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Cation–π interactions in [Na(dibenzo-18-crown-6)]$_2$[Pd(SCN)$_4$]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.028
wR factor = 0.080
Data-to-parameter ratio = 11.0

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

The crystal structure of the title compound, bis[(dibenzo-18-crown-6)sodium] tetrathiocyanatopalladium(II), [Na($C_{20}H_{24}O_6$)]$_2$[Pd(SCN)$_4$], features an ion-pair-type species consisting of two [Na(dibenzo-18-crown-6)]$^+$ cations and a [Pd(SCN)$_4$]$^{2-}$ dianion which occupies a special position on the inversion centre. The Pd atom has a square-planar coordination formed by four S atoms [Pd—S 2.3241 (9) and 2.3319 (8) Å, S—Pd—S 90.15 (3)°]; the ion pairs are held together through Na···N interactions [2.423 (3) Å] involving the N atoms of two (out of four) thiocyanate groups. The Na$^+$···π interactions reaching out to the aromatic nucleus of the neighbouring ion pair [Na···C 3.077 (4) and 3.082 (4) Å] are responsible for the formation of infinite chains stretching along the [1$\bar{1}$0] direction of the crystal.

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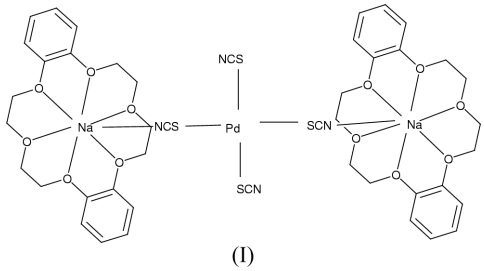
Comment

Cation–π interactions have attracted considerable attention as an important non-covalent binding force. Studies in the gas phase (Sunner *et al.*, 1981), aqueous media (Petti *et al.*, 1988; Forman *et al.*, 1995), solid state (Clark *et al.*, 1992; Beer *et al.*, 1994; Werner *et al.*, 1996), biological systems (Ma & Dougherty, 1997; Dougherty & Stauffer, 1990), as well as theoretical calculations (Mecozzi *et al.*, 1996; Jiang *et al.*, 1998, 1999) established the broad scope and significance of these interactions. We have reported the first examples of crown ether complexes, [K(DB18C6)]$_2$[Pd(SCN)$_4$] (DB18C6 is dibenzo-18-crown-6) (Dou *et al.*, 2000) and [K(DB18C6)]$_2$[Pt(SCN)$_4$] (Li *et al.*, 2000), which exhibit cation–π interactions responsible for the formation of infinite chains in crystals. However, in spite of the growing interest, the X-ray evidence for the existence of the analogous Na$^+$···π interaction is still limited. Bock and co-workers synthesized two compounds containing interactions of this kind, namely [$(C_6H_5)_2C{=}CH$-$C(C_6H_5)_2$]$^-$[Na$^+$O$(C_2H_5)_2$] (Bock *et al.*, 1990) and [$(C_6H_5)_2C{=}C(C_6H_5)_2$]$^{2-}$2[Na$^+O(C_2H_5)_2$] (Bock *et al.*, 1989). In the present paper, we report the synthesis and crystal structure of the complex of DB18C6 with Na$_2$[Pd(SCN)$_4$], (I), which provides a new example of Na$^+$···π interaction.



(I)

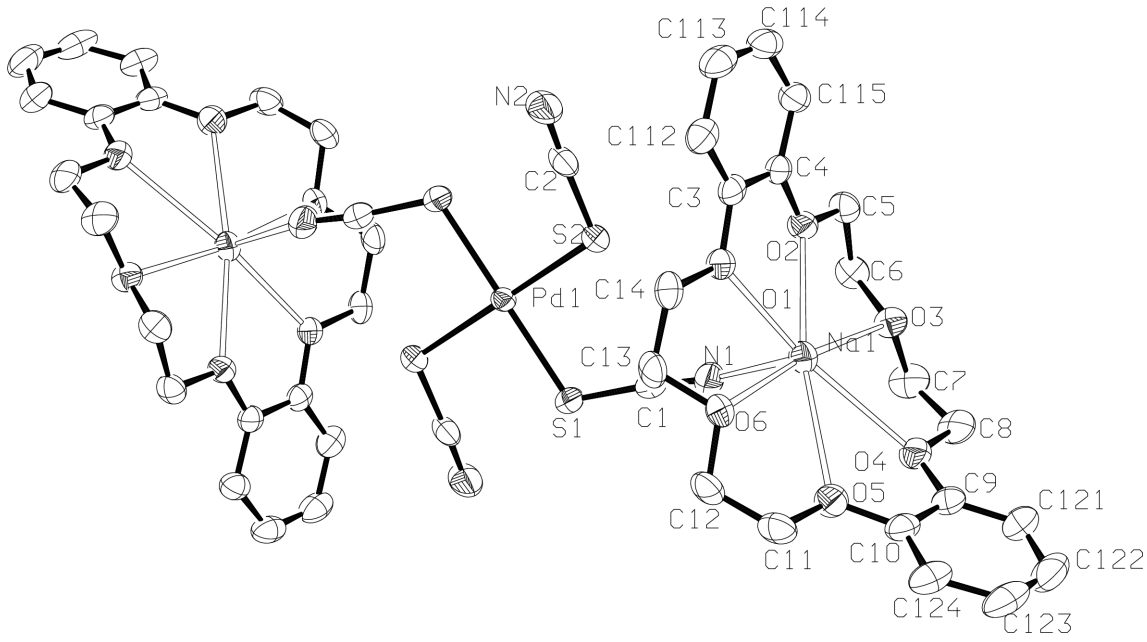


Figure 1
The structure of $[Na(DB18C6)]_2[Pd(SCN)_4]$ showing 30% probablity displacement elliposoids. H atoms have been omitted for clarity.

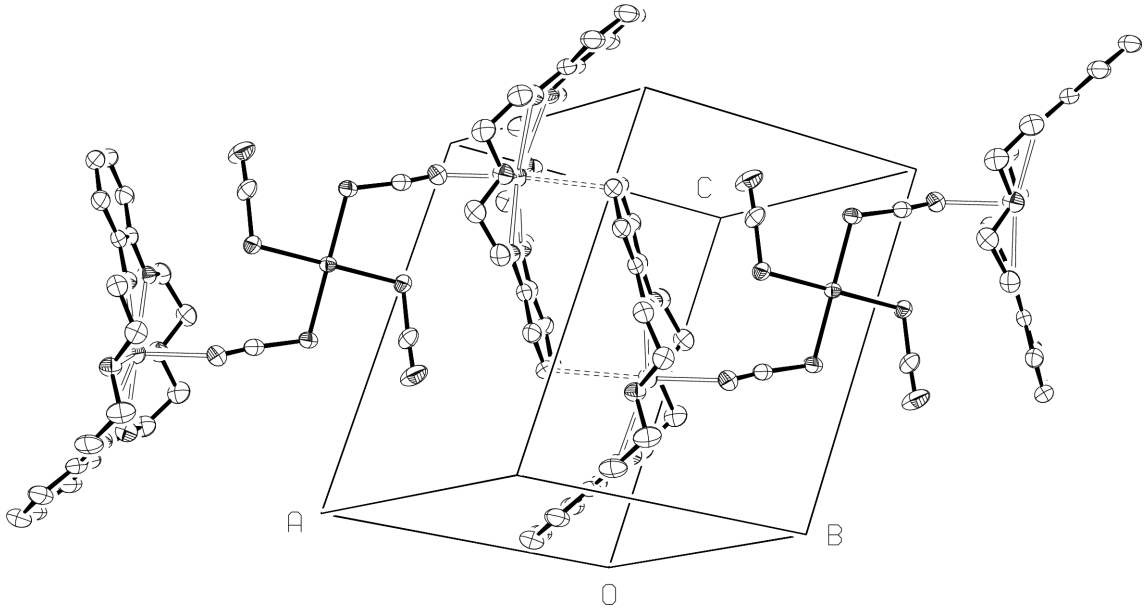


Figure 2
A fragment of the infinite chain in the crystal packing of $[Na(DB18C6)]_2[Pd(SCN)_4]$.

The structure of the title complex (Fig. 1) features an ion-pair-type species consisting of two $[Na(DB18C6)]^+$ cations and a $[Pd(SCN)_4]^{2-}$ dianion. The Pd atom occupies a special position on the inversion centre and has a square-planar coordination environment formed by four S atoms [Pd1—S1 2.3241 (9) and Pd1—S2 2.3319 (8) Å, S1—Pd1—S2 90.15 (3)°]. The average Pd—S, S—C and C—N bond lengths (2.3270, 1.671 and 1.133 Å, respectively) are consistent with the corresponding values in $[K(DB18C6)]_2[Pd(SCN)_4]$ (Dou *et al.*, 2000) and $[K(DB18C6)]_2[Pd(SCN)_4]\cdot H_2O$ (Wu *et al.*, 1991).

In the $[Na(DB18C6)]^+$ cation, the Na—O bond lengths span the range 2.559–2.853 Å. The Na^+ ion is also coordinated by the N atom of one of the SCN groups at a distance of 2.423 (3) Å, which is consistent with the Na—N distance [2.472 (8) Å] in $[Na(B15C5)]_2[Pd(SCN)_4]$ (B15C5 is benzo-15-crown-5) (Zhu *et al.*, 2000). The remainder of its coordination sphere is made up of the Na···$C113^{i}$ 3.077 (4) Å and Na···$C114^{i}$ 3.082 (4) Å [symmetry code: (i) $2-x, -y, 1-z$] close contacts involving one of the phenylene rings of the DB18C6 ligand of the neighbouring $[Na(DB18C6)]_2[Pd(SCN)_4]$ ion pair. These interactions give rise to the formation

of infinite chains stretching along the [1$\bar{1}$0] direction in the crystal (Fig. 2). Similar infinite chains formed due to Na$\cdots\pi$ interactions with even shorter Na$\cdots$C distances were observed in the above-mentioned complexes reported by Bock *et al.* (1989, 1990) (the average Na$\cdots$C distances are 2.86 and 2.88 Å respectively).

Experimental

The synthesis of the title complex was effected by adding 10 ml of aqueous mixture of $PdCl_2$ (0.025 *M*) and NaSCN (2 *M*) to 10 ml of 0.1 *M* solution of DB18C6 in 1,2-dichloroethane. The reaction mixture was stirred for 2 h at room temperature and then filtered. The precipitate was dissolved in acetone. M. p. 485–487 K. Found: C 47.51, H 4.25, N 4.72, S 11.23%; $C_{44}H_{48}Na_2N_4O_{12}PdS_4$ requires: C 47.79, H 4.38, N 5.07, S 11.58%. Selected FT–IR ν/cm^{-1}: 2920, 2850, 2111, 1695, 1595, 1504, 1251, 1213, 1125, 960, 940, 751. The single-crystal was obtained from a 4:1 diethyl ether/acetone solution.

Crystal data

$[Na(C_{20}H_{24}O_6)]_2[Pd(SCN)_4]$	$Z = 1$
$M_r = 1105.48$	$D_x = 1.487$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.5695$ (10) Å	Cell parameters from 25 reflections
$b = 8.568$ (3) Å	$\theta = 10.5$–$13.5°$
$c = 12.976$ (2) Å	$\mu = 0.63$ mm^{-1}
$\alpha = 81.58$ (2)°	$T = 293$ (2) K
$\beta = 104.804$ (10)°	Prism, orange
$\gamma = 96.85$ (2)°	0.60 × 0.50 × 0.40 mm
$V = 1225.7$ (5) Å^3	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.020$
$\theta/2\theta$ scans	$\theta_{max} = 25.2°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = -13 \rightarrow 13$
$T_{min} = 0.834$, $T_{max} = 0.884$	$k = -10 \rightarrow 10$
4622 measured reflections	$l = 0 \rightarrow 15$
4406 independent reflections	3 standard reflections every 200 reflections
3190 reflections with $I > 2\sigma(I)$	frequency: 3600 min
	intensity decay: 5.0%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.4501P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.080$	$\Delta\rho_{max} = 0.41$ e Å^{-3}
$S = 1.0$	$\Delta\rho_{min} = -0.43$ e Å^{-3}
4406 reflections	
400 parameters	
All H-atom parameters refined	

Table 1
Selected geometric parameters (Å, °).

Pd1—S1	2.3241 (9)	Na1—O4	2.853 (2)
Pd1—S2	2.3319 (8)	Na1—O5	2.841 (3)
S1—C1	1.663 (4)	Na1—O6	2.559 (2)
S2—C2	1.664 (4)	Na1—C113^{i}	3.077 (4)
Na1—N1	2.423 (3)	Na1—C114^{i}	3.082 (4)
Na1—O1	2.572 (2)	N1—C1	1.151 (4)
Na1—O2	2.559 (2)	N2—C2	1.133 (4)
Na1—O3	2.597 (2)		
S1^{ii}—Pd1—S2	90.15 (3)	O5—Na1—O4	52.46 (7)
O2—Na1—O3	64.23 (7)	O6—Na1—O1	64.00 (7)
O2—Na1—O1	59.40 (7)	O6—Na1—O5	60.17 (7)
O3—Na1—O4	59.83 (7)	C113^{i}—Na1—C114^{i}	25.32 (11)

Symmetry codes: (i) $2-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$.

The H atoms were located in the difference map and were refined isotropically; the C—H bond lengths span the range 0.88–1.08 Å.

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988); cell refinement: *CAD*-4 *Manual*; data reduction: *SDP-Plus* (Frenz, 1985); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1996); software used to prepare material for publication: *SHELXL*97.

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