Vapochromism

Vapochromic Behavior Accompanied by Phase Transition between Charge-Polarization and Charge-Density-Wave States in a Quasi-One-Dimensional Iodine-Bridged Dinuclear Platinum Compound**

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One-dimensional (1D) materials have attracted great attention for several decades in the fields of chemistry and physics, because they exhibit characteristic optical properties that originate from 1D electronic structures as well as magnetic and transport properties.[1] Some 1D materials have been reported to show striking and reversible changes in color and/or luminescence upon exposure to volatile organic compounds and water vapor. This spectroscopic change in the presence of vapor is called vapochromism, which is a promising phenomenon for chemical-vapor-sensing devices.[2] Typical vapochromic materials are the series of compounds $[Pt(CNR)_4][Pt(CN)_4]$ ($R = p\text{-CN-C}_6H_4\text{-C}_nH_{2n+1}$; $n = 1, 2, 6, 10, 12, 14$), which are square-planar Pt^{II} compounds that form linear chains of alternating $[Pt(CNR)_4]^{2+}$ dications and $[Pt(CN)_4]^{2-}$ dianions.[2b,d] The vapochromism of these complexes is suggested to be a result of the change in the Pt···Pt distance,[2d] which is not related to instabilities of 1D electronic structures such as Peierls and spin-Peierls instabilities. Herein, we report a new type of vapochromism driven by the phase-transition characteristic of 1D electronic systems. A 1D halogen-bridged dinuclear platinum compound was studied, which displays a reversible phase transition on exposure to water vapor with a remarkable change in structural and optical properties. This compound has a 1D chain structure composed of repeating metal–metal–halogen (MMX) units, in which M = Pt and X = I, called an MMX chain.

A 1D electronic structure is formed in the MMX chain compound by the d_{z^2} orbitals of the M atoms and the p_z orbitals of the X atoms. The formal valence of M is 2.5+, and three electrons exist per two d_{z^2} orbitals. The following four charge-ordering (CO) states are theoretically expected in this system:[3]

a) $\text{-M}^{2.5+}\text{-M}^{2.5+}\text{-X-M}^{2.5+}\text{-M}^{2.5+}\text{-X-}$
average-valence (AV) state

b) $\cdots\text{M}^{2+}\text{-M}^{2+}\cdots\text{X-M}^{3+}\text{-M}^{3+}\text{-X}\cdots$
charge-density-wave (CDW) state

c) $\cdots\text{M}^{2+}\text{-M}^{3+}\text{-X}\cdots\text{M}^{2+}\text{-M}^{3+}\text{-X}\cdots$
charge-polarization (CP) state

d) $\cdots\text{M}^{2+}\text{-M}^{3+}\text{-X-M}^{3+}\text{-M}^{2+}\cdots\text{X}\cdots$
alternating charge-polarization (ACP) state

Two families of the MMX chain compounds, namely, $A'_4[Pt_2(pop)_4X]\cdot n\,H_2O$ ($A' = K, NH_4$; pop $= P_2O_5H_2^{2-}$; X = Cl, Br)[4] and $[M_2(dta)_4I]$ (M = Pt, Ni; dta $= CH_3CS_2^-$),[5] were reported in the early stage of the studies. The ground state of the former was revealed to be the CDW state. For $[Pt_2(dta)_4I]$, a transition from the CP to the ACP state was suggested to occur at 80 K,[5d] while $[Ni_2(dta)_4I]$ was considered to have the AV state.[5c] The I-bridged compounds have a larger hybridization between the p orbital of the X atom and the d orbital of the M atom than the Cl- or Br-bridged compounds, so various CO states are expected to be stabilized. In preceding papers,[6,7] we reported on the synthesis of about 20 compounds of the type $A'_4[Pt_2(pop)_4I]\cdot n\,H_2O$ and $A''_2[Pt_2(pop)_4I]\cdot n\,H_2O$, with different countercations (A' = Na, NH$_4$, Rb, Cs, $C_nH_{2n+1}NH_3$, and $(C_nH_{2n+1})_2NH_2$; $A'' = NH_3(C_nH_{2n})NH_3$). We demonstrated that substitution of these compounds widely changes the Pt···I···Pt distance (d(Pt-I-Pt)) and that the electronic structures of PtPtI chains are controlled between the diamagnetic CDW and paramagnetic CP states. Moreover, we reported the pressure- and photoinduced phase transition between the CP and CDW states in $[(C_2H_5)_2NH_2]_4[Pt_2(pop)_4I]$.[7] The target material in the present study is $[NH_3(C_4H_8)NH_3]_2[Pt_2(pop)_4I]\cdot 4\,H_2O$ (**1**), which shows vapochromic behavior accompanied by a transition between the paramagnetic CP state and the diamagnetic CDW state.

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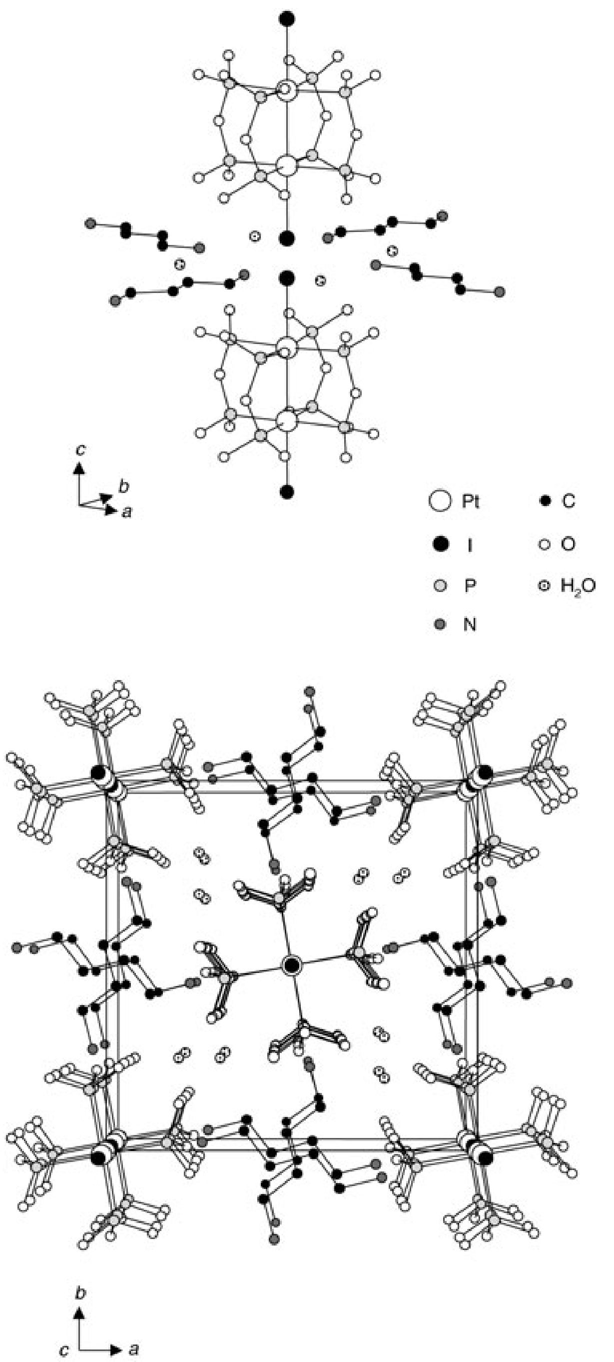

Figure 1. Crystal structure of **1**. H atoms have been omitted for clarity.

Figure 1 shows a perspective view of the crystal structure of **1** at 296 K. Two Pt atoms are linked by four pop ligands to form a $\{Pt_2(pop)_4\}$ unit. The two neighboring $\{Pt_2(pop)_4\}$ units are bridged by I ions, thus forming a PtPtI linear chain along the *c* axis. The bridging I ions are disordered with half occupancies from the midpoints between the neighboring Pt–Pt units, because the displacement of I ions is not three-dimensionally ordered. Therefore, it is difficult to determine from the X-ray structural analysis whether the ground state of **1** is the CDW or CP state. The Pt···Pt distance is 2.837 Å, which is between between that in $K_4[Pt_2^{II}(pop)_4]\cdot 2H_2O$ (2.925 Å)[8a] and that in $K_4[Pt_2^{III}(pop)_4I_2]$ (2.754 Å),[8b] and the Pt···I distance is 2.722 Å. The countercations $[NH_3(C_4H_8)NH_3]^{2+}$ are located in the spaces among the four chains and form hydrogen bonds to the pop ligands. Four H_2O molecules are also located in the spaces.

Raman spectra were measured to obtain information about the CO structure of **1**. Figure 2a shows the polarized Raman spectra of **1** in the usual laboratory humidity at 296 and 340 K. The strong signals at 80–100 cm^{-1} are attributed to the Pt–Pt stretching mode ν(Pt–Pt) of the Pt–Pt unit. An overtone progression of ν(Pt–Pt) up to fourth order is observed in both spectra. At 296 K, a single ν(Pt–Pt) band is observed at 98 cm^{-1}, which indicates the formation of only one kind of Pt–Pt unit. A relatively weak band is also observed at around 115 cm^{-1}. This band can be assigned to the Pt–I stretching mode, which is activated by the displacement of I ions from the midpoint between the neighboring Pt–Pt units. This fact is consistent with the crystal structure of **1** discussed above. Therefore, the ground state of **1** at 296 K can be considered as the CP state. The ν(Pt–Pt) band clearly splits into two components when the temperature is increased from 296 to 340 K, which indicates that there are two kinds of Pt–Pt units, in the present case Pt^{II}–Pt^{II} (86 cm^{-1}) and Pt^{III}–Pt^{III} (94 cm^{-1}), while the Pt–I stretching mode seems to be still activated. Therefore, the electronic phase at 340 K is reasonably classified as the CDW phase.

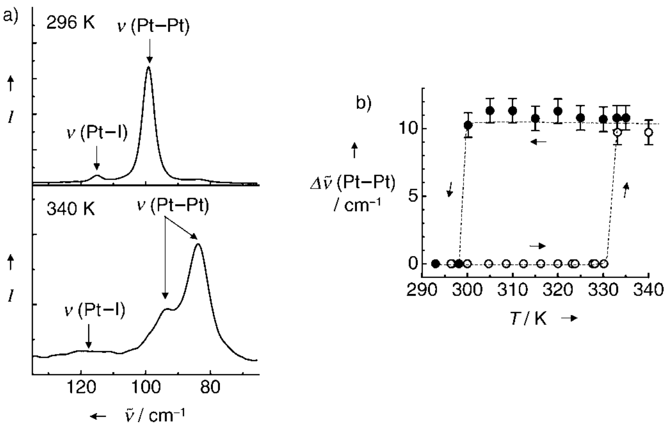

Figure 2. a) Polarized Raman spectra for the polarization of $z(x,x)z$ ($x \parallel c$ axis) at 296 and 340 K. b) Temperature dependence of the magnitude of splitting in the Pt–Pt stretching Raman band $\Delta\tilde{\nu}$(Pt–Pt).

The temperature dependence of the magnitude of splitting in the Pt–Pt stretching Raman band $\Delta\tilde{\nu}$(Pt–Pt) is shown in Figure 2b. When heated from room temperature, $\Delta\tilde{\nu}$(Pt–Pt) remains at zero within the temperature range from 296 to 330 K but abruptly increases to about 10 cm^{-1} at 333 K. In the cooling run, $\Delta\tilde{\nu}$(Pt–Pt) does not change even at 333 K, but returns to zero at 300 K. This result indicates that the CDW phase can return to the original CP phase by cooling the crystal to room temperature. We confirmed this reversibility by repeating the heating and cooling processes several times. It should be noted that the reversibility largely depends on the humidity. In fact, the CDW phase does not recover to the CP phase on lowering the temperature in a fully dry atmosphere.

We can, however, revive the reversibility by exposing the crystal to water vapor. Thus, the reversibility is not a simple function of temperature. Further studies will be necessary to clarify how the transition between the CP and CDW phases depends on the values of temperature and humidity.

The most striking feature of **1** is that the CP-to-CDW transition is accompanied by a marked color change of the crystal. The polarized reflectivity spectra and corresponding microscope images of the sample are presented in Figure 3a.

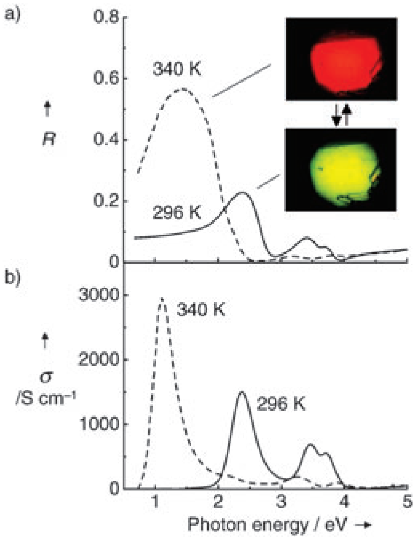

Figure 3. a) Polarized reflectivity and b) optical conductivity spectra with polarization of light parallel to the *c* axis in **1** at 296 and 340 K. The insets in (a) show the corresponding microscope images for the single crystal taken in reflection mode.

Compound **1** is yellow–green at 296 K as a result of the peak at 2.37 eV; on increasing the temperature up to about 340 K, the color changes to red–brown. This color is primarily a result of the strong reflection band from the near-infrared to the visible region. Such clear chromism is also confirmed by the optical conductivity (σ) spectra (Figure 3b). The peak energy of the lowest charge-transfer (CT) band (E_{CT}) drastically shifts from 2.37 (520 nm) to 1.12 eV (1110 nm). This spectral change is anomalously larger than that of the previously reported vapochromic materials. From a previous theoretical study on the optical excitation in the MMX chain compounds,[3c] the lowest CT band observed at 2.37 eV in the CP phase can be assigned to intradimer CT excitation from [-I$\cdots$Pt^{2+}-Pt^{3+}-I$\cdots$Pt^{2+}-Pt^{3+}-I-] to [-I-Pt^{3+}-Pt$^{2+}\cdots$I$\cdots$Pt^{2+}-Pt^{3+}-I-], while the CT band at 1.12 eV in the CDW phase is attributable to the interdimer CT band from [-I$\cdots$Pt^{2+}-Pt$^{2+}\cdots$I-Pt^{3+}-Pt^{3+}-I-] to [-I$\cdots$Pt^{2+}-Pt^{3+}-I$\cdots$Pt^{2+}-Pt^{3+}-I-]. The CP-to-CDW transition and the resultant change of the origin for the optical gap are responsible for the observed chromism. The gap energy $E_{CT} = 1.12$ eV at 340 K is nearly equal to that of other compounds in the CDW phase.[7] The *d*(Pt-I-Pt) value is relatively small in the CDW compounds compared to that in the CP compounds. Therefore, it is reasonable to consider that the observed CP-to-CDW transition is driven by the decrease in the value of *d*(Pt-I-Pt).

Thermogravimetric analysis (TGA) was performed in a dry nitrogen atmosphere to gain an insight into the mechanism of the phase transition (Figure 4). Compound **1** shows a gradual weight loss when the temperature is increased from room temperature, and has lost 5.450 % of its weight at 395 K. This value is in good agreement with that calculated (5.365 %) for the loss of four H_2O molecules per formula unit. The compound then shows a minor weight loss ($< 0.5\%$) up to approximately 500 K. There is a discrepancy in the temperature dependence of the water losses observed in TGA (Figure 4) and the valence changes observed in the Raman spectra (Figure 2b). This discrepancy is considered to be for the following reason: It is natural to consider that the water molecules near the surface of the crystal are lost more readily than those inside the crystal. The total water loss of the sample is probed in the TGA measurement, whereas the Raman spectra sensitively reflect changes in the penetration depth of the pump light (1.96 eV), which is much smaller than the thickness of the crystal ($\geqslant 10$ μm). These optical and TGA results demonstrate that the transition between the CP and CDW states is triggered by desorption and absorption of water molecules. Powder X-ray diffraction measurements were also performed to investigate the vapochromic structural changes. The diffraction pattern of **1** heated at 353 K in vacuum shows that the crystal has converted into some new, and as yet unidentified, crystal structure. Further studies will be necessary to determine the details of this structural transition.

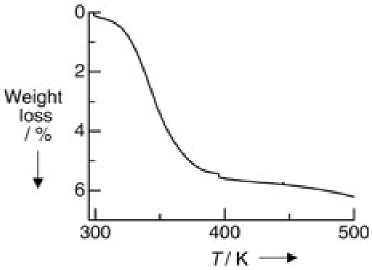

Figure 4. TGA trace of **1** under a dry nitrogen purge at 5 K min^{-1}.

In conclusion, we have found a novel reversible vapochromic behavior accompanied by a phase transition between the paramagnetic CP state and the diamagnetic CDW state in the MMX compound $[NH_3(C_4H_8)NH_3]_4[Pt_2(pop)_4I]\cdot 4H_2O$. The results presented here lead us to expect that the MMX chain compound is a versatile candidate for future chemical-vapor-sensing devices.

Experimental Section

The starting compounds $K_4[Pt_2(pop)_4]\cdot 2H_2O$ and $K_4[Pt_2(pop)_4I_2]$ were prepared according to the methods previously described.[4b] Single crystals of **1** were grown by the standard diffusion method using an H-shaped glass cell. Aqueous solutions (2 mL each) of $[NH_3(C_4H_8)NH_3]SO_4$ (2 mg) and of $K_4[Pt_2(pop)_4]\cdot 2H_2O$ (20 mg) and $K_4[Pt_2(pop)_4I_2]$ (20 mg) were loaded at the ends of the cell and allowed to slowly diffuse in water at room temperature. After about a week, yellow–green needle crystals were obtained. Elemental analysis (%) calcd for $C_{10}H_{48}IN_4O_{24}P_8Pt_2$: C 7.14, H 3.30, N 4.16; found: C 7.15, H 3.20, N 4.13.

X-ray structural analysis of **1** was performed by using a Rigaku RAXIS-RAPID imaging-plate diffractometer with graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å). Crystal data for **1** at 296 K: $M_r = 1343.31$, tetragonal, space group $I4/m$, $a = 13.3474(8)$, $c = 9.8091(7)$ Å, $V = 1747.5(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.553$ g cm^{-3}, final $R = 0.0351$, $wR = 0.138$, GOF = 1.587 with $I > 3.00\sigma(I)$. CCDC-245189 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polarized Raman spectra of **1** were measured by using a Renishaw Ramascope 1000B Raman spectrometer with a continuous-wave He–Ne laser (1.96 eV) and an optical microscope. Polarized reflectivity spectra were obtained by using a specially designed spectrometer with a 25-cm-grating monochromator and an optical microscope. TGA was carried out under a dry nitrogen atmosphere using the Rigaku Thermo plus2 TG 8120 analyzer.

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