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Key indicators

Single-crystal X-ray study
 T = 193 K
 Mean $\sigma(C-C)$ = 0.004 Å
 R factor = 0.060
 wR factor = 0.108
 Data-to-parameter ratio = 17.0

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis(*N,N*-dimethylformamide- κO)bis[1-phenyl-3-methyl-4-benzoyl-1*H*-pyrazol-5(4*H*)-onato- $\kappa^2 O, O'$]nickel(II)

In the crystal structure of the title complex, $[Ni(C_{17}H_{13}N_2O_2)_2(C_3H_7NO)_2]$ or $[Ni(PMBP)_2(DMF)_2]$, where HPMBP is 1-phenyl-3-methyl-4-benzoyl-1*H*-pyrazol-5(4*H*)-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.

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Comment

Many β -diketonate complexes, such as acetylacetonate, hexafluoroacetonate, 1,1,1-trifluoro-3-(2-thenyl)acetonate and benzoylacetonate (Dong *et al.*, 1999; Li *et al.*, 1999, 2003), have been reported. 1-Phenyl-3-methyl-4-benzoyl-1*H*-pyrazol-5(4*H*)-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).

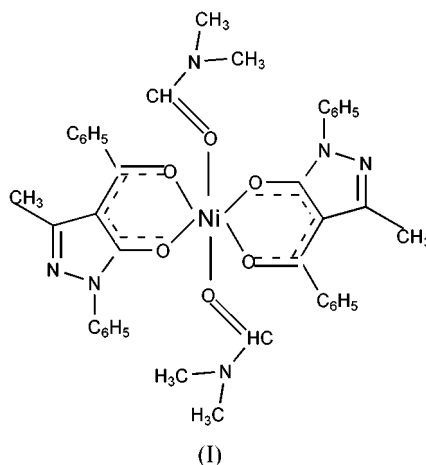


Fig. 1 shows the coordination geometry of the nickel(II) centre in (I) and Fig. 2 shows the crystal packing. The complex molecule has a centre of symmetry, with the Ni^{II} atom lying on an inversion centre. The coordination geometry of the Ni^{II} atom is distorted octahedral; it is coordinated equatorially 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

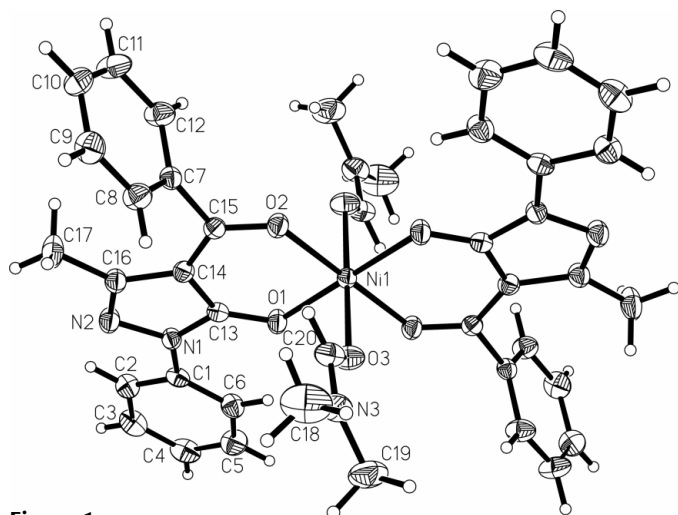


Figure 1

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

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 system of PMBP in (I).

The pyrazole ring is nearly planar, with a maximum deviation of 0.0056 (15) Å for atom C13. The maximum deviations from the C1–C6 and C7–C12 phenyl ring planes are 0.006 (2) Å for atom C4 and 0.0087 (19) Å for atom C7. The three rings (two phenyl rings and one pyrazole ring) of one PMBP ligand are not coplanar. The dihedral angle between the two phenyl planes is 81.50 (9)°. The dihedral angles between the pyrazole plane and the C1–C6 and C7–C12 phenyl planes are 12.95 (15) and 88.01 (9)°, respectively. The O1, O2, and C13–C15 atoms are almost coplanar, with a maximum deviation of 0.0272 (16) Å for atom C15. The dihedral angles between the O1/O2/C13–C15 plane and the pyrazole, C1–C6 phenyl and C7–C12 phenyl rings are 2.07 (14), 13.89 (14) and 86.24 (9)°, respectively, suggesting that the pyrazole and C1–C6 phenyl rings, with their low twisting angles, participate in the π delocalization of the β -diketonate enol ring.

Experimental

An aqueous solution (10 ml) of Ni(NO₃)₆H₂O (0.291 g, 1.0 mmol) was added to an ethanol solution (10 ml) of HPMBP (0.556 g,

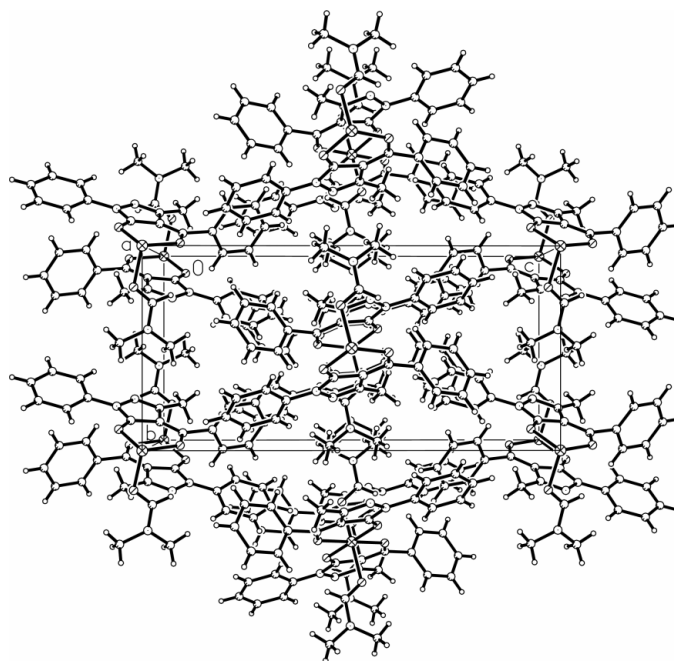


Figure 2

The crystal packing in (I).

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 11.04%; calculated for C₄₀H₄₀N₆NiO₆: C 63.26, H 5.31, N 11.07%.

Crystal data

[Ni(C₁₇H₁₃N₂O₂)₂(C₃H₇NO)₂]
M_r = 759.47
 Monoclinic, *P*2₁/*n*
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

D_x = 1.402 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 4719 reflections
 θ = 3.0–27.5°
 μ = 0.60 mm⁻¹
T = 193.2 K
 Block, green
 0.42 × 0.40 × 0.12 mm

Data collection

Rigaku Mercury CCD diffractometer
 ω scans
 Absorption correction: multi-scan (North *et al.*, 1968)
T_{min} = 0.765, *T_{max}* = 0.928
 13 949 measured reflections

4093 independent reflections
 3708 reflections with *I* > 2 σ (*I*)
R_{int} = 0.040
 θ_{max} = 27.5°
h = –13 → 11
k = –12 → 12
l = –21 → 24

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.060
wR(*F*²) = 0.108
S = 1.10
 4093 reflections
 241 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0253P)^2 + 2.859P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.35 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

| | | | |
|------------------------|-------------|-------------------------|-----------|
| Ni1—O1 | 2.0320 (17) | N1—N2 | 1.404 (3) |
| Ni1—O2 | 2.0442 (17) | N1—C1 | 1.421 (3) |
| Ni1—O3 ⁱ | 2.0776 (19) | N2—C16 | 1.308 (3) |
| O1—C13 | 1.263 (3) | C13—C14 | 1.437 (3) |
| O2—C15 | 1.259 (3) | C14—C15 | 1.407 (3) |
| O3—C20 | 1.227 (3) | C14—C16 | 1.434 (3) |
| N1—C13 | 1.373 (3) | | |
| O1—Ni1—O1 ⁱ | 180 | O2—Ni1—O3 ⁱ | 87.75 (7) |
| O1—Ni1—O2 | 92.32 (7) | O1—Ni1—O3 | 91.45 (8) |
| O1—Ni1—O2 ⁱ | 87.68 (7) | O2—Ni1—O3 | 92.25 (7) |
| O2—Ni1—O2 ⁱ | 180 | O3 ⁱ —Ni1—O3 | 180 |
| O1—Ni1—O3 ⁱ | 88.55 (8) | | |

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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (phenyl rings and C20), and C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ (methyl).

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (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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