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Synthesis and Synchrotron Radiation Structure Analysis of Tetra-Dithiopropanato-Diplatinum(II) with Infinite Linear Chain Structure

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Diplatinum(II) complex, $Pt_2(EtCS_2)_4$, is synthesized and characterized by X-ray crystal structure analysis using a synchrotron radiation at SPring-8. The crystal structure consists of diplatinum units stacking in columns along the four-fold axis, with intra and interdimer Pt-Pt distances of 2.764(1) and 3.428 (1) Å, respectively.

Keywords: diplatinum(II) complex; crystal structure; synchrotron radiation; linear chain structure

INTRODUCTION

Halogen-bridged one-dimensional diplatinum complex, $Pt_2(dta)_4I$ (dta = $MeCS_2^-$), which was first prepared and characterized by Bellitto et al.,[1] shows anomalous electrical conducting behavior (> 300 K, metallic)[2] and structural phase-transition at 371–372 K.[3] In order to clarify the anomalous structural and solid-state properties observed for $Pt_2(dta)_4I$, it should be an effective approach to investigate the correlation between the solid-state properties and the geometric and electronic structures systematically for a series of the chemically modified halogen-bridged

one-dimensional diplatinum complexes. In order to study such chemistry, it is necessary to synthesis the precursor complex, $Pt_2(RCS_2)_4$. Here we report the synthesis and crystal structure of the complex, $Pt_2(EtCS_2)_4$, containing dithiopropanate ($EtCS_2^-$) as a bidentate ligand.

EXPERIMENTAL

Synthesis

To a solution of dithiopropanoic acid[14] (1.95 g, 18.4 mmol) in 300mL of toluene was added $PtCl_2(NCPh)_2$ (2.16 g, 4.58 mmol) under argon atmosphere. The mixture was refluxed for 2h with stirring. The solution turned dark red. On cooling, the brownish olive needles separated from the solution was collected, washed with toluene. The crude product was recrystallized from toluene to afford 1.41 g (71% yield based on $PtCl_2(NCPh)_2$) of $Pt_2(EtCS_2)_4$ as brownish olive needles with copper luster. IR (KBr, cm^{-1}): 2978 (w), 2929 (w), 2910 (vw), 2868 (vw), 1456 (w), 1450 (w), 1425 (m), 1365 (w), 1298 (w), 1273 (w), 1157 (s), 1099 (vw), 1045 (m), 962 (s), 947 (m), 939 (m), 783 (vw), 615 (vw), 538 (w). Anal. Calcd for $C_{12}H_{20}Pt_2S_8$: C, 17.77; H, 2.49. Found: C, 17.77; H, 2.44.

X-ray Crystal Structure Analysis

A crystal of $Pt_2(EtCS_2)_4$ having dimensions of 40 x 50 x 100 μm^3 was mounted on a glass fiber with epoxy resin. The measurement was carried out using a vacuum X-ray camera and a synchrotron radiation (20 keV, λ = 0.62 Å) monochromated by a Si(111) double crystal and a

mirror at beam line BL02B1 at SPring-8. The data was collected with ϕ-oscillation method with imaging plate (IP) area detector at 298 K. 25 frames of 8 ° oscillation range were used, starting at 0, 7 °, etc. in ϕ. Indexing and integration of intensities were made by applying the DENZO program. The unit cell was determined using the SCALEPACK program. The crystallographic data are tetragonal with space group $P4/n$, a = 13.122 (1) Å, c = 6.192 (1) Å, V = 1066.2 (2) Å^3, Z = 2, and D_{calc} = 2.526 g cm^{-3}. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were placed in the calculated positions. 2077 reflections were collected, of which 836 unique reflection were used for refinement. Structural analysis was made by the teXsan, converging to R = 0.043, R_w = 0.063.

RESULTS AND DISCUSSION

An ORTEP diagram of $Pt_2(EtCS_2)_4$ is shown in FIGURE 1 and a stereoview of the unit cell is shown in FIGURE 2. The crystal structure consists of diplatinum units stacking in columns on the crystallographic four-fold axis parallel to the c axis, with interdimer

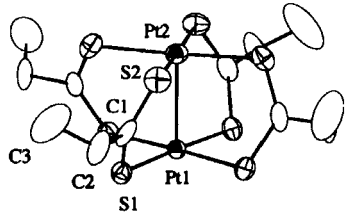

FIGURE 1 ORTEP diagram of $Pt_2(EtCS_2)_4$ with atomic numbering scheme and 50 % thermal ellipsoids.

Pt···Pt distance of 3.428 (1) Å. Similar linear chain structures were observed for $Pt_2(RCS_2)_4$ (R = Me[5], *i*-Pr[6,7], *n*-C_6H_{13}[8], $PhCH_2$[7]). Two platinum atoms are bridged by four dithiopropanato ligands and the Pt–Pt distance is 2.764 (1) Å, which is ca. 0.09 Å shorter than the distance between the mean planes defined by the four sulfur atoms. This intramolecular Pt–Pt bonding interaction would be attributed to hybridization of the vacant Pt–Pt pσ or pσ* orbital and the occupied Pt–Pt dσ or dσ* orbital, as has been pointed out Kawamura et al.. [8] Furthermore, the interaction of the vacant pσ and occupied dσ* orbitals of adjacent diplatinum units would contribute to intermolecular Pt–Pt binding interactions. [8] The Pt–S distances are 2.322 (4) and 2.324 (4)

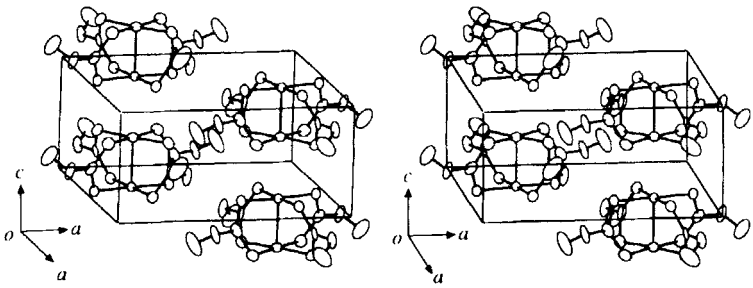

FIGURE 2 A streoview of the unit cell of $Pt_2(EtCS_2)_4$.

Å and the Pt–Pt–S angle is 91.1 °. In the dithiopropanato ligand, the C–S distances are 1.68 (2) and 1.71 (1) Å, the S–C–S angle is 127 (1) °, and the Pt–S–C angle is 109.6 (6) and 110.0 (6) °. The torsion angle concerning Pt–Pt axis is S(1)–Pt(1)–Pt(2)–S(2) = 26.4 (2) ° and then the two PtS_4 planes are twisted by ca. 26 ° from the eclipsed D_{4h} structure. The interdimer S···S distance is 3.503 (6) Å, which is shorter than the van der Waals contact distance of sulfur atoms (3.60 Å).

The electronic absorption spectra in the toluene solution and

solid-state (dispersed in KBr) are shown in FIGURE 3. The solid-state spectrum shows a low energy band (17.0 x 10^3 cm^{-1}) below the lowest transition energy in solution. Similar behavior was observed for $Pt_2(RCS_2)_4$ (R = Me[5], *i*-Pr[6,7], *n*-C_6H_{13}[8], $PhCH_2$[7]). The low energy band observed in the solid-state should arise from electronic interactions between diplatinum units in the linear stack. [7,8]

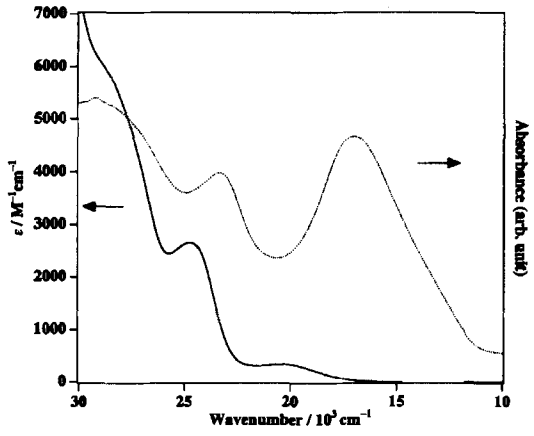

FIGURE 3 Electronic absorption spectra of $Pt_2(EtCS_2)_4$ in toluene solution (—) and solid state (dispersed in KBr) (·····).

TABLE 1 Electronic Absorption Spectral Data

	λ_{max} / 10^3 cm^{-1} ($\log(\varepsilon$ / $M^{-1}cm^{-1})$)
toluene solution	20.2 (2.52), 24.8 (3.42), 28.2 (3.73)(sh), 32.7 (4.51)
solid state	17.0, 23.4, 29.2

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