Crystal structure of tetranitropalladato(II)tetrakis[(15-crown-5)sodium] tetranitropalladate(II), $\{[Na(C_{10}H_{20}O_5)]_4Pd(NO_2)_4\}[Pd(NO_2)_4]$

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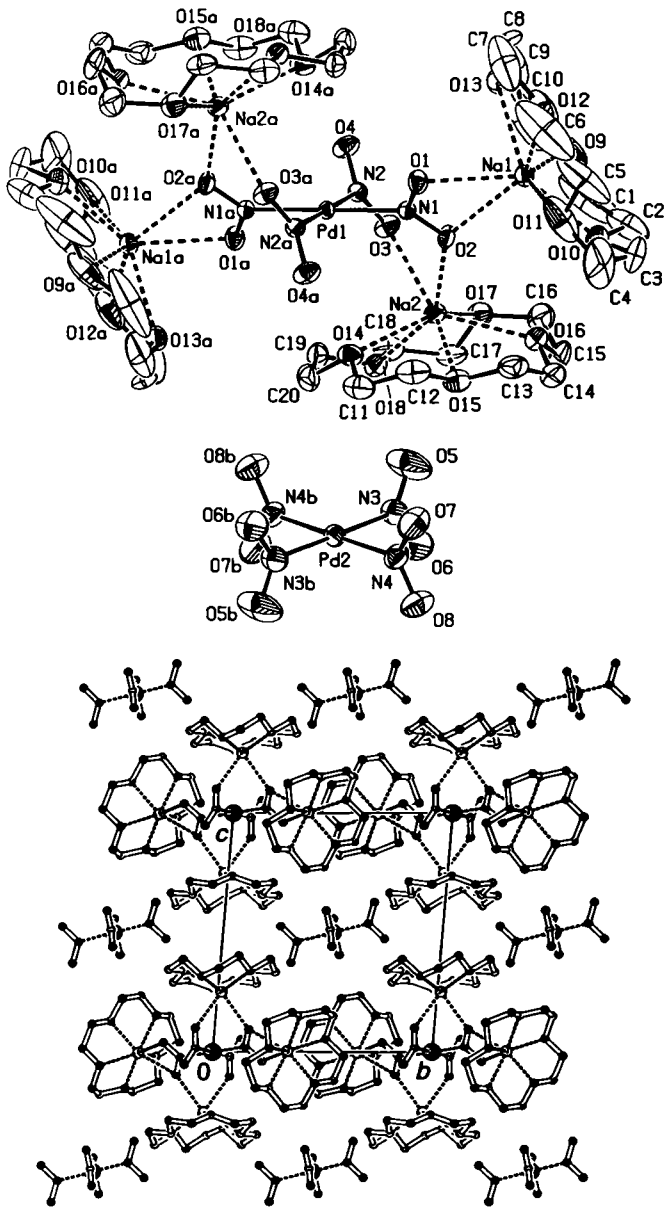

Abstract

$C_{40}H_{80}N_8Na_4O_{36}Pd_2$, triclinic, $P\bar{1}$ (no. 2), $a = 10.530(4)$ Å, $b = 11.955(5)$ Å, $c = 13.698(6)$ Å, $\alpha = 85.036(7)°$, $\beta = 74.511(6)°$, $\gamma = 89.404(7)°$, $V = 1655.4$ Å^3, $Z = 1$, $R_{gt}(F) = 0.062$, $wR_{ref}(F^2) = 0.152$, $T = 293$ K.

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Source of material

The title compound was prepared by adding 10 ml aqueous mixture of 0.025 M $PdCl_2$ and 2 M $NaNO_2$ solutions to 10 ml 0.1 M solution of 15-crown-5 (15-cr-5) in 1,2-dichloroethane solution. The reaction mixture was stirred for 4 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. 169-171 °C).

Elemental analysis: found – C, 30.92 %; H, 5.19 %; N, 7.21 %; calc. for $C_{40}H_{80}N_8O_{36}Pd_2Na_4$ – C, 30.67 %; H, 5.11 %; N, 7.33 %.

Discussion

The extensive pioneering studies of Pedersen [1] has led to a virtual explosion of solution and solid-state investigation of crown ethers with metal ions. The metal ions include alkali metal, alkali earth metal, other main-group and transition-metal ions. We now report the crystal structure of another 15-crown-5 ether complex: $\{[Na(15\text{-cr-}5)]_4[Pd(NO_2)_4]\}[Pd(NO_2)_4]$ which was established by X-ray diffraction analysis.

The structure consists of one $\{[Na(15\text{-cr-}5)]_4Pd(NO_2)_4\}^{2+}$ complex cation and one $[Pd(NO_2)_4]^{2-}$ complex anion (figure, top and middle, respectively). In the complex anion, the Pd2 atom is coordinated by four N atoms from four NO_2 groups. The N3–Pd2–N3′, N4–Pd2–N4″ bond angles are both 180°, implying the $[Pd(NO_2)_4]^{2-}$ anion has square planar configuration. The mean Pd2—N and N—O bond lengths are 2.012 Å and 1.205 Å, respectively, which are comparable to those of $[K(18\text{-cr-}6)]_2[Pd(NO_2)_4](H_2O)$ [2] (2.042 Å and 1.185 Å, respectively) and $[Pd(dien)(NO_2)]NO_3$ (2.028 Å and 1.225 Å, respectively) [3].

Four [Na(15-cr-5)] groups and one $[Pd(NO_2)_4]$ unit form the large $\{[Na(15\text{-cr-}5)]_4Pd(NO_2)_4\}^{2+}$ complex cation through Na–O interactions. The $[Pd1(NO_2)_4]$ group is also square planar with the Pd1—N1, N1—O1 and N1—O2 distances of 2.027(5) Å, 1.240(6) Å and 1.225(6) Å, respectively. In each [Na(15-cr-5)] group, the sodium ion is bonded to five ether oxygen atoms with Na—O distances ranging from 2.324 Å to 2.490 Å with an average value of 2.416 Å which is consistent with that of $[Na(b15\text{-cr-}5)]_2[Pd(SCN)_4]$ [4] (average 2.445 Å). The remainders of the coordinating sphere of Na1 atom are occupied by O1 and O2 atoms of a NO_2 group with the O1–Na1–O2 and O1–N1–O2 bond angles of 48.6(1)° and 118.0(5)°, respectively. The Na1—O1 and Na1—O2 bond lengths are 2.495(5) Å and 2.629(5) Å, respectively. Besides the five Na—O(ether) bonds the Na2 atom is bonded to O2 and O3 atoms from two NO_2 groups with the Na2—O2 and Na2—O3 distances of 2.563(5) Å and 2.489(5) Å, respectively.

The $\{[Na(15\text{-cr-}5)]_4Pd(NO_2)_4\}^{2+}$ complex cation and the $[Pd(NO_2)_4]^{2-}$ complex anion form the neutral complex salt without any solvents (figure, bottom).

Table 1. Data collection and handling.

Crystal:	yellowish rod, size 0.24 × 0.30 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.66 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, ω/φ
$2\theta_{max}$:	52.74°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9529, 6510
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3851
$N(param)_{refined}$:	409
Programs:	SHELXS-97 [5], SHELXL-97 [6]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.5378	0.2078	0.1327	0.374
H(1B)	2*i*	0.3859	0.1794	0.1564	0.374
H(2A)	2*i*	0.4180	0.3408	0.2372	0.364
H(2B)	2*i*	0.4907	0.4012	0.1308	0.364
H(3A)	2*i*	0.3561	0.5451	0.1369	0.307
H(3B)	2*i*	0.2741	0.5037	0.2479	0.307
H(4A)	2*i*	0.0839	0.4999	0.2013	0.375
H(4B)	2*i*	0.1506	0.6158	0.1541	0.375
H(5A)	2*i*	0.2811	0.6234	−0.0151	0.321
H(5B)	2*i*	0.1345	0.6605	−0.0029	0.321
H(6A)	2*i*	0.1162	0.5360	−0.1217	0.437
H(6B)	2*i*	0.2296	0.6255	−0.1703	0.437
H(7A)	2*i*	0.3221	0.4918	−0.2802	0.459
H(7B)	2*i*	0.2191	0.3973	−0.2231	0.459
H(8A)	2*i*	0.4208	0.3127	−0.2976	0.413
H(8B)	2*i*	0.4933	0.3867	−0.2389	0.413
H(9A)	2*i*	0.5653	0.2592	−0.1726	0.413
H(9B)	2*i*	0.4976	0.1523	−0.1961	0.413
H(10A)	2*i*	0.4042	0.1054	−0.0180	0.386
H(10B)	2*i*	0.5588	0.1176	−0.0390	0.386
H(11A)	2*i*	−0.2751	0.0487	0.3696	0.125
H(11B)	2*i*	−0.2943	0.0722	0.2598	0.125
H(12A)	2*i*	−0.1195	0.1931	0.2149	0.115
H(12B)	2*i*	−0.2197	0.2302	0.3139	0.115
H(13A)	2*i*	−0.0348	0.3138	0.3649	0.123
H(13B)	2*i*	0.0604	0.2781	0.2634	0.123
H(14A)	2*i*	0.1756	0.2921	0.3849	0.130
H(14B)	2*i*	0.0806	0.2017	0.4582	0.130
H(15A)	2*i*	0.2120	0.0497	0.4649	0.150
H(15B)	2*i*	0.3296	0.1356	0.4211	0.150
H(16A)	2*i*	0.4160	0.0294	0.2907	0.138
H(16B)	2*i*	0.3961	−0.0455	0.3938	0.138
H(17A)	2*i*	0.1659	−0.1451	0.4521	0.108
H(17B)	2*i*	0.2833	−0.2207	0.3997	0.108
H(18A)	2*i*	0.1682	−0.2548	0.2780	0.111
H(18B)	2*i*	0.0922	−0.3031	0.3886	0.111
H(19A)	2*i*	−0.1048	−0.2815	0.3242	0.104
H(19B)	2*i*	−0.0293	−0.2149	0.2212	0.104
H(20A)	2*i*	−0.2415	−0.1562	0.2595	0.120
H(20B)	2*i*	−0.2375	−0.1334	0.3700	0.120

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)	1*a*	0	0	0	0.0339(3)	0.0419(3)	0.0438(4)	−0.0004(2)	−0.0134(3)	−0.0078(3)
Pd(2)	1*h*	½	½	½	0.0597(5)	0.0781(5)	0.0583(5)	−0.0055(4)	−0.0253(4)	0.0037(4)
Na(1)	2*i*	0.2572(2)	0.3392(2)	0.0038(2)	0.052(1)	0.051(1)	0.068(2)	−0.004(1)	−0.016(1)	−0.011(1)
Na(2)	2*i*	0.0933(2)	0.0166(2)	0.2517(2)	0.056(2)	0.076(2)	0.051(1)	0.002(1)	−0.016(1)	−0.010(1)
N(1)	2*i*	0.0781(4)	0.1469(4)	0.0225(4)	0.045(3)	0.048(3)	0.048(3)	−0.004(2)	−0.012(2)	−0.010(2)
N(2)	2*i*	0.1608(4)	−0.0812(4)	0.0187(4)	0.038(3)	0.055(3)	0.053(3)	0.007(2)	−0.013(2)	−0.009(3)
N(3)	2*i*	0.6843(7)	0.4874(7)	0.5129(6)	0.062(4)	0.144(6)	0.083(5)	0.000(4)	−0.033(4)	0.004(5)
N(4)	2*i*	0.4942(7)	0.6602(6)	0.5378(6)	0.106(5)	0.085(5)	0.070(5)	−0.006(4)	−0.037(4)	−0.006(4)
O(1)	2*i*	0.0822(4)	0.2297(3)	−0.0394(3)	0.078(3)	0.047(2)	0.073(3)	−0.012(2)	−0.028(2)	0.000(2)
O(2)	2*i*	0.1246(4)	0.1568(3)	0.0944(3)	0.069(3)	0.062(3)	0.061(3)	−0.012(2)	−0.034(2)	−0.009(2)
O(3)	2*i*	0.1868(4)	−0.0894(4)	0.1009(3)	0.063(3)	0.093(3)	0.056(3)	0.026(2)	−0.034(2)	−0.011(2)
O(4)	2*i*	0.2324(5)	−0.1255(4)	−0.0523(4)	0.065(3)	0.108(4)	0.068(3)	0.034(3)	−0.019(2)	−0.033(3)
O(5)	2*i*	0.7773(8)	0.502(1)	0.4417(7)	0.070(5)	0.51(2)	0.135(7)	−0.029(8)	−0.034(5)	0.06(1)
O(6)	2*i*	0.7091(6)	0.4613(6)	0.5923(5)	0.101(5)	0.187(7)	0.107(5)	0.015(4)	−0.057(4)	0.009(5)
O(7)	2*i*	0.5228(9)	0.7399(5)	0.4742(5)	0.26(1)	0.093(4)	0.100(5)	−0.046(5)	−0.058(5)	0.014(4)
O(8)	2*i*	0.4592(7)	0.6794(5)	0.6270(5)	0.164(7)	0.119(5)	0.088(5)	0.016(4)	−0.023(4)	−0.028(4)
O(9)	2*i*	0.4607(6)	0.2567(6)	0.0178(8)	0.051(4)	0.135(6)	0.24(1)	0.004(3)	−0.017(5)	0.080(6)
O(10)	2*i*	0.3025(8)	0.385(1)	0.1525(5)	0.129(7)	0.30(1)	0.091(5)	−0.110(7)	−0.020(5)	−0.047(6)
O(11)	2*i*	0.1519(7)	0.5099(5)	0.056(1)	0.101(5)	0.060(4)	0.41(2)	−0.002(4)	0.019(8)	−0.056(7)
O(12)	2*i*	0.2922(8)	0.4796(8)	−0.1309(7)	0.135(7)	0.196(8)	0.165(8)	−0.097(6)	−0.090(6)	0.116(6)
O(13)	2*i*	0.3797(8)	0.272(1)	−0.1537(8)	0.121(7)	0.37(2)	0.187(9)	−0.151(9)	0.095(6)	−0.22(1)
O(14)	2*i*	−0.1382(5)	−0.0199(5)	0.2637(4)	0.057(3)	0.112(4)	0.063(3)	0.004(3)	−0.015(2)	−0.003(3)
O(15)	2*i*	−0.0599(6)	0.1572(4)	0.3400(4)	0.088(4)	0.088(4)	0.074(3)	0.012(3)	−0.012(3)	−0.012(3)
O(16)	2*i*	0.2005(5)	0.1392(5)	0.3393(4)	0.091(4)	0.100(4)	0.065(3)	−0.017(3)	−0.023(3)	−0.012(3)
O(17)	2*i*	0.2682(5)	−0.0801(5)	0.3171(4)	0.075(3)	0.107(4)	0.076(3)	0.011(3)	−0.029(3)	−0.011(3)
O(18)	2*i*	0.0148(5)	−0.1626(4)	0.3417(3)	0.083(3)	0.078(3)	0.063(3)	−0.007(3)	−0.025(3)	−0.008(2)
C(1)	2*i*	0.454(2)	0.235(2)	0.124(2)	0.081(9)	0.36(3)	0.42(4)	0.02(2)	−0.04(2)	0.30(3)
C(2)	2*i*	0.422(1)	0.347(2)	0.165(1)	0.12(1)	0.70(6)	0.092(9)	−0.18(2)	−0.08(1)	0.13(2)
C(3)	2*i*	0.282(2)	0.498(2)	0.176(1)	0.26(2)	0.35(3)	0.17(2)	−0.17(2)	−0.04(2)	−0.13(2)
C(4)	2*i*	0.158(2)	0.535(1)	0.151(1)	0.23(2)	0.20(2)	0.49(4)	−0.04(2)	0.01(2)	−0.28(2)
C(5)	2*i*	0.195(1)	0.5983(8)	−0.017(1)	0.12(1)	0.039(5)	0.52(4)	0.033(6)	0.11(2)	0.06(1)
C(6)	2*i*	0.201(2)	0.564(1)	−0.119(2)	0.13(2)	0.43(4)	0.51(5)	−0.05(2)	−0.15(3)	0.37(4)
C(7)	2*i*	0.301(2)	0.434(2)	−0.224(1)	0.44(5)	0.54(5)	0.23(2)	−0.38(4)	−0.28(3)	0.29(3)
C(8)	2*i*	0.411(2)	0.349(2)	−0.2355(9)	0.35(3)	0.54(5)	0.08(1)	−0.34(4)	0.11(2)	−0.17(2)
C(9)	2*i*	0.488(2)	0.211(1)	−0.150(2)	0.14(2)	0.30(2)	0.52(5)	−0.10(2)	0.14(2)	−0.35(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(10)	2*i*	0.479(1)	0.1570(9)	–0.042(2)	0.058(8)	0.043(6)	0.83(6)	0.027(5)	–0.08(2)	0.00(1)
C(11)	2*i*	–0.2294(8)	0.067(1)	0.2986(7)	0.063(5)	0.17(1)	0.076(6)	0.018(6)	–0.024(4)	0.012(6)
C(12)	2*i*	–0.1596(9)	0.1717(8)	0.2864(7)	0.094(7)	0.105(7)	0.081(6)	0.047(6)	–0.015(5)	0.003(5)
C(13)	2*i*	0.019(1)	0.2534(8)	0.3341(7)	0.116(8)	0.087(6)	0.087(6)	0.011(6)	0.006(6)	–0.024(5)
C(14)	2*i*	0.122(1)	0.2261(8)	0.3875(7)	0.126(8)	0.107(7)	0.084(6)	–0.030(6)	–0.005(6)	–0.031(6)
C(15)	2*i*	0.273(1)	0.083(1)	0.4029(8)	0.141(9)	0.17(1)	0.098(7)	–0.030(8)	–0.076(7)	–0.029(7)
C(16)	2*i*	0.3504(9)	–0.004(1)	0.3495(8)	0.074(6)	0.17(1)	0.116(8)	0.011(6)	–0.042(6)	–0.039(7)
C(17)	2*i*	0.2137(9)	–0.1720(8)	0.3878(6)	0.086(6)	0.124(7)	0.057(5)	0.027(5)	–0.016(4)	–0.004(5)
C(18)	2*i*	0.1233(9)	–0.2347(7)	0.3456(7)	0.102(7)	0.089(6)	0.082(6)	0.020(5)	–0.020(5)	0.002(5)
C(19)	2*i*	–0.0739(9)	–0.2077(6)	0.2921(6)	0.106(7)	0.078(5)	0.079(6)	–0.030(5)	–0.031(5)	–0.005(4)
C(20)	2*i*	–0.1855(9)	–0.1318(9)	0.2997(7)	0.087(6)	0.137(8)	0.086(6)	–0.038(6)	–0.043(5)	0.006(6)

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