Endo- and Exo-Coordinated Mercury(II) Complexes of O_3S_2 Macrocycles: Effect of Dibenzo-Substituents on Coordination Mode†

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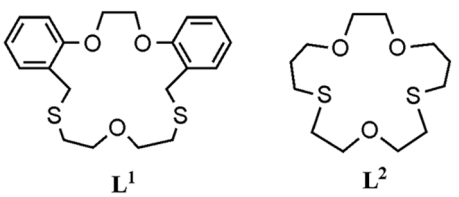
The reactions of mercury(II) chloride with O_3S_2-donor macrocyclic ligands with ($\mathbf{L^1}$) and without ($\mathbf{L^2}$) dibenzo-subunit afforded respective exo- (**1**) and endo-coordinated (**2**) complexes depending on the ring rigidity of the ligands. From the X-ray crystal structures and comparative NMR studies for the complexes **1** and **2**, it is confirmed that the resulting species with different coordination modes exist not only in solid state but also in solution state.

Key Words : O_3S_2-Donor macrocycles, Dibenzo-substituents, Mercury(II) complex, Exo- and endo-coordinations

Introduction

Modification of macrocyclic ligands as well as selection of the metal salt system make possible to generate diverse types of coordination topologies. Besides the cavity size that varies to tune a binding selectivity for a given metal ion, the introduction of hetero donor atoms and/or subunits into the macrocyclic ligands results in dramatic changes in both binding ability and geometry of the complexes.[1] We recently reported two NO_2S_2 macrocycles[2] showing affinity for mercury(II), with the latter being bound in an exo-[3] or endo-coordination manner. In the course of our ongoing studies of the sulfur containing mixed-donor macrocycles[4] we explore the possibility of generating rigidity-controlled coordination products through the modification of the macrocycles. This approach has received less attention especially for the thia-macrocycles.[4b] In connection with this reason, $\mathbf{L^1}$ and $\mathbf{L^2}$ were chosen as a model system.[5,6] Since these ligands are potentially pentadentate and show variation of rigidity due to the dibenzo-substituents, we reasoned that these may induce the rigidity-controlled products with soft metals, such as mercury(II). In particular, the coordination chemistry of mercury(II) has received increased attention lately, in part, because of the concerns regarding its environmental and toxicological impacts.[7] We herein report the synthesis of the mercury(II) chloride complexes with these ligands including the molecular structure determination of them by single-crystal X-ray diffraction. In an extension of the solid-state study, comparative NMR experiments were undertaken to explore the complexations in solution.



$\mathbf{L^1}$ $\mathbf{L^2}$

Results and Discussion

$\mathbf{L^1}$ and $\mathbf{L^2}$ were synthesized with the methods reported by us previously.[5,6] Two mercury(II) complexes **1** and **2** were prepared from the respective reactions of the ligands with mercury(II) chloride as crystalline products.

Preparation and Crystal Structure of $\mathbf{L^1}$ Complex with $HgCl_2$ (1). Colorless single crystals of complex **1** suitable for X-ray analysis were obtained by slow evaporation of reaction mixture of $\mathbf{L^1}$ and $HgCl_2$ in CH_3CN/CH_2Cl_2. The crystal structure of **1** is shown in Figure 1, and its selected geometric parameters are presented in Table 1. The ESI mass spectrum of the product **1** shows a peak at *m/z* 613 corresponding to $[Hg(\mathbf{L^1})Cl]^+$. The crystallographic analysis confirms that **1** is an exo-coordinated complex of formula $[Hg(\mathbf{L^1})Cl_2]$ with a metal:ligand:anion ratio of 1:1:2 in which the macrocycle is folded backward from the chlorine

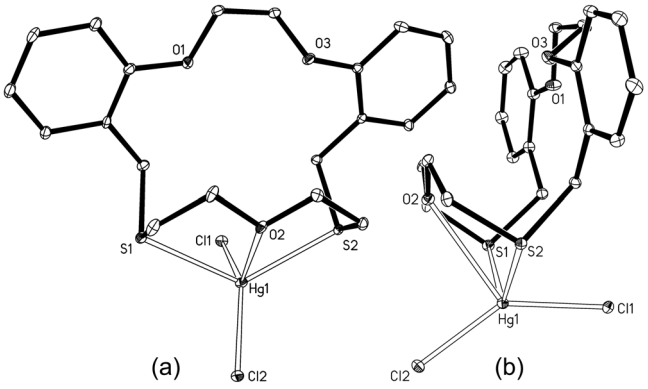


Figure 1. Molecular structure of **1**, $[Hg(\mathbf{L^1})Cl_2]$. (a) general view and (b) side view.

† This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

Table 1. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **1**, [Hg(**L**^{1})Cl$_2$]

Hg1-Cl1	2.430(3)	Hg1-Cl2	2.364(3)
Hg1-S1	2.760(3)	Hg1-S2	2.657(3)
Hg1-O2	2.864(7)	Hg1···O1	5.418(9)
Hg1···O3	5.591(9)		
S1-Hg1-S2	121.92(8)	S1-Hg1-Cl1	89.65(10)
S1-Hg1- Cl2	98.70(10)	S1-Hg1-O2	67.92(17)
S2-Hg1-O2	66.47(17)	S2-Hg1-Cl1	91.75(9)
S2-Hg1-Cl2	116.03(9)	O2-Hg1-Cl1	128.46(17)
O2-Hg1-Cl2	91.17(18)	Cl2-Hg1-Cl1	139.26(10)
O1-C1-C20-O3	−64.5(1)	S1-C9-C10-O2	−58.1(1)
O2-C11-C12-S2	52.3(1)		

position. The Hg atom in the outside of the cavity is five-coordinate, with coordinating to one O and two S atoms from **L**^{1}. The fourth and fifth sites are occupied by two Cl atoms. The two O atoms between dibenzo-subunit remain uncoordinated (Hg1···O1 5.42, Hg1···O3 5.59 Å). The mercury center in **1** is in the distorted square pyramidal environment. The Hg atom is located 1.143 Å above the S1-Cl1-S2-O2 square plane, with Cl2 atom occupying the apex. The bond lengths of Hg-S [2.657(7)-2.760(3) Å] and Hg-O [2.864(7) Å] are slightly longer than reported previously for such bonds.[8] The torsion angles between the respective donor atoms fall in the range of 52.3(1)-64.5(1)°, in keeping with *gauche* conformations for these fragments.

Preparation and Crystal Structure of L^2 Complex with HgCl$_2$ (2). The slow evaporation of the methanolic solution of **L**^{2} and HgCl$_2$ afforded pale yellow crystalline product **2** that proved suitable for X-ray analysis. The crystal structure of complex **2** is shown in Figure 2, and its selected geometric parameters are presented in Table 2. Unlike the case of **1**, complex **2** features three separated units of formula [Hg(**L**^{2})Cl]$_2$[Hg$_2$Cl$_6$]: two macrocyclic cation complex units and one mercury halide anion cluster. Since there is an imposed inversion at the center of [Hg$_2$Cl$_6$]$^{2-}$, the asymmetric unit contains one macrocyclic cation complex unit and half of the anionic unit. In macrocyclic complex cation unit, Hg atom is six-coordinate, being bound to O$_3$S$_2$ donor set from one **L**^{2}, with the macrocycle adopting an endo-conformation. One Cl atom is occupying the remaining

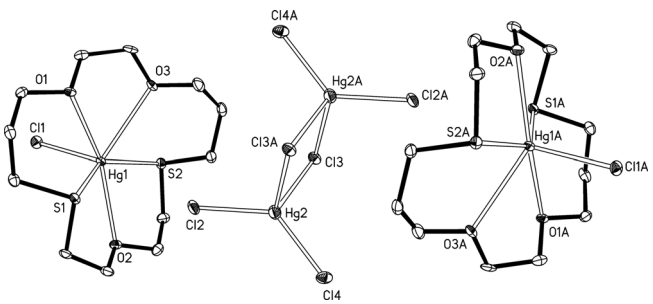


Figure 2. Molecular structure of **2**, [Hg(**L**^{2})Cl]$_2$[Hg$_2$Cl$_6$].

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **2**, [Hg(**L**^{2})Cl]$_2$[Hg$_2$Cl$_6$]

Hg1-S1	2.488(2)	Hg1-S2	2.480(2)
Hg1-O1	2.822(5)	Hg1-O2	2.657(5)
Hg1-O3	2.815(5)	Hg1-Cl1	2.455(2)
Hg2-Cl2	2.395(2)	Hg2-Cl3	2.632(2)
Hg2-Cl4	2.381(2)	Hg2-Cl3A	2.642(2)
S1-Hg1-S2	139.44(6)	S1-Hg1- Cl1	107.30(7)
S1-Hg1-O1	72.55(11)	S1-Hg1-O2	75.53(13)
S1-Hg1-O3	116.11(12)	S2-Hg1-O1	131.19(11)
S2-Hg1-O2	75.25(13)	S2-Hg1-O3	70.42(12)
S2-Hg1-Cl1	107.89(7)	Cl1-Hg1-O1	83.24(12)
Cl1-Hg1-O2	107.41(13)	Cl1-Hg1-O3	108.03(12)
O1-Hg1-O2	148.06(16)	O2-Hg1-O3	136.46(17)
O1-Hg1-O3	61.08(15)	Cl2-Hg2-Cl3	110.57(7)
Cl2-Hg2-Cl4	130.83(7)	Cl3-Hg2-Cl4	105.17(7)
Cl2-Hg2-Cl3A	100.92(7)	Cl3-Hg2-Cl3A	89.77(6)
Cl4-Hg2-Cl3A	112.02(7)	Hg2-Cl3-Hg2A	90.23(6)
O1-C1-C12-O3	-68.2(8)	S1-C5-C6-O2	70.2(8)
O2-C7-C8-S2	-61.9(8)		

Symmetry codes A: $-x+2, -y, -z$.

coordination position. The coordination sphere of the Hg atom in the center of the macrocyclic cation unit can be considered as a distorted pentagonal pyramid, where the O$_3$S$_2$ donor set defines the pentagonal basal plane (mean deviation from planarity: 0.305 Å), with the cation shifted 0.60 Å from the mean plane towards the apex. The apical site is occupied by one Cl atom, with Hg1-Cl1 being almost perpendicular to the average basal plane (angle subtended to the normal: 5.49°). It is noteworthy that the metal to donor bond lengths are shorter in **2** [Hg1-S1: 2.488(2), Hg1-S2 2.480(2), Hg1-O2 2.657(5) Å] than those in **1** [Hg1-S1 2.760(3), Hg1-S2 2.657(3), Hg1-O2 2.864(7) Å], indicating endo-coordinative bonds are stronger than those of exo-ones. Geometrical parameters for [Hg$_2$Cl$_6$]$^{2-}$, whose formation apparently aids the stabilization of [Hg(**L**^{2})Cl]$^+$ in the crystal lattice, are similar to those reported previously for this unit.[9] The shortest inter-ionic contact, corresponding to Hg1···Cl2, is 3.992(2) Å.

NMR Spectra of Complex System. For the comparison of above results in solid state with those in solution state, comparative ^{1}H NMR experiments in CD$_3$CN were carried out for the parallel system. The ^{1}H NMR signals of four methylene protons (H$_{1-4}$) for **L**^{1} and **L**^{2} were well resolved and identified, respectively. Upon complexation with HgCl$_2$, all peaks for both ligands shifted downfield (Figure 3). The ^{1}H NMR profiles of each methylene protons for complexes **1** and **2** were compared with those of free ligands (Figure 4). Importantly, upon complexation, the magnitudes of chemical shift change of all methylene protons for **L**^{2} are approximately twice larger than those of **L**^{1} except for H$_1$. In case of H$_1$, however, the chemical shift change in **L**^{1} ($\Delta\delta$ = 0.0138 ppm) is negligibly smaller than that of **L**^{2} ($\Delta\delta$ =

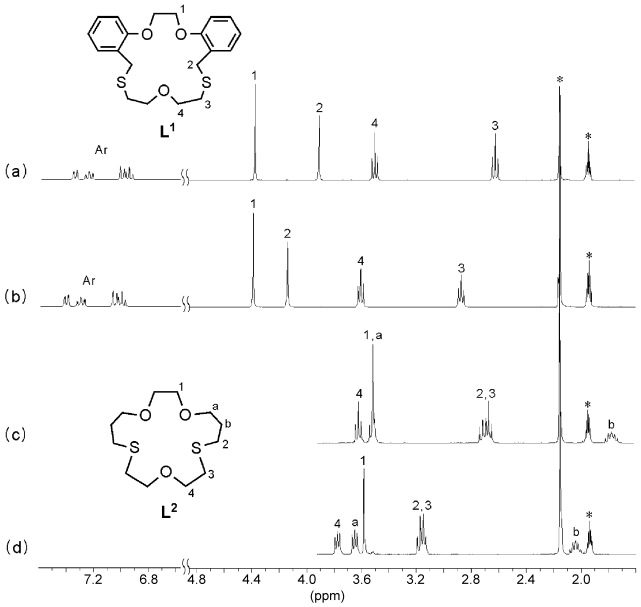


Figure 3. Comparative NMR spectra for (a) $\mathbf{L^1}$, (b) **1**, (c) $\mathbf{L^2}$ and (d) **2** in CD_3CN.

Table 3. Crystal data and structural refinement

	1	**2**
Formula	$C_{20}H_{24}Cl_2HgO_3S_2$	$C_{12}H_{24}Cl_4Hg_2O_3S_2$
M	648.00	823.41
T/K	298(2)	173(2)
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a/Å	8.6765(19)	7.2423(6)
b/Å	11.996(3)	10.4782(8)
c/Å	12.157(3)	14.9555(12)
α/°	60.437(3)	75.3150(10)
β/°	87.711(4)	78.8320(10)
γ/°	85.358(4)	88.5060(10)
V/Å^3	1097.0(4)	1076.74(15)
Z	2	2
μ(Mo-Kα)/mm^{-1}	7.468	14.939
Crystal size/mm	0.25 × 0.20 × 0.06	0.50 × 0.20 × 0.20
Absorption correction	SADABS	SADABS
Reflections collected	7245	5733
Independent reflections	5151	4055
Goodness-of-fit on F^2	1.023	1.047
Final *R*1, *wR*2 [$I > 2\sigma(I)$]	0.0667, 0.1804	0.0427, 0.1095
(all data)	0.0807, 0.1921	0.0473, 0.1120

0.0754 ppm). The much larger shift observed for H_1 in **2** than that in **1** suggests that the Hg atom strongly interacts with two ether O atoms adjacent to H_1 in $\mathbf{L^2}$ not with those in $\mathbf{L^1}$. From this comparison, it became evident that exo- (for **1**) and endo-coordinated (for **2**) structures are also remained in solution. Additionally, in both cases, the order of magnitudes of the downfield shift is $H_{2,3} > H_4 > H_1$, indicating that mercury(II) is strongly coordinated by S donors, similar to the case in the solid state.

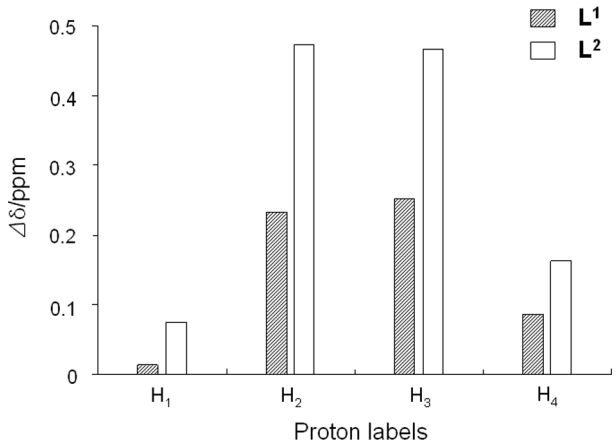


Figure 4. Differences in proton chemical shifts ($\Delta\delta$) between ligands ($\mathbf{L^1}$ and $\mathbf{L^2}$) and their $HgCl_2$ complexes (**1** and **2**).

Conclusions

A comparative study of the coordination behavior of two O_3S_2 macrocycles with ($\mathbf{L^1}$) and without ($\mathbf{L^2}$) dibenzo-subunit toward mercury(II) chloride has been presented. $\mathbf{L^1}$ forms exo-coordinated mononuclear complex [Hg($\mathbf{L^1}$)Cl_2] (**1**), in which the mercury atom lies outside the cavity exhibiting the distorted square pyramidal environment. Contrasting with **1**, $\mathbf{L^2}$ results in the formation of endo-coordinated complex [Hg($\mathbf{L^2}$)Cl]$_2$[Hg_2Cl_6] (**2**), in which the mercury center in the complex cation has a stable distorted pentagonal pyramidal environment. These results reflect that the rigidity of ring cavity due to the substitution of dibenzo-subunit plays an important role in the coordination modes of these compounds. Through the results from the comparative NMR study, it became evident that same structures are remained in solution state. It is also noticed that the endo-coordinated complex **1** is more stable than that of exo-coordinated **2** from the bond lengths and chemical shift data for the complexes.

Experimental Section

All commercial reagents including solvents were of analytical reagent grade where available. NMR spectra were recorded on a Bruker DRX-300 spectrometer (300 MHz). Infrared spectra were measured with a Mattson Genesis Series FT-IR spectrophotometer. Microanalyses were performed by LECO CHNS-932. The mass spectra were obtained on a JEOL JMS-700 spectrometer (FAB) and Applied Biosystems 4000 Q TRAP (ESI) at the Central Instrument Facility of Gyeongsang National University. Melting points are uncorrected.

[Hg($\mathbf{L^1}$)Cl_2] (1). $HgCl_2$ (25 mg, 0.093 mmol) was dissolved in acetonitrile and was added to the solution of $\mathbf{L^1}$ (30 mg, 0.093 mmol) in dichloromethane. The reaction mixture was stirred for 1 hr and filtered. The slow evaporation of the filtrate afforded colorless crystals. M.p. (decomp.) 181-182 °C. IR (KBr, cm^{-1}): 2921, 2854, 2352, 1598, 1492, 1244.

MS (ESI): m/z = 613 ($[Hg(\mathbf{L^1})Cl]^+$, $[C_{20}H_{24}Cl_2HgO_3S_2]^+$).

$[Hg(L^2)Cl]_2[Hg_2Cl_6]$(2). $HgCl_2$ (29 mg, 0.107 mmol) was dissolved in methanol and was added to the solution of $\mathbf{L^2}$ (30 mg, 0.107 mmol) in methanol. The reaction mixture was stirred for 1 hr and filtered. The slow evaporation of the filtrate afforded pale yellow crystals. M.p. (decomp.) 223-224 °C. IR (KBr, cm^{-1}): 2918, 2871, 1473, 1419, 1359, 1282, 1107, 1091, 1024, 987, 937, 851, 817. MS (FAB): m/z = 517 ($[Hg(\mathbf{L^2})Cl]^+$, $[C_{12}H_{24}ClHgO_3S_2]^+$).

Crystallograpy. A crystal suitable for X-ray diffraction was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo-Kα (λ = 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.[10] The intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for complexes using the program SADABS.[11] The structures were solved by a combination of the direct method and the difference Fourier methods provided by the program package SHELXTL,[12] 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 3.

Supplementary materials. CCDC 649431 and 649432 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.

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References

1. (a) Lindoy, L. F. *The Chemistry of Macrocyclic Complexes*; Cambridge University Press: Cambridge, U. K., 1989. (b) Lehn, J.-M. *Supramolecular Chemistry, Concept and Perspectives*; VCH: Weinheim, Germany, 1995.
2. Jin, Y.; Yoon, I.; Seo, J.; Lee, J.-E.; Moon, S.-T.; Kim, J.; Han, S. W.; Park, K.-M.; Lindoy, L. F.; Lee, S. S. *Dalton Trans.* **2005**, 788.
3. (a) Yoon, I.; Seo, J.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Choi, K. S.; Jung, O.-S.; Park, K.-M.; Lee, S. S. *Dalton Trans.* **2005**, 2352. (b) Park, K.-M.; Yoon, I.; Seo, J.; Lee, J.-E.; Kim, J.; Choi, K. S.; Jung, O.-S.; Lee, S. S. *Cryst. Growth Des.* **2005**, *5*, 1707. (c) Seo, J.; Yoon, I.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Park, S. H.; Kim, T. H.; Park. K.-M.; Kim, B. G.; Lee, S. S. *Inorg. Chem. Commun.* **2005**, *8*, 916. (d) Lee, J.-E.; Jin, Y.; Seo, J.; Yoon, I.; Song, M. R.; Lee, S. Y.; Park, K.-M.; Lee, S. S. *Bull. Korean Chem. Soc.* **2006**, *27*, 203.
4. (a) Yoon, I.; Seo, J.; Lee, J.-E.; Park, K.-M.; Kim, J. S.; Lah, M. S.; Lee, S. S. *Inorg. Chem.* **2006**, *45*, 3487. (b) Seo, J.; Lee, J.-E.; Song, M. R.; Lee, S. Y.; Yoon, I.; Park, K.-M.; Kim, J.; Jung, J. H.; Park, S. B.; Lee, S. S. *Inorg. Chem.* **2006**, *45*, 952. (c) Park, S. B.; Yoon, I.; Seo, J.; Kim, H. J.; Kim, J. S.; Lee, S. S. *Bull. Korean Chem. Soc.* **2006**, *27*, 713.
5. Lee, Y. H.; Lee, S. S. *J. Inclusion Phenom.* **2001**, *39*, 235.
6. Song, M. R.; Lee, J.-E.; Lee, S. Y.; Seo, J.; Park, K.-M.; Lee, S. S. *Inorg. Chem. Commun.* **2006**, *9*, 75.
7. (a) Von Burg, R. *J. Appl. Toxicol.* **1995**, *15*, 483. (b) Magos, L. *Met. Ions Biol. Syst.* **1997**, *34*, 321. (c) Wolfe, M. F.; Schwarzbach, S.; Sulaiman, R. A. *Environ. Toxicol. Chem.* **1998**, *17*, 146.
8. (a) Marchand, A. P.; Cal, D.; Mlinaric-Majerski, K.; Ejsmont, K.; Watson, W. H. *J. Chem. Cryst.* **2002**, *32*, 447. (b) Caltagirone, C.; Bencini, A.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Mariani, P.; Papke, U.; Tei, L.; Verani, G. *Dalton Trans.* **2003**, 901. (c) Afshar, S.; Marcus, S. T.; Gahan, L. R.; Hambley, T. W. *Aust. J. Chem.* **1999**, *52*, 1. (d) Byriel, K. A.; Gahan, L. R.; Kennard, C. H. L.; Sunderland, C. T. *J. Chem. Soc., Dalton Trans.* **1993**, 625.
9. (a) Bebout, D. C.; Bush II, J. F.; Crahan, K. K.; Kastner, M. E.; Parrish, D. A. *Inorg. Chem.* **1998**, *37*, 4641. (b) Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *Inorg. Chim. Acta* **1998**, *269*, 274. (c) Chessa, G.; Marangoni, G.; Pitteri, B.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Chem. Soc., Dalton Trans.* **1990**, 915.
10. Bruker *SMART and SAINT*: *Area Detector Control and Integration Software Ver. 5.0*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.
11. Sheldrick, G. M. *SADABS*: *Empirical Absorption and Correction Software*; University of Göttingen: Göttingen, Germany, 1999.
12. Bruker *SHELXTL*: *Structure Determination Programs Ver. 5.16*; Bruker Analytical X-ray Instruments: Madison, Wisconsin, 1998.