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

M.-J. Niu, D.-Q. Wang, D.-C. Li and J.-M. Dou*

Liaocheng University, Department of Chemistry, Liaocheng, 252059 P. R. China

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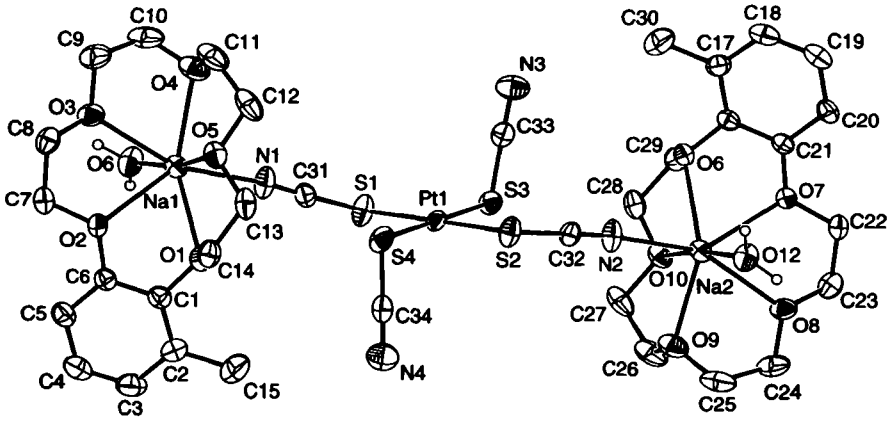

Abstract

$C_{34}H_{48}N_4Na_2O_{12}PtS_4$, monoclinic, $P12_1/c1$ (no. 14), a = 21.19(1) Å, b = 16.814(8) Å, c = 13.218(7) Å, β = 105.330(7)°, V = 4542.8 Å^3, Z = 4, $R_{gt}(F)$ = 0.032, $wR_{ref}(F^2)$ = 0.072, T = 298 K.

Source of material

The title compound was prepared by adding 10 ml aqueous mixture of 0.025 M Na_2PtCl_4 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 six hours at room temperature and then the organic phase was separated. The single crystal was obtained from 4:1 diethyl ether/1,2-dichloroethane solution (m.p. 154-156 °C).

Elemental analysis: found – C, 38.03 %; H, 4.50 %; N, 5.22 %; S, 11.94 %; calc. for $C_{34}H_{48}N_4O_{12}PtNa_2S_4$ – C, 38.24 %; H, 4.48 %; N, 5.18 %; S, 11.83 %. 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

The reported benzo-15-crown-5 (b15-cr-5) complexes structurally characterized by X-ray diffraction analysis have so far included: $[Na(b15\text{-}cr\text{-}5)(ClO_4)]$, $[Na(b15\text{-}cr\text{-}5)_2][ClO_4]$, $[Na(b15\text{-}cr\text{-}5)_2][BPh_4]$ [1], $[Na(b15\text{-}cr\text{-}5)H_2O]I$ [2], $[K(b15\text{-}cr\text{-}5)_2]pic$ [3], $[K(b15\text{-}cr\text{-}5)_2][InBr_4]$ [4], $[K(b15\text{-}cr\text{-}5)_2][InI_4]$ [5], $[K(b15\text{-}cr\text{-}5)_2]I$ [6], $[K(b15\text{-}cr\text{-}5)_2][Co(NCS)_4]$ [7]. However, complexes of methyl substituted benzo-15-crown-5 have not been reported in the literature.

We now report the novel 3-mb15-cr-5 complex $\{Pt(SCN)_4[Na(3\text{-}mb15\text{-}cr\text{-}5)(H_2O)]_2\}$. The structure consists of two $[Na(3\text{-}mb15\text{-}cr\text{-}5)(H_2O)]^+$ complex cations and one $[Pt(SCN)_4]^{2-}$ complex anion forming a stable neutral complex by coordination bonding. The Pt atom located on a general position is coordinated by four S atoms from four SCN groups, but not bonded directly to the O atoms of the crown ether. The bond angles of S2–Pt1–S1 and S4–Pt1–S3 are 179.41(5)° and 179.06(5)°, respectively, the average bond angles of other S–Pt–S are 90°, indicating that $[Pt(SCN)_4]^{2-}$ has a distorted planar, quadrangular configuration. The average bond lengths of Pt—S, S—C and C—N are 2.3235 Å, 1.6764 Å and 1.1463 Å, respectively, which is consistent with the corresponding values in the structures of $\{[K(18\text{-}cr\text{-}6)]_2[Pt(SCN)_4](H_2O)\}_n$ [8] and $\{[Na(b15\text{-}cr\text{-}5)][Na(b15\text{-}cr\text{-}5)(H_2O)][Pt(SCN)_4]\}$ [9]. In the complex cation $[Na(3\text{-}mb15\text{-}cr\text{-}5)(H_2O)]^+$, sodium ion is coordinated by five oxygen atoms of the crown ether rings. Na—O bond lengths are at the range from 2.437 Å to 2.590 Å, which are similar to those found in $[Na(b15\text{-}cr\text{-}5)ClO_4]$ [1], $[Na(b15\text{-}cr\text{-}5)H_2O]I$ [2] and $[Na(b15\text{-}cr\text{-}5)][Na(b15\text{-}cr\text{-}5)(H_2O)][Pt(SCN)_4]$ [9]. Na^+ ion is 0.826 Å deviated out of the ether oxygen plane. The five oxygen atoms in the ether ring are not in a perfect plane and the averaged deviation of oxygen atoms from the best plane is 0.486 Å. Na^+ ion is also coordinated by an O atom from H_2O molecule to form cone-shaped configuration. The distances of Na1—O11, Na2—O12 are 2.330(4) Å and 2.315(4) Å, respectively, which is slightly longer than that of the complex $[Na(b15\text{-}cr\text{-}5)H_2O]I$ [2] [2.29(1) Å]. The remainder of Na^+ coordinating position is occupied by an N atom from one SCN group of $[Pt(SCN)_4]^{2-}$ at the same side as the H_2O molecule. The distances of Na1—N1 and Na2—N2 are 2.432(5) Å and 2.425(5) Å, respectively, and the bond angles of O11–Na1–N1 and O12–Na2–N2 are 91.1(2)° and 90.2(2)°, respectively, which are similar to those found in $\{[Na(b15\text{-}cr\text{-}5)][Na(b15\text{-}cr\text{-}5)(H_2O)][Pt(SCN)_4]\}_n$ [9].

* Correspondence author (e-mail: jmdou@lctu.edu.cn)

Table 1. Data collection and handling.

Crystal:	orange prism, size 0.32 × 0.41 × 0.44 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	33.46 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	23358, 7998
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5610
$N(param)_{refined}$:	530
Programs:	SHELXS-97 [10], SHELXL-97 [11]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4e	0.8496	−0.0098	0.7307	0.095
H(4)	4e	0.9498	−0.0677	0.7690	0.083
H(5)	4e	1.0398	−0.0042	0.8765	0.068
H(7A)	4e	1.1140	0.1078	0.9121	0.067
H(7B)	4e	1.1127	0.0606	1.0144	0.067
H(8A)	4e	1.1416	0.1748	1.1151	0.070
H(8B)	4e	1.1938	0.1607	1.0518	0.070
H(9A)	4e	1.2185	0.3028	1.0349	0.095
H(9B)	4e	1.1785	0.3124	1.1190	0.095
H(10A)	4e	1.1726	0.4307	1.0306	0.103
H(10B)	4e	1.1499	0.3872	0.9221	0.103
H(11A)	4e	1.0805	0.4706	1.1119	0.103
H(11B)	4e	1.1006	0.3829	1.1484	0.103
H(12A)	4e	0.9926	0.4112	1.1580	0.097
H(12B)	4e	0.9720	0.4261	1.0361	0.097
H(13A)	4e	0.8951	0.3212	1.0181	0.079
H(13B)	4e	0.9168	0.2915	1.1350	0.079
H(14A)	4e	0.9519	0.1697	1.0735	0.073
H(14B)	4e	0.8758	0.1822	1.0326	0.073
H(15A)	4e	0.7759	0.0961	0.7470	0.175
H(15B)	4e	0.8096	0.1798	0.7581	0.175
H(15C)	4e	0.7952	0.1389	0.8562	0.175
H(18)	4e	0.6515	1.0313	0.7670	0.079
H(19)	4e	0.5468	1.0764	0.7334	0.075
H(20)	4e	0.4610	1.0029	0.6306	0.059
H(22A)	4e	0.3938	0.9337	0.4916	0.059
H(22B)	4e	0.3942	0.8824	0.5913	0.059
H(23A)	4e	0.3192	0.8264	0.4481	0.070
H(23B)	4e	0.3730	0.8213	0.3859	0.070
H(24A)	4e	0.3485	0.6802	0.3746	0.089
H(24B)	4e	0.3053	0.6798	0.4550	0.089
H(25A)	4e	0.3784	0.5993	0.5681	0.094
H(25B)	4e	0.3619	0.5585	0.4577	0.094
H(26A)	4e	0.4341	0.6128	0.3478	0.093
H(26B)	4e	0.4612	0.5284	0.3893	0.093
H(27A)	4e	0.5634	0.5858	0.4692	0.088
H(27B)	4e	0.5445	0.6007	0.3473	0.088
H(28A)	4e	0.6078	0.7283	0.3705	0.071
H(28B)	4e	0.6311	0.6992	0.4877	0.071
H(29A)	4e	0.6385	0.8401	0.4721	0.062
H(29B)	4e	0.5617	0.8428	0.4306	0.062
H(30A)	4e	0.7320	0.9354	0.7500	0.150
H(30B)	4e	0.7143	0.8927	0.6407	0.150
H(30C)	4e	0.7055	0.8479	0.7401	0.150
H(31)	4e	1.048(2)	0.245(3)	0.703(2)	0.08(2)
H(32)	4e	1.1071(8)	0.249(3)	0.786(3)	0.10(2)
H(33)	4e	0.4115(6)	0.743(3)	0.717(3)	0.08(2)
H(34)	4e	0.476(2)	0.758(3)	0.794(2)	0.09(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}
Pt(1)	4e	0.752219(9)	0.48820(1)	0.74390(1)	0.0318(1)	0.0447(1)	0.0473(1)	0.0016(1)	0.00430(8)	0.0079(1)
Na(1)	4e	1.01867(9)	0.2830(1)	0.9076(1)	0.055(1)	0.046(1)	0.039(1)	0.0020(9)	0.0085(9)	0.0011(8)
Na(2)	4e	0.50124(9)	0.72008(9)	0.5933(1)	0.056(1)	0.040(1)	0.0368(9)	0.0019(8)	0.0094(9)	0.0007(7)
N(1)	4e	0.9309(2)	0.3623(3)	0.7980(3)	0.057(3)	0.082(3)	0.071(3)	0.028(3)	0.023(3)	0.023(3)
N(2)	4e	0.5876(2)	0.6400(3)	0.7038(3)	0.066(3)	0.081(3)	0.067(3)	0.032(3)	0.020(3)	0.017(3)
N(3)	4e	0.7939(2)	0.7141(3)	0.6820(3)	0.091(4)	0.069(3)	0.072(3)	−0.027(3)	0.024(3)	0.003(3)
N(4)	4e	0.6882(3)	0.2775(3)	0.8212(4)	0.093(4)	0.078(3)	0.073(3)	−0.016(3)	0.030(3)	0.007(3)
O(1)	4e	0.9231(2)	0.2020(2)	0.9228(2)	0.055(2)	0.050(2)	0.052(2)	0.007(2)	0.016(2)	0.004(2)
O(2)	4e	1.0390(2)	0.1365(2)	0.9682(2)	0.045(2)	0.047(2)	0.058(2)	0.009(2)	0.014(2)	−0.002(2)
O(3)	4e	1.1330(2)	0.2486(2)	0.9963(2)	0.059(2)	0.063(2)	0.047(2)	−0.010(2)	−0.002(2)	−0.000(2)
O(4)	4e	1.0803(2)	0.3974(2)	0.9946(3)	0.100(3)	0.052(2)	0.051(2)	−0.013(2)	−0.001(2)	−0.001(2)
O(5)	4e	0.9912(2)	0.3119(2)	1.0741(2)	0.067(3)	0.058(2)	0.042(2)	0.011(2)	0.007(2)	−0.003(2)
O(6)	4e	0.5929(1)	0.8121(2)	0.5815(2)	0.050(2)	0.039(2)	0.049(2)	0.005(2)	0.014(2)	0.002(1)
O(7)	4e	0.4719(1)	0.8642(2)	0.5372(2)	0.042(2)	0.040(2)	0.054(2)	0.002(2)	0.013(2)	−0.003(1)
O(8)	4e	0.3858(2)	0.7437(2)	0.5017(2)	0.055(2)	0.055(2)	0.048(2)	−0.012(2)	−0.001(2)	0.002(2)
O(9)	4e	0.4502(2)	0.6010(2)	0.5021(3)	0.092(3)	0.050(2)	0.049(2)	−0.012(2)	0.002(2)	−0.001(2)
O(10)	4e	0.5349(2)	0.6969(2)	0.4298(2)	0.071(3)	0.039(2)	0.042(2)	0.001(2)	0.012(2)	−0.005(1)
O(11)	4e	1.0646(2)	0.2632(2)	0.7677(3)	0.062(3)	0.096(3)	0.041(2)	0.015(2)	0.004(2)	−0.012(2)
O(12)	4e	0.4548(2)	0.7370(2)	0.7320(3)	0.060(3)	0.082(3)	0.041(2)	0.010(2)	0.010(2)	−0.007(2)
S(1)	4e	0.82621(7)	0.44144(9)	0.6571(1)	0.0555(9)	0.093(1)	0.0535(8)	0.0267(8)	0.0138(7)	0.0114(7)
S(2)	4e	0.67768(7)	0.53371(8)	0.8302(1)	0.0534(8)	0.0767(9)	0.0576(8)	0.0222(7)	0.0209(7)	0.0226(7)
S(3)	4e	0.72219(6)	0.57627(7)	0.60258(9)	0.0478(8)	0.0557(8)	0.0490(7)	0.0001(6)	0.0034(6)	0.0123(6)
S(4)	4e	0.78227(7)	0.39865(8)	0.8830(1)	0.0468(8)	0.0712(9)	0.0646(9)	0.0049(7)	0.0007(7)	0.0269(7)
C(1)	4e	0.9289(2)	0.1266(3)	0.8828(4)	0.056(3)	0.045(3)	0.052(3)	−0.003(3)	0.022(3)	0.001(2)
C(2)	4e	0.8747(3)	0.0898(3)	0.8176(4)	0.052(4)	0.069(4)	0.076(4)	−0.009(3)	0.010(3)	−0.005(3)
C(3)	4e	0.8849(3)	0.0162(3)	0.7753(5)	0.077(5)	0.072(4)	0.086(4)	−0.024(4)	0.018(4)	−0.020(3)
C(4)	4e	0.9448(3)	−0.0182(3)	0.7975(4)	0.088(5)	0.051(3)	0.076(4)	−0.014(3)	0.035(4)	−0.011(3)
C(5)	4e	0.9986(3)	0.0193(3)	0.8621(4)	0.065(4)	0.046(3)	0.063(3)	0.002(3)	0.025(3)	0.003(3)
C(6)	4e	0.9901(2)	0.0921(3)	0.9048(3)	0.051(3)	0.041(3)	0.046(3)	−0.001(2)	0.018(3)	0.005(2)
C(7)	4e	1.1050(2)	0.1121(3)	0.9801(4)	0.057(3)	0.053(3)	0.058(3)	0.015(3)	0.017(3)	0.007(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(8)	4*e*	1.1483(2)	0.1735(3)	1.0453(4)	0.051(3)	0.076(4)	0.044(3)	0.008(3)	0.005(3)	0.002(3)
C(9)	4*e*	1.1751(3)	0.3109(3)	1.0444(4)	0.069(4)	0.091(5)	0.063(4)	–0.017(4)	–0.006(3)	–0.011(3)
C(10)	4*e*	1.1469(3)	0.3866(3)	0.9941(4)	0.094(5)	0.080(5)	0.068(4)	–0.040(4)	–0.004(4)	–0.010(3)
C(11)	4*e*	1.0712(3)	0.4149(3)	1.0951(5)	0.121(6)	0.053(4)	0.068(4)	–0.006(4)	–0.001(4)	–0.016(3)
C(12)	4*e*	1.0013(3)	0.3964(3)	1.0920(4)	0.128(6)	0.052(4)	0.056(4)	0.019(4)	0.014(4)	–0.012(3)
C(13)	4*e*	0.9257(3)	0.2873(3)	1.0669(4)	0.071(4)	0.072(4)	0.055(3)	0.029(3)	0.018(3)	0.001(3)
C(14)	4*e*	0.9180(3)	0.2027(3)	1.0296(4)	0.057(4)	0.070(4)	0.060(3)	0.009(3)	0.025(3)	0.008(3)
C(15)	4*e*	0.8076(3)	0.1299(4)	0.7924(6)	0.059(5)	0.118(6)	0.155(7)	0.001(4)	–0.005(5)	–0.038(5)
C(16)	4*e*	0.5820(2)	0.8865(2)	0.6213(3)	0.053(3)	0.035(3)	0.043(3)	–0.003(2)	0.012(2)	0.003(2)
C(17)	4*e*	0.6334(3)	0.9296(3)	0.6840(4)	0.050(3)	0.054(3)	0.061(3)	–0.009(3)	0.007(3)	0.000(3)
C(18)	4*e*	0.6179(3)	1.0010(3)	0.7248(4)	0.083(5)	0.051(4)	0.059(3)	–0.021(3)	0.012(3)	–0.010(3)
C(19)	4*e*	0.5552(3)	1.0282(3)	0.7050(4)	0.094(5)	0.039(3)	0.056(3)	–0.006(3)	0.024(3)	–0.006(2)
C(20)	4*e*	0.5038(3)	0.9847(3)	0.6431(4)	0.061(3)	0.036(3)	0.054(3)	0.004(2)	0.020(3)	0.007(2)
C(21)	4*e*	0.5173(2)	0.9134(2)	0.5999(3)	0.050(3)	0.033(3)	0.034(2)	–0.002(2)	0.013(2)	0.005(2)
C(22)	4*e*	0.4043(2)	0.8819(3)	0.5239(4)	0.047(3)	0.049(3)	0.050(3)	0.011(2)	0.012(3)	0.006(2)
C(23)	4*e*	0.3656(2)	0.8187(3)	0.4552(4)	0.052(3)	0.076(4)	0.044(3)	0.004(3)	0.008(3)	0.005(3)
C(24)	4*e*	0.3498(3)	0.6784(3)	0.4485(4)	0.067(4)	0.082(4)	0.061(4)	–0.028(3)	–0.004(3)	–0.005(3)
C(25)	4*e*	0.3834(3)	0.6039(3)	0.4975(4)	0.103(5)	0.059(4)	0.062(4)	–0.038(4)	0.000(4)	0.004(3)
C(26)	4*e*	0.4648(3)	0.5850(3)	0.4042(4)	0.123(6)	0.052(3)	0.047(3)	–0.010(3)	0.003(4)	–0.008(3)
C(27)	4*e*	0.5327(3)	0.6126(3)	0.4118(4)	0.119(6)	0.044(3)	0.053(3)	0.011(3)	0.014(4)	–0.010(3)
C(28)	4*e*	0.5981(3)	0.7298(3)	0.4382(4)	0.072(4)	0.056(3)	0.056(3)	0.019(3)	0.028(3)	–0.001(3)
C(29)	4*e*	0.5983(2)	0.8139(3)	0.4750(4)	0.053(3)	0.053(3)	0.054(3)	0.002(2)	0.025(3)	0.004(2)
C(30)	4*e*	0.7026(3)	0.8986(4)	0.7057(5)	0.058(4)	0.110(5)	0.117(5)	–0.007(4)	–0.001(4)	–0.022(4)
C(31)	4*e*	0.8864(3)	0.3934(3)	0.7446(4)	0.055(3)	0.044(3)	0.063(3)	0.005(3)	0.026(3)	0.004(2)
C(32)	4*e*	0.6254(2)	0.5967(3)	0.7515(4)	0.045(3)	0.058(3)	0.053(3)	0.004(3)	0.019(3)	0.002(2)
C(33)	4*e*	0.7651(2)	0.6570(3)	0.6525(4)	0.049(3)	0.057(3)	0.051(3)	0.003(3)	0.019(3)	0.014(3)
C(34)	4*e*	0.7263(3)	0.3276(3)	0.8443(4)	0.056(4)	0.058(3)	0.050(3)	0.015(3)	0.022(3)	0.012(3)

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