Synthesis and Characterization of a Novel Palladium(II) Complex Polymer Having Network Structure with Guest Water Molecules

Rong Cao,* Weiping Su, Maochun Hong,* and Kazuyuki Tatsumi†
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,
Fuzhou, Fujian 350002, P.R. China
†*Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602*

(Received August 6, 1999; CL-990692)

The polymeric palladium complex of $[Pd_3K_6(i\text{-mnt})_3(H_2O)_2]_n$ (i-mnt$=[(S_2C=C(CN)_2]^{2-})$ has been prepared from the reaction of $PdCl_2$ and $K_2[(S_2C=C(CN)_2]$ in CH_3CN. The complex has three dimensional network structure, in which two Pd, two K, four S, four N and twelve C atoms form a 24-membered ring, and the rings are further arranged in eclipsed configuration along *c* axis to give a channel with H_2O as guest molecules.

Over recent years, the investigation of complex polymers, especially those with conjugation systems, has become a subject of intensive research and has stimulated of much interest of synthetic and materials chemists due to their novel structural features and potential applications.[1,2] Much work using polypyridyl or pyrazines as exo-bidentate ligands to generate polymeric coordination complexes through bridging metal ions has been reported.[3-5] Isomalononitriledithiolate(i-mnt) is versatile ligand with rich coordination modes for syntheses of transition metal complexes and many reports have appeared in literatures.[6] Normally, i-mnt acts as chelating ligands coordinating metal ions via metal-sulfur bonds to get complex anions, which are neutralized by large cations, such as Et_4N^+, for instance, Long and coworkers used the large cation (benzo-15-crown-5)Na^+ to neutralize the anion and isolated a one-dimensional palladium complex $[\{(\text{benzo-15-crown-5})Na\}_2Pd(i\text{-mnt})_2]_n$.[7] Owing to the conjugated configuration along with the polydentate coordination ability for connecting multi-metal moieties, i-mnt is a good candidate for designing conjugated complex polymers. Considering the free N donor atoms of cyano groups, man can use metal ions, such as alkali and alkali earth ions or some transition metal ions, to bridge the desecrate $[Pd(i\text{-mnt})_2]^{2-}$ species for designing complex polymers with different structures. Herein we report the synthesis and structure of a novel palladium(II) complex polymer of $[Pd_3K_6(i\text{-mnt})_3(H_2O)_2]_n$ having three dimensional network structure with guest water molecules, in which K^+ ions are used as metal bridges.

The complex was synthesized as follows: 0.09 g(0.5 mmol) of solid $PdCl_2$ was added to 30 ml of CH_3CN and stirred for two hours, then 0.22 g(1 mmol) of K_2(i-mnt) was added and the stirring was continued for 5 hours. After filtration the bright red filtrate was evaporated in the air at room temperature for two weeks to give bright red crystals with high yield(85%). The complex is very stable and may be dissolved in polar solvents such as H_2O, MeOH, EtOH, CH_3CN etc..

The product was characterized by chemical analysis,[8] IR spectroscopy,[9] and X-ray crystallographic method.[10] The IR spectrum gives the characteristic absorptions of i-mnt ligand.

The complex is a polymer and the trinuclear species $[Pd_3K_6(i\text{-mnt})_3(H_2O)_2]$ constitutes the building block unit as shown in Figure 1. The trinuclear species possesses a crystallographic inverse center at the central palladium atom and is composed of three $[Pd(i\text{-mnt})_2]$ linked by three K^+ through K-NC bonds. The N atoms of the cyano groups in one building block further link the K atoms from the other building block and *vers visu* to form an infinite K-(i-mnt)-Pd-(i-mnt)-K three dimensional network structure of the complex (Figure 2). Each Pd atom is surrounded by four sulphur atoms from two i-mnt ligands in a square planar chromophores and every $[Pd(i\text{-mnt})_2]^{2-}$ is nearly the same as that in $[NEt_4]_2[Pd(i\text{-mnt})_2]$[11] and shows typical Pd-S distances in the range of 2.322 Å to 2.336 Å, very similar to those found in $[NEt_4]_2[Pd(i\text{-mnt})_2]$(2.323 Å)[11] and $[\{(\text{benzo-15-crown-5})Na\}_2Pd(i\text{-mnt})_2]_n$(2.326-2.333 Å).[7] The palladium atoms are separated by i-mnt ligands with distances longer than 10 Å, which is much longer than the value of any possible Pd-Pd interactions. Compared with free i-mnt ligand, no significant changes of C-C, C=C, and C≡N bond lengths are observed upon complexation, suggesting that the bonding characteristics of i-mnt in the complex are similar to those in free ligand with electron delocalization of π system. Each K atom are surrounded by nine atoms, five nitrogen atoms from cyano groups, two sulfur atoms of i-mnt ligands, and two oxygen atoms from two water molecules. The long K-S distance(*ca.* 3.44 Å) indicates that the interaction between K and S is very weak and can be neglected. The K-N and K-O distances are in the ranges of 2.860 to 3.128Å, and 2.776 to 2.960 Å, respectively. Based on the sum of the van der Waals radii(1.40 Å for O and 1.50 Å for N) and the effective ionic radii(1.33 Å for K^+), the 2.73 Å of K-O and 2.83 Å of K-N distances may be expected, thus the interactions of K-N and K-

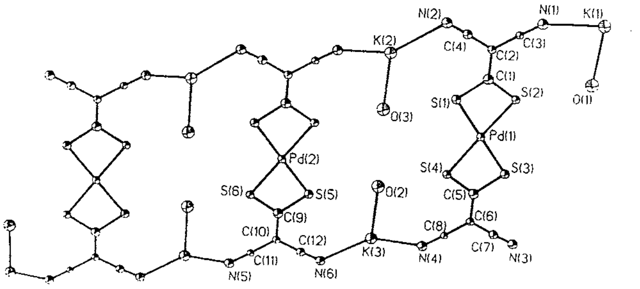

Figure 1. The labeling scheme of the basic unit in the complex. Selected bond distances(Å) and angles$(^0)$: Pd(1)-S(1), 2.335(2); Pd(1)-S(2), 2.331(1); Pd(1)-S(3), 2.323(2); Pd(1)-S(4), 2.336(1); Pd(2)-S(5), 2.327(1); Pd(2)-S(6), 2.333(1); N(1)-K(1), 2.910(5); N(2)-K(2), 3.124(5); N(4)-K(3), 3.128(5); N(6)-K(3), 3.070(5); K(1)-O(1), 2.776(4); K(2)-O(3), 2.867(5); K(3)-O(2), 2.931(5); S(1)-Pd(1)-S(2), 75.1(1); S(3)-Pd(1)-S(4), 75.1(1); S(5)-Pd(2)-S(6), 74.9(1).

O in the complex polymer are rather weak. Based on the solubility and the bonding characters, it is rational that the complex may exit as simple species in solution and its three dimensional network structure is formed upon crystallization.

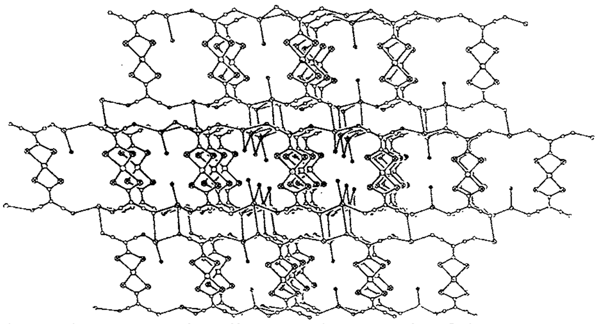

Figure 2. The packing diagram along *c* axis of the complex.

The significant feature of the complex polymer is that each two $[Pd(i\text{-}mnt)_2]^{2-}$ species and two K^+ ions form a 24-membered ring(two Pd, two K, four S, four N and 12 C atoms), in which all of the atoms except K are nearly co-planar(the largest deviation is *ca.* 0.35 Å) with the two K atoms being *ca.* 2.0 Å outside the plane and two water molecules being inserted (Figure 3). These rings further constitutes channels in the crystal, each water molecule in the channels loosely links two K^+ ions, e.g., the channels formed by the 24-membered rings may be viewed as hosts and the water molecules as guests.

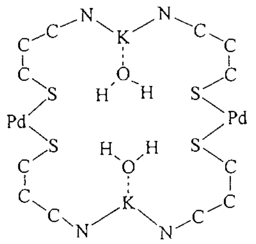

Figure 3. The 24-membered ring in the complex polymer.

The authors acknowledge the financial support from the National Natural Science Foundation of China and the Natural Science Foundation of Fujian Province. M.C.H. gratefully acknowledges Research Center for Material Science, Nagoya University for the finical support of the Visiting Professor.

References and Notes

1 J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1975); H.L. Anderson, S.J. Martin, and D.D.C. Bradley, *Angew. Chem., Int. Ed. Engl.*, **33**, 655 (1994).

2 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, **34**, 2311 (1995); O. M. Yaghi, Z. Sun, D. A. Richardson, and T. L. Groy, *J. Am. Chem. Soc.*, **116**, 807 (1994); M. Munakata, L. P. Wu, T. Kuroda-Sowa, M. Maekawa, K. Moriwaki, and S. Kitagawa, *Inorg. Chem.*, **36**, 5416 (1997).

3 O. S. Jung and C. G. Pierpont, *J. Am. Chem. Soc.*, **116**, 2229 (1994); T. Otieno, S. Rettig, R. C. Thompson, and J. Trotter, *Can. J. Chem.*, **68**, 1901 (1990); M. M. Turnbull, G. Pon, and R. D. Willett, *Polyhedron*, **10**, 1835 (1991).

4 T. Soma, H. Yuge, and T. Iwamoto, *Angew. Chem., Int. Ed. Engl.*, **33**, 1665 (1994); L. Carlucci, G. Ciani, D. M. Proserpio, and A. Sironi, *J. Am. Chem. Soc.*, **117**, 4562 (1995).

5 L. R. MacGillivray, S. Subramanian, and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, **1994**, 1325.

6 H.Y. Li and E.L. Amma, *Inorg. Chim. Acta*, **177**, 5 (1990); Md. N. I. Khan, S. Wang, and J.P. Fackler, *Inorg. Chem.*, **28**, 3579 (1989); J. P. Fackler, J.S. Richard, and A. Zerihun, *J. Chem. Soc., Chem. Commun.*, **1994**, 431; C.W. Liu, C.J. Mcneal, and J.P. Fackler, *J. Cluster Sci.*, **7**, 385 (1996).

7 D.L. Long, J.T. Chen, Y. Cui, and J.S. Huang, *Chem. Lett.*, **1998**, 172.

8 Anal. Found: C, 18.7; H, 0.89; N, 10.6%. Calcd for $C_{24}H_{12}N_{12}O_6K_6Pd_3S_{12}$: C, 19.2; H, 0.81; N, 11.2%.

9 Select. Spectroscopic data: IR(KBr pellets) ν/cm^{-1}: 3570(S), 2198(S), 2146(m), 1593(m), 1574(w), 1403(S), 1381(s), 1255(w), 947(w), 902(m), 604(m), 480(w), 515(w).

10 Crystal data for the complex: $C_{24}H_{12}N_{12}O_6K_6Pd_3S_{12}$, Mr=1502.8, monoclinic, space group $P2_1/n$, a = 12.122(2), b=9.448(2), c=21.557(4)Å , β=100.76(3)^0, V = 2425(12) Å^3, Z = 2, $R(Rw)$ =0.035 (0.039) for 3078 reflections with $F \geq 4.0\ \sigma(F)$. The intensity data were collected on a SIMENS SMART CCD diffractometer with Mo-Kα radiation. The structure analyses and calculations were performed using the SHELXTL PC version 5.5 package on an HP 5/75 computer.

11 D.L. Long, H.W. Hou, X.Q. Xin, K.B. Yu, B.S. Luo, and L.R. Chen, *J. Coord. Chem.*, **38**,15 (1996).