Instrumental Achievements

Crystal Structure of Bis(diethyldithiocarbamato)palladium(II) Benzene Solvate, $[\text{Pd}(\text{Et}_2\text{dtc})_2] \cdot (\text{C}_6\text{H}_6)$ Masahiko MAEKAWA*[†], Megumu MUNAKATA**[†], Takayoshi KURODA-SOWA** and Masanori MOTOKAWA***Research Institute for Science and Technology, Kinki University,
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Since palladium(II) belongs to a class *b* or a soft metal ion, it forms relatively stable complexes with sulfur- and phosphorous-containing ligands.¹ Many Pd(II) complexes with dithiolate ligands have already been prepared and characterized.¹ Although Pd(II) complexes with dithiocarbamate have been prepared and systematically characterized based on the IR and electronic spectra², the crystal structure has not been reported. In this study we have characterized bis(diethyldithiocarbamato)palladium(II) crystallographically.

Yellow single crystals of $[\text{Pd}(\text{Et}_2\text{dtc})_2] \cdot \text{C}_6\text{H}_6$ (Et_2dtc = diethyldithiocarbamate) (**1**) were obtained from a mixture solution of $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ (46 mg, 1.2×10^{-4} mol), sodium diethyldithiocarbamate (28 mg, 1.2×10^{-4} mol), triphenylphosphine (32 mg, 1.2×10^{-4} mol), NaBH_4 (27 mg, 7.2×10^{-4} mol) and trichloroethylene (1.1 ml, 1.2×10^{-2} mol) in benzene/methanol (16 ml, $v/v=3/5$) after two weeks. Data collection was performed on a Rigaku AFC-5R diffractometer under the conditions given in Table 1. The structure was solved by a direct method

(MITHRIL)³ and an empirical, spherical, absorption correction was performed using a program called DIFABS⁴ after an isotropic refinement for all of the non-hydrogen atoms. The scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 5. A refinement of the non-hydrogen atomic positional and thermal anisotropic parameters was performed by a full-matrix least-squares calculation. The positions of the hydrogen atoms were obtained from a difference Fourier synthesis. All of the calculations were performed using a TEXSAN⁶ crystallographic software package. The atomic positional parameters are given in Table 2.

The molecular structure of **1** is shown in Fig. 1, together with the solvated benzene molecule. Selected bond distances and angles are listed in Table 3. Complex **1** has symmetry center on a Pd(1) atom. The Pd atom is coordinated by four S atoms of two Et_2dtc ligands in a square-planar geometry. The average Pd-S distance of 2.3277(7) Å is within those (2.31–2.35 Å) of the Pd(II) complexes with the dithiolate ligand.⁷ The S(1)–Pd(1)–S(2) angle of 75.09(2)° is also close to those (73.6–75.4°) of the Pd(II) complexes with the dithiolate ligand.⁷ The

Table 1 Crystal and experimental data

Formula: $\text{PdS}_4\text{N}_2\text{C}_{16}\text{H}_{26}$
Formula weight: 481.04
Crystal system: triclinic
Space group: $P\bar{1}$ $Z=1$
$a=8.883(1)$ Å
$b=9.017(2)$ Å
$c=7.446(1)$ Å
$\alpha=111.88(1)^\circ$
$\beta=110.45(1)^\circ$
$\gamma=86.66(2)^\circ$
$V=516.8(4)$ Å ³
$D_{\text{calc}}=1.545$ g/cm ³
$R=0.026$, $R_w=0.038$
No. of reflections used=2198 ($I>3\sigma(I)$)
Measurement: Rigaku AFC-5R
Program system: TEXSAN
Structure determination: direct method (MITHRIL)
Refinement: full-matrix least-square

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters B_{eq} (Å²) of non-hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Pd(1)	1.0000	0	1.0000	3.495(6)
S(1)	0.96033(7)	0.18423(7)	0.8404(1)	4.47(2)
S(2)	1.20899(7)	-0.02717(7)	0.8718(1)	4.52(2)
N(1)	1.1903(2)	0.1784(2)	0.6806(3)	4.15(5)
C(1)	1.1291(2)	0.1203(3)	0.7812(3)	3.79(6)
C(2)	1.3356(3)	0.1165(3)	0.6348(4)	5.18(8)
C(3)	1.4880(3)	0.2127(5)	0.7956(5)	6.9(1)
C(4)	1.1153(3)	0.3070(3)	0.6116(4)	4.94(8)
C(5)	1.1694(5)	0.4716(4)	0.7734(5)	6.9(1)
C(6)	1.3577(5)	0.4374(6)	0.3439(5)	8.4(1)
C(7)	1.4845(6)	0.3476(4)	0.3677(5)	8.1(1)
C(8)	1.6267(4)	0.4089(5)	0.5227(7)	8.5(1)

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$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} (a_i \cdot a_j).$$

Fig. 1 Molecular structure of $[\text{Pd}(\text{Et}_2\text{dtc})_2] \cdot (\text{C}_6\text{H}_6)$ (1).

Table 3 Selected bond distances (Å) and bond angles (°)

Pd(1)-S(1)	2.3253(7)	Pd(1)-S(2)	2.3301(7)
S(1)-C(1)	1.716(2)	S(2)-C(1)	1.718(2)
N(1)-C(1)	1.319(3)	N(1)-C(2)	1.476(3)
N(1)-C(4)	1.472(3)		
S(1)-Pd(1)-S(2)	75.09(2)	S(1)-Pd(1)-S(2')	104.91(2)
Pd(1)-S(1)-C(1)	86.86(8)	Pd(1)-S(2)-C(1)	86.66(8)

intermolecular plane distance among the PdS_4 planes is far apart, and no specific intermolecular stacking was found. The close $\text{Pd} \cdots \text{S}$ distance between the Pd atom and the S atom of the neighboring PdS_4 plane is also 5.981 Å, not indicative of the intermolecular $\text{Pd} \cdots \text{S}$ interaction ($\text{Pd}-\text{S}=3.32$ Å) found in the bis(dithiobenzoato)palladium(II) complex.⁷ Four ethyl groups of

the coordinating Et_2dtc are perpendicular to the PdS_4 plane. Interestingly, two ethyl groups of each Et_2dtc ligand are directed to the same orientation. Two of the four ethyl groups are directed to the upper side of the PdS_4 plane; the other two ethyl groups are directed to the lower side of the PdS_4 plane. This conformation is different from that of free Et_2dtc ⁸, because two ethyl groups of free Et_2dtc are directed to the opposite orientation from each other. The solvated benzene molecule includes almost perpendicular to the PdS_4 planar, although an intermolecular $\pi-\pi$ interaction does not exist among the solvated benzene molecules.

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