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Synthesis and Crystal Structures of Mercury(II) and Copper(II) Complexes of Azathia-Macrocycle with Pyridylmethyl Arm

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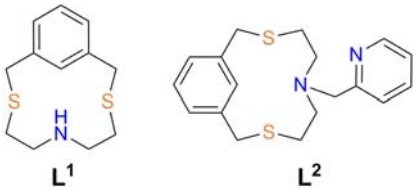
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Three dimensional cation binding with the armed macrocycles is one of the important topics not only in the area of the ion transport but also in the construction of new metallosupramolecules.[1] In patircular, N-pivot armed macrocycles with pyridine-type pendant tend to be able to direct their side arm toward the guest since the hetero N atom is directed toward the metal cation.[2] Sometimes the positions of the hetero N atom (N_{py}) in the pyridine arms affect the resulting topologies of the metallosupramolecules. Habata *et al.*[2b] reported the interesting bowl-type cyclic dimer and cylic trimer silver(I) complexes from 3'-pyridylmethyl- and 4'-pyridylmethyl-armed monoaza-12-crown-4, respectively.

On the other hand, a range of soft metal complexes of sulfur-containing mixed-donor macrocycles with supramolecular structures have been reported by us[3] and other groups.[4] For example, we recently reported three NS_2-donor macrocycle isomers including a *meta*-isomer **L**^{1} which show a leaf-shaped 1D network structure on complexation with mercury(II) halides.[3a] More recently, the mercury(II) complexes which give rise to different topologies depending on the anions and the heteronuclear Ag(I)/Pd(II) 2D network complex were also introduced by us for **L**^{1}.[3b]

The continuing interest in the metallosupramolecules based on **L**^{1} and the limited research in the area of the N-pivot thiamacrocycles so far has propmpted us to investigate the coordination behaviors of **L**^{2} in which one *ortho*-type pyridine side arm is attached to a tertiary amine nitrogen (N_{tert}) of the parent macrocycle. Herein, we report the synthesis and structural characterizaton of the three mercury and one copper complexes of **L**^{2}.



Experimental Section

General. All commercial reagents including solvents were of analytical reagent grade. The armed macrocycle **L**^{2} was prepared by 2-picolyl chloride hydrochloride and the parent macrocycle **L**^{1} which was prepared as described by us.[3a] The details for the synthetic procedure for **L**^{2} will be described elsewhere. The mass data were obtained on a Thermo Scientific LCQ Fleet spectrometer. The FT-IR spectra were measured with a Shimadzu FT-IR 1800 spectrophotometer.

[Hg(L^2)Cl$_2$], (1). $HgCl_2$ (18.4 mg, 0.068 mmol) was dissolved in acetone (2 mL) and was added to a solution of **L**^{2} (20.4 mg, 0.062 mmol) in acetone (2 mL). Slow evaporation of the solution at room temperature afforded the colorless crystalline product **1** suitable for X-ray analysis. mp 115-116 ºC (decomp.). IR (KBr, cm^{-1}): 3043, 2928, 1704, 1624, 1601, 1441, 1090, 1016, 768. ESI-MS: *m/z* 567.0 [Hg(**L**^{2})Cl]$^+$.

[Hg(L^2)(SCN)$_2$]·CH$_3$OH, (2). $Hg(SCN)_2$ (21.9 mg, 0.069 mmol) was dissolved in methanol (2 mL) and was added to a solution of **L**^{2} (20.7 mg, 0.063 mmol) in dichloromethane (2 mL). Slow evaporation of the solution at room temperature afforded the colorless crystalline product **2** suitable for X-ray analysis. mp 125-126 ºC (decomp.). IR (KBr, cm^{-1}): 3051, 2938, 2362, 2110, 1601, 1437, 1296, 1150, 1086, 767, 710. ESI-MS: *m/z* 590.2. [Hg(**L**^{2})SCN]$^+$.

[Hg(L^2)Br]$_2$[Hg$_2$Br$_4$(μ_2-Br$_2$)], (3). $HgBr_2$ (24.1 mg, 0.067 mmol) was dissolved in acetone (2 mL) and was added to a solution of **L**^{2} (20.1 mg, 0.061 mmol) in acetone (2 mL). Slow evaporation of the solution at room temperature afforded the colorless crystalline product **3** suitable for X-ray analysis. mp 169-170 ºC (decomp.). IR (KBr, cm^{-1}): 3053, 2919, 2829, 1601, 1444, 1299, 1088, 1016, 799. ESI-MS: *m/z* 611.1 [Hg(**L**^{2})Br]$^+$.

[Cu(L^2)Cl$_2$], (4). CuCl (6.9 mg, 0.069 mmol) was dissolved in acetone (2 mL) and was added to a solution of **L**^{2} (20.8 mg, 0.063 mmol) in acetone (2 mL). Slow evaporation of the solution at room temperature afforded the blue crystalline product **4** suitable for X-ray analysis. mp 237-238 ºC (decomp.). IR (KBr, cm^{-1}): 3057, 2960, 2822, 1598, 1477, 1437, 1289, 1106, 1088, 1011, 773. ESI-MS: *m/z* 428.02 [Cu(**L**^{2})Cl]$^+$.

Crystallography. All data were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å)

Table 1. Crystal Data and Structural Refinement for **1-4**

	1	**2**	**3**	**4**
Empirical formula	$C_{18}H_{22}Cl_2HgN_2S_2$	$C_{21}H_{26}HgN_4OS_4$	$C_{36}H_{44}Br_8Hg_4N_4S_4$	$C_{18}H_{22}Cl_2CuN_2S_2$
Fw	601.99	679.29	2102.63	464.94
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	$P2_1$	*P*-1	$P2_1/n$
a /Å	7.8985(11)	8.4988(7)	8.0535(8)	8.4741(6)
b /Å	8.4537(11)	14.1645(12)	11.9606(11)	10.7598(7)
c /Å	16.961(2)	10.3265(10)	27.234(3)	21.5615(14)
α /°	88.268(5)	90	92.978(5)	90
β /°	80.200(5)	102.602(6)	94.423(5)	91.725(3)
γ /°	63.824(6)	90	106.372(4)	90
V /Å^3	1000.2(2)	1213.17(19)	2502.0(4)	1965.1(2)
Z	2	2	2	4
D_{calc} / g cm^{-3}	1.999	1.860	2.791	1.572
F(000)	580	664	1904	956
μ /mm^{-1}	8.174	6.709	18.821	1.600
θ range /°	1.22-25.99	2.02-26.50	1.50-28.00	1.89-28.00
Reflns collected (R_{int})	18362	8832 (0.0532)	51239 (0.0576)	28722 (0.0355)
Independent reflns	3914	4266	12068	4742
R_1; wR_2 [$I > 2\sigma(I)$]	0.0252, 0.0869	0.0371, 0.0746	0.0376, 0.1110	0.0253, 0.0674
R_1; wR_2 (all data)	0.0259, 0.0873	0.0447, 0.0774	0.0441, 0.1148	0.0286, 0.0696
GOF (F^2)	1.164	0.999	1.047	1.040

generated by a rotating anode. Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of APEX2.[5] All of the calculations for the structure determination were carried out using the SHELXTL package.[6] In all cases, all nonhydrogen atoms were refined anisotropically and all hydrogen atoms were placed in idealized positions and refined isotropically in a riding manner along with the their respective parent atoms. Relevant crystal data collection and refinement data for the crystal structures of **1-4** are summarized in Table 1.

Results and Discussion

Self-assembly of $\mathbf{L^2}$ with mercury(II) salts with three different anions were attempted. First, reactions of $\mathbf{L^2}$ with HgX_2 (X = Cl and SCN) afforded the crystalline complexes **1** (X = Cl) and **2** (X = SCN) that proved suitable for crystallography. The X-ray analysis revealed that **1** and **2** are [M($\mathbf{L^2}$)X_2] type neutral dichloro and dithiocyanato complexes, respectivley, and these two have no major difference in the crystal structure (Figures 1 and 2). In each case, for example, the mercury(II) center is five-coordinate, being bound to one pyridine N atom and SN donors from the macrocyclic ring of $\mathbf{L^2}$ in a bent arragnement. Two remaining sites are occupied by two anions and one sulfur donor (S2) in the macrocyclic ring remains uncoordinated.

In case of the five-coordinated complex systems, many compounds can hardly be classified into square pyramid or trigonal bipyramid geometries because of their intermediate natures due to the orbital hybridization. According to the Addison's approach,[7] the Hg atoms in **1** and **2** have distortion parameter τ value 0.32 and 0.20, respectively: $\tau = (\theta_1-\theta_2)/60$, where θ_1 and θ_2 are the largest angles in the coordination sphere, then τ = 0 means perfect square pyramid and τ = 1 means perfect trigonal bipyramid. Thus, both of Hg(II) coordination in **1** and **2** can be best described as a distorted square pyramid. In **1**, S1, N1, N2, and Cl1 atoms form the basal square plane while Cl2 atom occupies the apex position. In case of **2**, similarly, N1, S1, S4, and N2 atoms form the basal square plane while one thiocyanato ligand (S3) occupies the apex position.

In both complexes, the distances between Hg and N_{py} [2.310(4) Å in **1** and 2.363(7) Å in **2**] are clearly shorter than those of Hg-N_{tert} [2.642(4) Å in **1** and 2.496(6) Å in **2**], suggesting the important role of the pyridine arm in the

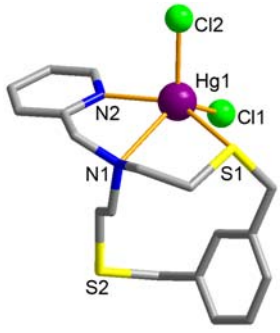


Figure 1. Crystal structure of **1**, [Hg($\mathbf{L^2}$)Cl_2] showing the distorted square pyramid coordination geometry (τ = 0.32). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Hg1-N2 2.310(4), Hg1-Cl1 2.478(1), Hg1-Cl2 2.4864(14), Hg1-S1 2.625(1), Hg1-N1 2.642(4), N2-Hg1-Cl1 98.30(1), N2-Hg1-Cl2 94.61(11), Cl1-Hg1-Cl2 115.18(6), N2-Hg1-S1 145.04(12), Cl1-Hg1-S1 101.20(5), Cl2-Hg1-S1 102.81(4), N2-Hg1-N1 68.95(15), Cl1-Hg1-N1 125.58(10), C12-Hg1-N1 118.37(10), S2-Hg1-N1 76.11(10).

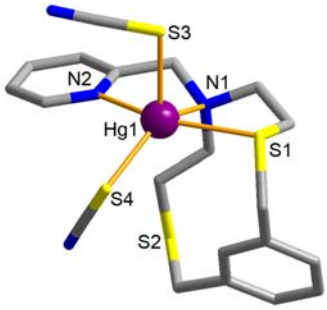


Figure 2. Crystal structure of **2**, $[Hg(\mathbf{L}^2)(SCN)_2]\cdot CH_3OH$ showing the distorted square pyramid coordination geometry (τ = 0.20). Hydrogen atoms and noncoordinating solvent molecule are omitted. Selected bond lengths (Å) and angles (º): Hg1-S1 2.638(3), Hg1-N1 2.496(6), Hg1-N2 2.363(7), Hg1-S3 2.576(2), Hg1-S4 2.493(3), N2-Hg1-S4 96.64(17), N2-Hg1-N1 71.2(2), S4-Hg1-N1 137.79(15), N2-Hg1-S3 95.47(19), S4-Hg1-S3 113.48(10), N1-Hg1-S3 107.93(16), N2-Hg1-S1 149.59(16), S4-Hg1-S1 107.87(9), N1-Hg1-S1 78.56(16), S3-Hg1-S1 91.08(9).

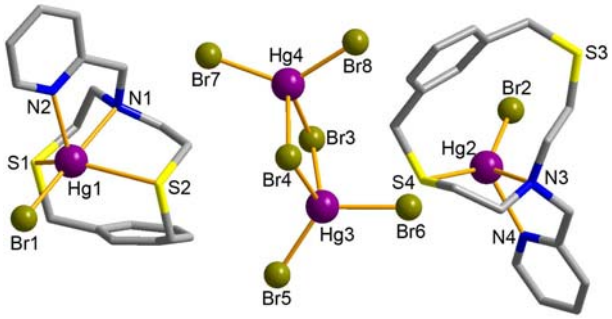


Figure 3. Crystal structure of **3**, $[Hg(\mathbf{L}^2)Br]_2[Hg_2Br_4(\mu_2\text{-}Br_2)]$ showing the distorted trigonal bipyramid coordination geometry for Hg1 (τ = 0.79) and the distorted tetrahedral coordination geometry for Hg2, Hg3, and Hg4. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (º): Hg1-N1 2.391(5), Hg1-N2 2.338(5), Hg1-S1 2.702(2), Hg1-S2 2.813(2), Hg1-Br1 2.517(1), Hg2-N3 2.485(5), Hg2-N4 2.328(5), Hg2-S4 2.491(2), Hg2-Br2 2.477(1), N2-Hg1-N1 72.84(19), N2-Hg1-Br1 106.25(15), N1-Hg1-Br1 177.84(13), N2-Hg1-S1 106.06(14), N1-Hg1-S1 80.20(13), Br1-Hg1-S1 101.96(5), N2-Hg1-S2 108.29(14), N1-Hg1-S2 76.76(13), Br1-Hg1-S2 101.81(4), S1-Hg1-S2 130.17(5), N4-Hg2-Br2 111.50(14), N4-Hg2-N3 71.95(18), Br2-Hg2-N3 121.50(13), N4-Hg2-S4 108.03(15), Br2-Hg2-S4 138.94(4), N3-Hg2-S4 81.00(13).

coordination sphere. The Hg-S_{ether} bond lengths [2.625(1) Å in **1**, 2.638(3) Å in **2**] are typical.[8] It is noteworthy that the anion coordination is predominant. For example, the Hg-Cl bond lengths [2.381(1) and 2.349(2) Å] in **1** are comparable with those reported previously for such bonds.[9] Accordingly, the strong binding of the anion toward the Hg atom inhibits the bond formation of Hg atom to S2 donor, resulting in the unsymmetrical products **1** and **2**.

Unlike **1** and **2**, the reaction of $HgBr_2$ with **L** afforded a pale yellow crystalline product **3** that features three separated unit of formula $[Hg(\mathbf{L})Br]_2[Hg_2Br_4(\mu_2\text{-}Br_2)]$: two monobromo macrocyclic complex cations and one mercury bromide anion cluster. The crystal structure of **3** is shown in Figure 3. Presumably, the occurrence of the inorganic anion cluster $[Hg_2Br_4(\mu_2\text{-}Br_2)]^{2-}$ make possible to form the two monobromo mercury(II) complex cations which show different coordination environments for the Hg centers.[3c,10] For instance, the Hg1 center is bound to all donor atoms of $\mathbf{L}^2$ and adopts a 'tight' conformation. The coordination environment is completed by one bromo atom to yield an overall metal coordination number of five. The Hg1 center in **3** has distortion parameter τ value 0.79. Thus, the coordination geometry of Hg1 atom can best be described as a distorted trigonal bipyramid with two S atoms and one pyridine N atom from $\mathbf{L}^2$ defining the trigonal plane and the axial positions occupied by the N_{tert} atom and one Br atom. The N1-Hg1-Br1 angle is 177.8(1)°.

Meanwhile, the Hg2 center in **3** is tetrahedrally coordinated by N_2S donors from $\mathbf{L}^2$ and one Br atom. In this case, one S donor (S3) of $\mathbf{L}^2$ remains uncoordinated. It is noteworthy that the Hg-S bond lengths for the Hg1 atom [Hg1-S1 2.702(2) and Hg1-S2 2.813(2) Å] are much longer than that of Hg2-S4 [2.491(2) Å] probably due to the higher coordination number and lager ring strain upon complexation for Hg1 center than Hg2. Typically, Hg-S_{ether} bond lengths are found in the range of 2.5-2.8 Å.[8] The bond distances for Hg-N_{py}, however, show no significant difference [Hg1-N2 2.338(5), Hg2-N4 2.328(5) Å] due to its flexible nature.

Having obtained three Hg(II) complexes, we proceeded to the preparation of the corresponding complex by employing Cu(I) system as another example of the soft metal ion. Since the copper(I) iodide and bromide complexes of $\mathbf{L}^2$ we tried to prepare were unstable in air, copper(I) chloride was used. In this case, unlike our expectation, blue single crystalline product **4** was obtained; generally, the copper(I) complexes show colorless or pale yellow color. So, the crystal color of **4** initially suggested that it was a copper(II) species and this was subsequently confirmed by a crystal structure determination.

Similar to the mercury(II) complexes **1** and **2**, the X-ray

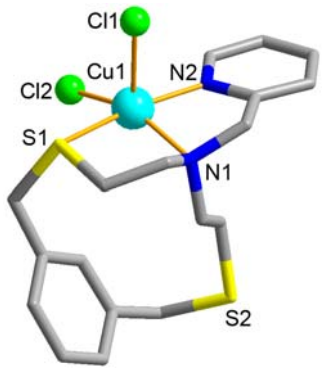


Figure 4. Crystal structure of **4**, $[Cu(\mathbf{L}^2)Cl_2]$ showing the distorted square pyramid geometry (τ = 0.23). Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (º): Cu1-N1 2.086(1), Cu1-N2 1.992(1), Cu1-S1 2.317(1), Cu1-Cl1 2.506(1), Cu1-Cl2 2.248(1), N2-Cu1-N1 82.10(5), N2-Cu1-Cl2 98.50(4), N1-Cu1-Cl2 155.27(4), N2-Cu1-S1 169.02(4), N1-Cu1-S1 87.12(4), Cl2-Cu1-S1 92.17(2), N2-Cu1-Cl1 92.47(4), N1-Cu1-Cl1 96.04(4), Cl2-Cu1-Cl1 108.60(2), S1-Cu1-Cl1 86.56(2).

analysis reveals that **4** is the [M($\mathbf{L^2}$)X_2] type neutral dichloro species. The crystal structure of **4** is shown in Figure 4. The Cu atom in **4** is five-coordinate, being bound to the two N and one S donors from $\mathbf{L^2}$. Two remaining sites are occupied by two Cl atoms; one S donor (S2) is not bound. The copper(II) center in **4** has distortion parameter τ value 0.23. Thus, the coordination geometry can best be described as a distorted square pyramid with N_2S donors from one $\mathbf{L^2}$ and one Cl atom defining the square plane and the apex position occupied by another Cl atom. The distance between Cu and the N_{py} atom (N2) [1.992(1) Å] is slightly shorter than that of Cu-N_{tert}(N1) [2.086(1) Å]. The Cu-S bond length [2.317(1) Å] is typical.[11] It is noteworthy that the bond length of Cu1-Cl1 [2.506(1) Å] is longer than that of Cu1-Cl2 [2.248(1) Å] due to the Jahn-Teller distortion. The preference of the copper(II) oxidation state in **4** may be due not only to the predominant anion binding but also to the cooperative coordination of N_2S donors toward the metal center which leads the five-coordinate system.

In summary, mercury(II) and copper(II) complexes of pyridylmethyl-armed monobenzo-NS_2-macrocycle have been prepared and structurally characterized by X-ray analysis. In all cases, the pyridine arms show important role in their three dimensional coordination behaviors via the strong N_{py}-M bonds. The coordination patterns depend markedly on the anion coordination. In case of the five-coordination system, the distortion parameter τ values were useful to classify their coordination geometries such as trigonal bipyramid or square pyramid.

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Supplementary Materials. CCDC 844548 (**1**) 844549 (**2**), 844550 (**3**), and 844551 (**4**) contain the supplementary crystallographic data. 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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