Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

N-Benzoyl-*N*′,*N*′-dibutylselenourea and its palladium(II) complex

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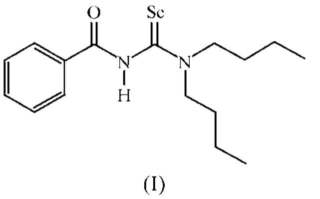
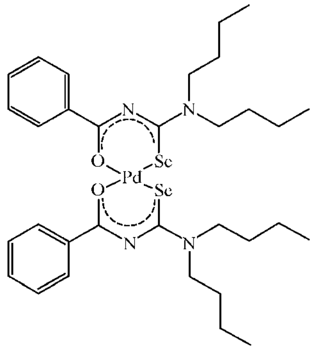
Received 11 September 2007
Accepted 27 October 2007
Online 14 December 2007

The crystal and molecular structures of *N*-benzoyl-*N*′,*N*′-dibutylselenourea (H*L*), $C_{16}H_{24}N_2OSe$, and the corresponding complex bis(*N*-benzoyl-*N*′,*N*′-dibutylselenoureato-κ^2Se,O)palladium(II), $[Pd(C_{16}H_{23}N_2OSe)_2]$, are reported. The selenourea molecule is characterized by intermolecular hydrogen bonds between the selenoamidic H atom and the Se atom of a neighbouring molecule forming a dimer, presumably as a consequence of resonance-assisted hydrogen bonding or π-bonding co-operativity. A second dimeric hydrogen bond is also described. In the palladium complex, the typical square-planar coordination characteristic of such ligands results in a *cis*-[Pd(*L*-*Se*,*O*)$_2$] complex.

Comment

The use of metal complexes in which the ligands contain either S or Se as single-source precursors for the synthesis of semiconducting quantum dots has recently attracted interest (Nair *et al.*, 2005; Malik *et al.*, 2005). In this context, we have recently reported the use of [*N*′-benzoyl-*N*,*N*-diethylthio(seleno)urea]cadmium(II) complexes as single-source precursors for the successful synthesis of CdS and CdSe nanoparticles (Bruce *et al.*, 2007). As part of our interest in extending this study to include other metal ions, we have prepared several *N*,*N*-dialkyl-*N*′-benzoylselenoureas and corresponding metal complexes with a view to using these as single-source precursors for nanoparticle synthesis. The related *N*,*N*-dialkyl-*N*′-benzoylthiourea ligands have been studied extensively and are well known to coordinate to a wide variety of first-row transition metal ions (Schuster & Koenig, 1987; Dietze *et al.*, 1991; Beyer *et al.*, 1981). The corresponding *N*,*N*-dialkyl-*N*′-benzoylselenoureas are relatively rare, although some metal complexes of Ni^{II} and Pd^{II} derived from *N*,*N*-dialkyl-*N*′-benzoylselenourea have been structurally characterized (Kampf *et al.*, 2004; Bensch & Schuster, 1994). Generally, both *N*,*N*-dialkyl-*N*′-benzoylthioureas and *N*,*N*-dialkyl-*N*′-benzoylselenoureas readily coordinate to metal ions with loss of a thioamidic or selenoamidic H atom, resulting in bidentate coordination through the S(Se) and O donor atoms. Surprisingly, relatively few crystal structures of the unbound ligand *N*,*N*-dialkyl-*N*′-benzoylthiourea and analogous *N*,*N*-dialkyl-*N*′-benzoylselenoureas are available in the literature. We report here the crystal and molecular structures of *N*,*N*-dibutyl-*N*′-benzoylselenourea (H*L*), (I) (Figs. 1 and 2), and its Pd^{II} complex, *cis*-[Pd(*L*-*Se*,*O*)$_2$], (II) (Fig. 3).


(I)


(II)

Compound (I) (Fig. 1) crystallizes in the space group $P2_1/c$. The O and Se donor atoms adopt an *anti* orientation relative to each other as a result of twisting about the N1—C8 bond, to give torsion angles O1—C7—N1—C8 = 0.5 (4)° and C7—N1—C8—Se1 = 121.1 (2)°. The C—N bonds are all shorter than the average C—N bond length of 1.472 (5) Å (Allen *et al.*, 1987) (Table 1); the alkyl-substituted selenourea C—N bond [C8—N2 = 1.316 (3) Å] is significantly shorter than the amide bond [C7—N1 = 1.397 (3) Å] and the acyl-substituted selenourea C—N bond [C8—N1 = 1.399 (3) Å]. This reflects the trend observed in the sulfur analogues, where *N*,*N*-dibutyl-*N*′-naphthoylthiourea (Koch *et al.*, 1995) and, more recently, *N*-acetyl-*N*′,*N*′-(butane-1,4-diyl)thiourea (Dillen *et al.*, 2006*a*) and *N*,*N*-di-*n*-butyl-*N*′-pivaloylthiourea (Dillen *et al.*, 2006*b*), show that the *R*,*R*N—C(S) bond length is, on average, the shortest, followed by the amidic *R*′C(O)—N bond, while the HN—C(S) thiourea bond is the longest. Moreover, these molecules usually adopt a conformation in the solid state such that the S and O donor atoms assume opposing orientations, the molecule being usually significantly twisted around the longest HN—C(S) thiourea bond.

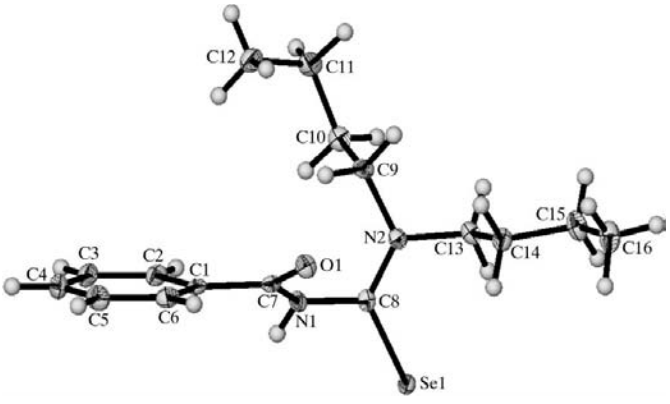


Figure 1
The molecular structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

DOI: 10.1107/S0108270107053711

As shown in Fig. 2, the molecules of (I) are linked through a hydrogen bond between the selenoamidic H atom of one molecule and the Se atom of its neighbour (see Table 2), so giving rise to a dimer linked through such hydrogen bonds in the crystal structure. The formation of this dimer represents an example of resonance-assisted hydrogen bonding (RAHB) or π-bond co-operativity (Steiner, 2002) since, in terms of hydrogen bonding, the selenourea moiety consists of donor–acceptor pairs which are connected by a resonant π system, manifested by the shortening of the amide and acyl-substituted C—N bonds. Such an arrangement is also observed in the closely related diethyl analogue, *N*′-benzoyl-*N*,*N*-diethylselenourea (Bruce *et al.*, 2007). This dimer forms an eight-membered ring structure where atoms H1/N1/C8/Se1/H1^{i}/N1^{i}/C8^{i}/Se1^{i} [symmetry code: (i) $-x, 1-y, 1-z$] lie in a plane, with a maximum deviation of 0.119 (2) Å for atom H1. A second dimeric hydrogen bond is present in (I) between the carbonyl O atom and a H atom on the benzene residue at ($-x$, $1-y$, $-z$) (see Table 2). Similarly to the first dimer, this forms a ten-membered ring structure where atoms O1/C7/C1/C6/H6/O1^{ii}/C7^{ii}/C1^{ii}/C6^{ii}/H6^{ii} [symmetry code: (ii) $-x, 1-y, -z$] again lie in a plane, with a maximum deviation of 0.241 (2) Å for atom O1, the angle between these two planes being 82.36 (2)°. It is interesting to note that the second hydrogen bond is not evident in the solid-state structures of other *N*′-benzoyl-*N*,*N*-dialkylselenoureas that have previously been analysed (*N*′-benzoyl-*N*,*N*-dihexylselenourea, *N*′-benzoyl-*N*,*N*-dioctylselenourea and *N*′-benzoyl-*N*-benzyl-*N*-methylselenourea; Bruce & Koch, 2007). These two dimers give rise to the hydrogen-bonded chains shown in Fig. 2 that form in the direction of the *c* axis. There is little interaction apparent between these chains.

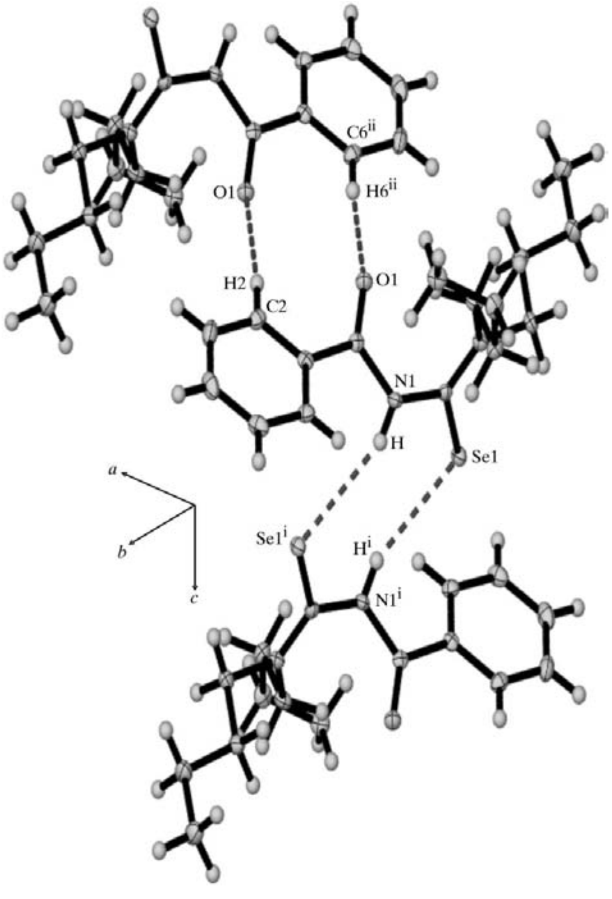


Figure 2
Neighbouring molecules of (I), showing the weak N—H···Se and C—H···O intermolecular hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, 1-y, -z$.]

The molecular structure of *cis*-[Pd(*L*-Se,O)$_2$], (II), which crystallizes in the space group $P\overline{1}$, is shown in Fig. 3. The generally expected mode of coordination of H*L*, with loss of an H atom and yielding a *cis*-square-planar complex, is observed. The four donor atoms and Pd metal centre lie in a single coordination plane involving atoms Se1*A*/O1*A*/Pd1/Se1*B*/O1*B*, with a mean deviation from planarity of only 0.024 Å; the two chelate rings are twisted at an angle of 4.6 (1)° relative to each other, and deviate slightly from perfect planarity by 0.096 and 0.085 Å for atoms Se1*A*/C8*A*/N1*A*/C7*A*/O1*A* and Se1*B*/C8*B*/N1*B*/C7*B*/O1*B*, respectively. The reduced planarity in the chelate rings is reflected in a puckering of the C7*A*/N1*A*/C8*A* and the C7*B*/N1*B*/C8*B* planes, with atoms N1*A* and N1*B*, respectively, lying 0.486 (2) Å below and 0.336 (2) Å above the Se1*A*/O1*A*/Pd1/Se1*B*/O1*B* plane.

The average Pd—Se and Pd—O bond lengths (Table 3) of 2.345 (3) and 2.041 (1) Å, respectively, in (II) compare well with those reported previously for bis[*N*′-(2-fluorobenzoyl)-*N*,*N*-diisobutylselenoureato]palladium(II) (Kampf *et al.*, 2004) and its difluoro analogue, bis[*N*′-(2,6-difluorobenzoyl)-*N*,*N*-diisobutylselenoureato]palladium(II) (Kampf *et al.*, 2005). The C=O and C=Se bonds in (II) are somewhat longer than the corresponding bonds in the ligand H*L*, as a result of a slight loss of double-bond character in these bonds, presumably due to electron delocalization in the six-membered chelate ring of the metal complex. The relative reduction in the C=Se bond

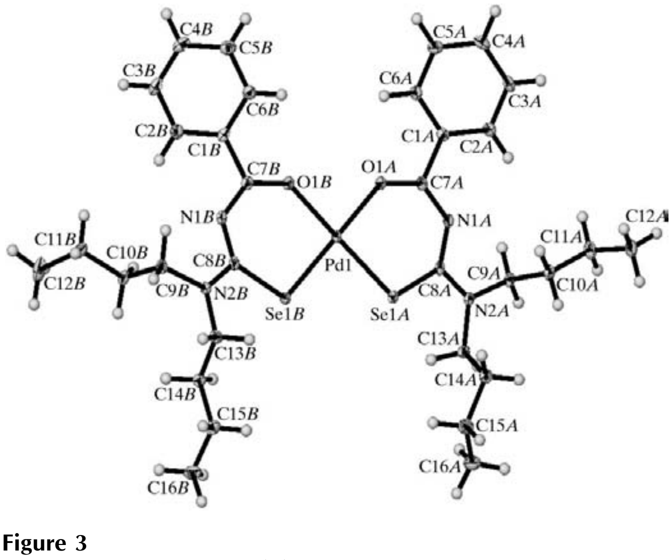


Figure 3
The molecular structure of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

order of (I) on coordination to Pd^{II} in the complex is also reflected by a significant reduction of the $^{1}J(^{77}Se-^{13}C)$ coupling constant, from 222 Hz in the ligand to 177 Hz in (II), in the ^{13}C NMR spectra of these substances in $CDCl_3$. The electron delocalization in the chelate ring of (II) is, in turn, shown by the slight shortening of the C—N bond lengths compared with the corresponding bonds in the unbound ligand.

Experimental

The ligand synthesis was formed according to a previously published procedure (Douglass, 1937).

For the synthesis of (II), a dichloromethane solution (25 ml) of (I) (1.278 mmol) was added to an aqueous solution (25 ml) of K_2PdCl_4 (0.639 mmol). The solutions were shaken together in a separating funnel after which an aqueous solution (10 ml) of sodium acetate (2.558 mmol) was added, followed by gentle shaking. Extraction and drying of the organic layer was followed by the addition of ethanol. Slow evaporation from this mixture yielded crystals suitable for analysis. ^{1}H NMR chemical shifts are quoted relative to the residual $CHCl_3$ solvent resonance at 7.26 p.p.m., and ^{13}C NMR chemical shifts are quoted relative to the $CDCl_3$ triplet at 77.0 p.p.m. (centre peak). Elemental analyses were performed on a Heraeus Universal Combustion Analyser, model CHN-Micro.

For *N*-benzoyl-*N*′,*N*′-dibutylselenourea, (I): yield 57.5%, m.p. 392.5–394.0 K. Analysis found: C 56.6, H 7.1, N 8.2%; $C_{16}H_{24}N_2OSe$ requires: C 56.6, H 7.1, N 8.3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (*t*, 3H, $^{3}J_{HH}$ = 7.4 Hz, H12/H16), 0.99 (*t*, 3H, $^{3}J_{HH}$ = 7.4 Hz, H12/H16), 1.28 (*m*, 2H, $^{3}J_{HH}$ = 7.5 Hz, H11/H15), 1.45 (*m*, 2H, $^{3}J_{HH}$ = 7.5 Hz, H11/H15), 1.67 (*q*, 2H, $^{3}J_{HH}$ = 7.4 Hz, H10/H14), 1.83 (*q*, 2H, $^{3}J_{HH}$ = 7.4 Hz, H10/H14), 3.55 (*t*, 2H, $^{3}J_{HH}$ = 7.4 Hz, H9/H13), 4.08 (*t*, 2H, $^{3}J_{HH}$ = 7.6 Hz, H9/H13), 7.46 (*t*, 2H, H3, H5), 7.57 (*t*, 1H, H4), 7.83 (*d*, 2H, H2, H6), 8.54 (*br s*, 1H, N—H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6 (C12/C16), 13.8 (C12/C16), 19.9 (C15/C11), 20.0 (C15/C11), 28.7 (C14/C10), 29.7 (C14/C10), 53.7 (C13/C9), 56.4 (C13/C9), 127.8 (C3, C5), 128.8 (C2, C6), 132.5 (C4), 133.0 (C1), 162.1 (C7), 180.9 (C8); $^{1}J(^{77}Se-^{13}C)$ = 222.1 Hz.

For *cis*-bis(*N*-benzoyl-*N*′,*N*′-dibutylselenoureato)palladium(II), (II): yield 94.2%, m.p. 423.5–424.4 K. Analysis found: C 49.1, H 5.8, N 7.1%; $C_{32}H_{46}N_4O_2PdSe_2$ requires: C 49.1, H 5.9, N 7.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (*t*, 6H, $^{3}J_{HH}$ = 7.4 Hz, H12*A*/*B* or H16*A*/*B*), 0.98 (*t*, 6H, $^{3}J_{HH}$ = 7.4 Hz, H12*A*/*B* or H16*A*/*B*), 1.38 (*m*, 8H, $^{3}J_{HH}$ = 7.6 Hz, H11*A*/*B*, H15*A*/*B*), 1.67 (*q*, 4H, $^{3}J_{HH}$ = 7.7 Hz, H10*A*/*B* or H14*A*/H14*A*/*B*), 1.76 (*q*, 4H, $^{3}J_{HH}$ = 7.8 Hz, H10*A*/*B* or H14*A*/*B*), 3.78 (*m*, 8H, $^{3}J_{HH}$ = 7.8 Hz, H9*A*/*B*, H13*A*/*B*), 7.40 (*t*, 4H, H3*A*/*B*, H5*A*/*B*), 7.49 (*t*, 2H, H4*A*/*B*), 8.23 (*d*, 4H, H2*A*/*B*, H6*A*/*B*); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 13.8, 13.9 (C12*A*/*B*, C16*A*/*B*), 20.2, 20.3 (C11*A*/*B*, C15*A*/*B*), 29.9, 30.0 (C10*A*/*B*, C14*A*/*B*), 51.8, 54.7 (C9*A*/*B*, C13*A*/*B*), 127.9 (C3*A*/*B*, C5*A*/*B*), 129.7 (C2*A*/*B*, C6*A*/*B*), 131.4 (C4*A*/B), 137.2 (C1*A*/*B*), 166.7 (C8*A*/*B*), 170.8 (C7*A*/*B*). $^{1}J(^{77}Se-^{13}C)$ = 176.5 Hz.

Compound (I)

Crystal data

$C_{16}H_{24}N_2OSe$
M_r = 339.33
Monoclinic, $P2_1/c$
a = 10.3880 (17) Å
b = 15.715 (3) Å
c = 10.1518 (16) Å
β = 98.423 (3)°
V = 1639.4 (5) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 2.29 mm^{-1}
T = 273 (2) K
0.20 × 0.16 × 0.14 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.651, T_{max} = 0.732
10228 measured reflections
3775 independent reflections
3031 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.085
S = 1.02
3775 reflections
187 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.55 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.33 e $Å^{-3}$

Table 1
Selected bond lengths (Å) for (I).

Se1—C8	1.848 (2)	N1—C8	1.399 (3)
O1—C7	1.212 (3)	N2—C8	1.314 (3)
C7—N1	1.397 (3)	N2—C13	1.470 (3)
C7—C1	1.492 (3)	N2—C9	1.480 (3)

Compound (II)

Crystal data

$[Pd(C_{16}H_{23}N_2OSe)_2]$
M_r = 783.05
Triclinic, $P\overline{1}$
a = 9.9302 (8) Å
b = 10.9315 (9) Å
c = 15.4119 (13) Å
α = 80.216 (1)°
β = 88.291 (1)°
γ = 81.867 (1)°
V = 1632.0 (2) $Å^3$
Z = 2
Mo $K\alpha$ radiation
μ = 2.83 mm^{-1}
T = 173 (2) K
0.09 × 0.08 × 0.08 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.785, T_{max} = 0.797
18809 measured reflections
7329 independent reflections
6802 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.056
S = 1.05
7329 reflections
374 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.55 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.38 e $Å^{-3}$

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Se1^{i}	0.83 (3)	2.76 (3)	3.539 (2)	159 (2)
C6—H6···O1^{ii}	0.93	2.48	3.407 (3)	174

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

Table 3
Selected bond lengths (Å) for (II).

Pd1—O1*A*	2.0395 (12)	N2*A*—C13*A*	1.469 (2)
Pd1—O1*B*	2.0439 (12)	N2*A*—C9*A*	1.478 (2)
Pd1—Se1*B*	2.3411 (3)	C9*B*—N2*B*	1.481 (2)
Pd1—Se1*A*	2.3489 (3)	N1*B*—C8*B*	1.334 (2)
Se1*A*—C8*A*	1.9076 (17)	N1*B*—C7*B*	1.335 (2)
Se1*B*—C8*B*	1.9006 (16)	N2*B*—C8*B*	1.338 (2)
O1*B*—C7*B*	1.260 (2)	N2*B*—C13*B*	1.473 (2)
O1*A*—C7*A*	1.266 (2)	C8*A*—N1*A*	1.333 (2)
N2*A*—C8*A*	1.341 (2)	C7*A*—N1*A*	1.329 (2)

H atoms involved in hydrogen bonding were located in difference electron-density maps and all other H atoms were placed in geometrically calculated positions, with C—H = 0.99 (for CH_2), 0.98 (for CH_3) or 0.95 Å (for aromatic H), and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ for CH_2 and aromatic, or $1.5U_{eq}(C)$ for CH_3 H atoms.

For both compounds, data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

Financial support from the University of Stellenbosch, the NRF (GUN 2046827), THRIP (project No. 2921) and Angloplatinum Ltd is gratefully acknowledged. JB acknowledges a Harry Crossley Bursary.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3058). Services for accessing these data are described at the back of the journal.

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