

Bis(tetra-*n*-butylammonium) (μ -*N,N'*-diselenium dinitride)bis[tribromo-palladate(II)]

Stephen M. Aucott, Sophie H. Dale, Mark R. J. Elsegood, Kathryn E. Holmes, Sarah L. M. James and Paul F. Kelly*

Chemistry Department, Loughborough University, Loughborough, Leicestershire LE11 3TU, England

Correspondence e-mail: p.f.kelly@lboro.ac.uk

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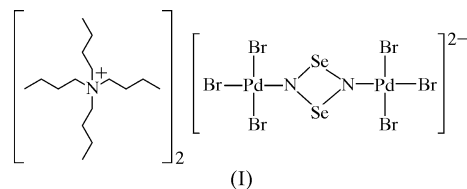
The reaction of Se_4N_4 with $(\text{Bu}_4\text{N})_2[\text{Pd}_2\text{Br}_6]$ gives the title compound, $(\text{C}_{16}\text{H}_{36}\text{N})_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]$, in good yield. The $[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]^{2-}$ anion lies on an inversion centre, and therefore the asymmetric unit contains half a formula unit. The crystal structure confirms the coordination of the Se_2N_2 unit to Pd through the N atoms, as previously assigned by IR spectroscopic analysis [Kelly, Slawin & Soriano-Rama (1997). *J. Chem. Soc. Dalton Trans.* pp. 559–562]. The title compound contains the longest Pd–N bond so far observed for such systems.

Comment

During the course of our work on the reactivity of Se_4N_4 towards metal centres, we have successfully demonstrated that, under the right circumstances, adducts of diselenium dinitride, Se_2N_2 , can be generated. Examples so far fully characterized by X-ray crystallography are $(\text{AlBr}_3)_2(\text{Se}_2\text{N}_2)$ (Kelly & Slawin, 1996), $(\text{PPh}_4)_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]$ (Kelly *et al.*, 1997) and $(\text{PPh}_4)_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Cl}_6]$ (Kelly & Slawin, 1995). All are of great interest due to the fact that, unlike its sulfur analogue (the four-membered ring S_2N_2), Se_2N_2 is unknown in the free state. Thus, these compounds have the potential to act as sources of the free material *via* appropriate substitution reactions.

In terms of performing such reactions, however, the aluminium compound is hampered by its extreme air-sensitivity, while the tetraphenylphosphonium salts of the air-stable palladium adducts form in rather poor yield. By far the best yield thus far obtained for one of these palladium adducts occurs when Se_4N_4 is reacted with $(\text{Bu}_4\text{N})_2[\text{Pd}_2\text{Br}_6]$ to give $(\text{Bu}_4\text{N})_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]$, (I) [typically *ca* 67% yield, compared with *ca* 20% for the tetraphenylphosphonium salts]. However, in our previous report on this compound, we used only IR spectroscopy and microanalysis as characterization techniques (Kelly *et al.*, 1997). Given that, thanks to its high yield, this compound is the obvious starting point for investigations into

the ability of such adducts to act as sources of the free nitride, and in the light of the general lack of structural data on complexes of Se_2N_2 , confirmation of the structure of (I) by X-ray crystallography becomes desirable.



The X-ray crystal structure of (I) confirms the presence of the four-membered Se_2N_2 ring, N-bound to the Pd centres, with the $[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]^{2-}$ anion situated on an inversion centre. The asymmetric unit therefore contains half a formula unit. The Se–N bond lengths are almost equivalent, in direct contrast with the other examples shown in Table 2. Co-crystallization of the anion with tetraphenylphosphonium cations results in a greater asymmetry in the Se–N bond lengths than seen in (I). In comparison with $(\text{PPh}_4)_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]$ (Kelly *et al.*, 1997), the presence of the tetrabutylammonium cations in (I) appears to result in a lengthening of the Pd–N bond, in addition to an increase in the symmetry of the Se_2N_2 unit.

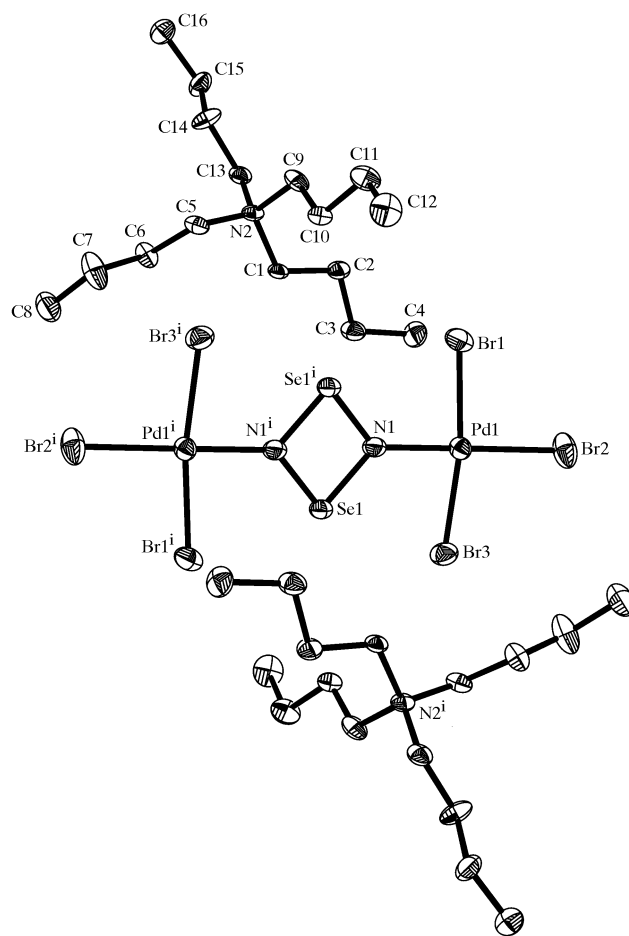


Figure 1

A view of (I), showing the atom-labelling scheme and with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, 1 - y, 2 - z$.]

Analysis of the salts $(\text{PPh}_4)_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]$ (Kelly *et al.*, 1997) and $(\text{PPh}_4)_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Cl}_6]$ (Kelly & Slawin, 1995) shows that there are interactions between the cations and anions which are absent from compound (I). In the case of $(\text{PPh}_4)_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Br}_6]$, there are C—H \cdots Se interactions having C \cdots Se distances of the order of 4.5 Å and C—H \cdots Br interactions having C \cdots Br distances in the range 3.8–3.95 Å. In addition, there is weak π – π stacking, with the Se_2N_2 unit held between two benzene rings, at a distance of 4.3 Å from each benzene ring. This weak π – π stacking is not observed in $(\text{PPh}_4)_2[\text{Pd}_2(\text{Se}_2\text{N}_2)\text{Cl}_6]$; instead, there are C—H \cdots Se interactions having C \cdots Se distances of the order of 4.3 Å and C—H \cdots Cl interactions having C \cdots Cl distances of the order of 3.6 Å. It is possible that the absence from (I) of relatively acidic C—H donors, such as the aromatic C—H groups of the tetraphenylphosphonium cations, may thus lead to a greater symmetry in the Se_2N_2 unit in the former.

A potentially important feature of (I) is the fact that the Pd—N bond is the longest so far observed for such systems (Tables 1 and 2). This fact, along with the high yield of the compound, suggests that it is likely to be the most effective starting material for studies into the liberation of the Se_2N_2 unit.

Experimental

The title compound was prepared according to the literature method of Kelly *et al.* (1997) and single crystals were grown by slow diffusion of diethyl ether into a CH_2Cl_2 solution.

Crystal data

$(\text{C}_{16}\text{H}_{36}\text{N})_2[\text{Pd}_2\text{Br}_6(\text{N}_2\text{Se}_2)]$	$Z = 1$
$M_r = 1363.12$	$D_x = 1.938 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.081 (2) \text{ \AA}$	Cell parameters from 2921 reflections
$b = 10.671 (3) \text{ \AA}$	$\theta = 2.4\text{--}27.2^\circ$
$c = 12.415 (3) \text{ \AA}$	$\mu = 7.49 \text{ mm}^{-1}$
$\alpha = 95.131 (4)^\circ$	$T = 150 (2) \text{ K}$
$\beta = 98.598 (4)^\circ$	Lath, orange
$\gamma = 98.689 (4)^\circ$	$0.30 \times 0.20 \times 0.09 \text{ mm}$
$V = 1168.1 (5) \text{ \AA}^3$	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	4049 independent reflections
ω rotation scans with narrow frames	3002 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.037$
$T_{\text{min}} = 0.195$, $T_{\text{max}} = 0.508$	$\theta_{\text{max}} = 25.0^\circ$
8065 measured reflections	$h = -10 \rightarrow 10$
	$k = -12 \rightarrow 12$
	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 10.845P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.85 \text{ e \AA}^{-3}$
4049 reflections	$\Delta\rho_{\text{min}} = -1.50 \text{ e \AA}^{-3}$
212 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Pd1—N1	1.978 (7)	Pd1—Br3	2.4316 (12)
Pd1—Br1	2.4299 (12)	Se1 ¹ —N1 ¹	1.806 (7)
Pd1—Br2	2.4066 (13)	Se1—N1	1.809 (7)
N1—Pd1—Br2	176.6 (2)	Br1—Pd1—Br3	170.88 (5)
N1—Pd1—Br1	85.4 (2)	Se1 ¹ —N1—Se1	97.9 (3)
Br2—Pd1—Br1	94.39 (4)	Se1 ¹ —N1—Pd1	130.5 (4)
N1—Pd1—Br3	85.7 (2)	Se1—N1—Pd1	130.2 (4)
Br2—Pd1—Br3	94.61 (4)	N1 ¹ —Se1—N1	82.1 (3)

Symmetry code: (i) $1 - x, 1 - y, 2 - z$.

Table 2

Selected bond lengths (Å) in (I) and related compounds.

Compound	Metal—N	Se—N	Reference
(I)	1.978 (7)	1.806 (7), 1.809 (7)	<i>a</i>
(AlBr ₃) ₂ (Se ₂ N ₂)	1.92 (2)	1.77 (1), 1.81 (1)	<i>b</i>
(PPh ₄) ₂ [Pd ₂ (Se ₂ N ₂)Br ₆]	1.875 (9)	1.809 (10), 1.920 (9)	<i>c</i>
(PPh ₄) ₂ [Pd ₂ (Se ₂ N ₂)Cl ₆]	1.946 (4)	1.804 (5), 1.779 (4)	<i>d</i>

(*a*) This work; (*b*) Kelly & Slawin (1996); (*c*) Kelly *et al.* (1997); (*d*) Kelly & Slawin (1995).

Methylene (C—H = 0.99 Å) and methyl (C—H = 0.98 Å) H atoms were placed in geometric positions and refined using a riding model. $U_{\text{iso}}(\text{H})$ values were set at $1.2U_{\text{eq}}(\text{C})$ for methylene and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. The data set was truncated at $2\theta = 50^\circ$, as only statistically insignificant data were present above this limit.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1591). Services for accessing these data are described at the back of the journal.

References

- Bruker (2001). SMART (Version 5.611) and SAINT (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.
- Kelly, P. F. & Slawin, A. M. Z. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1758–1759.
- Kelly, P. F. & Slawin, A. M. Z. (1996). *J. Chem. Soc. Dalton Trans.* pp. 4029–4030.
- Kelly, P. F., Slawin, A. M. Z. & Soriano-Rama, A. (1997). *J. Chem. Soc. Dalton Trans.* pp. 559–562.
- Sheldrick, G. M. (2000). SHELXTL. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (2003). SADABS. Version 2.08. University of Göttingen, Germany.