CHEMISTRY LETTERS, pp. 1167-1170, 1978. Published by the Chemical Society of Japan

STRUCTURE OF COMMENSURATE PEIERLS STATE OF $Rb_{1.67}Pt(C_2O_4)_2.1.5H_2O$

Akiko KOBAYASHI, Yukiyoshi SASAKI, and Hayao KOBAYASHI*

Department of Chemistry, Faculty of Science, The University of Tokyo, The Research Centre for Spectrochemistry, Hongo, Tokyo 113

*Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274

X-ray examination, chemical analyses and electrical conductivity measurements were made on the partially oxidized platinum complex $Rb_{1.67}Pt(C_2O_4)_2.1.5H_2O$(RbDOX). Sixfold modulated superstructure of RbDOX is confirmed as the newly found commensurate Peierls structure based on the agreement with the period of the Peierls distorted superlattice determined by the degree of partial oxidation.

In the one-dimensional metals, the charge density waves(CDWs) have a wave vector $q=2k_F$ in the chain direction, where k_F is the Fermi wave vector, and in the insulating state, the CDWs are correlated to form a three-dimensional static Peierls distortion, that is, the lattice modulation wave give rise to a three-dimensional superstructure at low temperature.[1] The period of the lattice modulation wave in the Peierls phase is commensurate or incommensurate with the period in the high-temperature metallic phase.

Recently we have reported that the modulated superstructure of $K_{1.81}Pt(C_2O_4)_2.2H_2O$(γ-KDOX) is the structure of the incommensurate Peierls state first determined three-dimensionally and is attributed to the condensation of the $2k_F$ phonon(CDW) of the one-dimensional metallic system.[2,3] In the present work we report the sixfold modulated commensurate Peierls structure of new salt $Rb_{1.67}Pt(C_2O_4)_2.1.5H_2O$.

RbDOX was prepared from $Rb_2Pt(C_2O_4)_2$ and Rb_2PtCl_6 by a diffusion method. The copper-colored needles were obtained after a month. Oscillation and Weissenberg

photographs showed that RbDOX crystallizes in the sixfold structure. The crystal and molecular structure of $Rb_{1.67}Pt(C_2O_4)_2.1.5H_2O$ has been determined by single crystal X-ray diffraction.

crystal data: triclinic, a=12.690(10), b=17.108(14), c=11.357(3) Å ; α=102.04(4), β=115.17(3), γ=43.58(4)°, space group $P\bar{1}$, Z=6, D_X=3.548 , D_m=3.5 g cm^{-3}, μ=230.6 cm^{-1}(Mo Kα).

Three dimensional intensity data were collected on a Rigaku automated four-circle diffractometer with Mo Kα radiation monochromated by a graphite plate. The diffracted intensity had gradually decreased to 93 % of the initial value during an exposure of X-ray radiation. The data were corrected for deterioration. The atomic parameters were refined by the block-diagonal and the full matrix least squares methods to an R value of 0.072. The anisotropic thermal parameters were used only for Pt and Rb atoms. Selected crystals were subjected to the chemical analyses. The contents of Rb and Pt atom were determined with the aid of atomic emission spectrometry (Jarrell Ash AA-1 MK-II) and atomic absorption spectrophotometry(Nippon-Jarrell Ash FLA-100). The results of chemical analyses are shown as follows.

Expected(%); Pt 36.07,Rb 26.39,C 8.88, H 0.56;

Found(%) ; Pt 37.5 ,Rb 27.1 ,C 9.0 , H 0.56; the ratio of Rb to Pt is 1.66±0.07.

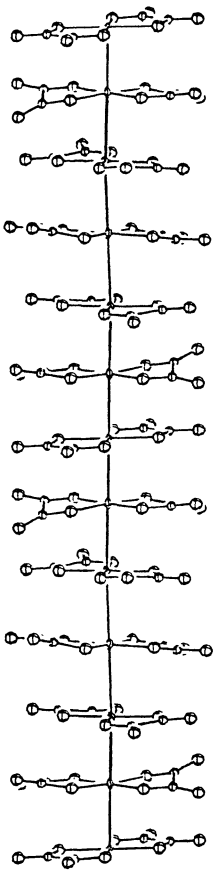

Fig. 1.
Two wavelengths of the Pt chain along the b axis show the chain distortion and ligand non-planarity.

The electrical conductivity was determined by a four probe method. RbDOX behaves as a semiconductor from 305K to 83K. The room temperature conductivity is 7×10^{-3} $(\Omega cm)^{-1}$ and the activation energy is 0.077 eV.

The planar bis(oxalato)platinate ions stack parallel to the b axis of the crystal. Pt atoms form a sixfold distorted chain along the b axis. The stacking of $Pt(ox)_2$ ions is shown in Fig. 1.

Partially oxidized tetracyanoplatinate and bis(oxalato)platinate salts so

far reported crystallize in one of the following forms; "twofold structure" $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$[4], $Mg_{0.82}Pt(C_2O_4)_2\cdot 5.2H_2O$[5], "threefold structure", β-KDOX[2], and "fourfold structure", $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$[6], α-KDOX[2]. RbDOX is the first example of the sixfold structure. Three independent Pt-Pt distances are 2.715(2) 2.832(3) and 3.014(2) Å. The Pt-Pt-Pt angles are 177.93(12) and 174.34(7)°. The Pt-Pt distance of 2.715(2) Å found in RbDOX is the shortest spacing so far observed in partially oxidized platinate salts and shorter than the 2.77 Å interatomic separation in Pt metal itself. The oxalate ligands are bidentate and are staggered (~45°,~60°,~90°) with respect to the ligands directly above and below them along the chain, while alternate ligands are eclipsed or staggered (~90°).

A one-dimensional metallic system is unstable in the presence of changes in the crystal lattice period which split a partly filled band into completely filled and empty subbands (Peierls transition). In other words, when the temperature is lowered, a one-dimensional metal should exibit lattice distortions with a wave number equal to twice the Fermi momentum. The period of the Peierls distorted cell is determined by the degree of partial oxidation(DPO)[7].

By the structure determination of RbDOX, six Pt atoms and ten Rb atoms are found in the unit cell and the ratio of the content of Rb atom to Pt atom is 1.67, while the result of chemical analyses show that this ratio is 1.66. Thus DPO of RbDOX is about 0.33. The possible period of the superlattice along the $Pt(ox)_2$ chain is $6nb_o$ ($=2nb_o/DPO$; n=1,2,3...), where b_o is the average Pt-Pt distance. The case for n=1 (≈17.1 Å) corresponds to the "$2k_F$-instability" of a one-dimensional metal. Thus the sixfold superstructure of RbDOX is confirmed as the structure of commensurate Peierls state, produced by the condensation of $2k_F$ phonon, on the basis of the crystal structure determination, chemical analyses and the measurements of electrical conductivity.

The longitudinal displacements of Pt modulation wave from the point (0.0, n/6, 0.0; n=0,...5) are (0.0,0.14,0.16,0.0,-0.16,-0.14 Å) respectively. These displacements can be approximately expressed in terms of the sinusoidal modulation wave. The amplitude of the modulation wave on the ℓ-th platinum atomic position in the n-th cell [$n=(n_1,n_2,n_3)$] is given as

$$0.17\sin\{(2\pi/6)(\ell-1)+n_2\} \qquad (\ell=1,\ldots 6).$$

This amplitude is as the same order of magnitude as that of γ-KDOX and grater than an order of magnitude in $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$. The transverse displacements of Pt

atoms are (0.0,0.04,0.16,0.0,-0.16,-0.04 Å). Since the longitudinal displacements are mainly influenced by intrachain interactions but the transverse displacements are also influenced by interchain interactions, it is natural that the transverse displacements can not be described as a simple sinusoidal wave.

References

1) "Chemistry and Physics of One-Dimensional Metals" ed. by H. J. Keller (Plenum Press, New York and London, 1977).
2) H. Kobayashi, I. Shirotani, A. Kobayashi and Y. Sasaki, Solid State Commun., 23, 409(1977).
3) A. Kobayashi, Y. Sasaki, I. Shirotani and H. Kobayashi, Solid State Commun., 26, 653(1978).
4) K. Krogmann and H. D. Hausen, Z. Anorg. Allg. Chem., 358, 67(1968).
5) K. Krogmann, Z. Anorg. Allg. Chem., 358, 97(1968).
6) J. M. Williams, K. D. Keefer, D. M. Washecheck and N. P. Enright, Inorg. Chem. 15, 2446(1976) ; A. H. Reis, Jr., S. W. Peterson, D. M. Washecheck and J. S. Miller, Inorg. Chem., 15, 2455(1976).
7) K. Krogmann, in "One-Dimensional Conductors", ed. by J. Ehlers, K. Hepp and H. A. Weidenmüller (Springer-Verlag,1975).

(Received August 21, 1978)