

Ling-Qian Kong,^{a,b} Jian-Min
Dou,^{a*} Cheng-Juan Li,^a
Da-Cheng Li^a and Da-Qi Wang^a^aDepartment of Chemistry, Liaocheng University, Liaocheng 252059, People's Republic of China, and ^bDongchang College, Liaocheng University, Liaocheng 252059, People's Republic of China

Correspondence e-mail: jmdou@lctu.edu.cn

Key indicators

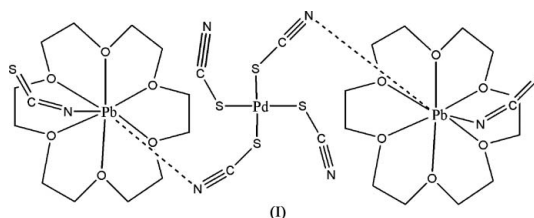
Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.014 \text{ \AA}$
R factor = 0.037
wR factor = 0.094
Data-to-parameter ratio = 15.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis[(18-crown-6)isothiocyanatolead(II)]
tetrathiocyanatopalladate(II)

The title complex, bis{[(1,4,7,10,13,16-hexaoxacyclooctadecane- $\kappa^6 O$)(isothiocyanato- κN)lead(II)] tetrakis(thiocyanato- κS)palladate(II)}, $[\text{Pb}(\text{NCS})(\text{C}_{12}\text{H}_{24}\text{O}_6)]_2[\text{Pd}(\text{NCS})_4]$, has been synthesized by the reaction of PdCl_2 and $\text{Pb}(\text{SCN})_2$ with 18-crown-6 in 1,2-dichloroethane. The complex is composed of two $[\text{Pb}(18\text{-crown-6})(\text{NCS})]^+$ complex cations and one $[\text{Pd}(\text{SCN})_4]^{2-}$ complex anion. The Pd atom lies on a centre of symmetry. The cation and anion are associated through a weak interaction between the Pb atom of the cation and an N atom of the anion.

Received 22 March 2006
Accepted 6 April 2006

Comment

Since the pioneering work of Pedersen (1967), crown ethers and their complexes with metal ions have attracted much attention, not only because crown ethers present unusual coordination ability to various metal ions but also because crown ethers and their complexes can act as building blocks to form polymeric supramolecular structures by crystal engineering (Pedersen & Frensdorff, 1972; Steed, 2001; Harrington *et al.*, 2004). Among crown ether complexes of main group metals, only a few structural characterizations of Pb^{II} -crown ether complexes have been published to date. These include the simple crown ether complexes $[\text{Pb}(18\text{-crown-6})(\text{NCS})(\text{SCN})]$ (Nazarenko & Rusanov, 1994*b*), $[\text{Pb}(15\text{-crown-5})_2][\text{Pb}(\text{NO}_3)_3(15\text{-crown-5})_2]$ (Rogers & Bond, 1992), $[\text{Pb}(18\text{-crown-6})(\text{OCCCCl}_3)_2](\text{Cl}_3\text{CCOOH})_2$ (Manlinovskii *et al.*, 1990), $\text{Pb}(18\text{-crown-6})\text{I}_2$ (Nazarenko *et al.*, 1995) and $[\text{Pb}(\text{DC18-crown-6})\text{Cl}_2]$ (DC18 is dicyclohexyl-18-crown-6; Nazarenko & Rusanov, 1994*a*), and crown ether complexes with a one-dimensional chain structure, such as $(18\text{-crown-6})[\text{Pb}(\text{OOCCH}_3)_2(\text{H}_2\text{O})]$ (Manlinovskii *et al.*, 1992), $\text{Pb}(\text{OOCCH}_3)_2(18\text{-crown-6})\cdot 3\text{H}_2\text{O}$ (Shin *et al.*, 1993) and $[\text{Pb}(\text{DC18-crown-6-}A)(\text{H}_2\text{O})][\text{Pd}(\text{SCN})_4]$ (Sun *et al.*, 2005). In our previous work, we have synthesized and characterized the first crown ether complex of lead(II) with a two-dimensional network, $[\text{K}(18\text{-crown-6})_2][\text{Pb}(\text{i-mnt})_2]$ (i-mnt is 1,1-dicyanoethane-2,2-dithiolate; Kong *et al.*, 2006). In this paper, we report a new crown ether complex, $[\text{Pb}(18\text{-crown-6})(\text{NCS})_2]_2[\text{Pd}(\text{SCN})_4]$, (I).



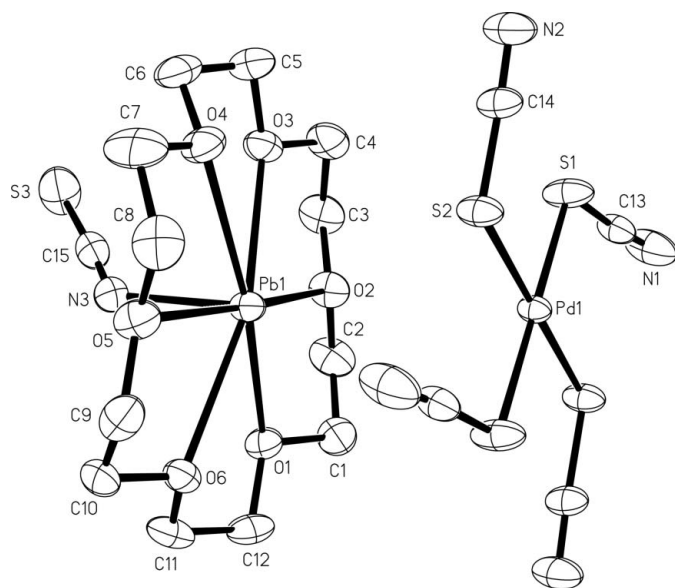


Figure 1

The structures of the complex cation and anion in (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Unlabelled atoms are related to labelled atoms by $(1-x, 1-y, 2-z)$.

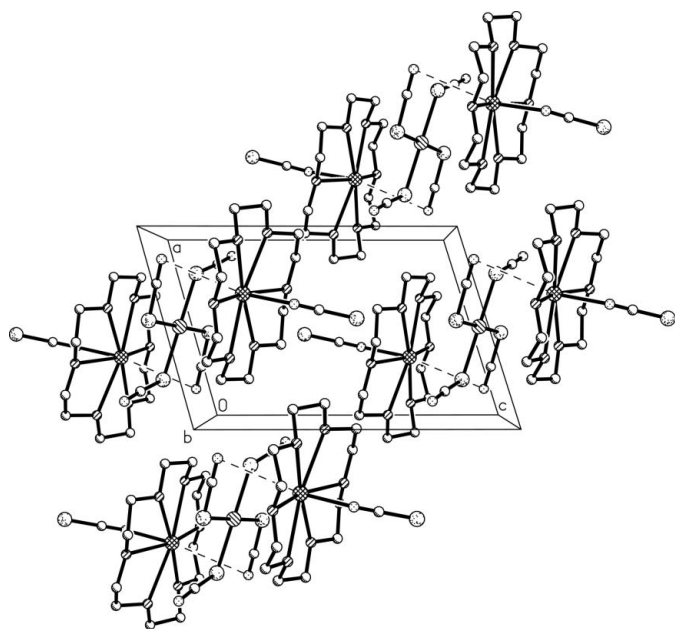


Figure 2

The crystal packing of (I). Dashed lines denote the weak interactions between cations and anions. H atoms have been omitted.

Compound (I) is composed of two $[\text{Pb}(18\text{-crown-6})(\text{NCS})]^+$ complex cations and one $[\text{Pd}(\text{SCN})_4]^{2-}$ complex anion. The structures of the cation and anion are shown in Fig. 1 and selected bond lengths and angles are listed in Table 1. In the anion, the Pd atom, which is located on a centre of symmetry in a square-planar geometry, is coordinated by four S atoms from the SCN ligands, with no direct bonds to the crown ether. The average Pd–S bond length is 2.325 Å, consistent with the corresponding values in the related complexes $[\text{Na}(\text{B15-}$

$\text{crown-5})_2][\text{Pd}(\text{SCN})_4]$ (B15-crown-5 is benzo-15-crown-5; Zhang *et al.*, 2002) and $[\text{Na}(\text{N15-crown-5})_2][\text{Pd}(\text{SCN})_4]$ (N15-crown-5 is 2,3-naphtho-15-crown-5; Dou *et al.*, 2004). In the cation, the Pb atom lying within the crown ether is seven-coordinated by six O atoms from the 18-crown-6 ligand and one N atom from the NCS ligand. The six O atoms are almost coplanar, the mean deviation from the plane being 0.145 Å, while the Pb atom is 0.254 (4) Å out of the ether-O plane. The Pb–O bond lengths are in agreement with the corresponding values in the complex $[\text{Pb}(\text{DC18-crown-6-A})(\text{H}_2\text{O})][\text{Pd}(\text{SCN})_4]$ (Sun *et al.*, 2005). The Pb–N3 bond length of 2.353 (7) Å is shorter than that in the complex $[\text{Pb}(18\text{-crown-6})(\text{NCS})(\text{SCN})]$ (2.445 Å; Nazarenko & Rusanov, 1994b).

It is found from the crystal packing (Fig. 2) that there is a weak interaction between the Pb atom and an N atom of the complex anion, with a $\text{Pb}\cdots\text{N}$ distance of 3.514 (8) Å; thus the anion links two cations to form a neutral complex molecule.

Experimental

All reagents used were commercially available and were used without further purification. Microanalytical data were obtained from a Perkin–Elmer 2400 II analyser. The title complex was prepared by adding an aqueous mixture (10 ml) of PdCl_2 (0.0445 g, 0.25 mmol) and $\text{Pb}(\text{SCN})_2$ (1.616 g, 5 mmol) to a solution of 18-crown-6 (0.364 g, 1 mmol) in 1,2-dichloroethane (10 ml). The reaction mixture was stirred for 3 h at room temperature. The organic phase was then separated from the reaction solution. Single crystals of (I) were obtained from a solution in diethyl ether–1,2-dichloroethane (4:1) [yield 241.2 mg, 69% (based on Pd); m.p. 530–531 K]. Analysis, calculated for $\text{C}_{30}\text{H}_{48}\text{N}_6\text{O}_{12}\text{Pb}_2\text{PdS}_6$: C 25.75, H 3.43, N 6.01%; found: C 25.95, H 3.72, N 5.95%.

Crystal data

$[\text{Pb}(\text{NCS})(\text{C}_{12}\text{H}_{24}\text{O}_6)]_2[\text{Pd}(\text{NCS})_4]$
 $M_r = 1397.88$
 Triclinic, $P\bar{1}$
 $a = 8.336$ (2) Å
 $b = 11.958$ (3) Å
 $c = 12.464$ (3) Å
 $\alpha = 92.043$ (4)°
 $\beta = 105.979$ (3)°
 $\gamma = 101.316$ (4)°

$V = 1165.9$ (5) Å³
 $Z = 1$
 $D_x = 1.991$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 7.91$ mm⁻¹
 $T = 293$ (2) K
 Block, red
 $0.39 \times 0.37 \times 0.33$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.148$, $T_{\text{max}} = 0.180$
 (expected range = 0.061–0.073)

6061 measured reflections
 4040 independent reflections
 3276 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.094$
 $S = 1.00$
 4040 reflections
 259 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0542P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.11$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pb1—N3	2.353 (7)	Pb1—O3	2.736 (5)
Pb1—O5	2.692 (5)	Pb1—O4	2.752 (5)
Pb1—O6	2.721 (5)	Pd1—S2	2.3214 (19)
Pb1—O2	2.727 (5)	Pd1—S1	2.329 (2)
Pb1—O1	2.733 (5)		
S2—Pd1—S2 ⁱ	180.0 (1)	S2—Pd1—S1	90.81 (7)
S2—Pd1—S1 ⁱ	89.19 (7)		

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

All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest density peak and deepest hole are located 0.99 and 0.97 Å, respectively, from atom Pb1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997b).

The authors acknowledge the financial support of the Natural Science Foundation of Shandong Province, China (grant No. Y2003B01).

References

- Dou, J. M., Gao, X. K., Dong, F. Y., Li, D. C. & Wang, D. Q. (2004). *J. Chem. Soc. Dalton Trans.* pp. 2918–2922.
- Harrington, J. M., Jones, S. B., White, P. H. & Hancock, R. D. (2004). *Inorg. Chem.* **43**, 4456–4461.
- Kong, L. Q., Dou, J. M., Li, D. C. & Wang, D. Q. (2006). *J. Mol. Chem.* **785**, 186–191.
- Manlinovskii, S. T., Simonov, Y. A. & Nazarenko, A. Y. (1990). *Kristallografiya*, **35**, 1410–1419.
- Manlinovskii, S. T., Simonov, Y. A. & Nazarenko, A. Y. (1992). *Kristallografiya*, **37**, 90–102.
- Nazarenko, A. Y., Kronikovski, O., Fonari, M. S., Kravtsov, V. C., Simonov, Y. A. & Malinovski, T. J. (1995). *Supramol. Chem.* **4**, 259–264.
- Nazarenko, A. Y. & Rusanov, E. B. (1994a). *Pol. J. Chem.* **68**, 1233–1241.
- Nazarenko, A. Y. & Rusanov, E. B. (1994b). *Polyhedron*, **13**, 2549–2553.
- Pedersen, C. (1967). *J. Am. Chem. Soc.* **89**, 7017–7036.
- Pedersen, C. J. & Frensdorff, H. K. (1972). *Angew. Chem. Int. Ed. Engl.* **11**, 16–19.
- Rogers, R. D. & Bond, A. H. (1992). *Inorg. Chim. Acta*, **192**, 163–171.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997a). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Shin, Y. G., Hampden, S. M. J. & Kodas, T. T. (1993). *Polyhedron*, **12**, 1453–1460.
- Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Steed, J. W. (2001). *Coord. Chem. Rev.* **215**, 171–178.
- Sun, Y.-M., Dong, F.-Y., Dou, J.-M., Gao, X.-K., Li, D.-C. & Wang, D.-Q. (2005). *Acta Cryst.* **E61**, m1787–m1788.
- Zhang, Z. H., Dou, J. M., Liu, Y., Wang, D. Q., Wang, Y., Zheng, P. J., Du, C. X. & Du, Y. (2002). *Acta Chim. Sinica*, **60**, 1649–1655. (In Chinese.)