

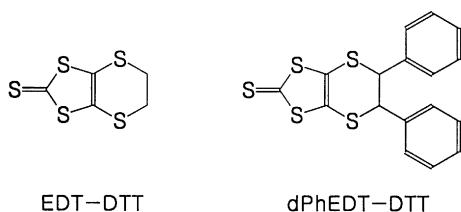
Dimeric Mercury(II) Chloride Complex of Sulfur-rich Ligand : Synthesis and X-ray Crystal Structure of $trans\text{-}[\{\text{Hg}(\mu\text{-Cl})\text{Cl}(\text{dPhEDT-DTT})\}_2] \cdot (\text{CH}_3\text{CN})_2$

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The coordination chemistry of mercury(II) with 5B, 6B and 7B family elements has been intensively studied because their structures mimic the interaction of mercury(II) ion in the biological systems as well as they exhibit the various coordination modes.¹⁻³ Among the ligating elements, sulfur is well known to bind tightly to mercury(II) as the word 'mercaptan' literally means *mercury capturer*.² Recently, we have focused our research interests on the synthesis of new sulfur-rich compounds and their metal complexes^{3,4}. A new sulfur-rich compound dPhEDT-DTT has been synthesized by a Diels-Alder type [2-4] cycloaddition reaction. It was also utilized as a precursor of bidentate thiolate ligand to prepare $[\text{NiL}_2]^{-4c}$ and $[\text{Hg}_2\text{L}_3]^{2-3}$ type metal complexes. Here, we report the synthesis and x-ray crystal structure of $trans\text{-}[\{\text{Hg}(\mu\text{-Cl})\text{Cl}(\text{dPhEDT-DTT})\}_2] \cdot (\text{CH}_3\text{CN})_2$ in which thio-carbonyl sulfur weakly coordinates to mercury(II) ion.



Experimental Section

Infrared spectra were obtained by KBr method on MIDAC FT-IR spectrometer, and UV-vis spectra in acetonitrile on HP 8452A diode array spectrometer. Elemental analysis was carried out at the Korea Basic Science Institute (KBSI).

Synthesis of $trans\text{-}[\{\text{Hg}(\mu\text{-Cl})\text{Cl}(\text{dPhEDT-DTT})\}_2]$. To a 3 mL of methylene chloride solution of dPhEDT-DTT (94 mg, 0.25 mmol) was added a 5 mL acetonitrile solution of HgCl_2 (136 mg, 0.5 mmol) with stirring at room temperature. Reddish orange precipitates were formed immediately. The mixture was heated until the precipitate was redissolved to form orange crystals. The precipitate was collected from filtrate. Diamond-shaped orange crystals suitable for x-ray structural analysis were occasionally obtained from the filtrate after a few minutes' standing. Yield 100%; mp. 136 °C (dec.); Elemental analysis (%) calc. for $\text{C}_{38}\text{H}_{24}\text{Cl}_4\text{Hg}_2\text{N}_2\text{S}_{10}$ C 33.12, H 2.19, S 23.26 found C 32.92, H 2.58, S 23.14; FT-IR (KBr, cm^{-1}) 1489, 1443 (Ar C-C), 1026 (C-S), 740,

714, 695 (Ar C-H); UV-vis (CH_3CN , nm) 222 (st) 276 (w) 406 (m).

X-ray Structural Analysis of $trans\text{-}[\{\text{Hg}(\mu\text{-Cl})\text{Cl}(\text{dPhEDT-DTT})\}_2] \cdot (\text{CH}_3\text{CN})_2$. X-ray crystallographic data of $trans\text{-}[\{\text{Hg}(\mu\text{-Cl})\text{Cl}(\text{dPhEDT-DTT})\}_2] \cdot (\text{CH}_3\text{CN})_2$ were collected on an Enraf-Nonius CAD-4 automatic diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. Intensities of 1830 [R(int) = 0.0929] independent reflections within θ range 2.19-29.02° were measured using $\omega/2\theta$ scan method for the range $-20 < h < 20$, $0 < k < 8$, $-22 < l < 22$. 1830 reflections were considered [$I > 2\sigma(I)$] and used in calculation performed on IBM PC using SHELXS-86 and SHELXS-93, and atomic scattering factors for all nonhydrogen atoms were supplied by the SHELXS-86 system.⁵ As the mixture of (*S,S*)- and (*R,R*)-dPhEDT-DTT enantiomer^{4b} was used as a ligand, the carbon atoms on the phenyl groups as well as C(4) and C(5) are highly disordered, and that they are fixed to $1.5 \pm 0.2 \text{ \AA}$. Crystal parameters and information for data collection are given in Table 1.

Table 1. Crystal data and structure refinement for $trans\text{-}[\{\text{Hg}(\mu\text{-Cl})\text{Cl}(\text{dPhEDT-DTT})\}_2] \cdot (\text{CH}_3\text{CN})_2$

Empirical formula	C38 H24 Cl4 Hg2 N2 S10
Formula weight	1372.17
Crystal system	monoclinic
Space group	Cm(No.8)
Unit cell dimensions	$a = 16.905(2) \text{ \AA}$ $b = 7.262(3) \text{ \AA}$ $c = 18.798(4) \text{ \AA}$ $\beta = 98.10(2) \text{ deg.}$
Volume	$2284.7(11) \text{ \AA}^3$
Z	2
Calculated density	1.995 Mg/m^3
Absorption coefficient	7.434 mm^{-1}
F(000)	1308
Crystal size	$0.10 \times 0.4 \times 0.5 \text{ mm}$
Reflections collected / unique	3362 / 1830 [R(int) = 0.0929]
Completeness to $2\theta = 29.02$	27.9%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1830 / 49 / 226
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0708$, $wR2 = 0.1873$
R indices (all data)	$R1 = 0.0733$, $wR2 = 0.1894$
Absolute structure parameter	0.11(4)
Largest diff. peak and hole	1.926 and $-1.682 \text{ e.\AA}^{-3}$

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$R_1 = \sum |F_o - F_c| / \sum F_o$, $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^2\}^{1/2}$, where $w = 1 / \{\sigma^2(F_o^2) + (0.1206P)^2 + 43.18P\}$ and where $P = \{\text{Max}(F_o^2, 0) + 2F_c^2\} / 3$.

Results and Discussion

Dimeric mercury(II) chloride complex of dPhEDT-DTT was readily prepared by mixing a dichloromethane solution of dPhEDT-DTT with an acetonitrile solution of HgCl₂ with two molar ratio, and isolated without washing with solvent. Interaction between mercury(II) and the ligand was confirmed by FT-IR: C=S frequency of the free ligand (1069 cm⁻¹)^{4b} was shifted to 1026 cm⁻¹, indicating that interaction between mercury(II) and thiocarbonyl sulfur can be assumed. When the product was treated with methanol after filtering, mercury(II) chloride was dissolved and washed out, and only the yellow dPhEDT-DTT ligand left on a fritted disk. It means that the ligand is weakly coordinated to mercury(II) ion and their interactions are easily broken up when dissolved in methanol. This was also confirmed by UV-vis measurement: the absorption for n → π* transition of thiocarbonyl group was observed at 406 nm for mercury complex, which is quite close to that of the free ligand (408 nm).^{4b} If the thiocarbonyl group is coordinated to Hg(II) ion even in the solution state, the electronic transition energy

Table 2. Atomic coordinates (× 10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for *trans*-[Hg(μ-Cl)Cl(dPhEDT-DTT)]₂ · (CH₃CN)₂

	x	y	z	U(eq) ^a
Hg(1)	-741(1)	5671(5)	5868(1)	61(1)
S(1)	-2166(3)	5720(2)	5784(3)	45(1)
S(2)	-1548(2)	5720(3)	4194(3)	46(1)
S(3)	-3217(3)	5680(2)	4693(3)	41(1)
S(4)	-1693(2)	5790(3)	2646(3)	51(2)
S(5)	-3753(2)	5740(3)	3277(3)	55(2)
Cl(1)	0	3233(14)	5000	45(4)
Cl(2)	0	8190(3)	5000	70(6)
Cl(3)	-155(3)	5710(3)	6933(3)	79(3)
C(1)	-2280(11)	5710(6)	4890(10)	40(5)
C(2)	-2164(10)	5740(8)	3509(11)	47(6)
C(3)	-2951(10)	5860(7)	3782(10)	36(5)
C(4)	-2541(13)	5180(3)	2153(12)	51(7)
C(5)	-3257(14)	6090(5)	2479(12)	71(9)
C(6)	-2193(14)	5440(4)	1414(11)	57(8)
C(7)	-1940(3)	3840(8)	968(18)	80(12)
C(8)	-1650(3)	3980(7)	305(18)	63(10)
C(9)	-1490(2)	5410(6)	7(18)	69(15)
C(10)	-1700(4)	7100(10)	420(2)	200(5)
C(11)	-2035(6)	7100(3)	1061(6)	110(3)
C(12)	-3821(6)	5370(3)	1964(6)	64(9)
C(13)	-4200(6)	3780(3)	1675(6)	83(14)
C(14)	-4892(6)	3920(3)	1182(6)	130(2)
C(15)	-5205(6)	5640(3)	978(6)	118(17)
C(16)	-4826(6)	7230(3)	1267(6)	71(13)
C(17)	-4134(6)	7090(3)	1760(6)	72(12)
N	2845(17)	5640(8)	2418(16)	94(11)
C(21)	4097(16)	5960(9)	3033(18)	76(10)
C(20)	3370(2)	5750(10)	2743(15)	81(11)

^aU(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

would be found at different energy.

The crystal structure of *trans*-[Hg(μ-Cl)Cl(dPhEDT-DTT)]₂ · (CH₃CN)₂ was analyzed by x-ray diffraction method. Atomic coordinates are given in Table 2 and selected bond lengths (Å) and angles (°) are given in Table 3. Its molecular structure with the atomic numbering scheme is shown in Figure 1. The mercury has an extremely distorted tetrahedral geometry with two bridging chlorides (Cl(1) and Cl(2)), one terminal chloride (Cl(3)) and one thiocarbonyl sulfur (S(1)). Surprisingly, the bond length of Hg(1)-Cl(3) (2.105(5) Å) is much shorter than that of the polymeric [Hg(μ-Cl)Cl(EDT-DTT)]₂ complex (2.381(1) Å)⁶ and even the shortest Hg-Cl bond (2.25 Å) in HgCl₂.² This is, to our knowledge, one of the shortest Hg-Cl bond ever reported. The bond lengths between mercury and bridging chlorides (2.818(7) Å for Hg(1)-Cl(1) and 2.856(14) Å for Hg(1)-Cl(2)) are close to the sum of ionic radii (2.83 Å).⁷ The Cl-Hg-Cl and Cl-Hg-S angles around Hg(1) are in the range of 110.4(5)-119.8(3)⁹ except that of Cl(1)-Hg(1)-Cl(2) (78.8(2)⁹). It means that Hg(1) adopts the distorted tetrahedral geometry with three chloride and one sulfur atoms, and Hg₂(μ-Cl)₂ core has rhombic geometry.

The C(1)=S(1) bond length (1.66(2) Å) is longer than that of the free ligand (1.634(4) Å)^{4b} because of the additional coordination of S(1) to Hg(1). Moreover, the overall bond lengths and angles of EDT-DTT unit of dPhEDT-DTT ligand deviate significantly from those of the free ligand^{4b} as can be seen in Table 3. For example, three angles around C(1) are 102.0(12), 124.2(11) and 133.8(10)⁹ while those of the free ligand are 124.3(3), 123.4(3) and 112.3(2)⁹. This distortion of the ligand structure can be attributed to the intramolecular close-contacts between sulfur and chloride atoms as shown

Table 3. Selected bond lengths[Å] and angles[deg] for *trans*-[Hg(μ-Cl)Cl(dPhEDT-DTT)]₂ · (CH₃CN)₂

Hg(1)-Cl(1)	2.818(7)	Hg(1)-Cl(2)	2.856(14)
Hg(1)-Cl(3)	2.105(5)	Hg(1)-S(1)	2.392(4)
S(1)-C(1)	1.66(2)	S(2)-C(2)	1.537(18)
S(2)-C(1)	1.92(2)	S(3)-C(1)	1.575(18)
S(3)-C(3)	1.84(2)	S(4)-C(4)	1.65(3)
S(4)-C(2)	1.91(2)	S(5)-C(3)	1.545(17)
S(5)-C(5)	1.837(17)	C(2)-C(3)	1.49(3)
C(4)-C(5)	1.577(19)		
Cl(3)-Hg(1)-S(1)	113.4(2)	Cl(3)-Hg(1)-Cl(1)	111.8(5)
S(1)-Hg(1)-Cl(1)	119.8(3)	Cl(3)-Hg(1)-Cl(2)	110.4(5)
S(1)-Hg(1)-Cl(2)	118.1(4)	Cl(1)-Hg(1)-Cl(2)	78.8(2)
C(1)-S(1)-Hg(1)	92.3(7)	Hg(1)-Cl(1)-Hg(1)#	102.2(4)
Hg(1)#-Cl(2)-Hg(1)	100.3(7)	C(2)-S(2)-C(1)	98.3(9)
C(1)-S(3)-C(3)	81.2(9)	C(4)-S(4)-C(2)	92.2(9)
C(3)-S(5)-C(5)	91.9(12)	S(3)-C(1)-S(1)	102.0(12)
S(3)-C(1)-S(2)	124.2(11)	S(1)-C(1)-S(2)	133.8(10)
C(3)-C(2)-S(2)	104.1(15)	C(3)-C(2)-S(4)	142.2(16)
S(2)-C(2)-S(4)	113.4(10)	C(2)-C(3)-S(5)	122.2(16)
C(2)-C(3)-S(3)	131.6(14)	S(5)-C(3)-S(3)	105.1(11)
C(5)-C(4)-S(4)	108.8(18)	C(4)-C(5)-S(5)	136(2)

Symmetry transformations used to generate equivalent atoms: # -x, y, 1-z

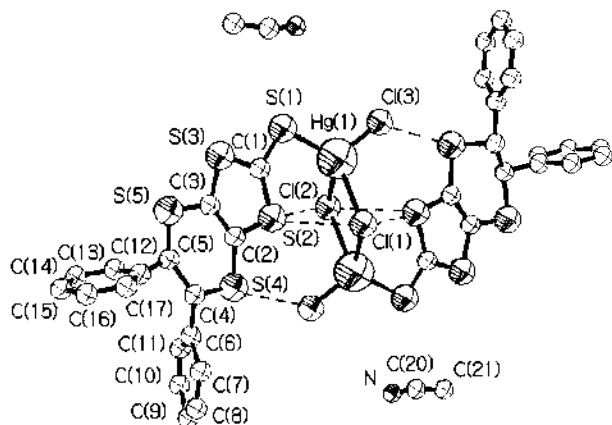


Figure 1. Molecular structure of $trans-[Hg_2(\mu-Cl)Cl(dPhEDT-DTT)]_2 \cdot (CH_3CN)_2$ with the atomic numbering scheme. The intramolecular secondary interactions between sulfur and chloride are denoted as a dashed line.

in Figure 1: $S(2) \cdots Cl(1)$ 3.361, $S(2) \cdots Cl(2)$ 3.352, $S(4) \cdots Cl(3)^*$ 3.113, $S(2)^* \cdots Cl(1)$ 3.361, $S(2)^* \cdots Cl(2)$ 3.352 and $S(4)^* \cdots Cl(3)$ 3.113 Å (symmetry transformation * : $-x, y, 1-z$). These intramolecular close-contacts are much shorter than the sum of van der Waals radii (3.7 Å).⁷ Due to these contacts, EDT-DTT units can get close to the rhombic $Hg_2(\mu-Cl)_2$ core and that $C(1)-S(1)-Hg(1)$ angle ($92.3(7)^\circ$) becomes much smaller than that of the polymeric $[Hg(\mu-Cl)Cl(EDT-DTT)]_2$ complex ($107.2(3)^\circ$).⁶ The diamond-shaped single crystal used for x-ray structure analysis was very brittle presumably due to these intramolecular close-contacts and thereby highly-distorted structure of dPhEDT-DTT ligand. The molecule lies in a plane except the phenyl groups and the bridging chlorides stacking along the b -axis as shown in Figure 2. Short intermolecular $S \cdots S$ contact is one of the important requirements for high electrical conductivity of sulfur-rich compound. The shortest intermolecular $S \cdots S$ contact observed in our complex is 3.791 Å for $S(1) \cdots S(3)^\dagger$ (symmetry operation \dagger : $-0.5-x, 0.5+y, 1-z$) and $S(3) \cdots S(1)^\ddagger$ (symmetry operation \ddagger : $-0.5-x, -0.5+y, 1-z$), which is longer than the sum of van der Waals radii (3.6 Å).⁸

In summary, we prepared the dimeric mercury(II) chloride complex of dPhEDT-DTT ligand, $trans-[Hg_2(\mu-Cl)Cl(dPhEDT-DTT)]_2$, by the direct mixing method. It crystallizes in the monoclinic system with space group Cm (No. 8), $Z = 2$ and unit cell parameters $a = 16.905(2)$, $b = 7.262(3)$, $c = 18.798(4)$ Å, and $\beta = 98.10(2)^\circ$. The central $Hg_2(\mu-Cl)_2Cl_2S_2$ unit adopts the $trans$ -centrosymmetric arrangement with the rhombic $Hg_2(\mu-Cl)_2$ core and the distorted tetrahedral geometry of $Hg(II)$ with the extremely short $Hg(1)-Cl(3)$ bond (2.105(5) Å) and the small angle of $Cl(1)-Hg(1)-Cl(2)$ ($78.8(2)^\circ$). Due to the short intramolecular $S \cdots Cl$ contacts (3.113–3.361 Å), dPhEDT-DTT ligand is highly-distorted compared to the free ligand.

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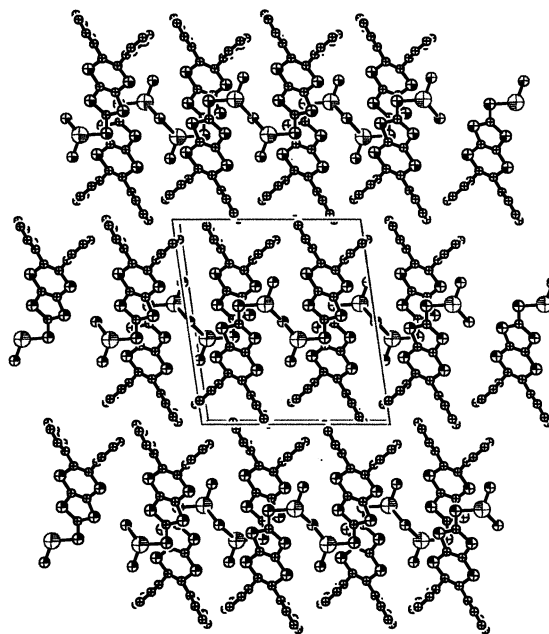


Figure 2. Crystal structure of $trans-[Hg_2(\mu-Cl)Cl(dPhEDT-DTT)]_2 \cdot (CH_3CN)_2$ normal to (010) direction.

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Supplementary Material Available. Tables of anisotropic displacement parameters for non-hydrogen atoms, full bond lengths and angles, and hydrogen coordinates and isotropic displacement parameters are available on request.

References

1. Wright, J. G.; Natan, M. J.; McDonnell, F. M.; Ralston, D. M.; O'Halloran, T. V. In *Prog. Inorg. Chem.*; Lippard, S. J., Ed.; John Wiley and Sons: NY, 1990; Vol 38, pp 323-412.
2. Grant, G. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley and Sons: Chichester, England, 1994; Vol 4, pp 2136-2145.
3. Noh, D. -Y.; Underhill, A. E.; Hursthouse, M. B. *J.C.S., Chem. Commun.* **1997**, 2211.
4. (a) Noh, D. -Y.; Lee, H. -J.; Hong, J.; Underhill, A. E. *Tetrahedron Lett.* **1996**, 37, 7603 (b) Lee, H. -J.; Noh, D. -Y. *Bull. Korean Chem. Soc.* **1998**, 19, 340 (c) Noh, D. -Y.; Lee, H. -J.; Underhill, A. E. *Synth. Metals* **1997**, 86, 1837.
5. (a) Sheldrick, G. M. SHELXS-86: A Program for Structure Determination; University of Gottingen, Germany, 1986. (b) Sheldrick, G. M. SHELXS-93: A Program for Structure Refinement; University of Gottingen, Germany, 1993.
6. Wang, Q. -H.; Long, D. -L.; Huang, J. -S. *Polyhedron* **1998**, 17, 3665.
7. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry - Principles of Structure and Reactivity*, 4th. ed.; Harper Collins: NY, 1993; pp 292.
8. Bondi, A. *J. Phys. Chem.* **1964**, 68, 441.