3. W.A. Aue and C.R. Hastings, *J. Chromatogr.*, **42**, 319 (1969).

4. L.L. Lamparski and T.J. Nestrick, *J. Chromatogr.*, **156**, 143 (1978).

5. L.L. Lamparski, T.J. Nestrick, and R.H. Stehl, *Anal. Chem.*, **51**, 1453 (1979).

6. T.J. Nestrick, L.L. Lamparski, and R.H. Stehl, *Anal. Chem.*, **51**, 2273 (1979).

7. W.A. Aue and P.P. Wiskramanayake, *J. Chromatogr.*, **200**, 3 (1980).

8. K. Grob, G. Grob, and K. Grob Jr., *J. Chromatogr.*, **211**, 243 (1981).

9. P. Sandra, G. Redant, E. Schacht, and M. Verzele, *J. HRC & CC*, **4**, 411 (1981).

10. K. Grob and G. Grob, *J. HRC & CC*, **4**, 491 (1981).

11. K. Grob and G. Grob, *J. Chromatogr.*, **213**, 211 (1981).

12. K. Grob and G. Grob, *J. HRC & CC*, **5**, 13 (1982).

13. L. Blomberg, J. Buijten, K. Markides, and T. Wann-

14. J.A. Huball, P. DiMauro, E.F. Barry, and E. Chabot, *J. HRC & CC*, **6**, 241 (1983).

15. K. Markides, L. Blomberg, J. Buijten and T. Wännman, *J. Chromatogr.*, **267**, 29 (1983).

16. K. Markides, L. Blomberg, S. Hoffmann, J. Buijten, and T. Wannman, *J. Chromatogr.*, **302**, 319 (1984).

17. J. Buijten, L. Blomberg, S. Hoffmann, K. Markides, and T. Wannman, *J. Chromatogr.*, **289**, 143 (1984).

18. J. Buijten, L. Blomberg, K. Markides, and T. Wannman, *J. Chromatogr.*, **237**, 465 (1982).

19. L. Blomberg, J. Buijten, K. Markides, and T. Wannman, *J. Chromatogr.*, **239**, 51 (1982).

20. W.M.L. Chow and B. Caddy, *J. Chromatogr.*, **318**, 255 (1985).

21. L. Ghaoui, H. Shanfield, and A. Zlatkis, *Chromatographia*, **18**, 11 (1984).

22. A. Zlatkis and K. Kim, *J. Chromatogr.*, **126**, 475 (1976).

man, *J. HRC & CC*, **4**, 578 (1981).

Preparation and Properties of New Metal-chain Compounds with Commensurate Peierls Structure

Kuk Haeng Lee*, and **Ja Hong Kim**

Department of Chemical Education, Chonbuk National University, Chonju 520

Masagi Mizuno

National Chemical Laboratory for Industry, Tsukuba Research Center, Yatabe Ibaraki 305, Japan
Received December 15, 1986

New platinum chain compounds, $[M(en)_2]_{0.80}$ $[Pt(ox)_2]$. $2H_2O$ where M = Cu or Pt, en = ethylenediamine and ox = oxalate, have been prepared and found to have a commensurate Peierls structure as evidenced by the five-fold Pt chain periodicity and unusually low electrical conductivity ($1.5 \times 10^{-5} \sim 5.7 \times 10^{-3}$ S/cm). Including two other compouds with the Peierls structure, their characteristic features were deduced and explained from the point of view of the band theory.

Introduction

Last decade has witnessed a renewed interest in the novel features of the linear platinum chain complexes. Peierls instability is one of the major characters to be related with the 1-D conductors as predicted by Peierls[1] and evidenced by Comes et al[2] in KCP (Br) using X-ray diffuse scattering technique.

Quasi-1-D compounds are inherently unstable to the lattice distortion with charge density wave $q = 2k_F$, where k_F is the Fermi wave vector. The importance of the lattice distortion is increasing with decreasing temperature and at certain temperature T_p the 1-D conductor goes to a semiconductor which is called as the Peierls transition.

However, when the original lattice periodicity is commensurate with respect to the Peierls distortion $2k_F$, the condensation of this phonon anomaly into a pattern of static displacements occurs. As a consequence a gap appears at the Fermi surface. The resultant structure is referred to the Peierls structure. Most of the partially oxidised platinum chain compounds studied so far have lattices incommen-surate with the charge density wave (CDW) $2k_F$. But some of them have the commensurate Peierls structures at room temperature.

α-Rb-OP[$Rb_{1.67}Pt(C_2O_4)_2 \cdot 1.5H_2O$] is the first compound found to have the Peierls structure and its 3-dimensional structure has been studied in detail[3]. The second one is $[(CH_3)_3NH]_{1.59}[Pt(C_2O_4)_2]$ (TriAm-OP) which has unusual five-fold Pt-chain structure[4]. In the present work, two new 1-D metal chain compounds with the commensurate Peierls structure, $[M(en)_2]_{0.80}$ $[Pt(C_2O_4)_2] \cdot 2H_2O$ where en = ethylenediamine and M = Cu or Pt, will be reported[5].

Experimental

Preparation of $[Cu(en)_2]$ $[Pt(C_2O_4)_2]$ (Cuen-OP(II)). 1g of $Ag_2[Pt(C_2O_4)_2] \cdot 2H_2O$ was suspended in 50 ml of water and heated to boiling. 0.47g of $Cu(C_2N_2H_8)_2Cl_2 \cdot 2H_2O$ dissolved in 10 ml of water was added slowly. The reaction mixture was stirred well until the white ppt of AgCl coagurates. The ppt was removed by a filtration and the blue filtrate was cooled down to room temperature to obtain red-brown glittering

needles. The crystals were collected by filtration, washed with cold water and dried in air.

Preparation of [Cu(en)₂]₀.₈₀ [Pt(C₂O₄)₂].2H₂O (Cuen-OP). Aqueous solution saturated with Cuen-OP(II) was electrolysed in a 100 ml beaker fitted with Pt wires at 1-2 μA for several weeks. Pale purple lath-shaped crystals appeared on anode. The product was filtered off and dried in air.

[Found: Cu, 9.18; Pt, 35.22; C, 15.92; H, 2.42; N, 8.08,
Calcd: Cu, 9.17; Pt, 35.21; C, 15.61; H, 3.06; N, 8.08%]

The typical size of the crystal is $1.5 \times 0.05 \times 0.02$ mm³. The crystals exhibit clear optical anisotropy which was examined under a polarized microscope.

The complexes [Pt(en)₂] [Pt(C₂O₄)₂].nH₂O and [Pt(en)₂]₀.₈₀ [Pt(C₂O₄)₂].2H₂O, (Pten-OP), were obtained by the similar ways. Partially oxidised salt Pten-OP crystalized on anode as dark brown needles which are likely to grow in a bundle form.

[Found: Pt, 53.18; C, 12.99; H, 2.36; N, 6.80; 0, 24.35
Calcd: Pt, 53. 26; C, 13.11; H, 2.57; N, 6.80; 0, 24.26%]

Platinum and copper analysis were carried out by atomic absorption spectroscopy and carbon, hydrogen, nitrogen and oxygen were determined microanalytically.

Physical Measurements. Electrical conduction studies were carried out using a four-probe d.c. technique with colloidal graphite as the contact material between crystal and gold wire leads. Variable temperature measurements were performed using an Oxford temperature controller DTC-2 and a cryostat with closed helium-circulation system made by Osaka Sanso Co. and with an Au-Fe-chromel thermocouple calibrated at three points. A Keithley 225 current source and a Keithley 614 electrometer were used to determine the conductivity. Single crystal X-ray diffraction measurements were made using a Rigaku Weissenberg camera and Cu-Kα radiation (λ = 1.54242 Å) to determine lattice constants.

Results and Discussion

Cuen-OP. The crystal structure of the integral oxidation salt Cuen-OP(II) was analysed in detail by Bekaroglu et al[6], where a zigzag chain was recognized with two kinds of Pt-Pt distance $\bar{d}_{Pt-Pt}$, 3.855 Å and 3.554 Å. From the preliminaly X-ray work on single crystal of partially oxidised complex, Cuen-OP, it was found that the crystal has an orthorhombic lattice and 5-fold platinum chain along the elongated axis. The averaged Pt-Pt separation is found to be 2.83 ± 0.01 Å which is one of the shortest distances found for the partially oxidised bis (oxalato) platinates (POBOP's). The crystal data are listed in Table 1.

Chemical analysis of Cuen-OP shows the cation deficiency corresponding to $2k_F = 0.80$. This indicates that within the experimental error the Peierls distortion is commensurate with respect to the original lattice and Cuen-OP corresponds to 4/5 filled band system. Thus the Peierls instability should have a wavelength corresponding to five Pt-Pt repeat distance which explains the unusual five-fold Pt chain structure.

The electrical conductivity σ was found to be $(1.5-3.5) \times 10^{-5}$ S/cm for Cuen-OP at room temperature (Table 1). The conductivity value is five order of magnitude lower than that of the other compounds of this series. This suggests that the Peierls transition has already took place in the crystal and produced a band gap which prevents Cuen-OP from having a

Table 1. Crystal Data and Conductivity

Compound		Cuen-OP	Pten-OP
Lattice		Orthorhombic	Orthorhombic
Cell Dimensions	a	21.52 ± 0.04	20.48 ± 0.06
(Å)	b	24.14 ± 0.04	26.52 ± 0.08
	c	14.16 ± 0.04	14.12 ± 0.21
Density d_{obs}		2.434 ± 0.003	2.913-003
(g/cm³) d_{calc}		2.504	2.855
Z		20	20
Pt-chain Periodicity		5	5
$\bar{d}_{Pt-Pt}$ (Å)		2.83 ± 0.01	2.82 ± 0.04
$\sigma_\parallel^{RT}$ (S/cm)		$(1.5-3.5) \times 10^{-5}$	$(3.4-5.7) \times 10^{-3}$

Figure 1. Vriation of ln$\sigma_\parallel$ with inverse temperature for a crystal of [Cu(en)₂]₀.₈₀ [Pt(C₂O₄)₂].2H₂O. Downward arrow indicates temperature-decreasing cycle and vice versa.

high electrical conduction. Thus the existence of the Peierls structure is supported by their unusually low conductivity.
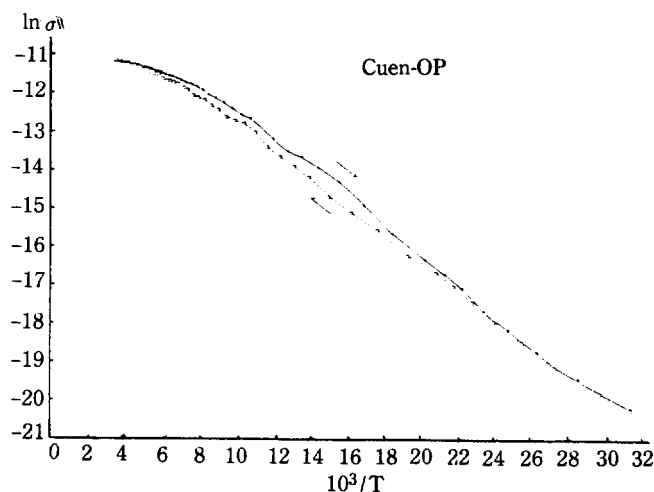
The variation of $\sigma_\parallel$ with inverse temperature is shown in Figure 1. The conductivity decreases slowly with decreasing temperature below room temperature to about 200K. Below 200K it behaves as a semiconductor with an averaged activation energy of 30 meV. At lower temperature the activation energy is reduced to 23 meV. Above room temperature the conductivity maximum was supposed to exist.

Pten-OP. Pten-OP has an orthorhombic crystal lattice and 5-fold platinum chain along the elongated axis. Crystal data are summarized in Table 1 together with those for Cuen-OP. The isostructural relation between Cuen-OP and Pten-OP is strongly supported by these crystal data and the chemical formulae, M₀.₈₀[Pt(C₂O₄)₂].2H₂O, for both compounds in common where M ≈ Cu or Pt, respectively. Pten-OP, therefore, is supposed to have a commensurate Peierls structure corresponding to 4/5 filled band system. The electrical conductivity of Pten-OP is $\sigma_\parallel = (3.4-5.7) \times 10^{-3}$ S/cm at room temperature which is third order of magnitude lower than that of the other POBOP's.

As is shown in Figure 2 the conductivity of Pten-OP exhibits a broad maximum around 280K and below this maximum down to about 55K it behaves linearly as inverse temperature with an activation energy of 47 meV. Below
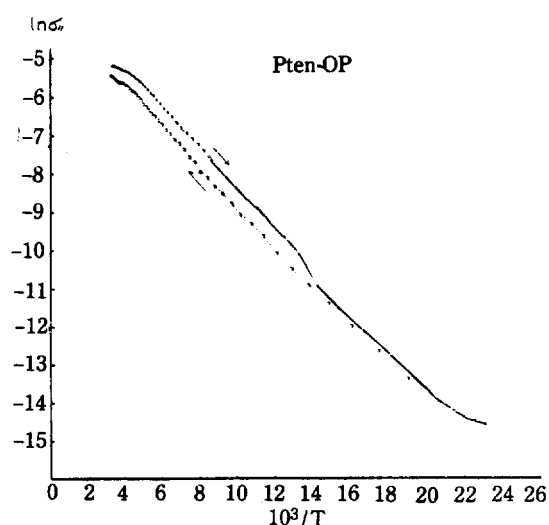
Figure 2. Variation of $\ln\sigma_t$ with inverse temperature for a crystal of $[Pt(en)_2]_{0.80}[Pt(C_2O_4)_2].2H_2O$.

Figure 3. (a) Equally spaced Pt chain of a 4/5 filled band. (b) A completely filled band and a vacant band at the Fermi surface.

55K it becomes less steep. The discrepancy of the conductivity between cooling and heating run is referred to the thermal hysteresis in conduction property and it varies from crystal to crystal even in the same batch of preparation. Above room temperature the crystal showed an abrupt decrease of conductivity which is supposed to be caused by dehydration of the sample upon elevated temperature.

Cuen-OP and Pten-OP have a complex cation as big as the complex anion $[Pt (C_2O_4)_2]^x$ which forms metal chain spine. It was proved in this study that a partially oxidised salt can exist even with such a big cations contained in the salt. It is not clear how the cation size effects on the commensurability between the lattice periodicity and the charge density wave $2k_F$. But an inclusion of big cation in a partially oxidised salt seems to have an effect to push the salt to the commensurate Peierls structure side.

Commensurability and Peierls Structure. Suppose that an equally spaced Pt chain forms a 4/5 filled band as illustrated in Figure 3 (a). Because of the one-dimensionality of the Pt chain, the Peierls instability occurs producing a charge density wave with $2k_F$ along the chains. This CDW is apparently commensurate with respect to the chain and has a
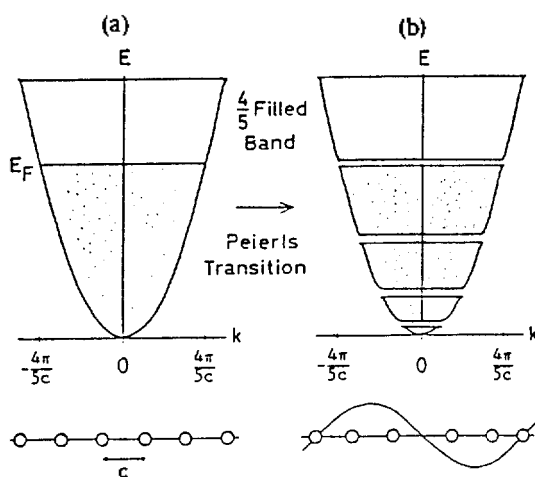
finite interaction potential with it causing the condensation of the phonon anomaly into a pattern of static displacement occurs. As this consequence a gap appears at the Fermi surface producing a completely filled band and a vacant band (Figure 3-b. The chain now has a five-fold periodicity with an enhanced alternation of Pt-Pt separation. The resultant structure is referred to Peierls structure.

Thus. from X-ray structural study, chemical analysis, and conductivity measurements, it is strongly suggested that both Cuen-OP and Pten-OP have the commensurate Peierls structure corresponding to 4/5 filled band and are isostructural to each other.

Kobayashi et al[3] has reported the commensurate Peierls structure of α-Rb-OP found for the first time. According to their result α-Rb-OP has a cation deficiency of 1.67 which correspond to 5/6 filled band system, and also sixfold Pt chain with an average Pt-Pt distance of 2.85Å. It has the three kinds of Pt-Pt distances among which there exists a very long distance of 3.015Å, thus explaining the low electrical conductivity of 7×10^{-3} S/cm for this salt. The commensurability of CDW with the crstal lattice results in the unusually low conductivity in this case also.

TriAm-OP has $2k_F = 0.795$ which correspond to 4/5 filled

Table 2. Crystal Data and Conductivity of Four Compounds with Commensurate Peierls Instability

Compounds	Lattice	Cell Dimensions (Å and °)		k_F (π/d_{Pt-Pt})	n	$\bar{d}_{Pt-Pt}$ (Å)	$\sigma^*(RT)$ (S/cm)	$\Delta\varepsilon$ (meV)	
α-Rb-OP $Rb_{1.67}[Pt(ox)_2].1.5H_2O$	Tri.	a) 12.690 b) 17.108 c) 11.357	a) 102.04 b) 115.17 r) 43.58	0.835	6	2.717 2.830 3.015	7×10^{-3}	77	Kobayashi et al. (1978)
TriMA-OP $[(CH_3)_3NH]_{1.59}[Pt(ox)_2]$	Orth.	a) 13.62 ± 0.01 b) 18.36 ± 0.05 c) 14.01 ± 0.04		0.795	5	2.80	5×10^{-3}	85	Mizuno & Underhill (1983)
Cuen-OP $[Cu(en)_2]_{0.80}[Pt(ox)_2].2H_2O$	Orth.	a) 21.52 ± 0.04 b) 24.14 ± 0.04 c) 14.16 ± 0.04		0.80	5	2.83	1.5×10^{-5} l 3.5×10^{-5}	35	This Work
Pten-OP $[Pt(en)_2]_{0.80}[Pt(ox)_2].2H_2O$	Orth.	a) 20.48 ± 0.06 b) 26.52 ± 0.08 c) 14.12 ± 0.21		0.80	5	2.82	3.4×10^{-3} l 5.7×10^{-3}	45	This work

band and actually has five-fold Pt chain structure[4]. It has a very low conductivity at room temperature as $\sigma_r = 5 \times 10^{-3}$ – 7×10^{-2} S/cm and it is also supposed to have a commensurate Peierls structure as a-Rb-OP.

All the partially oxidised platinum complexes with the commensurate Peierls structure are found in POBOP's so far as are summarized in Table 2. Their common features are deduced as follows;

(1) $k_f = \frac{n-1}{n} \cdot \frac{\pi}{d_{Pt-Pt}}$, where the Pt chain is n-fold.

(2) The room temperature conductivity σ is three to five order of magnitude less than that of the incommensurate salts of the same series.

(3) Averaged Pt-Pt separation $\bar{d}_{Pt-Pt}$ is relatively short compared with other compounds of this series with commensurate lattice modulation.

The first feature is the condition for the commensurability itself and the second one is the consequence of the above condition. The third one is the structural aspect of the commensurate Peierls structure where the individual Pt-Pt separation in the chain is supposed to be much deviated from the averaged one. This supposition is the structural expression of the second feature. From the point of view of the band theory, the big conductivity drop is explained as the consequence of the opening of a band gap at the Fermi surface as illustrated in Figure 3-b.

The further structural investigation of Pt spine is very desirable for these compounds to prove the present supposition about their strong bond alternation.

References

1. R.E. Peierls, "Quantum Theory of Solids" Oxford University Press, London 108 (1955).
2. R. Comes, M. Lambert, H. Launois and H.R. Zeller, *Phys. Rev.* **B8** 571 (1973).
3. A. Kobayashi, Y. Sasaki and H. Kobayashi, *Bull. Chem. Soc. Jpn.* **52** 3682 (1979).
4. M. Mizuno, A.E. Underhill and K. Carneiro, *J. Chem. Soc. Dalton Trans.* 1771 (1983).
5. Preliminary results was reported in Abstract of International Conference on Science and Technology of Synthetic Metals, ICSM'86 Kyoto, 454 (1986).
6. O. Bekaroglu, M. El Sharif, H. Endres and H.J. Keller, *Acta Cryst.* **B32** 2983 (1976).

Lewis Acid Catalysis of Coumarin and 5,7-Dimethoxycoumarin Photodimerization

Sang Chul Shim*, Eun Il Kim, and Ki Taek Lee

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131. Received December 23, 1986

The effect of Lewis acids on spectroscopic properties and photodimerization of coumarin and 5,7-dimethoxycoumarin was investigated. Quantum yields of coumarin photodimerization increase in the presence of $BF_3 \cdot OEt_2$ but those of 5,7-dimethoxycoumarin decrease. The spectroscopic properties of the coumarin-$BF_3 \cdot OEt_2$ and 5,7-dimethoxycoumarin-$BF_3 \cdot OEt_2$ complexes were studied by UV, IR, ^{1}H NMR and fluorescence spectroscopy.

Introduction

Lewis acids have been widely employed as catalysts for thermal Diels-Alder and ene reactions, especially those involving α,β-unsaturated esters.[1] The enhanced reactivity and stereoselectivity observed in many such reactions have been attributed to changes in frontier orbital energies and double bond polarity upon complexation of the carbonyl oxygen.[2]

The possobility that Lewis acid might serve as a catalyst for photochemical reactions have been recognized for many years, and the recent literature offers increasing number of reports about photochemical reactions accelerated by Lewis acids.

It is reported that the spectroscopic properties and unimolecular photoisomerization reactions of several α,β-unsaturated esters are profoundly changed by complexation with Lewis acids such as BF_3, $EtAlCl_2$ and $SnCl_4$.[3-6] Irradiation of several α,β-unsaturated esters in the presence of Lewis acids leads to photostationary states enriched in the thermodynamically less stable *cis* isomer.[3] From a mechanistic standpoint, selective *trans-cis* photoisomerization occurred via complexation of ester carbonyl oxygen with Lewis acids.[5] Such a complexation changes spectroscopic properties resulting in selective *trans-cis* photoisomerization upon irradiation of the ground state ester-Lewis acid complexes.

Lewis acids have also served as a catalyst for photochemical [2 + 2] cycloaddition reactions such as photodimerization of *trans,trans*-dibenzylidenacetone in the presence of UO_2^+ and $SnCl_4$[7,8] and photodimerization of coumarin and cinnamate esters in the presence of $BF_3 \cdot OEt_2$.[9,10]

To explain the effects of Lewis acids on [2 + 2] photocycloaddition reactions and possible role of Lewis acid catalysts in photochemical reactions, we investigated spectroscopic properties and photodimerization reactions of coumarin(I) and 5,7-dimethoxy-coumarin (DMC,II) in the presence and absence of Lewis acids.

Experimental

Materials. 5,7-Dimethoxycoumarin (Aldrich) was recry-