# Syntheses and Crystal Structures of Xylyl-Bridged $NO_2S_2$-Donor Macrocycles and Binuclear Mercury(II) Complex

**Ji-Eun Lee, Yongri Jin, Joobeom Seo, Il Yoon, Mi Ryoung Song, So Young Lee, Ki-Min Park, and Shim Sung Lee***

*Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University, Chinju 660-701, Korea*
**E-mail: sslee@gsnu.ac.kr*
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Isomeric series of dilinked $NO_2S_2$ macrocycles ($\mathbf{L^2}$: *para*-, $\mathbf{L^3}$: *meta*- and $\mathbf{L^4}$: *ortho*-linked) capable of binuclear complexing ability were prepared from its monomeric analog $\mathbf{L^1}$ in reasonable yields except *ortho*-type reaction, which led to mixture due to the formation of monomer-type macrocyclic quaternary ammonium bromide $\mathbf{L^5}$. Moreover, $\mathbf{L^2}$ (as $2HNO_3$ form) and $\mathbf{L^5}$ were confirmed by an X-ray crystallography. Reaction of $HgCl_2$ with $\mathbf{L^2}$ yielded a binuclear complex $[Hg_2(\mathbf{L^2})Cl_4]$. In the complex, each mercury(II) has a distorted tetrahedral environment made up of S and N donors from an *exodentate* $\mathbf{L^2}$ and two coordinated Cl atoms.

**Key Words :** Dilinked macrocycles, Crystal structure, Binuclear Hg(II) complex, Exo-coordination

## Introduction

Binuclear complexes are the inorganic systems of interest in diverse area, such as electron transport, charge transfer and allosteric behavior in biochemical systems.[1-3] Thus, particular attention has been devoted to the development of new ligand systems capable of forming binuclear complexes. In this regard, the covalently dilinked macrocycles can permit complexing properties to bind two metal ions in defined positions.[4-7] Although a wide variety of the linked macrocyclic ligands including the species covalently linked by secondary amines have been reported,[4-7] the systematic investigations for the monomeric and its *N,N'*-linked macrocycles with $NO_mS_n$ donor set are very rare.[8] We have been involved in a program of preparing new linked macrocyclic complexes based on a mixed-donor macrocyclic system.[9,10] Recently, we have reported the synthesis of $NO_2S_2$-donor macrocycle and its ditopic xylyl-bridged analog as well as the crystal structures of their heavy metal complexes.[11] Continuing with this study we have synthesized the isomeric series of xylyl-bridged macrocycles $\mathbf{L^2}$-$\mathbf{L^4}$ (Figure 1). Herein we report the preparation of the isomeric dilinked macrocycles based on the $NO_2S_2$ macrocyclic unit-particularly those capable of complexing ability with two heavy metal ions *eg.* mercury(II).

## Results and Discussion

The monomeric macrocycle $\mathbf{L^1}$ was obtained by coupling reaction of dibenzo-dichloride with the *N*-Boc-protected dithiol followed by deprotection as described by us previously.[11] The *N*-alkylation of the macrocyclic secondary amine with the corresponding dibromoxylene[12] using potassium carbonate in acetonitrile allows the linking of two rings leading *para*- ($\mathbf{L^2}$) and *meta*-type ($\mathbf{L^3}$) bismacrocycles in good yield (*ca.* 40%). Having successfully made the *meta*- and *para*-type analogs, we proceeded to the preparation of the *ortho*-type $\mathbf{L^4}$ (Figure 1). In the parallel reaction with *ortho*-dibromoxylene, however, the mono-macrocyclic quaternary ammonium bromide $\mathbf{L^5}$ was the major product, isolated in 71% and only small amount of the *ortho*-type linked macrocycle $\mathbf{L^4}$ (*ca.* 7%) was obtained. Apart from the tertiary amine formation *via N,N'*-bridging alkylation in cases of $\mathbf{L^2}$ and $\mathbf{L^3}$, the parallel reaction with *ortho*-dibromoxylene mainly resulted the quaternary ammonium derivative due to the preferential arrangement of leaving groups in 1,2-position. The formation of $\mathbf{L^5}$ was confirmed by an X-ray crystallography (see below). In the majority of cases, the desired products were simply purified by the column chromatography. The $^1H$ and $^{13}C$ NMR spectra clearly exhibited the characteristic singlets at 3.44 ($\mathbf{L^2}$), 3.43 ($\mathbf{L^3}$) ppm and 58.9 ($\mathbf{L^2}$), 58.3 ($\mathbf{L^3}$) ppm, respectively, due to the methylene moiety in the xylyl spacing groups.

The single crystals of $\mathbf{L^5}$ suitable for single crystal X-ray diffraction were isolated by crystallization from the reaction mixture. The crystal structure consists of macrocyclic quaternary ammonium cationic derivative and $Br^-$ together with one water and one dichloromethane molecules (Figure 2). The bond angles of C-N-C range 105.2(4)-113.2(4)°, which are not significantly different from that of the regular $sp^3$. As expected, two oxygen atoms orientated *endodentate*, while the two sulfur atoms are arranged *exodentate* with respect to the ring cavity. The S···S distance of $\mathbf{L^5}$ [7.272(3) Å] is longer than that of its linked analog [6.233(2) Å]. This result means that the macrocyclic ring cavity of $\mathbf{L^5}$ is relatively flat compared with that of its linked analogs. The aliphatic segment S1-C-C-N-C-C-S2 shows an *anti-anti* arrangement between donors.

The single crystals of $\mathbf{L^2}$ as its $2HNO_3$ salt were obtained by slow evaporation of a dichloromethane/$HNO_3$ (3-4 drops) solution of $\mathbf{L^2}$ and structurally characterized by crystallography (Figure 3). In crystal, two macrocyclic units locate at the opposite side, indicating that an imposed inversion symmetry exists at the center of aromatic ring in the xylyl group. Each macrocyclic ring is twisted with its two oxygen atoms orientated *endodentate*, while the two sulfur atoms are

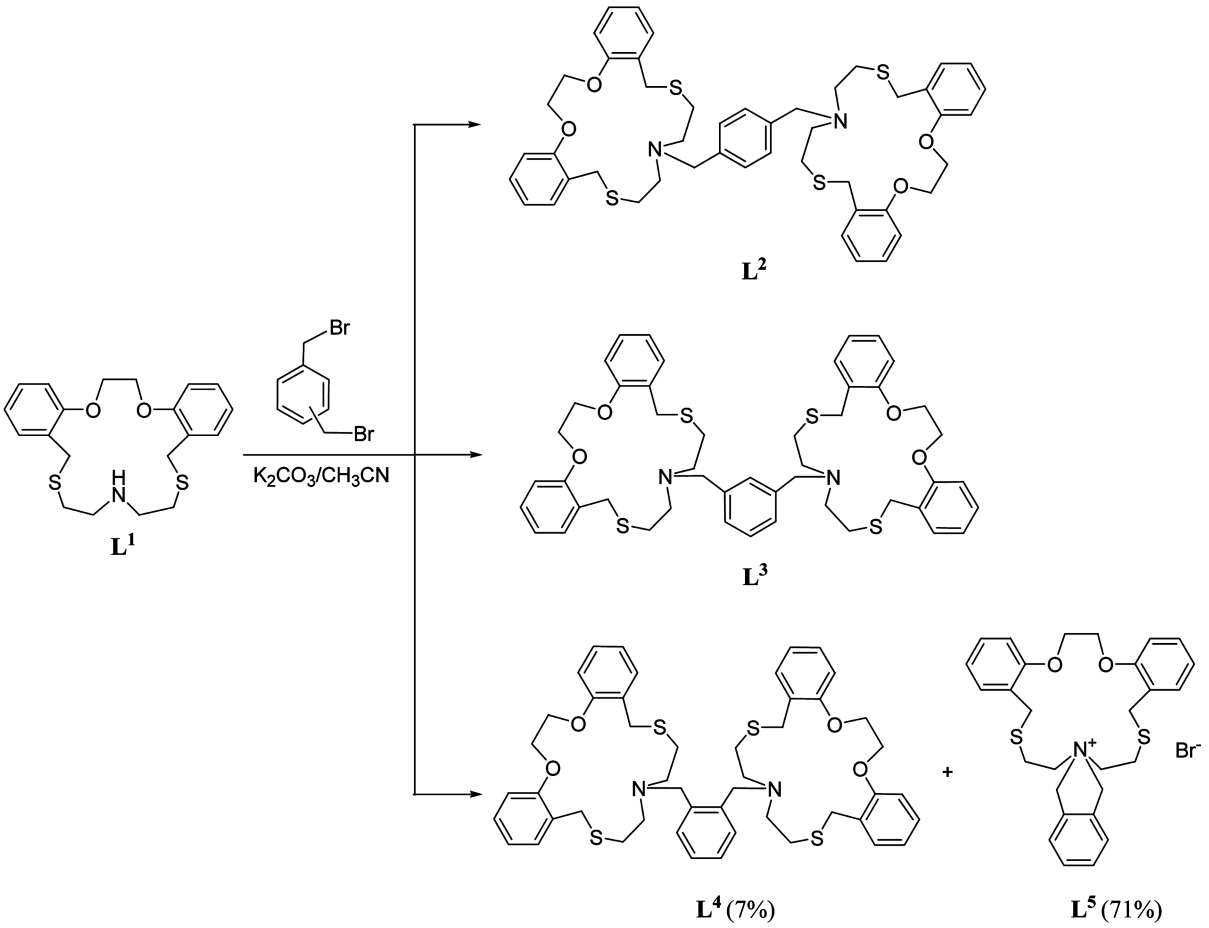


**Figure 1**. Syntheses of the xylyl-bridged macrocyclic isomers.

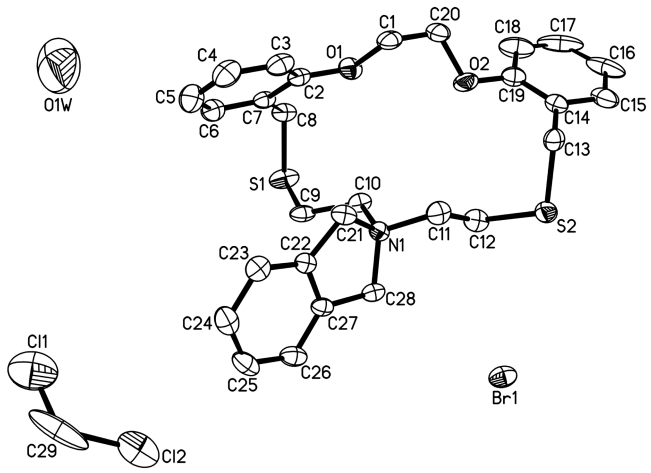


**Figure 2**. Molecular structure of the macrocyclic quaternary ammonium bromide $\mathbf{L}^5 \cdot CH_2Cl_2 \cdot H_2O$.

arranged *exodentate* with respect to the ring cavity. The torsional angles for the ligand between donor atoms are indicative of *gauche* arrangements [O1-C-C-O2 67.7(4)° and S2-C-C-N1 −52.6(4)°] except that of N1-C-C-S1 [179.9(2)°]. The cavity to cavity distance is 10.765 Å (measured as the distance between the two mid-points of lines joining S1···S2 and S1A···S2A and the distance of N1

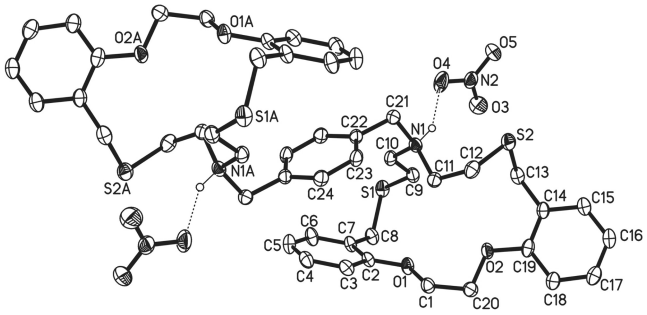

**Figure 3**. Molecular structure of $[\mathbf{L}^2H_2] \cdot 2NO_3$.

···N1A is 7.430(6) Å. As mentioned, $\mathbf{L}^2$ is a potent ditopic ligand for the heavy metal ions. Therefore, the binding study of $\mathbf{L}^2$ with the mercury ion has been focused (see below).

Reaction of $\mathbf{L}^2$ with two molar equivalent of $HgCl_2$ afforded colorless X-ray quality crystalline product $[Hg_2(\mathbf{L}^2)Cl_4]$. X-ray structure shows that the complex has a 1 : 2 ($\mathbf{L}^2$ : Hg) stoichiometry and an imposed inversion at the center of its xylyl group. Thus, the asymmetric unit contains a half molecule of $\mathbf{L}^2$, one mercury and two chloride atoms (Figure 4). Each mercury atom is in a tetrahedral geometry with two coordination sites occupied by one S and one N atom from one $\mathbf{L}^2$ which is present in an *exodentate* conformation. One S and two O atoms in the ring remain uncoordinated.

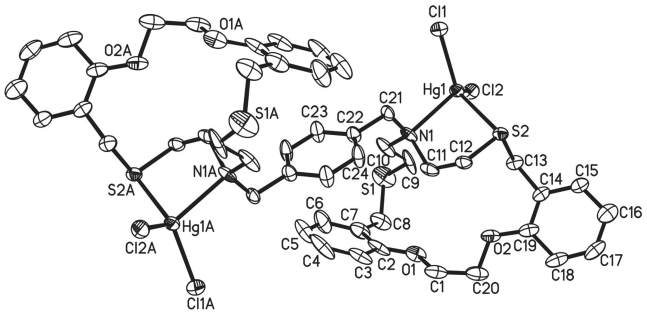


**Figure 4**. Molecular structure of $[Hg_2(\mathbf{L}^2)Cl_4]$.

Instead, two chloride anions occupy two coordination sites on the Hg atom. The coordination sphere of the mercury ion is considerably distorted from regular tetrahedral: the bond angles range from 82.3(2)° for N1-Hg1-S2 to 121.1(1)° for Cl1-Hg1-S2. This distortion may reflect the conformational steric demand of the five-membered ring formed by the chelating of mercury ion to the NS donor set. The Hg-S bond length [2.541(3) Å] agrees well with those values (2.52-2.58 Å) for the related system reported previously.[13,14] The Hg-N bond length [2.431(7) Å] is, however, slightly longer than reported previously for such bonds [2.28-2.35 Å].[13-16] The Hg1···Hg1A separation is 12.040(1) Å.

It is of interest to compare the structural features of the parent macrocycle before and after the complexation. The cavity to cavity distances in the ligand (as $2HNO_3$ form, see Figure 3) and the complex are 10.765 and 11.286 Å, respectively, with the N1 ···N1A distances in the ligand and the complex are 7.430(6) and 7.674(17) Å, respectively. Upon complexation the elongation of ligands by unfolding is also observed previously by us.[11] In both cases, the aliphatic segment S1-C-C-N-C-C-S2 shows an *anti-gauche* arrangement between donors and the related torsion angles are not so different. Consequently, the binuclear complexation induced no remarkable conformational change of the ligand except the elongation of cavity to cavity distance.

## Experimental Section

**General procedure for dialkylation.** A solution of corresponding dibromoxylene in acetonitrile was added dropwise to a refluxing suspension of $\mathbf{L}^1$ and potassium carbonate in acetonitrile. The reaction mixture was maintained at reflux condition for additional 24 h, allowed to cool to room temperature, then filtered. The filtrate was evaporated and the residue was partitioned between water and dichloromethane. The aqueous phase was separated and extracted with two further portions of dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and the solution then evaporated to dryness. Flash column chromatography ($SiO_2$; *n*-hexane/ethyl acetate) afforded the product.

***Meta*-type linked macrocycle ($\mathbf{L}^3$).** The flash column chromatography ($SiO_2$, *n*-hexane : ethyl acetate/7 : 3) afforded the product as a colorless solid in 40% yield. mp: 53-54 °C. IR (KBr, $cm^{-1}$) 3056, 3020, 2922, 1688, 1598, 1490, 1449, 1364, 1240, 1103, 750. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.37-6.87 (m, 20 H, aromatic), 4.34 (s, 8 H, $CH_2O$), 3.84 (s, 8 H, $SCH_2Ar$), 3.43 (s, 4 H, $NCH_2Ar$), 2.55 (m, 16 H, $SCH_2CH_2N$). $^{13}$C-{$^1$H} NMR (125 MHz, $CDCl_3$): $\delta$ 156.0, 138.6, 130.3, 127.7, 127.6, 127.1, 121.0, 111.2, 66.9, 58.3, 53.2, 29.8, 29.3. HRMS (*m/z*) calcd. for $C_{48}H_{56}N_2O_4S_4$ :

**Table 1**. Crystal data and structural refinement

| | $\mathbf{L}^5 \cdot CH_2Cl_2 \cdot H_2O$ | $[\mathbf{L}^2H_2] \cdot 2NO_3$ | $[Hg_2(\mathbf{L}^2)Cl_4]$ |
|---|---|---|---|
| Formula | $C_{22}H_{36}BrCl_2NO_3S_2$ | $C_{24}H_{29}N_2O_5S_2$ | $C_{48}H_{56}Cl_4Hg_2N_2O_4S_4$ |
| M | 661.52 | 489.61 | 1396.17 |
| T/K | 298(2) | 298(2) | 173(2) |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | *P*-1 | $P2_1/n$ | $P2_1/n$ |
| *a*/Å | 8.5779(9) | 11.7213(16) | 11.0496(13) |
| *b*/Å | 14.2138(15) | 13.6925(19) | 15.3327(17) |
| *c*/Å | 14.8922(16) | 14.771(2) | 15.2528(18) |
| $\alpha$/° | 108.029(2) | | |
| $\beta$/° | 102.718(2) | 100.068(3) | 100.718(2) |
| $\gamma$/° | 107.285(2) | | |
| *V*/Å$^3$ | 1548.1(3) | 2334.1(6) | 2539.1(5) |
| Z | 2 | 2 | 2 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 1.666 | 0.134 | 6.459 |
| Crystal size/mm | 0.4 × 0.4 × 0.4 | 0.2 × 0.2 × 0.1 | 0.4 × 0.3 × 0.2 |
| Absorption correction | | | SADABS |
| Reflections collected | 10101 | 14869 | 14629 |
| Independent reflections | 7125 | 5527 | 5147 |
| Goodness-of-fit on $F^2$ | 0.933 | 0.938 | 1.013 |
| Final *R*1, *wR*2 [$I > 2\sigma(I)$] | 0.0665, 0.1820 | 0.0661, 0.1239 | 0.0571, 0.1292 |
| (all data) | 0.1620, 0.2384 | 0.1689, 0.1549 | 0.1194, 0.1523 |

852.3123; found: 852.3116.

***Ortho*-type linked macrocycle ($L^4$) and macrocyclic quaternary ammonium bromide ($L^5$).** After reduce the volume of the filtrate the colorless quaternary ammonium salt $L^5$ was isolated as a colorless crystalline solid. Flash column chromatography ($SiO_2$, *n*-hexane : ethyl acetate / 7 : 3) afforded $L^4$ as a glassy solid (yield: 7%). For $L^4$; IR (KBr, $cm^{-1}$) 3063, 3033, 2924.6, 2362, 1687, 1492, 1242, 1105, 751. $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.22-6.83 (m, 20 H, aromatic), 4.30 (s, 8 H, $CH_2O$), 3.79 (s, 8 H, $ArCH_2S$), 3.71 (s, 4 H, $NCH_2Ar$), 2.80 (t, 8 H, $J$ = 10.0, $SCH_2CH_2$), 2.59 (t, 8 H, $J$ = 10.0, $NCH_2CH_2$). $^{13}C$-{$^1H$} NMR (125 MHz, $CDCl_3$): $\delta$ 155.4, 138.7, 129.4, 127.5, 126.6, 125.7, 125.3, 120.0, 111.1, 66.1, 57.9, 54.7, 29.7. HRMS (*m/z*) calcd. for $C_{48}H_{56}N_2O_4S_4$ : 852.3123; found: 853.3197 (M+1).

For $L^5$. (yield: 71%). mp: 185-186 ºC. Elemental analyses: for $C_{28}H_{34}BrNO_3S_2$, calc: C, 58.32; H, 5.94; N, 2.43; S, 11.12 Found: C, 58.44; H, 5.55; N, 2.12; S, 11.12%. IR (KBr, $cm^{-1}$) 3459, 3395, 2937, 2246, 1638, 1489, 1244, 759, 734. $^1H$ NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.00-7.39 (m, 12 H, aromatic), 4.49 (s, 4 H, $CH_2O$), 3.90 (s, 4 H, $ArCH_2S$), 3.62 (t, 4 H, $J$ = 5.0, $NCH_2CH_2$), 3.33 (s, 4 H, $NCH_2Ar$), 2.72 (t, 4 H, $J$ = 5.0, $SCH_2CH_2$). $^{13}C$-{$^1H$} NMR (125 MHz, DMSO-$d_6$): $\delta$ 156.3, 133.1, 130.5, 128.8, 122.6, 121.4, 113.1, 68.0, 66.7, 61.4, 29.3, 24.6 MS (FAB): *m/z* 478.0 $M^+$.

**$[Hg_2(L^2)Cl_4]$.** Colorless crystals suitable for X-ray analysis were grown over three days of the mixture formed by the layered diffusion of a solution of $HgCl_2$ in acetonitrile on $L^2$ in dichloromethane. Mp: 174-175 ºC. IR (KBr, $cm^{-1}$) 3441, 2933, 1597, 1495, 1445, 1234, 1111, 1053, 936, 755, 675.

**Crystallograpy.** A crystal suitable for X-ray diffraction was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo-K$\alpha$ ($\lambda$ = 0.71073 Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 30 sec. The frame data were processed to give structure factors by the program SAINT.[17] The intensity data were corrected for Lorentz and polarization effects. Using the program SADABS,[18] empirical absorption correction was also applied for $[Hg_2(L^2)Cl_4]$. The structures were solved by a combination of the direct method and the difference Fourier methods provided by the program package SHELXTL,[19] and refined using a full matrix least square against $F^2$ for all data. All the non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. Crystallographic data are summarized in Table 1.

**Supplementary materials.** CCDC 272853, 272854, and 272855 contain the supplementary crystallographic data, respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request @ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

**Table 2**. Selected bond lengths (Å), bond angles (º) and torsional angles (º)

| | | | |
|---|---|---|---|
| $L^5 \cdot CH_2Cl_2 \cdot H_2O$ | | | |
| S1-C9 | 1.800(5) | S1-C8 | 1.800(6) |
| S2-C12 | 1.803(7) | S2-C13 | 1.816(6) |
| O1-C2 | 1.363(7) | O1-C1 | 1.424(7) |
| O2-C19 | 1.356(8) | O2-C20 | 1.428(8) |
| N1-C10 | 1.515(6) | N1-C28 | 1.518(6) |
| N1-C21 | 1.522(7) | N1-C11 | 1.544(7) |
| C9-S1-C8 | 103.5(2) | C12-S2-C13 | 106.2(3) |
| C2-O1-C1 | 119.7(5) | C19-O2-C20 | 114.7(5) |
| C10-N1-C28 | 111.6(4) | C10-N1-C21 | 110.6(4) |
| C28-N1-C21 | 105.8(4) | C10-N1-C11 | 110.2(4) |
| C28-N1-C11 | 113.2(4) | C21-N1-C11 | 105.2(4) |
| O1-C1-C20-O2 | −72.7(7) | S1-C9-C10-N1 | 177.4(4) |
| S2-C12-C11-N1 | −167.2(4) | | |
| $[L^2H_2] \cdot 2NO_3$ | | | |
| S1-C8 | 1.814(4) | S1-C9 | 1.809(4) |
| S2-C12 | 1.806(4) | S2-C13 | 1.822(4) |
| O1-C1 | 1.438(4) | O1-C2 | 1.381(4) |
| O2-C19 | 1.377(4) | O2-C20 | 1.431(4) |
| N1-C10 | 1.503(4) | N1-C11 | 1.501(4) |
| N1-C21 | 1.520(4) | | |
| C9-S1-C8 | 101.8(2) | C2-O1-C1 | 117.3(3) |
| C19-O2-C20 | 118.1(3) | C11-N1-C10 | 111.4(3) |
| C11-N1-C21 | 112.7(3) | C10-N1-C21 | 112.3(3) |
| O1-C1-C20-O2 | 67.7(4) | S1-C9-C10-N1 | 179.9(2) |
| S2-C12-C11-N1 | −52.6(4) | O4···H | 1.985 |
| Symmetry codes A: | $-x+1, -y, -z$. | | |
| $[Hg_2(L^2)Cl_4]$ | | | |
| Hg1-S2 | 2.541(3) | Hg1-N1 | 2.431(7) |
| Hg1-Cl1 | 2.396(3) | Hg1-Cl2 | 2.426(3) |
| N1-Hg1-S2 | 82.3(2) | Cl1-Hg1-N1 | 106.5(2) |
| Cl2-Hg1-N1 | 117.7(2) | Cl1-Hg1-S2 | 121.1(1) |
| Cl2-Hg1-S2 | 112.6(1) | Cl1-Hg1-Cl2 | 113.2(1) |
| O1-C1-C20-O2 | 69.8(1) | S1-C9-C10-N1 | 178.4(9) |
| S2-C12-C11-N1 | −57.9(12) | | |
| Symmetry codes A: | $-x+1, -y, -z$. | | |

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