

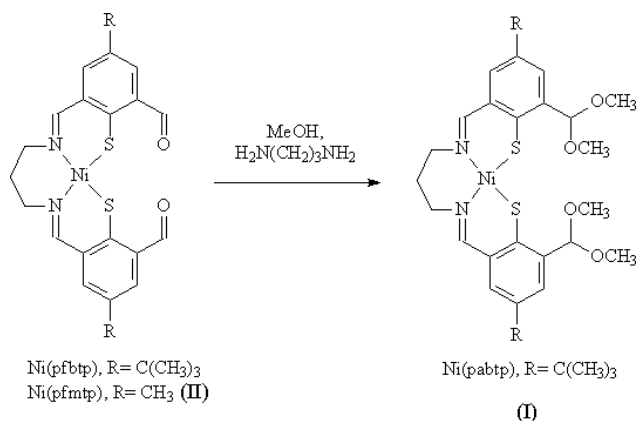
Jens K. Bjernemose,^a Christine J. McKenzie,^{a*} Paul R. Raithby^b and Simon J. Teat^c^aDepartment of Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark, ^bDepartment of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, England, and ^cCLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, England

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Key indicators

Single-crystal synchrotron study
T = 150 K
Mean $\sigma(C-C)$ = 0.004 Å
R factor = 0.084
wR factor = 0.228
Data-to-parameter ratio = 53.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**{4,4'-Di-*tert*-butyl-6,6'-bis(dimethoxymethyl)-2,2'-[propane-1,3-diylbis(nitrilomethylidene)]-bis(thiophenolato)- κ^4 S,N,N',S'}nickel(II)**The title compound, [Ni(C₃₁H₄₄N₂O₄S₂)], is an N₂S₂ four-coordinated nickel(II) complex. The coordination geometry of the metal, on a twofold rotation axis, is more distorted from square planar than in related compounds.Received 11 October 2004
Accepted 8 November 2004
Online 20 November 2004

Comment

The title compound, Ni(pabtp), (I), was isolated from a mixture of the dialdehyde [*N,N'*-propane-1,3-diyl(6-formyl-4-*tert*-butyl-2-methyliminatothiophenolato)]nickel(II) (Christensen & McKenzie, 2004), Ni(pfbtp) and 1,3-diaminopropane in methanol (see scheme). This reaction was an unsuccessful attempt to prepare a ring-closed Schiff base derivative of Ni(pfbtp) under conditions analogous to those in which we prepared 2 + 2 and 4 + 4 thiophenolate macrocyclic complexes using Ni(pfmp), (II), which is homologous to Ni(pfbtp) [Cambridge Structural Database, Version 5.25 of November 2003 with three updates (Allen, 2002) reocode NULPOZ; Christensen *et al.*, 1997].Comparing (I) and (II), it is immediately evident that no change in the length of the coordinating bonds has occurred, but although the coordination geometry at the Ni atom in (I) may be described as square planar, it is far more distorted towards tetrahedral than in (II). This can be seen from the change in bond angles around the Ni atom, which lies on a twofold rotation axis, but is more strikingly described by looking at the volume of the (irregular) tetrahedron spanned by the four donor atoms (N₂S₂). This is 1.544 Å³ for (I) but only 0.159 Å³ for (II). A space-filling model shows no direct interaction between the two (MeO)₂CH— groups on either side of the Ni atom, thus this distortion from square planar is apparently not due to the bulkier dimethylacetal groups replacing the formyl groups. The distortion is then more likely to be due to packing effects. Inspection of the packing diagrams for (I) and (II) reveals a number of similarities. The

molecules in (I) essentially stack along *c*, alternating their direction in either layer, but, whereas molecules in (II) have the Ni atoms directly above one another, they are more displaced in (I). These stacks then pack in a head-to-tail fashion along *b*, with the central methylene group nestled between the two S atoms of the next molecule [$C-H \cdots S = 3.64 \text{ \AA}$ compared to 3.20 \AA in (II)]. These *ab* layers then have *tert*-butyl groups on both sides along *c* in (I) [methyl groups in the case of (II)]. This is probably the origin of the distortion around Ni, for while (II) shows only very modest interaction between the methyl and formyl groups, (I) has a much closer approach of the *tert*-butyl groups to the dimethoxymethyl group.

Experimental

Crystals of (I) were isolated from a 1:1 mixture of Ni(pfbtp) (Christensen & McKenzie, 2004) and 1,3-diaminopropane in methanol after several days standing in a closed vessel.

Crystal data

[Ni(C₃₁H₄₄N₂O₄S₂)]
M_r = 631.51
 Monoclinic, *C*2/*c*
a = 28.352 (4) Å
b = 9.1532 (11) Å
c = 12.1556 (15) Å
 β = 102.178 (2)°
V = 3083.5 (7) Å³
Z = 4
D_x = 1.36 Mg m⁻³

Synchrotron radiation
 λ = 0.6881 Å
 Cell parameters from 6249 reflections
 θ = 2.8–29.2°
 μ = 0.80 mm⁻¹
T = 150 (2) K
 Needle, orange-red
 0.22 × 0.02 × 0.01 mm

Data collection

Bruker SMART 1K CCD diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2000)
T_{min} = 0.843, *T_{max}* = 0.992
 9981 measured reflections

9981 independent reflections
 8220 reflections with $I > 2\sigma(I)$
 θ_{\max} = 27.5°
 h = -37 → 38
 k = -12 → 12
 l = -16 → 16

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.084$
 $wR(F^2) = 0.228$
 $S = 1.04$
 9981 reflections
 188 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.169P)^2 + 0.2945P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.77 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.23 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Ni1–N1	1.907 (2)	Ni1–S1	2.1742 (8)
N1–Ni1–N1 ¹	90.49 (14)	N1–Ni1–S1	95.30 (7)
N1–Ni1–S1 ¹	163.52 (7)	S1 ¹ –Ni1–S1	83.41 (4)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The crystals turned out to be twinned. *ROTAX* (Parsons & Gould, 2001) identifies the twinning as 180° rotation about the *a* axis. The twin scale is [101, 010, 001]. The batch scale factor refines to 0.2786 (18). The non-merohedral twinning prevents merging of equivalent reflections before refinement. The maximum and minimum electron-density peaks are located 0.88 and 0.76 Å, respectively, from atom Ni1.

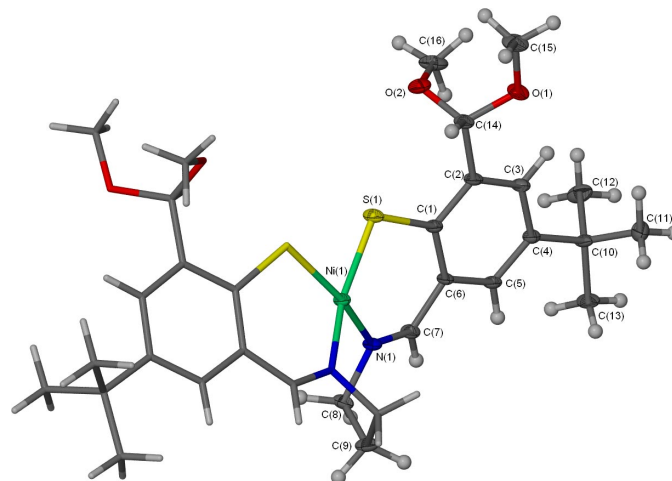


Figure 1

View of (I), with 50% probability displacement ellipsoids shown only for atoms of the asymmetric unit. Unlabelled atoms are related to labelled atoms by $-x, y, 1/2 - z$.

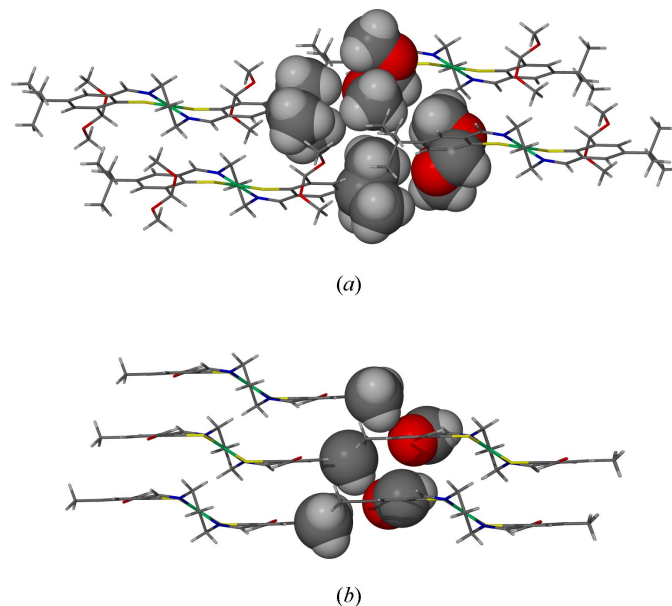


Figure 2

The packing of (a) Ni(pabtp), (I), (b) Ni(pfmp), (II). View down *b* with *tert*-butyl (a) or methyl (b) groups shown as space-filling on the left and dimethoxymethyl (a) or formyl (b) groups on the right.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-Seed* (Barbour, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We are grateful to the CCLRC Daresbury Laboratory for the award of beamtime to carry out the diffraction experiment.

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