

A novel Pt^{II}-dibenzo-18-crown-6 (DB18C6) complex

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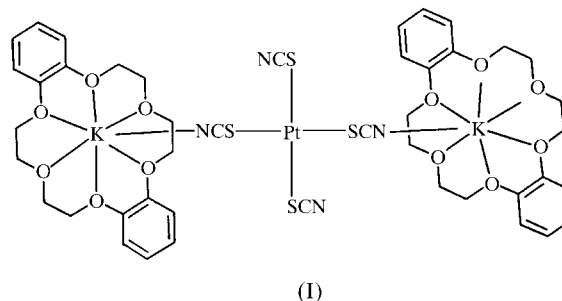
The novel Pt^{II}-dibenzo-18-crown-6 (DB18C6) title complex, μ -[tetrakis(thiocyanato-*S*)platinum(II)]-*N,N'*-bis[[2,5,8,15,18,21-hexaoxatricyclo[20.4.0.1^{9,14}]hexacos-1(22),9(14),10,12,23,25-hexaene- κ^6 O]potassium(I)], [K(C₂₀H₂₄O₆)₂][Pt(SCN)₄], has been isolated and characterized by X-ray diffraction analysis. The structure analysis shows that the complex displays a quasi-one-dimensional infinite chain of two [K(DB18C6)]⁺ complex cations and a [Pt(SCN)₄]²⁻ anion, bridged by K⁺⋯ π interactions between adjacent [K(DB18C6)]⁺ units.

Comment

In 1981, Sunner showed for the first time that K⁺ binds to benzene in the gas phase (Sunner *et al.*, 1981). The cation- π interaction has become a major goal in physical organic chemistry (Ma & Dougherty, 1997). The potential for such an interaction has always been evident from an electrostatic analysis of benzene. Some X-ray single-crystal diffraction analyses of this kind of compound also demonstrated the K⁺⋯ π interaction, for example, K⁺-benzene or K⁺-phenyl (Eaborn *et al.*, 1995), K⁺-phospholide anions (Paul *et al.*, 1996), K⁺-boratabenzene (Hoic *et al.*, 1997) and K⁺-calixarenes (Beer *et al.*, 1994). We have also synthesized and characterized a series of metal complexes with macrocyclic ligands (Wang *et al.*, 1987, 1991). We report here the synthesis and crystal structure of the novel complex of DB18C6 with K₂[Pt(SCN)₄], namely μ -[tetrakis(thiocyanato-*S*)platinum(II)]-*N,N'*-bis[[2,5,8,15,18,21-hexaoxatricyclo[20.4.0.1^{9,14}]hexacos-1(22),9(14),10,12,23,25-hexaene- κ^6 O]potassium(I)], (I), which has cation- π interactions.

The title compound consists of two [K(DB18C6)]⁺ complex cations and a [Pt(SCN)₄]²⁻ complex anion (Fig. 1). The Pt atom lies on a crystallographic center of symmetry and is

coordinated by four S atoms from four SCN groups to form the regular square-planar complex anion [Pt(SCN)₄]²⁻. The coordination environment of the K⁺ cation is, however, very unusual. The K⁺ ion is anchored in the crown-ether cavity forming the [K(C₁₂H₂₄O₆)]⁺ complex cation (Beer *et al.*, 1994).



The principal interactions of the K⁺ cation involve the six O atoms of the crown [K1—O bond lengths vary from 2.716 (3) to 2.795 (3) Å] and one N atom from the SCN group at a distance of 2.792 (5) Å. The remainder of its coordinating sphere is made up of close K⁺⋯C contacts with the phenyl ring of the DB18C6 in another molecule, thus forming a K⁺⋯C-bridged quasi-one-dimensional infinite chain (Fig. 2). The K1⋯C172 and K1⋯C173 distances of 3.288 (6) and 3.279 (6) Å, respectively, are similar to those in other quasi-one-dimensional infinite-chain structures, such as K[Nd(O-2,6-*t*Pr₂-C₆H₃)₄] (3.30 Å; Wang *et al.*, 1987) and KBPh₄ (3.29 Å; Clark *et al.*, 1992).

In the crown-ether ring, the average C—C and C—O bond distances are 1.432 and 1.426 Å, and the average O—C—C and C—O—C angles are 109.3 and 111.2°, respectively. These values are similar to those reported elsewhere (Wang *et al.*, 1987, 1991).

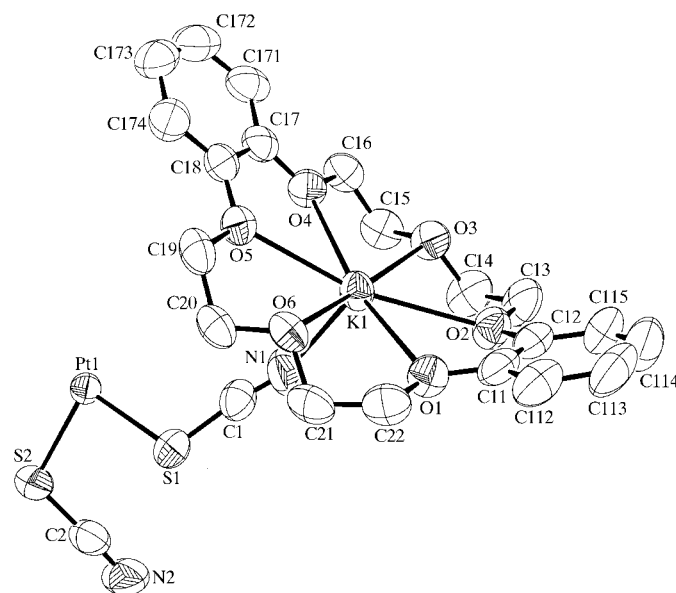
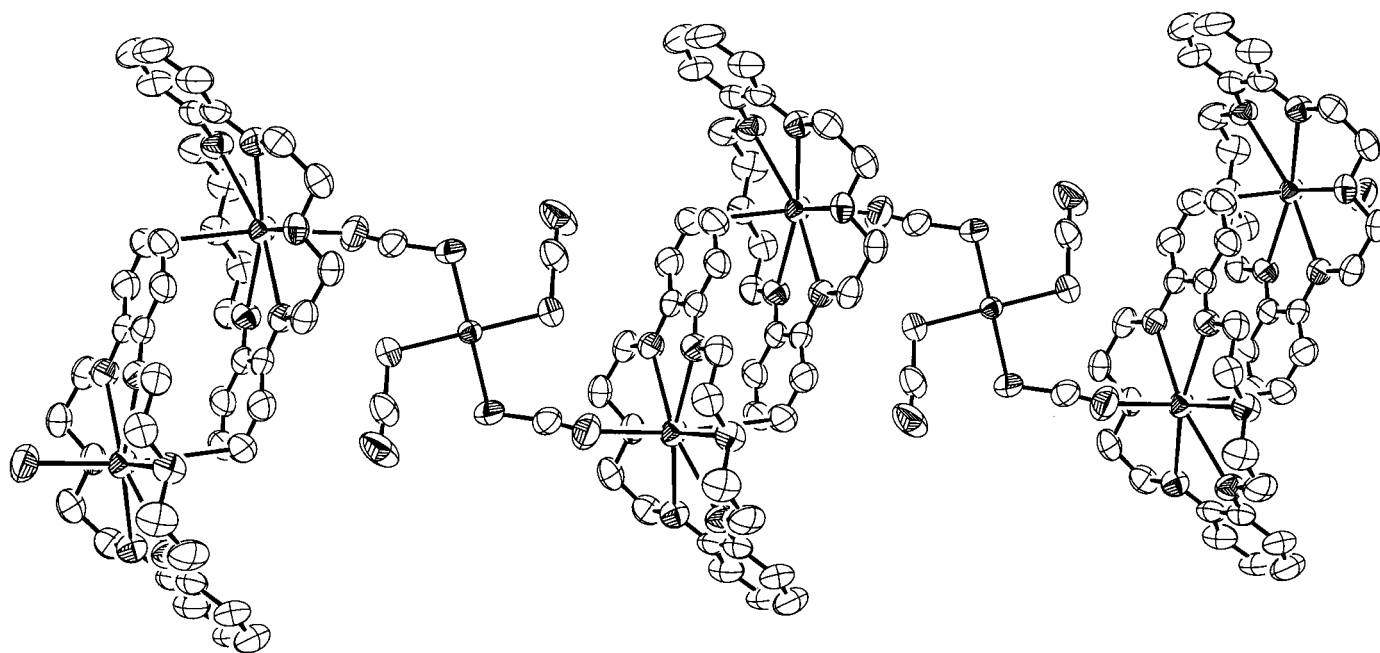


Figure 1
The structure of (I) showing 30% probability displacement ellipsoids.


Figure 2

The quasi-one-dimensional infinite chain structure of (I) shown with 30% probability displacement ellipsoids.

Experimental

[K(DB18C6)₂][Pt(SCN)₄] was prepared by adding an aqueous mixture of K₂PtCl₄ (0.025 mol l⁻¹, 10 ml) and KSCN (2 mol l⁻¹, 10 ml) to dibenzo-18-crown-6 (0.1 mol l⁻¹, 10 ml) in 1,2-dichloroethane. The reaction mixture was stirred for 2 h at room temperature and then filtered. The single crystal used for analysis was obtained from a 4:1 diethyl ether/acetone solution.

Crystal data

[K(C ₂₀ H ₂₄ O ₆) ₂][Pt(SCN) ₄]	<i>Z</i> = 1
<i>M_r</i> = 1226.40	<i>D_x</i> = 1.627 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 8.553 (5) Å	Cell parameters from 25 reflections
<i>b</i> = 13.127 (3) Å	<i>θ</i> = 11.08–14.39°
<i>c</i> = 11.819 (3) Å	<i>μ</i> = 3.199 mm ⁻¹
<i>α</i> = 106.21 (2)°	<i>T</i> = 293 (2) K
<i>β</i> = 82.77 (3)°	Prism, orange
<i>γ</i> = 99.72 (3)°	0.30 × 0.25 × 0.25 mm
<i>V</i> = 1251.6 (8) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω/2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
*T*_{min} = 0.400, *T*_{max} = 0.449
 4702 measured reflections
 4487 independent reflections
 4124 reflections with *I* > 2σ(*I*)

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.025
wR (*F*²) = 0.075
S = 0.906
 4487 reflections
 304 parameters
 H-atom parameters constrained

*R*_{int} = 0.014
*θ*_{max} = 25.17°
h = -10 → 10
k = 0 → 15
l = -14 → 13
 3 standard reflections every 200 reflections
 intensity decay: 3.9%

w = 1/[σ²(*F_o*²) + (0.0595*P*)² + 0.5854*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 1.17 e Å⁻³
 Δρ_{min} = -0.56 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pt1–S1	2.3064 (13)	O4–C16	1.437 (5)
Pt1–S2	2.3232 (13)	O4–K1	2.716 (3)
N1–K1	2.792 (5)	O5–C18	1.380 (5)
O1–C11	1.360 (6)	O5–C19	1.436 (5)
O1–C22	1.440 (6)	O5–K1	2.729 (3)
O1–K1	2.795 (3)	O6–C20	1.416 (6)
O2–C12	1.377 (6)	O6–C21	1.430 (6)
O2–C13	1.433 (6)	O6–K1	2.720 (3)
O2–K1	2.793 (3)	C172–K1 ⁱ	3.288 (6)
O3–C14	1.425 (6)	C173–K1 ⁱ	3.279 (6)
O3–C15	1.428 (6)	K1–C173 ⁱ	3.279 (6)
O3–K1	2.749 (3)	K1–C172 ⁱ	3.288 (6)
O4–C17	1.372 (5)		
S1 ⁱⁱ –Pt1–S2	90.10 (5)	O5–K1–O2	163.19 (10)
O4–K1–O6	118.27 (10)	O3–K1–O2	61.05 (10)
O4–K1–O5	56.68 (9)	O4–K1–O1	165.05 (10)
O6–K1–O5	61.67 (10)	O6–K1–O1	61.33 (10)
O4–K1–O3	62.10 (10)	O5–K1–O1	121.47 (10)
O6–K1–O3	170.96 (10)	O3–K1–O1	115.70 (10)
O5–K1–O3	118.43 (10)	O2–K1–O1	54.79 (9)
O4–K1–O2	121.89 (10)	C173 ⁱ –K1–C172 ⁱ	23.67 (16)
O6–K1–O2	115.92 (10)		
S2–Pt1–S1–C1	159.79 (19)		

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

The H atoms of the phenyl and CH₂ groups were included in riding positions, with C–H = 0.93 and 0.97 Å, and *U*(H) = 1.2*U*_{eq}(C).

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: *DIRDIF-96.3* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1101). Services for accessing these data are described at the back of the journal.

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