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STRUCTURAL STUDY ON NOVEL MOLECULAR SYSTEM WITH HYDROGEN-BONDINGS

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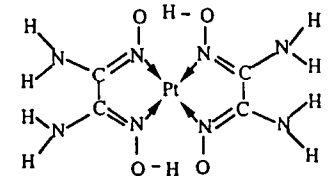
Abstract The crystal structure of [Pt(H_2DAG)(HDAG)]TCNQ (H_2DAG = diaminoglyoxime) was determined at 150K by use of a newly developed X-ray system based on an imaging plate with a closed cycle He refrigerator. The compound showed unusual changes in the crystal structure that the interplanar spacings between the transition-metal-complex stacks were extended from 3.4(r.t.) to 3.6(150K)Å. The TCNQ molecules exhibit large distortions in the bond lengths and angles. In [Pt(H_2DAG)(HDAG)]TCNQ, a decreasing of the Pt-N distance was observed. The charge transfer from Pt (*d* electronic chains) to TCNQ (π electronic chains) was suggested by these experimental results.

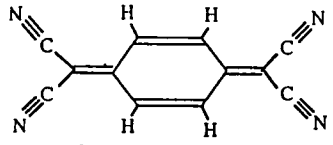
INTRODUCTION

A novel molecular system has been proposed, in which *d* and π electronic states are interacting through H-bonding networks. As a typical material of this system, we have investigated [M(H_2DAG)(HDAG)]TCNQ (M=Pt, Pd, or Ni) which consists of segregated stacks of 1-D transition-metal-complex and organic-acceptor chains with interchain H-bondings.

Figure 1 shows a projection of the structure along the stacking axis *a* in the Pt salt. This salt shows a metal-insulator transition around 250K[1]. From XPS measurements the valency of Pt was confirmed to change from Pt^{II} mono valence to Pt^{II}-Pt^{IV} mixed valence. Vibrational spectra of CN stretching mode indicate the occurrence of large distortions in TCNQ molecules with decreasing temperature[1]. In order to obtain the structural information under low temperature, single-crystal X-ray analysis was performed at 150K and r.t.



Transition metal complex
$Pt(H_2DAG)(HDAG)$



Organic acceptor
TCNQ

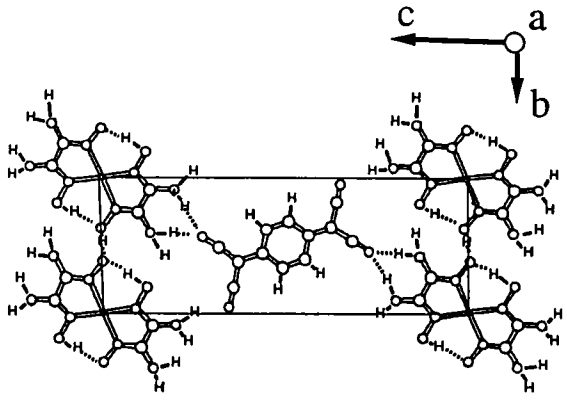


FIGURE 1 The projection of the crystal structure of $[Pt(H_2DAG)(HDAG)]TCNQ$ along the stacking axis (*a*)

EXPERIMENTS

The single crystal of $[Pt(H_2DAG)(HDAG)]TCNQ$ was obtained by the same method as reported by H.Endress[2]. A needle crystal with a size of 0.1 x 0.1 x 0.2 mm^3 was put on a steel chip, which was attached to the copper stick on the cold head of He refrigerator. All measurements were made on an imaging-plate system (MAC Science Co., Inc.) with the monochromatic MoKα radiation using the cryostat (DAIKIN Industries, Ltd.). In order to cool to 4K, this cryostat was equipped with three shields made of carbon fibers and organic films around the sample. In our X-ray system, the centering of crystals can be performed automatically by measuring total intensity of selected reflections with changing the sample position. So, it is easy to measure X-ray diffractions with opaque carbon shield at low temperatures. For the measurement of 150K, only the outside carbon shield was used.

From 30 Weissenberg photographs taken at 150K and r.t., 1252 independent reflections ($I > 3\sigma I$) were obtained. The crystal structures were determined by the direct method. The absorption correction was not carried out. The structure was refined with anisotropic temperature factors for the non-H atoms. A difference Fourier map revealed the two positions out of seven H atoms at 150K; oxime hydrogens and four H

atoms of an amino group did not show up at 150K. As all of the H positions could not be located, all H atoms were omitted in the final calculations. The final R (Rw) values at 150K and r.t. were 0.045 (0.074) and 0.036 (0.044), respectively. No cell doubling, unusual change in cell dimensions, or change in diffraction symmetry (symmetric reflection absences) was detected in scattering patterns. Unit cell dimensions were shown at Table 1.

TABLE1 Crystal data for [Pt(H_2DAG)(HDAG)]TCNQ

$PtC_{16}N_{12}O_4H_{15}$		M=634.47
Triclinic		
$P\bar{1}$		
Z=1		
T(K)	150	295
a (Å)	3.808	3.811
b (Å)	7.561	7.565
c (Å)	17.375	17.382
α (°)	89.078	89.123
β (°)	87.647	87.673
γ (°)	85.418	85.434

RESULTS AND DISCUSSION

Intermolecular Displacements

On cooling to 150K the transition-metal-complex spacing are increased from 3.4 to 3.6 Å in spite of the stacking-axis (a) contraction. The TCNQ spacing, on the other hand, changes less on cooling(the distance is 3.2 Å). In spite of the contraction of the a-axis, the interplanar spacing is extended. This is compensated by the large change (about 10 degrees) in the angle that the transition-metal-complex mean molecular plane makes with the a-axis. The interplanar change of the tilt in transition-metal-complex causes an increase of dz^2 orbital-to-orbital overlap for Pt, which suggests a decrease of repulsion of dz^2 electrons. This change corresponds to a partial oxidation for filled dz^2 orbitals of

Pt observed by XPS measurements.

Intramolecular Displacements

Intramolecular bond lengths and angles in both the transition-metal-complex molecule and organic-acceptor molecule also show unique changes (Figure 2-a). In Pt complex, distances of Pt-N become shortened about 0.01-0.02 Å. The decreasing of this bond length may also indicate a partial oxidation for Pt.

The TCNQ molecule exhibits unusual distortions. The two C-C≡N bond lengths, in which N atoms are interacting with N atoms in Pt complexes through H-bondings, are extended and the ring is also asymmetrically distorted. The N(TCNQ) - N(Pt complex) distances become shortened from r.t. to 150K. In other words, interchain H-bondings become stronger. Asymmetric distortions are caused by the interchain H-bondings. In fig.2-b changes from $TCNQ^0$ to $TCNQ^-$, which obtained by the semi-empirical MO calculation (MOPAC), was shown. The agreement between the observed and calculated change is essentially confirmed. This result indicates the reduction of TCNQ.

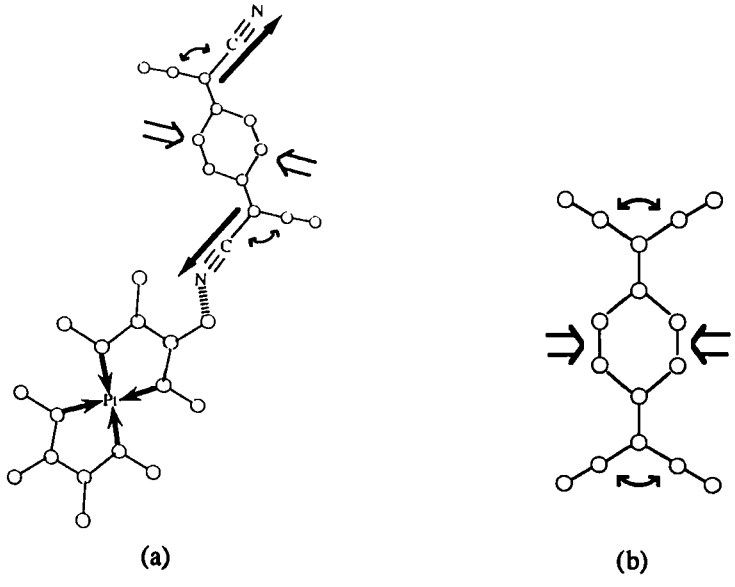


FIGURE 2 (a) The transformation of $Pt(H_2DAG)(HDAG)$ and TCNQ from room temperature to 150K (b) Changes of TCNQ from $TCNQ^0$ to $TCNQ^-$

The charge transfer from d to π electronic states was confirmed by these experimental results. The degree of charge transfer (about 0.7) at room temperature was estimated by using of infrared-absorption, Raman-scattering and X-ray-diffraction measurements. It may be predicted that the degree changed from 0.7 to 1.0 with decreasing temperature because of the charge transfer from d to π. It is suggested that the metal-insulator transition in this complex may be caused by the charge transformation on TCNQ from $\rho \approx 0.7$ to $\rho \approx 1.0$ (half-filling).

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