Crystal structure of bis(benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene)-bis(thiocyanato)disodium(I), $\text{Na}_2(\text{SCN})_2(\text{C}_{14}\text{H}_{20}\text{O}_5)_2$, a benzo-15-crown-5 complex

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Abstract

$\text{C}_{30}\text{H}_{40}\text{N}_2\text{Na}_2\text{O}_{10}\text{S}_2$, monoclinic, $C12/c1$ (no. 15), $a = 17.708(5)$ Å, $b = 11.236(3)$ Å, $c = 17.821(5)$ Å, $\beta = 106.816(4)^\circ$, $V = 3394.2$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.038$, $wR_{\text{ref}}(F^2) = 0.065$, $T = 293$ K.

Source of material

All chemicals were commercial products and were used as supplied. The title compound was prepared by adding 10 mL aqueous mixture of CoCl_2 (0.050 mol/L) and NaSCN (2 mol/L) to 10 mL benzo-15-crown-5 (0.1 mol/L) in 1,2-dichloroethane solution. The reaction mixture was stirred for 2 hours at room temperature and then the organic phase was separated and the title compound was yielded as an unexpected product (m.p. 99–100 °C). Elemental analysis: found – C, 51.52 %; H, 5.20 %; N, 3.88 %; S, 9.32 %, calc. for $\text{C}_{15}\text{H}_{20}\text{NO}_5\text{NaS}$ – C, 51.56 %; H, 5.72 %; N, 4.00 %; S, 9.16 %. Selected FT-IR data are available in the CIF file.

Discussion

The extensive pioneering study of Pedersen [1] has led to a virtual explosion of solution and solid-state investigation of crown ethers and metal ions like alkali metal, alkali earth metal, other main-group and transition-metal ions. It is shown that single-crystal X-ray diffraction analysis is a most powerful technique for the characterization of these complexes and numerous solid-state structural studies have appeared through the years. The reported

sodium benzo-15-crown-5 complexes (Na-b15c5) structurally characterized by X-ray diffraction analysis have so far included: $[\text{Na}(\text{b15c5})\text{ClO}_4]$, $[\text{Na}(\text{b15c5})_2]\text{ClO}_4$, $[\text{Na}(\text{b15c5})_2][\text{BPh}_4]$ [2], $[\text{Na}(\text{b15c5})\text{H}_2\text{O}]$ [3]. We have also reported b15c5 complexes $[\text{Na}(\text{b15c5})]_2$ and $[\text{Pd}(\text{SCN})_4]$ [4], and now report the novel b15c5 complex $[\text{Na}(\text{b15c5})]_2(\text{SCN})_2$.

The complex consists of two $[\text{Na}(\text{b15c5})]^+$ complex cations and two SCN^- anions. Na^+ ion is coordinated by five O atoms of b15c5 and Na–O bond lengths range from 2.4716(4) Å to 2.5202(4) Å, which are similar to that found in $[\text{Na}(\text{b15c5})\text{ClO}_4]$ [2] and $[\text{Na}(\text{b15c5})\text{H}_2\text{O}]$ [3]. The five oxygen atoms in the ether ring are not good least-square plane and the deviations of oxygen atoms from the plane is 1.264 Å and Na^+ ion is 1.158 Å out of the ether oxygen plane. Na^+ ion is also coordinated by one N atom from the SCN group at the distance of 2.495(2) Å, which is slightly longer than that found in $[\text{Na}(\text{b15c5})]_2[\text{Pd}(\text{SCN})_4]$ [Na–N: 2.472(8) Å] [4], $[\text{Na}(\text{18c6})_2][\text{M}(\text{SCN})_4] \cdot \text{H}_2\text{O}$ ($M = \text{Pd}, \text{Pt}$) [Na–N: 2.417(4) Å, 2.421(5) Å, respectively] [5]. The same N atom of SCN group is also connected with another $[\text{Na}(\text{b15c5})]^+$ complex cation. Thus, two $[\text{Na}(\text{b15c5})]^+$ complex cations and two SCN^- anions form a dimer structure. Similar structures are found in b18c6 or 18c6 complexes $[\text{Rb}(\text{b18c6})]_2(\text{SCN})_2$ [6], $[\text{Rb}(\text{18c6})]_2(\text{SCN})_2$ [7] and $[\text{Cs}(\text{18c6})]_2(\text{SCN})_2$ [8], in which two complex cations are also bridged by two SCN^- ligands to form 2:2 dimer structure.

Table 1. Data collection and handling.

Crystal:	colorless rod, size 0.20 × 0.30 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	2.39 cm ^{−1}
Diffractometer, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	50.06°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8734, 2997
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1709
$N(\text{param})_{\text{refined}}$:	288
Programs:	SHELXS-97 [9], SHELXL-97 [10]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(2A)	8f	0.339(1)	0.114(2)	0.770(1)	0.044(6)
H(3A)	8f	0.452(1)	0.222(2)	0.785(1)	0.059(7)
H(4A)	8f	0.539(1)	0.251(2)	0.910(1)	0.063(7)
H(5A)	8f	0.509(1)	0.162(2)	1.016(1)	0.052(7)
H(7A)	8f	0.478(1)	0.072(2)	1.109(1)	0.066(7)
H(8A)	8f	0.405(1)	−0.062(2)	1.153(1)	0.094(9)

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Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(9A)	8f	0.278(1)	0.188(2)	1.085(1)	0.080(9)
H(10A)	8f	0.139(1)	0.167(2)	1.078(1)	0.064(8)
H(11A)	8f	0.052(1)	0.097(2)	0.956(1)	0.051(7)
H(12A)	8f	0.033(1)	−0.011(2)	0.838(1)	0.073(7)
H(13A)	8f	0.127(1)	−0.081(2)	0.758(1)	0.067(7)
H(14A)	8f	0.256(1)	−0.020(2)	0.764(1)	0.082(9)
H(7B)	8f	0.395(1)	0.168(2)	1.096(1)	0.09(1)

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(8B)	8f	0.397(1)	0.077(2)	1.199(2)	0.11(1)
H(9B)	8f	0.267(1)	0.163(2)	1.168(1)	0.057(7)
H(10B)	8f	0.156(1)	0.036(2)	1.104(1)	0.056(7)
H(11B)	8f	0.071(1)	−0.034(2)	0.978(1)	0.067(8)
H(12B)	8f	0.109(1)	0.081(2)	0.849(1)	0.068(9)
H(13B)	8f	0.192(1)	−0.164(2)	0.809(1)	0.058(8)
H(14B)	8f	0.207(1)	0.084(2)	0.795(1)	0.073(9)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Na(1)	8f	0.25822(5)	−0.08803(7)	0.99121(5)	0.0545(5)	0.0414(5)	0.0599(6)	0.0010(4)	0.0207(5)	0.0010(4)
N(1)	8f	0.1878(1)	−0.2276(2)	1.0567(1)	0.081(2)	0.048(1)	0.087(2)	0.004(1)	0.041(1)	0.008(1)
O(1)	8f	0.28939(8)	0.0072(1)	0.87694(8)	0.0504(9)	0.0483(9)	0.0366(9)	−0.0068(8)	0.0053(8)	−0.0002(7)
O(2)	8f	0.38400(8)	0.0378(1)	1.01638(8)	0.0502(9)	0.055(1)	0.0360(9)	−0.0091(8)	0.0111(8)	0.0021(8)
O(3)	8f	0.29898(9)	0.0215(1)	1.12002(9)	0.058(1)	0.063(1)	0.062(1)	0.005(1)	0.0234(9)	−0.0030(9)
O(4)	8f	0.16449(8)	0.0764(1)	0.99679(9)	0.052(1)	0.059(1)	0.061(1)	0.0002(8)	0.0211(9)	−0.0026(9)
O(5)	8f	0.14242(9)	−0.0785(1)	0.87396(9)	0.055(1)	0.054(1)	0.067(1)	−0.0007(9)	0.0143(9)	−0.0052(9)
S(1)	8f	0.10625(4)	−0.22470(7)	1.16871(4)	0.0738(5)	0.1003(6)	0.0623(5)	−0.0167(4)	0.0235(4)	−0.0159(4)
C(1)	8f	0.3551(1)	0.0738(2)	0.8818(1)	0.045(1)	0.034(1)	0.045(2)	0.004(1)	0.018(1)	0.000(1)
C(2)	8f	0.3733(2)	0.1258(2)	0.8188(2)	0.065(2)	0.058(2)	0.045(2)	0.008(2)	0.021(2)	0.003(1)
C(3)	8f	0.4420(2)	0.1900(2)	0.8298(2)	0.075(2)	0.060(2)	0.067(2)	0.014(2)	0.042(2)	0.018(2)
C(4)	8f	0.4925(2)	0.2031(2)	0.9028(2)	0.052(2)	0.046(2)	0.090(2)	−0.000(1)	0.037(2)	0.007(2)
C(5)	8f	0.4752(1)	0.1531(2)	0.9665(2)	0.042(2)	0.048(2)	0.062(2)	0.002(1)	0.015(2)	−0.000(2)
C(6)	8f	0.4067(1)	0.0889(2)	0.9568(1)	0.041(1)	0.034(1)	0.046(1)	0.004(1)	0.016(1)	−0.000(1)
C(7)	8f	0.4191(2)	0.0870(3)	1.0928(2)	0.057(2)	0.090(2)	0.043(2)	−0.010(2)	0.011(2)	−0.006(2)
C(8)	8f	0.3828(2)	0.0285(3)	1.1481(2)	0.060(2)	0.094(3)	0.054(2)	−0.004(2)	0.013(2)	−0.003(2)
C(9)	8f	0.2573(2)	0.1300(3)	1.1148(2)	0.085(2)	0.055(2)	0.051(2)	−0.004(2)	0.020(2)	−0.007(2)
C(10)	8f	0.1727(2)	0.1038(3)	1.0770(2)	0.078(2)	0.050(2)	0.066(2)	0.019(2)	0.038(2)	0.002(2)
C(11)	8f	0.0876(2)	0.0393(3)	0.9533(2)	0.050(2)	0.059(2)	0.090(2)	0.011(2)	0.024(2)	0.004(2)
C(12)	8f	0.0884(2)	0.0167(3)	0.8716(2)	0.055(2)	0.069(2)	0.078(2)	0.002(2)	0.006(2)	0.000(2)
C(13)	8f	0.1700(2)	−0.0864(3)	0.8071(2)	0.065(2)	0.074(2)	0.059(2)	−0.005(2)	−0.001(2)	−0.018(2)
C(14)	8f	0.2301(2)	0.0056(3)	0.8034(2)	0.060(2)	0.078(2)	0.047(2)	−0.008(2)	0.007(2)	−0.006(2)
C(15)	8f	0.1545(1)	−0.2264(2)	1.1033(1)	0.051(2)	0.039(2)	0.060(2)	−0.003(1)	0.011(1)	0.003(1)

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