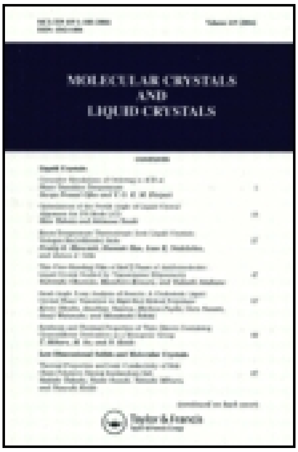

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Structural and Optical Properties of Pt 2 (dtp) 4 Br 2 (dtp =dithiopropionato) and its Halogen-Replacement Effect

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Structural and Optical Properties of $Pt_2(dtp)_4Br_2$ (*dtp* = dithiopropionato) and its Halogen-Replacement Effect

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A novel binuclear Pt(III) complex, $Pt_2(dtp)_4Br_2$ (*dtp* = $CH_3CH_2CS_2^-$, dithiopropionato), was synthesized by a reaction of $Pt_2(dtp)_4$ and Br_2 in refluxing toluene, which could be used as starting material for a new MMX-chain system such as a possible mixed-valence $Pt_2(dtp)_4Br$. The title complex has been characterized by X-ray single-crystal structure analysis, UV-Visible-NearIR, IR, and polarized Raman spectroscopies. The $Pt_2(dtp)_4Br_2$ crystallized in monoclinic $P2_1/a$ and this structure is almost same as $Pt_2(dtp)_4I_2$. Halogen-replacement effect from X = I to Br on $Pt_2(dtp)_4X_2$ has been examined. The Pt-Pt distance in X = Br is slightly shorter than that in X = I. Raman peak of the ν(Pt-Pt) mode is slightly shifted to higher wavenumber from X = I to Br. These changes are considered to be mainly caused by the difference of electron densities of antibonding $d_{\sigma*}$ orbitals.

Keywords MMX chain; mixed valence; diplatinum(III) complex; binuclear complex

INTRODUCTION

Halogen-bridged (X) one-dimensional (1-D) binuclear-metal (MM) complexes (MMX-chain complexes) have drawn much attention because of their interesting physical properties such as metallic conduction, metal-insulator transition with 1-D charge ordering, and so on [1]. MMX-chain complexes are classified to two systems with the terminal ligand, the *dta* (*dta* = dithioacetato; $CH_3CS_2^-$) and the *pop* (*pop* = $H_2P_2O_5^{2-}$; diphosphonato) systems [2]. In the *dta* system, there are three main structural components, centric metal, terminal ligand, and bridging halogen. Until now, there have been several reports on the *dta* system with X = I of which alkyl-chain of terminal ligand is lengthened [3], but no report on this system using bromide or chloride as a bridging halide ion. The halogen replacements from X = I to Br or Cl in MMX-chain would bring significant change of physical properties, because the bridging halogen plays an important role in the superexchange or supertransfer interaction between the metal dimers. From these reasons, we have synthesized a Pt(III) complex, Pt_2(*dtp*)$_4Br_2$ (*dtp* = dithiopropionato; $CH_3CH_2CS_2^-$) which could be used as starting material to obtain a new MMX-chain complex with X = Br. In this paper, we report on the structural and optical properties of Pt_2(*dtp*)$_4Br_2$ and the halogen-replacement effect from X = I to Br by X-ray single-crystal structure analysis, UV-Visible-NearIR, IR, and polarized Raman spectroscopies.

EXPERIMENTAL

SYNTHESES

Pt_2(*dtp*)$_4Br_2$ (1): Tetra-dithiopropionato-diplatinum(II), Pt_2(*dtp*)$_4$ [4] , (170.1 mg, 0.213 mmol) was dissolved in 50 ml of toluene under reflux in argon atmosphere. To this strong reddish orange solution was added a solution of bromine (0.43 g, 2.7 mmol) in 10 ml of toluene. The mixture was refluxed for 30 min. with stirring. On cooling, bright red needle crystals with metallic luster separated from the resulting light red solution were collected by suction filtration, washed with toluene, and dried in *vaccuo* (yield 102.2 mg, 50 %). IR (KBr, cm^{-1}): 2970(s), 2922(m), 2864(m), 1450(s), 1373(m), 1326(vw), 1263(w), 1159(s), 1087(m), 1038(m), 972(s), 936(m), 763(vw), 543(vw). Anal. Caled for $C_{12}H_{20}S_8Pt_2Br_2$: C, 14.85; H, 2.08. Found: C, 14.88: H, 2.05.

$Pt_2(dtp)_4I_2$ (2): The $Pt_2(dtp)_4I_2$ was prepared according to the procedure reported [3] .

X-RAY CRYSTAL STRUCTURE DETERMINATION

Intensity data of **(1)** were collected on an Enraf Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 293 K. The structure was solved and refined by using the Crystal Structure software package [5]. Crystal data; crystal dimensions $1.20 \times 0.20 \times 0.10$ mm^3, $C_{12}H_{20}Br_2Pt_2S_8$, fw = 970.76, monoclinic, $P2_1/a$, $Z = 4$, $T = 293$ K, $a = 9.755(7)$, $b = 15.67(1)$, $c = 15.87(2)$ Å, $\beta = 85.03(9)$°, $V = 2417.3(33)$ Å^3, μ(Mo Kα) = 155.19 cm^{-1}, $F(000) = 1784.00$, 10372 reflections measured ($2\theta_{\max} = 52.7$°), of which 10163 were independent and 2202 were observed with $I > 3\sigma(I)$, 239 refined parameters, $R = 0.073$, $Rw = 0.078$.

ELEMENTAL ANALYSIS

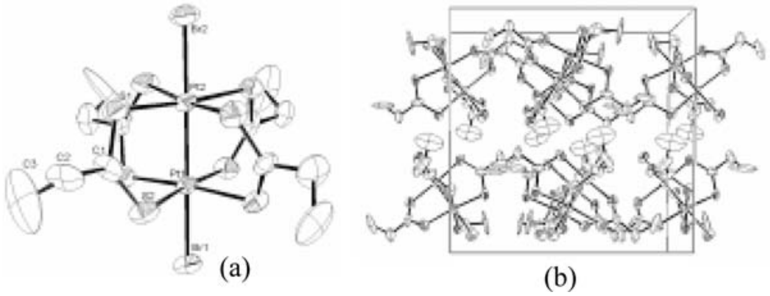
Elemental analysis was performed by a Perkin-Elmer 2400 series II CHNS/O analyzer at the Chemical analysis Center, University of Tsukuba.

OPTICAL MEASUREMENTS

UV-Visible-NearIR spectra of the complexes as KBr pressed disks and toluene solution were recorded on a Jasco V-570 spectrometer. IR spectra were recorded as KBr pressed disks on ThermoNicolet NEXUS 670 FT-IR spectrometer. Polarized Raman spectra were recorded with a Jasco NR-1800 subtractive-dispersion triple (filter single) polychromator using a microscope. A Spectra Physics model 2017 Ar^+ laser provided the exciting line (514.5 nm). Detection of the scattered radiation was made by a cooled Photometrics CC200 CCD camera system with operating temperature of 153 K. Wavenumber calibration was made based on the emission lines of Ne lamp.

RESULT AND DISCUSSION

The ORTEP and packing diagrams of **(1)** are shown in FIGURE 1. The complex **(1)** crystallized in the monoclinic $P2_1/a$. Two platinum atoms of the complex are bridged by four *dtp* ligands. Each platinum atom is six coordinated in a tetragonally distorted octahedral geometry and being surrounded by four sulfur atoms in an approximately square-planar arrangement and a bromide and the other platinum atom in apical positions. The two PtS_4 planes are twisted by the angle of ca. 25.6° from the eclipsed D_{4h} structure. The structure of **(1)** is almost equal to that of **(2)** [3]. The Pt-Pt distance of 2.572(4) Å in **(1)** is slightly shorter than that in **(2)** (2.582(1) Å) [3]. This is due to the difference in the electron densities of antibonding $d_{\sigma*}$ orbital, that is the difference in the σ-donations from axial halide p_z orbital. The Br-Pt-Pt-Br sequence is almost linear. The two Pt-Br distances (2.573(5) and 2.578(5) Å) are the same within standard deviations.



(a)

(b)

FIGURE 1 (a) ORTEP diagram of **(1)** with 50% thermal ellipsoids. (b) Packing diagram projected along the *a* axis for **(1)**.

Electronic spectra of **(1)** and **(2)** are shown in FIGURE 2. The spectra of two complexes are very similar both in solid and solution state. An important feature of the absorption spectra is the intense band at ca. 2.5 eV. These bands are assigned to LMCT (Ligant-to-Metal Charge Transfer) transition, $p_\sigma(X) \rightarrow d_{\sigma*}(M)$. The energy of LMCT band is higher in **(1)** than that in **(2)**, because the energy level of $p_\sigma(X)$ is shifted to lower energy with changing X from I to Br.

The observed bands around at 3.5 and 4.2 eV are also assigned to $d_{\pi^*}(M) \rightarrow d_{\sigma^*}(M)$ and $d_{\pi^*}(M) \rightarrow p_\sigma(M)$ transitions, respectively.

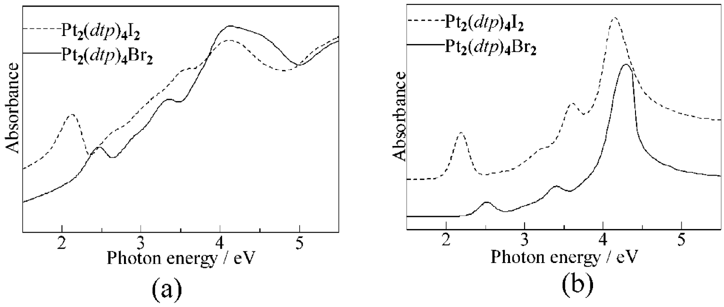


FIGURE 2 Electronic spectra of **(1)** and **(2)** in KBr disk (a) and in toluene solution (b).

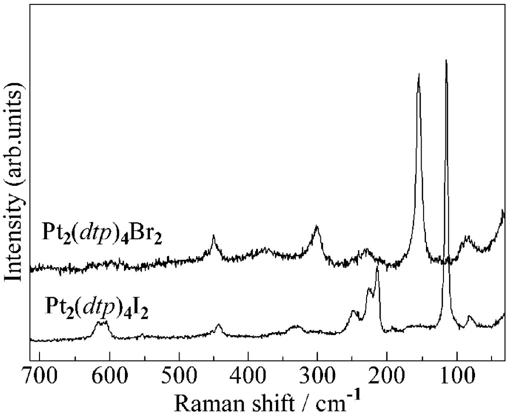


FIGURE 3 Polarized Raman spectra of **(1)** and **(2)**.

Polarized Raman spectra of **(1)** and **(2)** are shown in FIGURE 3. The peaks at 154 and 300 cm^{-1} in **(1)** are assigned to ν(Pt-X) mode and its overtone. The strong peak at 114 and 226 cm^{-1} in **(2)** is also assigned as well, which is shifted to lower wavenumber than that in **(1)**. The weak peaks at 86 cm^{-1} in **(1)** and 81 cm^{-1} in **(2)** are assigned to the ν(Pt-Pt) modes. This slight shift is due to the difference in the electron densities of antibonding d_{σ^*} orbitals of **(1)** and **(2)**.

Acknowledgements

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