z$; (ii) $-x, -y, -z$.

Amino H atoms, H1N and H2N, were located in a difference Fourier map and their parameters (x, y, z and U_{iso}) were refined [N—H = 0.91 (3)–0.94 (3) Å]. The remaining H atoms were placed in calculated positions and allowed to ride on their parent C atoms, with C—H distances in the range 0.93–0.96 Å; the $U_{iso}(H)$ values were set equal to $1.5U_{eq}$(parent atom) for the methyl H atoms and $1.2U_{eq}$(parent atom) for the others. A rotating-group model was used for the methyl group.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlisCCD*; data reduction: *CrysAlisRED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST*97 (Nardelli, 1995).

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