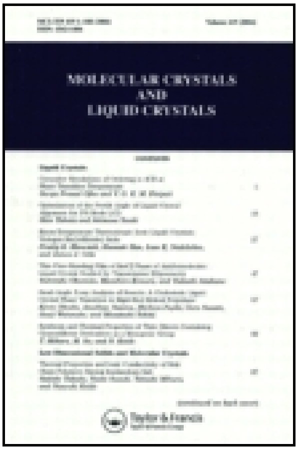

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High Pressure Studies on One-Dimensional Platinum Complexes-Periodical Modulation and Phase Transition

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HIGH PRESSURE STUDIES ON ONE-DIMENSIONAL PLATINUM COMPLEXES—PERIODICAL MODULATION AND PHASE TRANSITION

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The correlation between the superstructures observed at ambient pressure and the possible high-pressure modifications of the crystal structures of partially oxidized platinum complexes was examined. The examples of the $2k_F$-modulation of the platinum chains and the planar platinum complexes were presented. Besides the Peierls and mixed-valence transitions, another type of pressure-induced modulation of the platinum chain was observed in KCP(Br) and RbCP(FHF), which appears to show that there is a real phase transition at the pressure and temperature where the fluctuating periodical lattice distortion wave begins to appear in the crystal. The brief description of the high pressure X-ray single crystal structure analyses at 6, 14 and 21 Kbar will be presented.

POSSIBLE HIGH-PRESSURE MODIFICATION OF PLATINUM CHAIN

The partially oxidized platinum complexes are familiar for their one-dimensional metallic properties and have been intensively studied for the past decade. Although various types of the modulated structures have been obtained, their complete description has been rarely made. In this paper, we will examine the correlation between the superstructures observed at ambient pressure and the possible high-pressure modifications of the Pt-chains. we will also present the high pressure studies of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ (KCP(Br)) and $Rb_2[Pt(CN)_4](FHF)_{0.4}$ (RbCP(FHF)).

The periodicity of the Pt-chains

The high-pressure conducting studies by Thielemans et al. has shown that the high pressure suppresses the fluctuation of the periodical lattice modulation to bring about a sharp Peierls transition of KCP(Br).[1] Thus, high pressure may induce the transition between regular chain and ($2k_F$-)modulated chain structures. Although the $2k_F$-structure of KCP(Br) can be obtained only under the condition of high pressure (>20 Kbar) and low temperature (<120 K), similar modulated structures have been observed in some platinum complexes at ambient pressure. For example, the crystal of $K_{1.81}[Pt(C_2O_4)_2]\cdot 2H_2O$ (γ-KDOX) has a sinusoidally modulated structure and can be considered to be a model of the Peierls structure of KCP(Br).[2] The amplitude of the modulation wave is 0.17 A and the wave length along the Pt-chain is equal to that of $2k_F$-wave (10.5xR(Pt...Pt)) calculated from the degree of partial oxidation of 0.19.

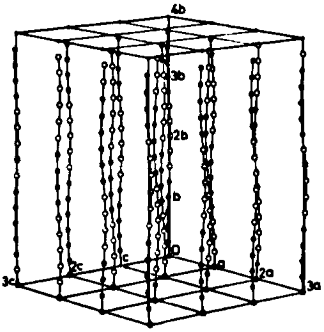


FIGURE 1 Schematic drawing of the modulation wave in γ-KDOX. The average structure has tetradic units of $[Pt(C_2O_4)_2]$.

When the applied pressure becomes large enough, the modulation wave may disappear and the system will transform to a "better metal". In fact, Thielemans et al. have proposed the possibility of the superconducting state of KCP(Br) above 70 Kbar (T_c~6K).[1] However, in KCP(Br), the conductivity decreases above 30 Kbar.[3] There may be some serious structural change(or dehydration of the crystal water).

The change of the mixed-valence state

The mixed-valence complex, $CsAuCl_3(Cs_2Au^IAu^{III}Cl_6)$ transforms to the uni-valent complex at 52Kbar.[4] At ambient pressure, Au^I and Au^{III} alternate to form the (Au···Cl-Au-Cl···Au) chain.

$$Cl\text{-}Au^{I}\text{-}Cl\cdots Au^{III}\cdots Cl\text{-}Au^{I}\text{-}Cl \xRightarrow[52Kbar]{} \text{-}Au^{II}\text{-}Cl\text{-}Au^{II}\text{-}Cl\text{-}Au^{II}\text{-}$$

Above 52 Kbar, X-ray diffraction spots indicating the unequivalence of the two Au atoms disappear and the system changes to be metallic.

Similar mixed-valence transition may occur at ambient pressure in the platinum complex. $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$(K(def)TCP) has a four-fold structure.[5] Since the Pt...Pt distance in K(def)TCP is relatively large(2.96 A), the Coulomb repulsion between excess charges in the Pt-chain tends to make "Wigner crystal-like arrangement". Then the arrangement of the Pt atoms can be represented as:

$$(Pt^{II}Pt^{II}Pt^{II}Pt^{III})\ldots\ldots$$

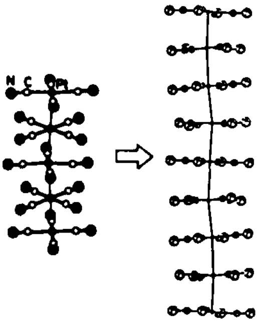


FIGURE 2 The "four-fold ↔ eight-fold transition" of K(def)TCP at 294 K.

The four-fold structure transforms to eight-fold structure below 294 K.[6] The eight-fold structure can be easily interpreted in terms of the mixed-valence:

$$(Pt^{II}PT^{II}Pt^{II}Pt^{II}Pt^{II}Pt^{II}Pt^{II}Pt^{IV})....$$

Relatively unstable valence state Pt^{III} will tend to transform to more stable states, Pt^{II} and Pt^{IV}. Thus, the 294 K transition of K(def)TCP is a mixed-valence transition.

Unlike KCP, the packing of the Pt-chains has a slightly modified hexagonal symmetry. Although

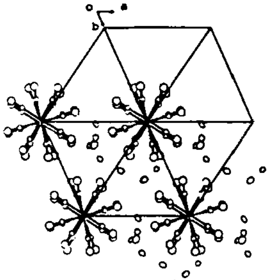


FIGURE 3 Projection of K(def)TCP along the PT-chain

the packing is considered to become more compact at high pressure, the single crystal X-ray studies could obtain no indication of the transition. At 20 Kbar, the X-ray spots become diffuse.

Molecular deformation

The detailed examination of the $2k_F$-structure of $Rb_{1.67}[Pt(C_2O_4)_2]\cdot1.5H_2O$ (RbDOX) shows that the $2k_F$-wave accompanies the molecular deformation.[7]

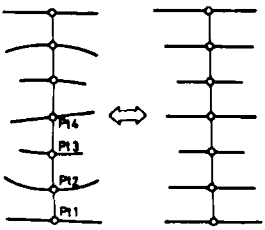


FIGURE 4 Schematic drawing of the molecular distortion in RbDOX and the possible phase transition

The bending of the molecules will disappear at high pressure.

PRESSURE INDUCED PHASE TRANSITION IN KCP(Br)

The pressure dependence of the lattice constants of KCP(Br) has been already reported by Interrante and Bundy.[3] But we have redetermined them by use of a precession camera and a miniature diamond anvil pressure cell.

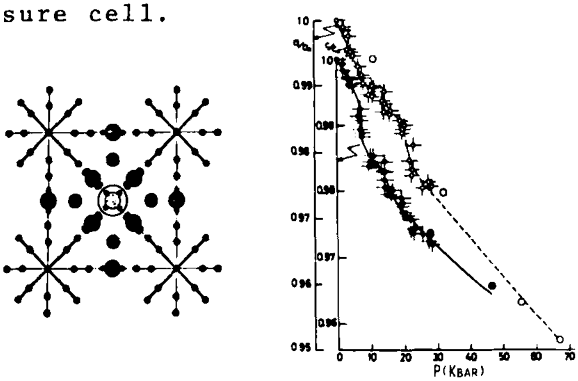


FIGURE 5 Pressure dependence of the lattice constants and the crystal structure of KCP(Br) at ambient pressure

Two anomalous pressures were obtained (7 and 20 Kbar). Using the reflection data collected with precession camera (and partly diffractometer), the high pressure structures were determined at 6, 14 and 21 Kbar. The crystal structure at 6 Kbar is almost identical to that at ambient pressure (Fig.6).

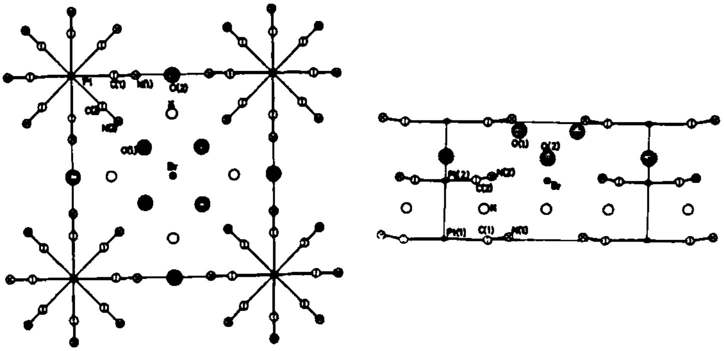
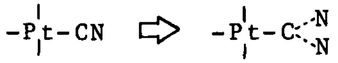


FIGURE 6 Structure at 6 Kbar

However, above 7 Kbar a water molecule (O(2)) is shifted about 0.5 A from the original position. Difference Fourier synthesis calculated based on the intensity data collected at 21 Kbar by precession camera suggested that the molecular structure of $Pt(CN)_4$ is strongly deformed.[8] However,



$$-\mathrm{Pt}-\mathrm{CN} \Rightarrow -\mathrm{Pt}-\mathrm{C}\langle^{\mathrm{N}}_{\mathrm{N}}$$

the least-square refinement could not be made satisfactorily. So that the refinement was repeated using the data newly collected by diffractometer. Although the difference synthesis calculated based on the final atomic parameters shows large peaks around N, the crystal structure thus obtained is similar to that at 14 Kbar (Fig. 7). Interrante and Bundy have found that the conductivity decreases above 30 Kbar.[8] There may be some serious structural change around this pressure.

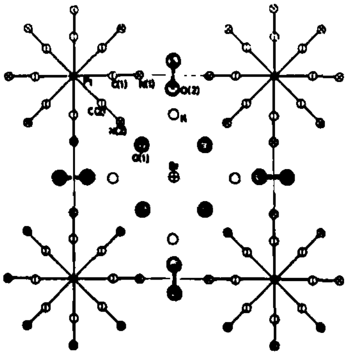


FIGURE 7 Structure above 7 Kbar

The anomalous pressure of 7 Kbar (Fig. 5) agrees with the pressure where the room-temperature transverse conductivity is maximum(Fig. 8).[1] Accord-

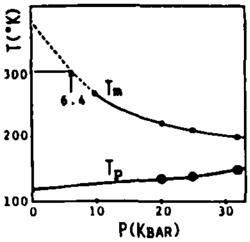


FIGURE 8 Pressure dependence of T_p and T_m

ing to Thielemans et al., at T_m the periodical distortion wave appears. The temperature interval $T_m - T_p$ (fluctuation depressed Peierls transition) is the domain of fluctuation. The agreement between the transition pressure of 7 Kbar and 6.4 Kbar in the phase diagram appears to show that there is a real phase transition at the pressure and temperature where the fluctuating lattice modulation wave begins to appear in the crystal.

The transverse compressibility anomaly around 20 Kbar may be associated with the fact that 3-D Peierls transition has been observed above 20 Kbar.

Compressibilities of $Rb_2[Pt(CN)_4](FHF)_{0.4}$ (RbCP(FHF))

RbCP(FHF) exhibits a high conductivity ($1600(\Omega cm)^{-1}$). The crystal structure has been determined by J. Williams et al.[9] However, we have found the extra reflections forbidden by the reported space group(I4/mcm). The redetermined structure is shown in Fig. 9 (space group $P4_2/mmc$). The periodical modulation of the occupancy probabilities of anion(FHF) sites and the positions of Rb sites are observed. The compressibilities parallel and perpendicular to the Pt-chain were determined up to 30 Kbar. Anomalous compression of the Pt-chain was obtained around 13 Kbar, which resembles the anomaly observed in KCP(Br) at 7 Kbar. The Pt...Pt distance become very short. At 30 Kbar it is 2.72A, which is 0.05 A shorter than the nearest-neighbor Pt...Pt distance in the platinum metal.

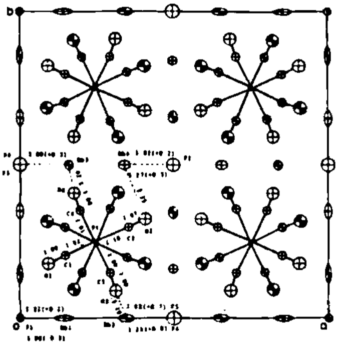


FIGURE 9 Structure of RbCP(FHF) at ambient pressure

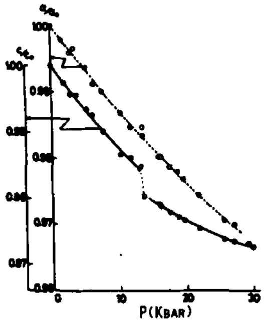


FIGURE 10 Pressure dependence of the lattice constants

REFERENCES

1. M. Thielemans, R. Deltour, D. Jerome and J. R. Cooper, Solid State Commun., 19, 21 (1976)
2. H. Kobayashi, I. Shirotani, A. Kobayashi and Y. Sasaki, Solid State Commun., 23, 409(1977); A. Kobayashi, Y. Sasaki, I. Shirotani and H. Kobayashi, Solid State Commun., 26, 653 (1978)
3. L. V. Interrante and F. P. Bundy, Solid State Commun., 11, 1641 (1972)
4. W. Denner, H. Schulz and H. d'Amour, Acta Cryst., A35, 360 (1979)
5. J. Williams, K. D. Keefer, D. M. Washecheck and N. P. Enright, Inorg. Chem., 15,2446 (1976) ; A. H. Reis, S. W. Peterson, D. M. Washecheck and J. S. Miller, Inorg. Chem., 15, 2455 (1976)
6. H. Kobayashi, Y. Hano, T. Danno, A. Kobayashi and Y. Sasaki, Chem. Letters, 1980, 177; A. J. Epstein and J. S. Miller, Solid State Commun., 29, 345 (1970)
7. A. Kobayashi, Y. Sasaki and H. Kobayashi, Bull. Chem. Soc. Japan, 52, 3682 (1979)
8. H. Kobayashi, A. Kobayashi, K. Asaumi and S. Minomura, Solid State Commun., 35, 293 (1980)
9. A. J. Schultz, C. C. Coffey, G. C. Lee and J. Williams, Inorg. Chem., 16, 2129 (1977)