Crown Ether-half-capped Sodium Ions as Bridges in the Formation of Complex Polymer, Structure of [{(Benzo-15-crown-5)Na}$_2$Pd(i-mnt)$_2$]$_n$ {i-mnt = [S$_2$C=C(CN)$_2$]$^{2-}$}

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The reaction of Na$_2$Pd(i-mnt)$_2$ and benzo-15-crown-5 leads to an unprecedented infinite chain-like [{(benzo-15-crown-5)Na}$_2$ Pd(i-mnt)$_2$]$_n$, in which the conjugated species Pd(i-mnt)$_2$ are linked by crown ether-half-capped sodium ions *via* Na–NC bonds.

Complex polymers, especially low dimensional conjugated ones, possess novel structural features and potential application of their solid state anisotropic properties. Investigation in this area has stimulated much interesting of synthetic and materials chemists.[1] The conjugated ligand isomalononitriledithiolate (i-mnt) is a versatile and classic ligand for metal ion in synthesizing complexes and cluster compounds, about which a number of research reports were raised in the last two decades.[2] It was thought that another metal ion, for example alkali and alkali earth metal ions or some transition metal ions, could connect the complex anions of this ligand by bonding to its cyano groups to form complex polymer. To obtain low dimensional polymer, partially coordinated ions are more preferred. Benzo-15-crown-5 with five oxygen atoms on its cycle and suitable diameter of cavity reacting with sodium ions offers very usually the sandwiched structure [(benzo-15-crown-5)$_2$Na]$^+$ [3,4] and half-capped structure [(benzo-15-crown-5)Na]$^+$.[3-5] In the later case the coordination of sodium ion is saturated by bonding to other anions to form discrete molecules. In this paper, We present a special bridging fashion of [(benzo-15-crown-5)Na]$^+$ and the structure of one-dimensional [{(benzo-15-crown-5)Na}$_2$Pd(i-mnt)$_2$]$_n$ 1 derived from palladium complex anions of i-mnt.

The compound was synthesized as follows: to a solution of suspended Na$_2$Pd(i-mnt)$_2$ in CH$_2$Cl$_2$, a double molar amount of benzo-15-crown-5 was added with stirring.[6] The mixture was heated and stirred and then filtered. The filtrate was layered with iso-propanol and stored in a refrigerator. Reddish-orange crystals of the polymer 1 with four dichloromethane included in the unit cell were obtained in 57% yield.

The product was characterized by chemical analysis,[7] IR spectroscopy[8] and X-ray crystallography.[9] The IR spectra exhibit the characteristic absorptions for i-mnt ligand. The important feature is the presence of three v(C≡N) stretching bands at 2214, 2202, and 2189 cm^{-1}. The v(C≡N) stretching absorptions of [NEt$_4$]$_2$[Pd(i-mnt)$_2$], which has high symmetric anions, appear as a degenerated single band at 2199 cm^{-1}.[10] The difference suggests the coordination of cyano groups to sodium ions in 1.

The labelling scheme and ORTEP diagram of the asymmetric unit are shown in Figure 1. A drawing of polymer chain 1 is demonstrated in Figure 2. The special structural feature of the polymer is stressed by four Na–NC bonds. The N atoms from four cyano groups of two i-mnt units link the [(benzo-15-crown-5)Na]$^+$ cations and [Pd{S$_2$C=C(CN)$_2$}$_2$]$^{2-}$ anions to form an infinite -Pd-(i-mnt)-[(benzo-15-crown-5)Na]$_2$-(i-mnt)- chain. The structures of [(benzo-15-crown-5)Na]$^+$ moieties in 1 are similar to that of [(benzo-15-crown-5)NaClO$_4$] reported by Owen[4] and that of [(benzo-15-crown-5)NaC$_6$H$_2$N$_3$O$_7$] by Donald et al.[5] Each of the sodium ions is half-capped by one benzo-15-crown-5 cycle through coordinated oxygen atoms and additionally coordinated by two N atoms from cyano groups of complex anion [Pd(i-mnt)$_2$]$^{2-}$. The Na–O distances are in the range of 2.409(4) to 2.496(4) Å with a mean value of 2.460(5) Å. From the sum of the van der Waals radii (1.40 Å for O and 1.50 Å for N) and the effective ionic radii (1.02 Å for Na$^+$), one may expect distances Na–O of 2.42 Å and Na–N of 2.52 Å. The mean value for the ten Na–O distances is in perfect agreement with the predicted value. The four Na–N distances vary from 2.436(6) to 2.598(6) Å. Except for Na1–N11, they are all shorter than the predicated value of 2.52 Å, which indicates the strong interactions between sodium ions and cyano groups.

There are two polymer chains in a cell, related to each other through the cell center (1/2, 1/2, 1/2). One Pd atom (½Pd1 + ½Pd2) was found in the asymmetric unit of the polymer. Pd1 and Pd2 are individually located at the inverse centers (1/2, 0, 1/2) and (0,1/2,0). They are symmetrically coordinated in square

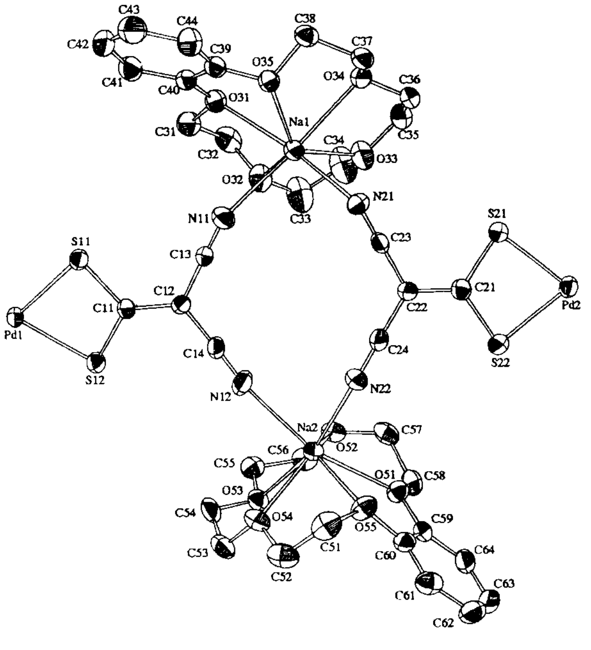

Figure 1. The labelling scheme and ORTEP diagram of the asymmetric unit for 1. Selected bond distances (Å) and angles (°): Pd1–S12, 2.329(2); Pd1–S11, 2.332(2); Pd2–S22, 2.326(2); Pd2–S21, 2.331(2); Na1–N11, 2.598(6); Na1–N21, 2.445(6); Na2–N22, 2.436(6); Na2–N12, 2.513(6); N21–Na1–N11, 85.0(2); N22–Na2–N12, 78.8(2). Hydrogen atoms are omitted for clarity.

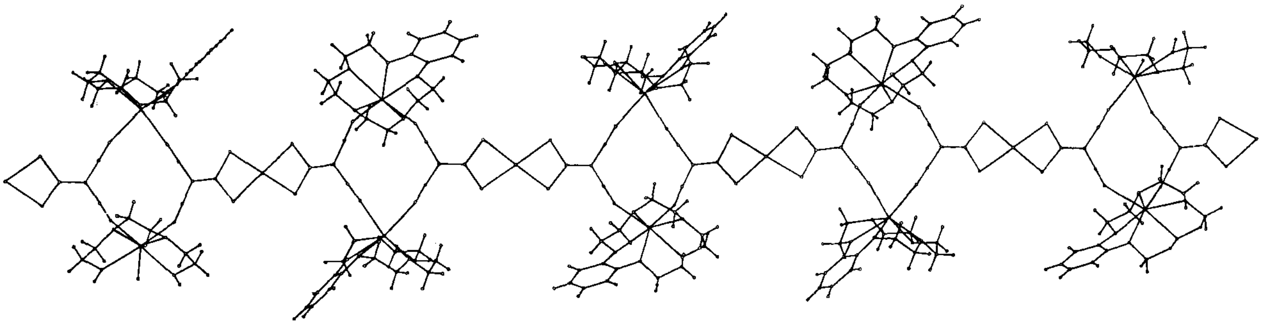

Figure 2. A drawing of polymer chain of 1.

planar chromophores by four S atoms of two i-mnt units. The Pd–S distances are regularly in the range of 2.326(2) to 2.333(2) Å, which are slightly longer than 2.323(1) Å found in $[NEt_4]_2[Pd(i\text{-}mnt)_2]$.[10] The alkyl portions of crown ether efficiently separate from each other with the shortest interchain Pd–Pd distance of 10.680(2) Å, which is far longer than the value for possible metal-metal interaction.[11]

The geometry of the i-mnt ligands in **1** is nearly the same as that appears in $[NEt_4]_2[Pd(i\text{-}mnt)_2]$.[10] The atoms in complex anion involving Pd1 and atoms in anion involving Pd2 are separately in least-squares planes, I and II, with deviates from individual plane not larger than 0.1 Å. Na1 is away from plane I and II for about 1.5 and 1.7 Å, respectively; while Na2 is for about 0.6 and 1.2 Å. The dihedral angle between plane I and II is about 23°. Compared with the values in a free ligand i-mnt, the C–C, C=C, C≡N bond distances primarily maintain unchanged after the complexation. This indicates that the bondings in the complex anions are similar to that in the free ligand with the delocalization of the π system.

In conclusion, the successful synthesis of **1** provides an example of the role of crown ether-half-capped metal ions as bridges in forming complex polymer and also illustrates the coordinating ability of the cyano groups to make a conjugated system. Further studies including the use of partially coordinated rare earth metal or other transition metal ions will probably exploit new low dimensional complex polymers of this kind of ligands, which may promote the investigation of materials science.

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6 Excessive benzo-15-crown-5 leads to the dianion product characterized as $[(benzo\text{-}15\text{-}crown\text{-}5)_2Na]_2[Pd(i\text{-}mnt)_2]$.

7 Anal. Found: C, 39.9; H, 3.7; N, 4.8%. Calcd for $C_{38}H_{44}Cl_4N_4Na_2O_{10}PdS_4$: C, 40.1; H, 3.9; N, 4.9%.

8 Selected spectroscopic data: IR (KBr pellets) ν/cm^{-1}, 2918w, 2214m, 2202m, 2189m, 1506s, 1500s, 1458m, 1400s, 1371s, 1255s, 1122s, 1093m, 1043m, 939s, 897m, 752m.

9 Crystal data for $1\cdot 2CH_2Cl_2$: $C_{38}H_{44}Cl_4N_4Na_2O_{10}PdS_4$, F.W. = 1139.19, triclinic, space group $P\text{-}1$, a = 10.689(1), b = 12.252(1), c = 21.092(2) Å, α = 90.614(1), β = 95.667(1), γ = 114.434(1)°, V = 2498.6(3) Å^3, Z = 2, D_c = 1.514 g cm^{-3}. A total of 6697 absorption-corrected reflections were collected at 293 K on a Siemens Smart-CCD area-detecting diffractometer using graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. The unique 5137 reflections with $I>2.0\sigma(I)$ were used in the structure solution and refinement. The final cycle of full-matrix least-squares refinement (on F^2) converged with $R1$ = 0.048, w$R2$ = 0.134, S = 1.125, and $(\Delta/\sigma)_{max}$ = 0.002.

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