J|A|C|S
COMMUNICATIONS

New Partially Oxidized 1-D Platinum Chain Complexes Consisting of Carboxylate-Bridged *cis*-Diammineplatinum Dimer Cations

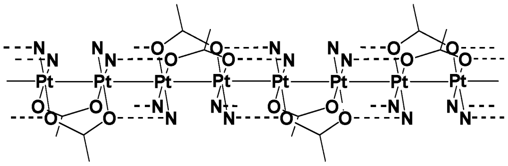
Ken Sakai,*,† Eri Ishigami,† Yosuke Konno,† Takashi Kajiwara,‡ and Tasuku Ito‡

Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan, and Department of Chemistry, Tohoku University, Sendai 980-8578, Japan

Received July 3, 2002

Crystals of 1-D metal chain complexes have attracted considerable attention due to their highly anisotropic physical properties.[1] One of the promising metals to attain such systems is Pt, since square-planar Pt(II) complexes often stack in the crystal to give 1-D $\mathrm{Pt(II)}_\infty$ chains.[2] The special affinity between the Pt(II) centers, that is, the weak metal−metal bonding character is now believed to be due to the mixing of filled $5d_{z^2}$ and vacant 6p orbitals.[3] Moreover, metal−metal bonds are efficiently reinforced by partial oxidation at the metal centers to afford highly delocalized mixed-valence systems exhibiting metallic conductivity (formally $[\mathrm{Pt(II)}_x\mathrm{Pt(III)}_y]_\infty$).[4] Nevertheless, *mononuclear anions*, such as $[\mathrm{Pt(CN)_4}]^{2-}$ and $[\mathrm{Pt(C_2O_4)_2}]^{2-}$, are the only examples affording such systems (e.g., $\mathrm{Pt(2.3+)}_\infty$).[1] Thus, the ability of chemists to rationally synthesize such systems is quite limited. Therefore, it must be questioned if it is possible to obtain such systems by use of other types of repeating units.

In the above context, we previously reported on some carboxylate-bridged *cis*-diammineplatinum *dimer cations* $[\mathrm{Pt(II)_2(NH_3)_4}(\mu\text{-carboxylato})_2]^{2+}$ (carboxylate = acetate, **1**; glycolate, **2**) which do afford 1-D $[\mathrm{Pt(II)_2}]_\infty$ chains in the crystal (see below; see also Table 1).[5]



We also pointed out that the dimer−dimer associations are effectively stabilized by the *quadruple hydrogen bonds* formed between the ammines and the oxygen atoms of carboxylates. However, the preparation of partially oxidized chains extended with more effective Pt−Pt bonds had been unsuccessful. Two years ago, we found that controlled-current electrolysis is an appropriate method to obtain such compounds. Here we communicate the syntheses, crystal structures, and electronic properties of acetate- and propionate-bridged 1-D $[\mathrm{Pt(2.2+)_2}]_\infty$ chain complexes, as the first report of 1-D mixed-valence chains consisting of *dinuclear cations*. It must be emphasized that this is an extended work for the so-called "platinum blues" ($[\mathrm{Pt(2.25+)_2(NH_3)_4}(\mu\text{-amidato})_2]_n^{5n+}$, $n = 2$ and 4), that is, the tetraplatinum[6] and octaplatinum[7] chain complexes made up of amidate-bridged dinuclear cations.

The title compounds $[\mathrm{Pt(2.2+)_2(NH_3)_4}(\mu\text{-acetato})_2](\mathrm{NO_3})_{2.4}\cdot 2\mathrm{H_2O}$ (**3**) and $[\mathrm{Pt(2.2+)_2(NH_3)_4}(\mu\text{-propionato})_2](\mathrm{NO_3})_2(\mathrm{ClO_4})_{0.4}\cdot 2\mathrm{H_2O}$ (**4**) were prepared as follows. An aqueous solution of *cis*-$[\mathrm{Pt(NH_3)_2(OH_2)_2}]\mathrm{X_2}$ ($\mathrm{X} = \mathrm{ClO_4^-}$) and sodium acetate (or propionate) was separated into two phases with an agar $\mathrm{NaNO_3}$ bridge, and was electrolyzed (2 μA, 30 °C, in air) for 3 weeks to give dark brown needles of **3** (or **4**) (Figure 1).[8] At the final stage of electrolysis, the color of the anodic solution turned dark brown, while that of the cathodic turned dark blue. To clarify the optimum synthetic conditions,[8] experiments were repeatedly performed by changing (i) the concentrations of the starting materials, (ii) the counterion X, (iii) the concentration/kind of salt in the agar separator ($\mathrm{NaClO_4}$ and $\mathrm{Na_2SO_4}$ were also tested), (iv) the temperature, and (v) the current applied. The most important finding is that the $\mathrm{NO_3^-}$ involved in **3** and **4** as the counterion must be added only to the salt bridge, for a much smaller amount of crystals having a lower quality deposited when $\mathrm{X} = \mathrm{NO_3^-}$. Therefore, slow diffusion of $\mathrm{NO_3^-}$ from the salt bridge into the anodic solution plays a key role in the growth of quality crystals in a higher yield (20−30%).

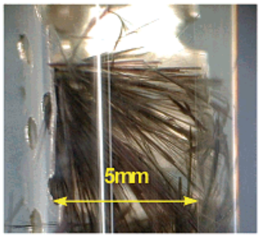


Figure 1. Dark brown needles of **3** grown on the surface of the anode.

Compounds **3**[9] and **4**[10] are judged to be pure and are stable in air at room temperature. Due to the severe disorder phenomena together with the slight batch dependence observed during the structure refinement studies,[11] there still remain uncertainties about the formulations of **3** and **4**. However, the reported formulas do explain the analytical data obtained thus far as well as the results of our disorder analysis.[12] The crystal of **3**[13] involves two independent dimer units. Each dimer forms an infinite chain of its own. One grows a chain with inversion symmetry (**3-i**), the other, with glidal symmetry (**3-g**) (Figure 2). Nevertheless, the structural features well resemble each other (Table 1). On the other hand, a very similar $\mathrm{Pt(2.2+)}_\infty$ chain is found in the crystal of **4**[14] (Table 1; Figure 2), suggesting that the average Pt oxidation levels of **3** and **4** are roughly the same. Both the bridged and nonbridged Pt−Pt distances in **3** and **4** are much shorter than those in the $[\mathrm{Pt(II)_2}]_\infty$ chains in **1** and **2** (see Table 1). Moreover, the linearity of chain is significantly improved in **3** and **4**. Thus, the partial oxidation at the Pt centers is effectively promoted in **3** and **4**. In addition, all the Pt−Pt distances observed for **1**−**4** well fit the correlation between the Pt−Pt distance and the average Pt oxidation state which has been reported thus far for the amidate-bridged platinum-blue family (Figure S4).[6b]

The XPS spectrum of **4** at the Pt 4f region consists of two sets of doublets ($4f_{7/2}$ and $4f_{5/2}$), confirming the presence of both Pt(II)

---

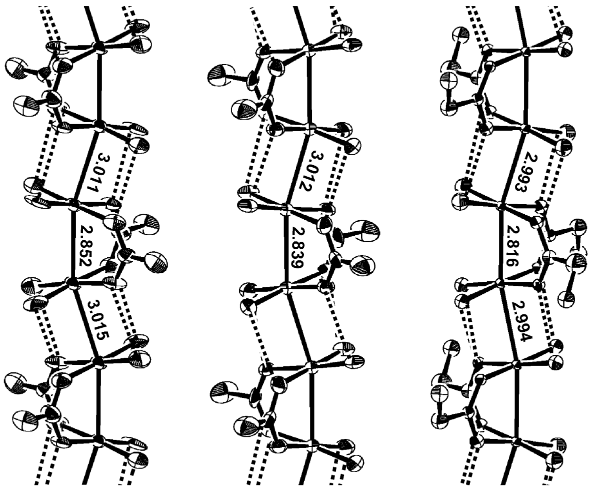
* To whom correspondence should be addressed. E-mail: ksakai@rs.kagu.tus.ac.jp.
† Tokyo University of Science.
‡ Tohoku University (X-ray Diffractometry).

10.1021/ja0275461 CCC: $22.00 © 2002 American Chemical Society

Table 1. Comparison of the Structural Features of **1**−**4**

compound		Pt–Pt(intra) distance (Å)	Pt–Pt(inter) distance (Å)	Pt–Pt–Pt angle (deg)	τ^a (deg)	ω^b (deg)	interdimer O···N distance[c](Å)
$[Pt(2.0+)_2(NH_3)_4(\mu\text{-acetato})_2](SiF_6)\cdot 4H_2O$ (**1**)[d]		2.9713(8)	3.1760(10)	148.58(2)	36.3(3)	7.2	3.02(1), 3.05(1)
			3.2265(9)	158.16(2)			3.09(1), 3.09(1)
$[Pt(2.0+)_2(NH_3)_4(\mu\text{-glycolato})_2](SiF_6)\cdot 4H_2O$ (**2**)[d]		2.9892(9)	3.2735(9)	150.30(1)	35.7(3)	1.9	3.16(1), 3.16(1)
$[Pt(2.2+)_2(NH_3)_4(\mu\text{-acetato})_2](NO_3)_{2.4}\cdot 2H_2O$ (**3**)	**3−i**	2.8517(11)	3.0107(14)	162.89(4)	29.9(5)	0.9	2.94(2), 2.89(2)
			3.0148(13)	161.93(4)			2.87(2), 2.92(2)
	3−g	2.8385(11)	3.0121(11)	163.31(3)	28.4(4)	1.1	2.96(2), 2.98(2)
				163.28(3)			2.94(2), 2.87(2)
$[Pt(2.2+)_2(NH_3)_4(\mu\text{-propionato})_2](NO_3)_2(ClO_4)_{0.4}\cdot 2H_2O$ (**4**)		2.8163(7)	2.9929(10)	163.52(4)	26.7(7)[e]	3.1[e]	2.87(3)[e], 2.91(3)[e]
			2.9938(10)	167.29(4)			2.88(3)[e], 2.92(3)[e]
					27.1(8)[f]	1.8[f]	2.89(3)[f], 2.89(3)[f]
							2.84(3)[f], 2.93(3)[f]

[a] Dihedral cant between the bridged Pt coordination planes. [b] Twist angle about the Pt−Pt vector of the bridged Pt coordination planes. [c] O(carboxylate)···N(ammine) distances. [d] Values reported in ref 5. [e] Values for one of two disordered structures. [f] Values for the other disordered structure.



3-i **3-g** **4**

Figure 2. Partially oxidized platinum chains in **3** and **4**, where only one of two disordered structures in **4** is shown for clarity.

and Pt(III) (Figure S5). ESR (113−300 K) measurements reveal the diamagnetic characters of **3** and **4**, indicating that the unpaired electrons derived from Pt(III)s are predominantly coupled. The solid-state absorption spectra of **3** and **4** (Nujol mull method) display a fairly broad band ranging from 500 to 3200 nm (Figure S6). The room-temperature single-crystal electrical conductivities (4 probe, d.c.) of **3** (0.01 S/cm) and **4** (0.001 S/cm) reveal semiconducting characters of the materials.

Combined results obtained thus far deny a simpler description of $Pt(2.25+)_\infty$ (formally $[Pt(II)_3Pt(III)]_\infty$) for the present systems, and rather support the reported mixed-valency of $Pt(2.2+)_\infty$ (formally $[Pt(II)_4Pt(III)]_\infty$), which has an implication of a one-dimensional superstructure along the *c* axis (e.g., $^5/_2c$).[15] Work in progress aims to more fully understand these new electronic systems by using other possible physical techniques to fully characterize various related compounds obtained during these studies, and also to extend this chemistry to new materials science.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 10149248, 11136246, and 12023247 “Metal-assembled Complexes”) from the Ministry of Education, Science, Sports, and Culture of Japan. We thank Dr. Hiroshi Kitagawa (Tsukuba University, Japan) for helpful discussions on the electrical conductivity measurements.

Supporting Information Available: Crystallographic and other relevant data for **3** and **4** (PDF). Crystallographic information files for **3** and **4** (CIF). This material is available free of charge via the Internet at http://pub.acs.org.

References

(1) Miller, J. S., Ed. *Extended Linear Chain Compounds*; Plenum Press: New York, 1982 and references therein.

(2) Bailey, J. A.; Hill, M. G.; Marsh, R. E.; Miskowski, V. M.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4591 and references therein.

(3) Novoa, J. J.; Aullón, G.; Alemany, P.; Alvarez, S. *J. Am. Chem. Soc.* **1995**, *117*, 7169.

(4) Butler, M. A.; Rousseau, D. L.; Buchanan, D. N. E. *Phys. Rev. B* **1973**, *7*, 61.

(5) Sakai, K.; Takeshita, M.; Tanaka, Y.; Ue, T.; Yanagisawa, M.; Kosaka, M.; Tsubomura, T.; Ato, M.; Nakano, T. *J. Am. Chem. Soc.* **1998**, *120*, 11353.

(6) (a) O’Halloran, T. V.; Mascharak, P. K.; Williams, I. D.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1987**, *26*, 1261. (b) Sakai, K.; Tanaka, Y.; Tsuchiya, Y.; Hirata, K.; Tsubomura, T.; Iijima, S.; Bhattacharjee, A., *J. Am. Chem. Soc.* **1998**, *120*, 8366 and references therein.

(7) (a) Sakai, K.; Matsumoto, K. *J. Am. Chem. Soc.* **1989**, *111*, 3074. (b) Matsumoto, K.; Sakai, K.; Nishio, K.; Tokisue, Y.; Ito, R.; Nishide, T.; Shichi, Y. *J. Am. Chem. Soc.* **1992**, *114*, 8110.

(8) The electrolysis was performed using a two-electrode system (platinum plates, 6 × 15 mm^2) and a U-shaped glass tube (11 mm in diameter). The anodic and cathodic compartments were separated with an agar salt bridge (ca. 40 mm in length; $NaNO_3$, 3.4 g; agar, 0.4 g; H_2O, 10 mL). To each compartment was added 1.5 mL of an aqueous solution containing both *cis*-$[Pt(NH_3)_2(OH_2)_2](ClO_4)_2$ (0.11 mmol) and sodium carboxylate (0.11 mmol), so as to cancel the mutual diffusion between the two phases. In the earlier studies, three different types of aqueous *cis*-$[Pt(NH_3)_2(OH_2)_2]X_2$ ($X = ClO_4^-$, NO_3^-, and $^1/_2SO_4^{2-}$) solutions, prepared as previously described in ref 5, were tested.

(9) Dark brown needles (**3**). Anal. Calcd for $Pt_2O_{13.2}N_{6.4}C_4H_{22}$: C, 6.31; H, 2.91; N, 11.78. Found: C, 6.31; H, 2.78; N, 11.24. Nitrate content determined by ion chromatography: 19.5 (Calcd); 18.9 (Found) %. Loss of water in thermal gravimetry: 5.5 (Calcd); 5.8 (Found) %.

(10) Dark brown plate-needles (**4**). Anal. Calcd for $Pt_2Cl_{0.4}O_{13.6}N_6C_6H_{26}$: C, 8.96; H, 3.26; N, 10.45. Found: C, 8.88; H, 3.09; N, 10.12. IR(single-crystal): $\nu(NO_3) = 1457$ (br); $\nu(ClO_4) = 1081$ (br) cm^{-1}. Counterion content (ion chromatography): NO_3^-, 15.4 (Calcd), 15.0 (Found); ClO_4^-, 4.9 (Calcd), 5.2 (Found) %.

(11) For both **3** and **4**, several data sets were collected on a Bruker Smart APEX CCD-detector X-ray diffractometer. In both cases, severe disorder phenomena were observed, especially around the counterion and water geometries. Low-temperature measurements were not successful due to the crystal decomposition at lower temperature. In **4**, all the atoms except for two Pts are disordered over two sites with each having an equal population.

(12) The KenX program (a GUI for SHELXL-97; freely available at http://www.ch.kagu.tus.ac.jp/OK/), developed by K.S., was used to solve the disordered structures. PLATON (Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578.) was also used to carefully examine the Fourier maps. Other details are reported in Supporting Information.

(13) Complex **3**: Monoclinic, $P2_1/c$, $a = 9.8930(13)$ Å, $b = 33.172(4)$ Å, $c = 11.4474(15)$ Å, $\beta = 102.410(2)°$, $V = 3668.9(8)$ Å^3, $Z = 8$, data/restraints/params = 5284/28/444, R1 = 0.0470 (for $I > 2\sigma(I)$), wR2 = 0.1086 (for all data), GOF = 1.023.

(14) Complex **4**: Triclinic, $P\bar{1}$, $a = 9.4102(8)$ Å, $b = 10.0776(8)$ Å, $c = 11.4257(9)$ Å, $\alpha = 101.489(2)°$, $\beta = 103.882(2)°$, $\gamma = 99.534(2)°$, $V = 1004.53(14)$ Å^3, $Z = 2$, data/restraints/params = 2878/258/411, R1 = 0.0519 (for $I > 2\sigma(I)$), wR2 = 0.1455 (for all data), GOF = 1.049.

(15) The Pt chains in both **3** and **4** grow along the *c* axis. Diffuse scattering was obvious around the Bragg spots collected on a CCD area detector. The detailed investigations concerning a possible superstructure is now in progress.

JA0275461