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Crystal structure of bis(μ-thiocyanato-*N*,*S*)bis[aqua(3-methyl-benzo-15-crown-5)sodium]bis(thiocyanato-*S*)palladium(II), $[Na(C_{15}H_{22}O_5)(H_2O)]_2[Pd(SCN)_4]$

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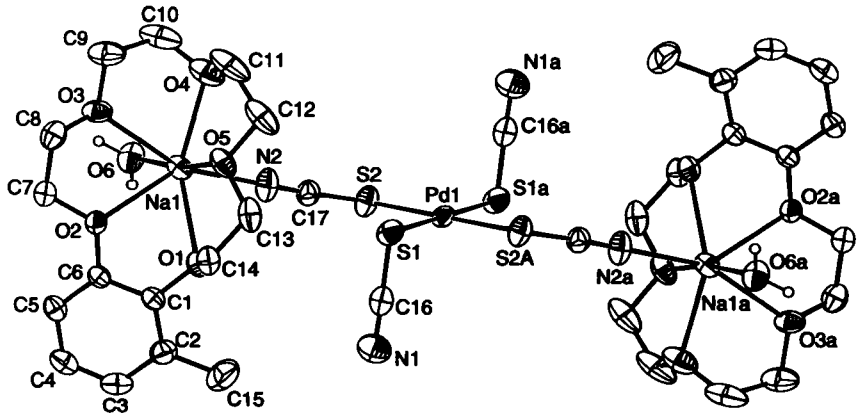

Abstract

$C_{34}H_{48}N_4Na_2O_{12}PdS_4$, monoclinic, $P12_1/c1$ (no. 14), $a = 10.88(2)$ Å, $b = 16.90(2)$ Å, $c = 13.21(2)$ Å, $\beta = 110.47(2)°$, $V = 2275.6$ Å^3, $Z = 2$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.091$, $T = 298$ K.

Source of material

The title compound was prepared by adding 10 ml aqueous mixture of 0.025 M $PdCl_2$ and 2 M NaSCN solutions to 10 ml 0.1 M 3-methylbenzo-15-crown-5 (3-mb15-cr-5) solution in 1,2-dichloroethane. The reaction mixture was stirred for 4 hours at RT and then the organic phase was separated. The single crystal was obtained from 4:1 diethyl ether/1,2-dichloroethane solution (m.p. 82-84 °C). Elemental analysis: found – C, 41.44 %, H, 4.91 %, N, 5.69 %, S, 13.01 %; calc. for $C_{34}H_{48}N_4O_{12}PdNa_2S_4$ – C, 41.69 %; H, 4.90 %; N, 5.53 %; S, 12.81 %. Selected FT-IR and ^{1}H NMR data are available in the CIF file.

Experimental details

While hydrogen atoms bound to carbon atoms were restrained during calculations, aqua H atoms were freely refined.

Discussion

Since the pioneering work of Pedersen [1], crown ethers and their metal cations have attracted much attention, which is not only because crown ethers are able to impose unusual coordination numbers and arrangements on various metal ions, but also because they and their cations, especially those involving aromatic rings, can act as building blocks to form 1D – 3D supramolecular structures by coordinative covalent bonds, hydrogen bonds, π-π stacking, cation-π interactions and other weak interactions [2-4]. The reported complexes of b15-cr-5 structurally characterized by X-ray diffraction analysis have so far included: $[Na(b15\text{-}cr\text{-}5)ClO_4]$, $[Na(b15\text{-}cr\text{-}5)_2]ClO_4$, $[Na(b15\text{-}cr\text{-}5)_2][BPh_4]$ [5], $[Na(b15\text{-}cr\text{-}5)H_2O]I$ [6], $[K(b15\text{-}cr\text{-}5)_2]$picrate [7], $[K(b15\text{-}cr\text{-}5)_2][InBr_4]$ [8], $[K(b15\text{-}cr\text{-}5)_2][InI_4]$ [9] and $[K(b15\text{-}cr\text{-}5)_2]I$ [10], $[K(b15\text{-}cr\text{-}5)_2][Co(NCS)_4]$ [11] and $[Na(b15\text{-}cr\text{-}5)]_2[Pd(SCN)_4]$ [12]. However, methyl-benzo-15-crown-5 complexes have not been reported in literature. We now report the novel 3-methylbenzo15-crown-5 complex $\{Pd(SCN)_4[Na(3\text{-}mb15\text{-}cr\text{-}5)(H_2O)]_2\}$.

The structure consists of two $[Na(3\text{-}mb15\text{-}cr\text{-}5)(H_2O)]^+$ complex cations and one $[Pd(SCN)_4]^{2-}$ complex anion forming a stable neutral complex. The Pd atom is located on the inversion centre and is not bonded to the O atoms of the crown ether. It is coordinated by four S atoms from four SCN groups. The bond angles of S2–Pd1–S2′ and S1–Pd1–S1′ are 180° and the other S–Pd–S bond angle are 86.0(1)° and 94.0(1)°, indicating that $[Pd(SCN)_4]^{2-}$ is square planar configuration. The average bond lengths of Pd—S, S—C and C—N are 2.328 Å, 1.667 Å and 1.149 Å, respectively, which are consistent with the corresponding values in the structure of $[Na(b15\text{-}cr\text{-}5)]_2[Pd(SCN)_4]$ [12]. In the complex cation $[Na(3\text{-}mb15\text{-}cr\text{-}5)(H_2O)]^+$, the sodium ion is coordinated by five crown ether oxygen atoms. Na—O bond lengths are at the range from 2.428 Å to 2.582 Å, which is similar to that found in $[Na(b15\text{-}cr\text{-}5)ClO_4]$ [5], $[Na(b15\text{-}cr\text{-}5)H_2O]I$ [6] and $[Na(b15\text{-}cr\text{-}5)]_2[Pd(SCN)_4]$ [12]. The Na^+ ion is 0.849 Å deviated out of the ether oxygen plane. The five oxygen atoms in the ether ring are not perfectly co-planar and the average deviation of the oxygen atoms from the best plane is 0.494 Å. The Na^+ ion is also coordinated by O6 atom from one H_2O molecule to form cone-shaped configuration. The distance of Na—O6 is 2.428(5) Å, which is slightly longer than that of the complex $[Na(b15\text{-}cr\text{-}5)H_2O]I$ [6] [2.2985(1) Å]. The remainder of Na^+ coordinating position is occupied by N atom from the SCN group of $[Pd(SCN)_4]^{2-}$ at the same side as the H_2O molecule. The distance of Na1—N2 is 2.428(5) Å and the bond angle of O6–Na1–N2 is 90.8(1)°, which are similar to that found in $[Na(b15\text{-}cr\text{-}5)]_2[Pd(SCN)_2]$ [12].

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Table 1. Data collection and handling.

Crystal:	salmon pink rod, size 0.07 × 0.27 × 0.41 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.69 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	50.16°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11214, 4021
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2409
$N(param)_{refined}$:	267
Programs:	SHELXS-97 [13], SHELXL-97 [14]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3)	4e	0.8040	0.5205	0.8852	0.093
H(4)	4e	0.5967	0.5710	0.8157	0.083
H(5)	4e	0.4213	0.5030	0.8344	0.067
H(7A)	4e	0.2790	0.3880	0.7999	0.069
H(7B)	4e	0.2798	0.4365	0.9018	0.069
H(8A)	4e	0.2282	0.3243	0.9784	0.082
H(8B)	4e	0.1233	0.3338	0.8617	0.082
H(9A)	4e	0.0836	0.1900	0.8302	0.112
H(9B)	4e	0.1648	0.1853	0.9548	0.112
H(10A)	4e	0.1873	0.0658	0.8805	0.127
H(10B)	4e	0.2262	0.1076	0.7903	0.127
H(11A)	4e	0.3828	0.0304	1.0518	0.132
H(11B)	4e	0.3343	0.1158	1.0674	0.132
H(12A)	4e	0.5542	0.0960	1.1793	0.116
H(12B)	4e	0.5916	0.0828	1.0758	0.116
H(13A)	4e	0.7364	0.1904	1.1330	0.088
H(13B)	4e	0.6912	0.2195	1.2276	0.088
H(14A)	4e	0.6088	0.3366	1.1258	0.075
H(14B)	4e	0.7624	0.3295	1.1620	0.075
H(15A)	4e	0.9573	0.4185	0.9747	0.183
H(15B)	4e	0.8965	0.3333	0.9566	0.183
H(15C)	4e	0.9216	0.3769	1.0668	0.183
H(1)	4e	0.306(2)	0.253(2)	0.691(3)	0.07(2)
H(2)	4e	0.434(4)	0.257(3)	0.677(4)	0.12(2)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd(1)	2a	0	0	0	0.0378(2)	0.0517(3)	0.0558(3)	−0.0003(2)	0.0179(2)	−0.0095(3)
Na(1)	4e	0.4816(2)	0.21942(9)	0.8977(1)	0.071(1)	0.045(1)	0.0554(9)	0.0004(8)	0.0351(8)	−0.0007(8)
N(1)	4e	1.1019(5)	0.2154(3)	1.1209(3)	0.107(4)	0.079(3)	0.080(3)	−0.014(3)	0.040(3)	−0.011(3)
N(2)	4e	0.6563(4)	0.1402(3)	0.8748(3)	0.072(3)	0.085(3)	0.072(3)	0.031(2)	0.021(2)	0.000(2)
O(1)	4e	0.6703(3)	0.3058(2)	1.0051(2)	0.063(2)	0.046(2)	0.054(2)	0.009(1)	0.024(1)	0.000(1)
O(2)	4e	0.4321(3)	0.3645(2)	0.9314(2)	0.048(2)	0.052(2)	0.056(2)	0.004(1)	0.016(1)	0.007(1)
O(3)	4e	0.2512(3)	0.2492(2)	0.8731(2)	0.069(2)	0.069(2)	0.080(2)	−0.018(2)	0.046(2)	−0.010(2)
O(4)	4e	0.3693(4)	0.1033(2)	0.9305(3)	0.133(3)	0.056(2)	0.101(3)	−0.019(2)	0.079(3)	−0.009(2)
O(5)	4e	0.5430(3)	0.1939(2)	1.0933(2)	0.100(3)	0.048(2)	0.064(2)	0.013(2)	0.048(2)	0.011(2)
O(6)	4e	0.3872(4)	0.2369(2)	0.7117(3)	0.070(3)	0.094(3)	0.065(2)	0.014(2)	0.038(2)	0.018(2)
S(1)	4e	0.9364(1)	0.08586(7)	1.11173(9)	0.0541(7)	0.0704(9)	0.0769(8)	0.0006(6)	0.0312(6)	−0.0197(7)
S(2)	4e	0.8505(1)	0.04604(8)	0.83862(9)	0.0569(8)	0.0860(9)	0.0580(7)	0.0207(7)	0.0174(6)	−0.0052(6)
C(1)	4e	0.6538(4)	0.3804(2)	0.9575(3)	0.058(3)	0.042(3)	0.050(2)	0.000(2)	0.021(2)	−0.002(2)
C(2)	4e	0.7598(5)	0.4193(3)	0.9460(4)	0.059(3)	0.068(4)	0.081(3)	−0.006(3)	0.028(3)	−0.004(3)
C(3)	4e	0.7346(5)	0.4920(3)	0.8928(4)	0.075(4)	0.073(4)	0.087(3)	−0.028(3)	0.032(3)	−0.004(3)
C(4)	4e	0.6105(5)	0.5226(3)	0.8515(3)	0.094(4)	0.049(3)	0.064(3)	−0.010(3)	0.028(3)	0.005(2)
C(5)	4e	0.5057(4)	0.4822(2)	0.8625(3)	0.068(3)	0.047(3)	0.052(2)	0.004(2)	0.020(2)	−0.001(2)
C(6)	4e	0.5277(4)	0.4108(2)	0.9157(3)	0.056(3)	0.040(3)	0.044(2)	−0.001(2)	0.020(2)	−0.005(2)
C(7)	4e	0.2980(4)	0.3852(3)	0.8773(3)	0.054(3)	0.059(3)	0.058(3)	0.007(2)	0.018(2)	0.002(2)
C(8)	4e	0.2153(4)	0.3235(3)	0.9020(4)	0.060(3)	0.087(4)	0.063(3)	0.009(3)	0.029(2)	0.000(3)
C(9)	4e	0.1712(5)	0.1852(3)	0.8834(5)	0.100(4)	0.094(5)	0.109(4)	−0.038(4)	0.064(4)	−0.017(4)
C(10)	4e	0.2345(7)	0.1104(3)	0.8657(5)	0.152(6)	0.074(5)	0.127(5)	−0.053(4)	0.096(5)	−0.034(4)
C(11)	4e	0.3946(7)	0.0864(3)	1.0421(5)	0.207(8)	0.049(4)	0.122(5)	−0.017(4)	0.118(5)	0.002(3)
C(12)	4e	0.5318(7)	0.1101(3)	1.1038(4)	0.174(7)	0.051(4)	0.093(4)	0.011(4)	0.082(4)	0.016(3)
C(13)	4e	0.6725(5)	0.2224(3)	1.1503(4)	0.091(4)	0.077(4)	0.057(3)	0.035(3)	0.031(3)	0.015(3)
C(14)	4e	0.6800(4)	0.3059(3)	1.1173(3)	0.070(3)	0.061(3)	0.051(3)	0.013(2)	0.014(2)	−0.003(2)
C(15)	4e	0.8963(5)	0.3838(4)	0.9900(5)	0.063(4)	0.142(6)	0.163(6)	0.001(4)	0.042(4)	0.033(5)
C(16)	4e	1.0349(4)	0.1611(3)	1.1158(3)	0.060(3)	0.073(4)	0.045(2)	0.015(3)	0.018(2)	−0.002(2)
C(17)	4e	0.7387(4)	0.1029(3)	0.8650(3)	0.054(3)	0.061(3)	0.048(2)	0.004(2)	0.010(2)	0.003(2)

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