# metal-organic papers

# Weak intermolecular hydrogen bonding in the pyridine adduct of a nickel(II) complex with a sterically demanding $\beta$-diketonate ligand

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The nickel(II) complex *trans*-bis(2-benzyl-1,3-diphenylpropane-1,3-dionato)dipyridinenickel(II), [Ni(C$_{22}$H$_{17}$O$_2$)$_2$(C$_5$H$_5$N)$_2$], with a bulky $\beta$-diketonate ligand, 2-benzyl-1,3-diphenylpropane-1,3-dione, has an octahedral nickel(II) centre. Molecules are held together by C—H···O and C—H···$\pi$ interactions to form layers.

## Comment

Coordination complexes of divalent transition metal ions with $\beta$-diketonate ligands have proven useful in a wide range of applications (Soldatov *et al.*, 2003). Notably, the ability to bind additional ligands to the monomeric complexes forms the basis for their often observed catalytic ability (Parkanyl *et al.*, 1981). In this context, modification of the steric properties of the $\beta$-diketonato ligand is significant as a means of controlling the ability for additional ligand binding. With that in mind, we have prepared and structurally characterized the bis(pyridine) adduct of a Ni$^{II}$ complex with a sterically demanding ligand, 2-benzyl-1,3-diphenylpropane-1,3-dione, $\alpha$(Bzl)dbm.



(I)
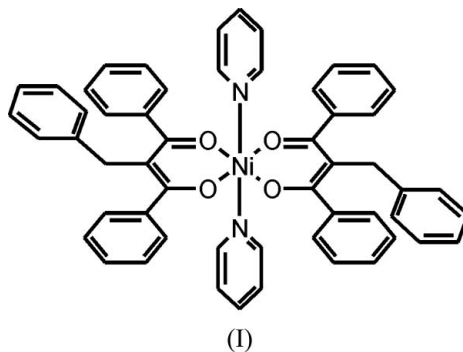
The coordination of the Ni$^{II}$ centre (Fig. 1) is distorted octahedral, with the O donor atoms of the $\beta$-diketonate ligand occupying equatorial positions and N atoms of two pyridine ligands in the axial positions. The metal-to-ligand bond distances (Table 1) are in good agreement with analogous values found in corresponding Ni$^{II}$ $\beta$-diketonato complexes (Cambridge Structural Database, Version 5.26, update of August 2005; Allen *et al.*, 2002).

The benzyl groups of both ligands in the molecule are twisted out of the plane of the respective $\beta$-diketone fragment and establish C—H···$\pi$ contacts involving the aromatic ring H atoms of the benzyl group and the $\pi$-systems of the pyridine ligands. The chelate ring planes, *i.e.* involving atoms O11, O12 and C11–C13 as well as O21, O22 and C21—C23, are tilted with respect to the central metal coordination plane involving atoms Ni, O11, O12, O21 and O22, forming angles of 17.8 (1) and 13.3 (1)°, respectively. The observed tilting may be
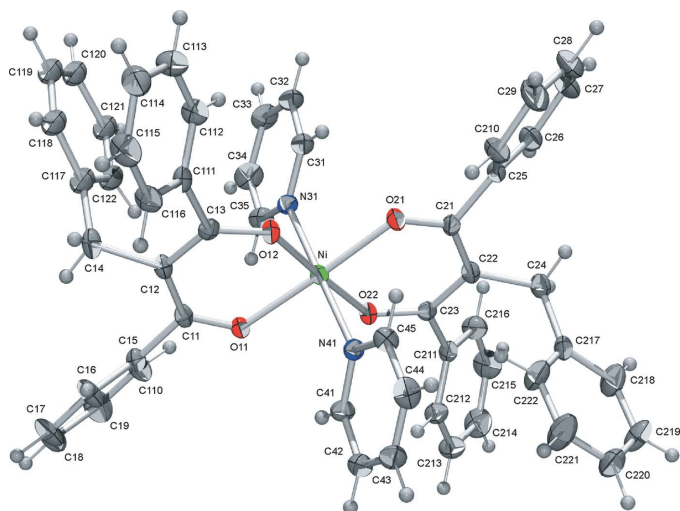
**Figure 1**
View of the title complex, showing the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level. For clarity, only the major component of the disordered aromatic ring is shown.
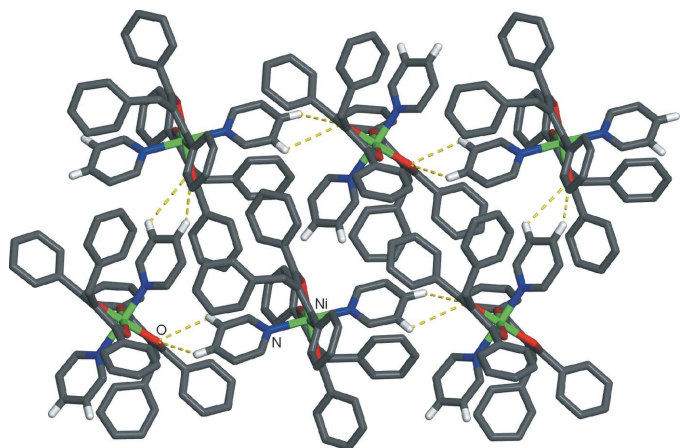


**Figure 2**
Crystal packing diagram showing four C—H···O interactions (dashed lines) between neighbouring complex molecules that lead to the formation of layers. H atoms have been omitted.



**Figure 3**
Crystal packing diagram showing C—H···$\pi$ interactions (dashed lines) between phenyl and benzyl groups of complex molecules derived from adjacent layers. H atoms have been omitted.

An analysis of the crystal packing indicated four C—H···O interactions between neighbouring complex molecules (two cooperative pairs, Table 2) involving the pyridine ring H atoms and $\beta$-diketonate O atoms. These contacts lead to the formation of layers (Fig. 2). The layers thus formed interact by way of C—H···$\pi$ contacts [C28···C121$^{iii}$ = 3.61 (2) Å; symmetry code: (iii) $x, \frac{1}{2} - y, \frac{1}{2} + z$] between phenyl and benzyl groups from adjacent layers (Fig. 3).

## Experimental

The complex was obtained by reacting Ni$^{II}$ nitrate (1 mmol) with 2-benzyl-1,3-diphenylpropane-1,3-dione ligand (2 mmol) in ethanol (25 ml), in the presence of a few drops of triethylamine. The resulting precipitate was redissolved in hot pyridine (10 ml). Slow evaporation of the pyridine solution yielded the bis(pyridine) adduct as small yellow irregular prisms.

*Crystal data*

| | |
|---|---|
| [Ni(C$_{22}$H$_{17}$O$_2$)$_2$(C$_5$H$_5$N)$_2$] | $D_x = 1.279$ Mg m$^{-3}$ |
| $M_r = 843.60$ | Mo $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 36 |
| $a = 10.8449$ (11) Å | reflections |
| $b = 15.2308$ (16) Å | $\theta = 10.0–13.6°$ |
| $c = 26.770$ (2) Å | $\mu = 0.49$ mm$^{-1}$ |
| $\beta = 97.900$ (8)° | $T = 295$ (1) K |
| $V = 4379.8$ (7) Å$^3$ | Prism, yellow |
| $Z = 4$ | $0.2 \times 0.1 \times 0.1$ mm |

*Data collection*

| | |
|---|---|
| Philips PW1100 diffractometer | $R_{int} = 0.062$ |
| $\omega$ scans | $\theta_{max} = 27.0°$ |
| Absorption correction: $\psi$ scan | $h = -13 \rightarrow 13$ |
| (North *et al.*, 1968) | $k = 0 \rightarrow 19$ |
| $T_{min} = 0.879$, $T_{max} = 0.946$ | $l = 0 \rightarrow 34$ |
| 9686 measured reflections | 3 standard reflections |
| 9483 independent reflections | frequency: 60 min |
| 3236 reflections with $I > 2\sigma(I)$ | intensity decay: 6.5% |

partially explained by the action of C—H···$\pi$ interactions with neighbouring complexes, which also result in short C···C contacts [C35···C45$^i$ = 3.463 (8) Å and C42···C216$^{ii}$ = 3.391 (7) Å; symmetry codes (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. In addition, the bending could also be partially stabilized by the aforementioned intramolecular C—H···$\pi$ interactions involving the benzyl groups and coordinated pyridine ligands.

The torsion angles involving atoms of the carbonyl groups and corresponding terminal phenyl groups are significantly larger [−50.0 (6), 63.0 (6), 42.0 (6) and −56.5 (6)°] than those found in the free ligand [19.56 (17) and 26.97 (8)°; Judaš & Kaitner, 2005]. Such distortion may be due to coordination to Ni, which enforces coplanarity of the chelate ring atoms, whereas in the free ligand each terminal phenyl group achieves maximum possible coplanarity with the neighbouring carbonyl system, with twisting occurring around the C$_\alpha$ atom of the molecule.
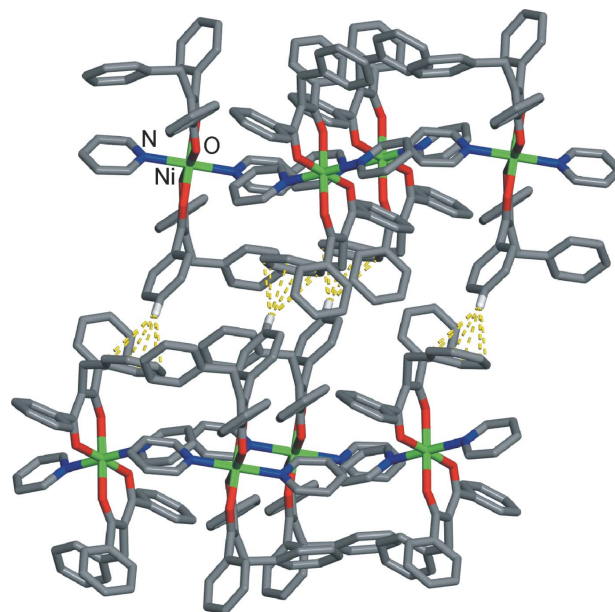
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## Refinement

Refinement on $F^2$  
$R[F^2 > 2\sigma(F^2)] = 0.070$  
$wR(F^2) = 0.159$  
$S = 0.95$  
9483 reflections  
596 parameters

H-atom parameters constrained  
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$  
where $P = (F_o^2 + 2F_c^2)/3$  
$(\Delta/\sigma)_{max} = 0.007$  
$\Delta\rho_{max} = 0.37$ e Å$^{-3}$  
$\Delta\rho_{min} = -0.35$ e Å$^{-3}$

## Table 1
Selected geometric parameters (Å, °).

| Ni—O11 | 2.033 (3) | Ni—O22 | 2.021 (3) |
|---|---|---|---|
| Ni—O12 | 2.023 (3) | Ni—N31 | 2.131 (4) |
| Ni—O21 | 2.003 (3) | Ni—N41 | 2.103 (4) |

| O11—Ni—O12 | 88.01 (12) | O12—Ni—N41 | 91.58 (14) |
|---|---|---|---|
| O11—Ni—O21 | 177.25 (13) | O21—Ni—O22 | 88.47 (12) |
| O11—Ni—O22 | 94.19 (12) | O21—Ni—N31 | 88.30 (14) |
| O11—Ni—N31 | 91.01 (14) | O21—Ni—N41 | 92.00 (14) |
| O11—Ni—N41 | 88.79 (14) | O22—Ni—N31 | 89.55 (14) |
| O12—Ni—O21 | 89.34 (12) | O22—Ni—N41 | 88.39 (13) |
| O12—Ni—O22 | 177.80 (12) | N31—Ni—N41 | 177.91 (16) |
| O12—Ni—N31 | 90.49 (14) | | |

## Table 2
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C34—H34$\cdots$O12$^i$ | 0.93 | 2.86 | 3.488 (7) | 126 |
| C35—H35$\cdots$O12$^i$ | 0.93 | 2.94 | 3.524 (6) | 123 |
| C42—H42$\cdots$O22$^{ii}$ | 0.93 | 3.14 | 3.652 (6) | 117 |
| C43—H43$\cdots$O22$^{ii}$ | 0.93 | 2.83 | 3.500 (6) | 130 |

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

The H atoms were included in the riding-model approximation with C—H(aromatic) = 0.93 Å, C—H(methylene) = 0.97 Å and $U_{iso}$(H) = 1.2$U_{eq}$(C). One of the benzyl groups, with the ispo-C117 atom, was found to be disordered over two sites, with relative occupancies fixed at 0.53 for C118–C122 and 0.47 for C123–C127, respectively. The values of the occupation parameters were determined in the early stages of refinement and were later fixed at these values. The displacement parameters of the non-H atoms belonging to the minor component of the disorder were constrained to be equal to those of the major component.

Data collection: *STADI4* (Stoe & Cie, 1995); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) *MERCURY* (Version 1.2.1; Bruno *et al.*, 2002) *RasTop* (Valadon, 2004) and *POVRay* (Persistence of Vision, 2004); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.  
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
Farrugia, L. J. (1999). *Appl. Cryst.* **32**, 837–838.  
Judaš, N. & Kaitner, B. (2005). *Acta Cryst.* E**61**, o4008–o4010.  
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.  
Parkanyl, C., Sturm, P., Jeffries, A. T. & Pannel, K. H. (1981). *J. Coord. Chem.* **11**, 153–158.  
Persistence of Vision (2004). *POV-Ray*. Version 3.6. Persistence of Vision Pty. Ltd., Victoria, Australia. http://www.povray.org/.  
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
Soldatov, D. V., Tinnemans, P., Enright, G. D., Ratcliff, C. I., Diamente, P. R. & Ripmeester, J. A. (2003). *Chem. Mater.* **15**, 3826–3840.  
Stoe & Cie (1995). *STADI4* (Version 1.05b) and *X-RED* (Version 1.05). Stoe & Cie, Darmstadt, Germany.  
Valadon, P. (2004). *RasTop*. Version 2.0.3. Philippe Valadon, PO Box 928064, La Jolla, CA 92192-8064, USA. http://www.geneinfinity.org/rastop/.