

[Pt(CN)₂·2Me₃SnCN·2Me₃SnOH·bpe]_n (bpe=*trans*-1,2-bis(4-pyridyl)ethylene), the First Double-Sinusoidal Platinum-Tin Coordination Polymer

Wanzhi Chen,* Liu Fenghui, and Xiaozeng You

The State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Department of Chemistry, Nanjing University, Nanjing 210093, P. R. China

(Received April 9, 2002; CL-020301)

The coordination polymer [Pt(CN)₂·2Me₃SnCN·2Me₃SnOH·bpe]_n was prepared and structurally characterized by X-ray diffraction analysis which consists of one-dimensional double-sinusoidal chains.

Metal coordination-driven self-assembly and hydrogen bonding have been used as powerful tools for the formation of a wide variety of discrete supramolecular materials.¹ The synthesis of coordination polymers of well-defined shape and functions via metal complexation and nonbonding intermolecular interactions is of particular interests since their potential applications in catalysis, ion-exchange process and gas absorption and separation.² The variety of metal coordination geometries, as well as ligand size, shape and functionality, has led to the generation of thousands of 1-, 2-, and 3-D compounds.³ We have been interested for some time in the formation of one-dimensional coordination polymers which are expected to be useful as nano wires.⁴ Here we report the synthesis and structural characterization of a novel quadruple adduct, [Pt(CN)₂·2Me₃SnCN·2Me₃SnOH·bpe]_n (**1**), which is revealed to have a double-stranded sinusoidal structure.⁵

The compound **1** was obtained as yellow air-stable crystals by spontaneous self-assembly in reacting K₂[Pt(CN)₄] with Me₃SnCl and bpe in a ratio of 1 : 2 : 1. Suitable single crystals were grown by slow evaporation of its acetone/H₂O solution. The composition of [Pt(CN)₂·2Me₃SnCN·2Me₃SnOH·bpe]_n was confirmed by elemental analysis. To our knowledge it is the first one-dimensional quadruple coordination polymer of sinusoidal structure containing platinum and organotin fragments.

The structure of **1** is a sinusoidal chain consisting of the four alternate building blocks, [Pt(CN)₂], Me₃SnOH, Me₃SnCN, and *trans*-1,2-bis(pyridyl)ethylene (bpe), which are mutually bridged. The observed sinusoidal structure is derived from the primary structure of [Pt(CN)₄]²⁻ [(Me₃Sn)₂OH]⁺, and bpe units. Thus these mutually bridged building blocks form the quadruple platinum-tin heterometallic sinusoidal polymer (Figure 1). As in many earlier described cyanometallate-tin coordination polymers,⁶ the Sn(IV) ions are pentacoordinated with N and O atoms occupying axial site of the bridging Me₃Sn⁺ units, and thus making the coordination sphere of each Sn atom trigonal bipyramidal. The Sn(2)–N(3) (pyridyl, 2.509(6) Å) bond is much longer than the Sn(1)–N(2) (cyanide, 2.433(7) Å). The pyridyl ring and cyanide ion are approximately perpendicular to the Me₃Sn⁺ planar moiety, and the N(2)–Sn(1)–O(1) (177.0(2)°) and N(3)–Sn(2)–O(1) (174.4(2)°) angles deviate from 180°, but are quite close to the ideal value. The hydrolysis of R₃SnCl to R₃SnOH or R₃SnOSnR₃ often occurs in the presence of water, and the oxonium [(Me₃Sn)₂OH]⁺ building block of **1** strongly

resembles the corresponding units present in other polymeric Me₃Sn⁺ derivatives.^{6b,7} The two Sn–O bond distances are 2.162(5), 2.140(5) Å for Sn(1)–O(1) *trans* to cyanide group and for Sn(2)–O(1) *trans* to pyridyl ring respectively. The former is comparable with reported values in [(ⁿBu₄N)(Me₃Sn)₂OH][Ni(CN)₄]^{7a} and the later is relatively shorter.

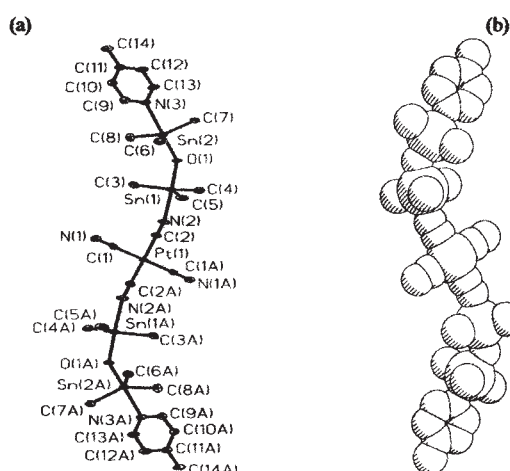


Figure 1. (a) A thermal ellipsoid plot of a portion of the chain. Hydrogen atoms have been omitted for clarity. Selected bond distances and angles: C(1)–Pt(1) 1.990(8), C(2)–Pt(1) 1.996(7), C(1)–N(1) 1.140(10), C(2)–N(2) 1.135(10), N(2)–Sn(1) 2.433(7), N(3)–Sn(2) 2.509(6), O(1)–Sn(2) 2.140(5), O(1)–Sn(1) 2.162(5), N(1)–C(1)–Pt(1) 179.3(7), N(2)–C(2)–Pt(1) 178.9(8), C(1)–Pt(1)–C(1A) 180.000(1), C(1)–Pt(1)–C(2) 90.8(3), C(1)–Pt(1)–C(2A) 89.2(3), Sn(2)–O(1)–Sn(1) 137.4(2), O(1)–Sn(2)–N(3) 174.4(2), O(1)–Sn(1)–N(2) 177.0(2). A -x, -y+1, -z+2; B, -x+1, -y-1, -z. (b) A space-filling view of the sinusoidal chain.

As expected, the [Pt(CN)₄]²⁻ unit remains square planar with normal Pt–C (average 1.993 Å), C–N (average 1.140 Å) bond lengths and Pt–C–N angles (nearly 180°), which are similar to those of related [Pt(CN)₄]²⁻ salts.⁸ The bridging and the terminal CN⁻ ions do not show significant difference for their Pt–C and C–N distances. Platinum atoms are located at the crystallographic center of symmetry (at 0.5, -0.5, 0) with refined site occupancy factor of 0.5. Obviously, the multiplicity of the special platinum position is half the multiplicity of the general position of the space group P $\bar{1}$.

The coordination polymer exhibits a sinusoidal architecture in the solid state. The sinusoidal corrugation is generated along

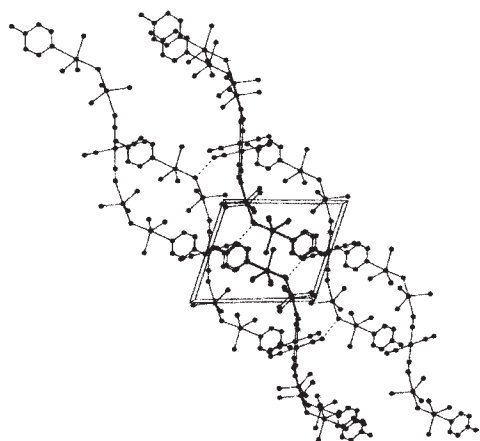


Figure 2. Crystal packing diagram of $[\text{Pt}(\text{CN})_2 \cdot 2\text{Me}_3\text{SnCN} \cdot 2\text{Me}_3\text{SnOH} \cdot \text{bpe}]_n$ showing the double-sinusoidal corrugation and hydrogen bonds.

the crystallographic $\text{Pt} \cdots \text{Pt} \cdots \text{Pt}$ axis. The alignment of Pt atoms forms the central axis of its corresponding sinusoidal chain. Each two sinusoidal chains are interwrapped along their $\text{Pt} \cdots \text{Pt} \cdots \text{Pt}$ axes (Figure 2). The adjacent chains are linked via hydrogen bonds, and the shortest contacts between neighboring chains are observed to be $\text{N}(1) \cdots \text{O}(1)$ (2.802 Å). It seems that the double sinusoidal structure is governed by the weak hydrogen bonds.

In summary, the compound presented here is the only example reported to date of a double stranded sinusoidal structure formed by $[\text{Pt}(\text{CN})_4]^{2-}$ anion and R_3Sn^+ cations. The composition of the polymer is unprecedented. The formation of the corrugations via self-assembly using the coordination motif is truly remarkable, since the four building units have to be linked together properly in the sequence and manner, and simultaneously the oxonium ions have to be formed.

We thank the National Natural Science Foundation of China for financial support for this work.

References and Notes

- a) C. J. Kuehl, F. M. Tabellion, A. M. Arif, and P. J. Stang, *Organometallics*, **20**, 1956 (2001) and references therein. b) T. Yamaguchi, F. Yamazaki, and T. Ito, *J. Am. Chem. Soc.*, **123**, 743 (2001).
- a) S. Noro, R. Kitauro, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, and M. Yamashita, *J. Am. Chem. Soc.*, **124**, 2568 (2002). b) X. Bu, W. Weng, J. Li, W. Chen, and R. Zhang *Inorg. Chem.*, **41**, 413 (2002).
- a) C. Livage, N. Guillo, J. Marrot, and G. Férey, *Chem. Mater.*, **13**, 4387 (2001). b) D. B. Leznoff, B. Xue, R. J. Batchelor, F. W. B. Einstein, and B. O. Patrick, *Inorg. Chem.*, **40**, 6026 (2001).
- a) H. Cai, H. Hu, W. Chen, H. Zhu, and X. You, *Chem. Lett.*, **1999**, 221. b) W. Chen, F. Liu, and X. You, *Bull. Chem. Soc. Jpn.*, in press.
- Elemental analysis Calcd for $\text{C}_{14}\text{H}_{24}\text{N}_3\text{OPt}_{0.5}\text{Sn}_2$: C 28.73; H 4.13; N 7.18%. Found: C 28.47; H 3.78; N 6.88%. X-ray crystal structure analysis of 1: MW = 585.29 for $\text{C}_{14}\text{H}_{24}\text{N}_3\text{OPt}_{0.5}\text{Sn}_2$, pale-yellow prism crystal of size $0.12 \times 0.23 \times 0.29$ mm, triclinic, space group $\text{P}\bar{1}$, $a = 9.1559(15)$ Å, $b = 9.7970(16)$ Å, $c = 11.924(2)$ Å, $\alpha = 106.339(2)^\circ$, $\beta = 108.397(3)^\circ$, $\gamma = 93.245(3)^\circ$, $V = 961.4(3)$ Å³, $Z = 2$, $D_{\text{calcd}} = 2.022$ Mg/m³, $T = 123(2)$ K. Siemens Smart CCD diffractometer; Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å); Of 6098 reflections measured, 4219 were unique. $R1 = 0.0556$, $wR2 = 0.1476$, $GOF = 1.087$.
- a) J. Lu, W. T. A. Harrison, and A. J. Jacobson, *Angew. Chem. Int. Ed. Engl.*, **34**, 2557 (1995). b) E. Siebel, R. D. Fischer, J. Kopf, N. A. Davis, D. C. Apperley, and R. K. Harris, *Inorg. Chem. Commun.*, **1**, 346 (1998).
- a) $[\text{Me}_3\text{Sn}]_2\text{OH}(\mu\text{-NCO})$: J. B. Hall and D. Britton, *Acta Crystllogr., Sect. B*, **28**, 2133 (1972). b) $[(\text{Me}_3\text{Sn})_2\text{OH}(\mu\text{-Me}_3\text{SnOCrO}_3)]$: A. M. Domingos and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, **1974**, 477. c) $[(\text{Me}_3\text{Sn})_2\text{OH}(\mu\text{-N}(\text{MeSO}_2)_2)]$: A. Blaschette, E. Wieland, P. G. Jones, and I. Hippel, *J. Organomet. Chem.*, **445**, 55 (1993).
- a) A. Loosli, M. Wermuth, H. Güdel, S. Capelli, J. Hauser, and H. Bürgi, *Inorg. Chem.*, **39**, 2289 (2000) and references therein. b) C. A. Daws, C. L. Exstrom, J. R. Sowa, Jr., and K. R. Mann, *Chem. Mater.*, **9**, 363 (1997).

1 a) C. J. Kuehl, F. M. Tabellion, A. M. Arif, and P. J. Stang,