Bis(N,N-dimethylformamide-κO)bis[1-phenyl-3-methyl-4-benzoyl-1H-pyrazol-5(4H)-onato-κ²O,O]nickel(II)

Xiao-Ping Shen and Ai-Hua Yuan
Bis((N,N-dimethylformamide-κO)bis[1-phenyl-3-methyl-4-benzoyl-1H-pyrazol-5(4H)-onato-κ²O,O']nickel(II))

In the crystal structure of the title complex, [Ni(C_{17}H_{13}N_{2}O_{2})_{2} (C_{2}H_{4}NO)] or [Ni(PMBP)_{2}(DMF)]_{2}, where HPMBP is 1-phenyl-3-methyl-4-benzoyl-1H-pyrazol-5(4H)-one, the Ni^{II} atom, which lies on an inversion centre, is six-coordinated in a distorted octahedral coordination environment by coordinating four O atoms from two symmetry-related chelating bidentate PMBP ligands and two O atoms from two symmetry-related DMF ligands.

Comment

Many β-diketonate complexes, such as acetylacetone, hexafluoroacetone, 1,1,1-trifluoro-3-(2-thenyl)acetone and benzoylacetonate (Dong et al., 1999; Li et al., 1999, 2003), have been reported. 1-Phenyl-3-methyl-4-benzoyl-1H-pyrazol-5(4H)-one (HPMBP) has also been widely studied as an extractant and chelating agent of metal ions (Okafor, 1981; Barkat et al., 2004). Recently, PMBP-metal complexes have attracted the attention of chemists because of the potentially biological activities of these compounds, for example, as antibacterial, antimalarial and antiviral agents (Xu et al., 2003). However, few PMBP-metal complexes have been structurally characterized (Miao et al., 1991; Xu et al., 2003).

We report here the preparation and the crystal structure of the title complex, [Ni(PMBP)_{2}(DMF)]_{2}, (I).

Fig. 1 shows the coordination geometry of the nickel(II) centre in (I) and Fig. 2 shows the crystal packing. The complex molecule has a centre of symmetry, with the Ni^{II} atom lying on an inversion centre. The coordination geometry of the Ni^{II} atom is distorted octahedral; it is coordinated equatorially by four O atoms from two symmetry-related chelating bidentate PMBP ligands, and axially by two O atoms from two symmetry-related DMF molecules. The Ni―O bond lengths in
the axial positions are 2.0776 (19) Å, slightly longer than the Ni—O distances [2.0320 (17) and 2.0442 (17) Å] in the equatorial positions. The O—Ni—O angles [87.68 (7)—92.32 (7)°] are close to 90°.

The N1—N2, N1—C13, C13—C14 and C14—C16 bond lengths in the pyrazole ring are in the range 1.373 (3)—1.437 (3) Å, showing partial double-bond character. The shorter N2—C16 bond length in the pyrazole ring [1.308 (3) Å] shows a relatively stronger double-bond character. The C14—C15 [1.407 (3) Å] and N1—C1 [1.421 (3) Å] bond lengths also suggest partial double-bond character. The O1—C13 [1.263 (3) Å] and O2—C15 [1.259 (3) Å] bond lengths are longer than O3—C20 [1.227 (3) Å] in DMF. All of these data illustrate the characteristic large conjugation lengths in the β-diketonate enol ring.

The coordination geometry of the Ni II atom in (I) is monodentate, with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are related by the symmetry operator (—x, —y, —z).

Experimental

An aqueous solution (10 ml) of Ni(NO₃)₂·6H₂O (0.291 g, 1.0 mmol) was added to an ethanol solution (10 ml) of HPMBP (0.556 g, 2.0 mmol). The mixture was adjusted to pH 6 with an NaOH aqueous solution and was stirred for 30 min at room temperature. The green precipitate that formed was filtered off and washed with a small amount of ethanol. The products were recrystallized from DMF at room temperature and well shaped single crystals suitable for X-ray diffraction analysis were obtained after two weeks. Analysis found: C 63.19, H 5.33, N 11.07%; calculated for C₄₀H₄₀N₆NiO₆: C 63.26, H 5.31, N 11.07%.

Crystal data

[Ni(C₁₇H₁₃N₂O₂)₂(C₃H₇NO)₂]

Mᵣ = 759.47
Mo Kα radiation
Cell parameters from 4719 reflections
a = 10.048 (2) Å
b = 9.3746 (19) Å
c = 19.101 (4) Å
β = 90.87 (3)°
V = 1799.0 (6) Å³
Z = 2

Data collection

Rigaku Mercury CCD diffractometer
4093 independent reflections
3708 reflections with I > 2σ(I)
R(int) = 0.040
θ(max) = 27.5°
h = −13 to 11
k = −12 to 12
l = −21 to 24

Refinement

Refinement on F²
R(F²) = 0.060
wR(F²) = 0.108
S = 1.10
4093 reflections
241 parameters
H-atoms parameters constrained

Figure 1
The coordination geometry of the NiII atom in (I), with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are related by the symmetry operator (—x, —y, —z).

Figure 2
The crystal packing in (I).
Table 1
Selected geometric parameters (Å, °).

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<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
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<tbody>
<tr>
<td>Ni1−O1</td>
<td>2.0320 (17)</td>
<td></td>
</tr>
<tr>
<td>Ni1−O2</td>
<td>2.0442 (17)</td>
<td></td>
</tr>
<tr>
<td>Ni1−O3i</td>
<td>2.0776 (19)</td>
<td></td>
</tr>
<tr>
<td>O1−C13</td>
<td>1.263 (3)</td>
<td></td>
</tr>
<tr>
<td>O2−C15</td>
<td>1.259 (3)</td>
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</tr>
<tr>
<td>O3i−C20</td>
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<tr>
<td>N1−C13</td>
<td>1.373 (3)</td>
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<tr>
<td>O1−Ni1−O1i</td>
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<td>O1−Ni1−O3i</td>
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<tr>
<td>O2−Ni1−O2i</td>
<td>87.75 (7)</td>
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</table>

Symmetry code: (i) = x, −y, z.

H atoms were placed in idealized positions and refined in a riding-model approximation, with C−H = 0.93 Å and Uiso(C) = 1.2Ueq(C) (phenyl rings and C20), and C−H = 0.96 Å and Uiso(C) = 1.5Ueq(C) (methyl).

Data collection: CrystalClear (Rigaku, 2000); cell refinement: CrystalClear; data reduction: CrystalClear; program(s) used to solve structure: SHELX97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); software used to prepare material for publication: SHELXTL.

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References


