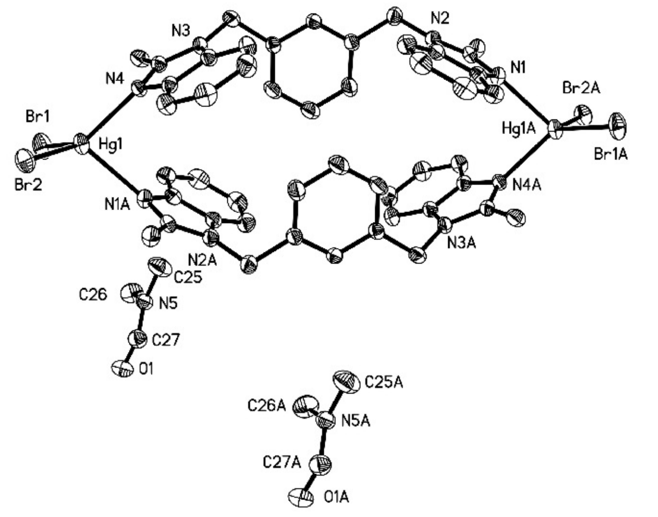
Crystal structure of bis{dibromo[μ-1-(3-((2-methyl-1*H*-benzimidazol-1-yl)methyl)benzyl)-2-methyl-1*H*-benzimidazole-$\kappa^2 N,N''$]mercury(II)} — *N*,*N*-dimethylformamide (1:2), $[HgBr_2(C_{24}H_{22}N_4)]_2 \cdot 2C_3H_7NO$

Jiyong Hu[*,I], Chunli Liao[II], Jin'an Zhao[I] and Haipeng Zhao[I]

[I] Department of Chemistry and Chemical Industry, Henan University of Urban Construction, Henan 467036, P. R. China
[II] Department of Biological Engineering, Henan University of Urban Construction, Henan 467036, P. R. China

Received April 18, 2011, accepted and available on-line December 20, 2011; CCDC no. 1267/3535



Abstract

$C_{54}H_{58}Br_4Hg_2N_{10}O_2$, triclinic, $P\bar{1}$ (no. 2), $a = 9.551(2)$ Å, $b = 12.774(3)$ Å, $c = 13.357(3)$ Å, $\alpha = 64.42(3)°$, $\beta = 86.81(3)°$, $\gamma = 71.66(3)°$, $V = 1389.1$ Å^3, $Z = 1$, $R_{gt}(F) = 0.046$, $wR_{ref}(F^2) = 0.128$, $T = 293$ K.

Source of material

A solution of $HgBr_2$ (0.0072 g, 0.02 mmol) in methanol (5 mL) and an equivalent amount of the ligand 1-(3-((2-methyl-1*H*-benzimidazol-1-yl)methyl)benzyl)-2-methyl-1*H*-benzimidazole in DMF (1.5 mL) were mixed and the colorless crystals were obtained at ambient temperature after four weeks.

Experimental details

The structures were solved by direct methods and expanded with Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections.

Discussion

The benzimidazole group has strong coordination ability, and the $\pi \cdots \pi$ interactions between their aromatic rings are of benefit for the stabilizations of the supra-molecular system as well [1,2]. Thus, benzimidazole derivatives together with their complexes attract much attention [3]. Moreover, the functional group and geometry of ligands are crucial for the construction of structure-specific coordination architectures, which is a key factor for their properties and functions. By contrast, the discrete polynuclear supra-molecules have unique applications, such as molecular catalysis, molecular instrument, and molecular recognition. Especially for clamp-type ligands, these molecules with stretched arms are conducive to the formation of such zero-dimensional motifs with pore or macrocycle [4,5]. Accordingly, molecules bearing bis(benzimidazole) groups are good candidates for the formation of novel architectures.

The title complex has a binuclear structure with macrocycle motif, the asymmetric unit contains on Hg^{2+} cation, one 1-(3-((2-methyl-1*H*-benzimidazol-1-yl)methyl)benzyl)-2-methyl-1*H*-benzimidazole (mbibix), two bromine anions and one *N*,*N*-dimethylformamide (DMF) solvent molecule. The mercury adopts a distorted tetrahedral coordination, which is completed by two mbibix nitrogen atoms and two bromine ions. The bromine anions serve as terminal groups, which separate the mercury from other bridging synthons. The bidentate mbibix bridges two mercury centers, which are separated by 13.98 Å. The separation of two parallel benzene rings bridging the benzimidazole moieties is 5.20 Å. The dihedral angle of two terminal benzimidazole groups is 53.12° within one mbibix. Two free solvent molecules are located on the two sides of the complex. Along [010], the separation between the centroids of benzene ring (C3-C8) of benzimidazole and imidazole ring (C2′-N3′–C8′–C3′–N4′) of another benzimidazole moiety is 3.74 Å with a dihedral angle of 0°. This indicates the presence of $\pi \cdots \pi$ interactions. The distance of Br2···H9b is 2.94 Å, suggesting hydrogen bonding. Based on these hydrogen bonds and $\pi \cdots \pi$ interactions, the chains are formed. In the *a*,*b* plane, the separations are 3.42 Å, 3.41 Å, 3.38 Å for C1···O1, C9···O1, C22···O1, respectively, and these intra-chain hydrogen bonds cause the chains to generate 2D supra-molecules [5,6]. Benzimidazole moieties play crucial roles in the formation and stabilization of this complex.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.11 × 0.17 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	84.46 cm^{-1}
Diffractometer, scan mode:	Rigaku Saturn 724 CCD, ω
$2\theta_{max}$:	55.78°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17477, 6609
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5404
$N(param)_{refined}$:	329
Programs:	SHELXS-97, SHELXL-97 [7]

* Correspondence author (e-mail: hujiyong688@yahoo.com.cn)

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(20)	2*i*	0.8661	1.2976	0.7368	0.061
H(21)	2*i*	0.9811	1.0908	0.7916	0.074
H(22)	2*i*	0.8518	0.9684	0.7847	0.072
H(23)	2*i*	0.6018	1.0500	0.7230	0.065
H(16A)	2*i*	0.3392	1.2267	0.5864	0.061
H(16B)	2*i*	0.2283	1.3271	0.6163	0.061
H(13)	2*i*	0.2874	1.2485	0.8455	0.072
H(12)	2*i*	0.2650	1.0928	1.0113	0.084
H(11)	2*i*	0.2636	0.9098	1.0188	0.066
H(15)	2*i*	0.3104	1.0359	0.6929	0.048
H(9A)	2*i*	0.1712	0.8466	0.8473	0.055
H(9B)	2*i*	0.3187	0.8334	0.7893	0.055
H(1A)	2*i*	0.1074	0.6179	1.1066	0.077
H(1B)	2*i*	0.0868	0.6833	0.9759	0.077
H(1C)	2*i*	0.0820	0.7591	1.0430	0.077

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7)	2*i*	0.5996	0.7805	0.8505	0.059
H(6)	2*i*	0.8383	0.6625	0.9318	0.072
H(5)	2*i*	0.8810	0.4916	1.1009	0.069
H(4)	2*i*	0.6884	0.4330	1.1950	0.061
H(26A)	2*i*	0.2617	0.0345	0.4526	0.113
H(26B)	2*i*	0.2588	0.1651	0.4339	0.113
H(26C)	2*i*	0.2418	0.1395	0.3313	0.113
H(25A)	2*i*	−0.1036	0.1683	0.5067	0.128
H(25B)	2*i*	0.0265	0.2044	0.5348	0.128
H(25C)	2*i*	0.0447	0.0661	0.5717	0.128
H(27)	2*i*	−0.1304	0.2347	0.3252	0.072
H(17A)	2*i*	0.3218	1.5930	0.5790	0.075
H(17B)	2*i*	0.2292	1.5088	0.6494	0.075
H(17C)	2*i*	0.2572	1.5268	0.5272	0.075

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*i*	0.5656(6)	1.4174(5)	0.6605(4)	0.037(3)	0.037(3)	0.048(3)	−0.014(2)	0.002(2)	−0.014(2)
N(2)	2*i*	0.4415(6)	1.2993(5)	0.6544(4)	0.041(3)	0.042(3)	0.042(3)	−0.016(2)	0.002(2)	−0.014(2)
N(3)	2*i*	0.3492(5)	0.7278(5)	0.9539(4)	0.039(3)	0.035(3)	0.038(3)	−0.015(2)	0.002(2)	−0.010(2)
N(4)	2*i*	0.3899(5)	0.5632(5)	1.1169(4)	0.038(3)	0.039(3)	0.032(2)	−0.016(2)	0.005(2)	−0.009(2)
C(18)	2*i*	0.4346(7)	1.4143(6)	0.6362(5)	0.038(3)	0.038(3)	0.035(3)	−0.013(3)	0.010(3)	−0.012(2)
C(19)	2*i*	0.6629(6)	1.2974(6)	0.6973(5)	0.033(3)	0.042(3)	0.037(3)	−0.009(3)	0.008(2)	−0.015(3)
C(20)	2*i*	0.8135(7)	1.2485(7)	0.7342(6)	0.044(4)	0.056(4)	0.049(4)	−0.012(3)	0.001(3)	−0.022(3)
C(21)	2*i*	0.8810(8)	1.1257(7)	0.7664(6)	0.044(4)	0.062(5)	0.058(4)	0.003(4)	0.006(3)	−0.023(4)
C(22)	2*i*	0.8026(9)	1.0515(7)	0.7624(6)	0.060(5)	0.046(4)	0.058(4)	−0.001(4)	0.008(4)	−0.020(3)
C(23)	2*i*	0.6541(8)	1.0990(7)	0.7261(6)	0.059(4)	0.048(4)	0.060(4)	−0.016(3)	0.012(4)	−0.028(3)
C(24)	2*i*	0.5860(8)	1.2232(6)	0.6943(5)	0.052(4)	0.042(4)	0.036(3)	−0.016(3)	0.007(3)	−0.015(3)
C(16)	2*i*	0.3194(8)	1.2580(7)	0.6420(6)	0.054(4)	0.051(4)	0.047(4)	−0.027(3)	−0.002(3)	−0.013(3)
C(14)	2*i*	0.3002(7)	1.1588(6)	0.7514(5)	0.043(3)	0.048(4)	0.038(3)	−0.021(3)	0.001(3)	−0.012(3)
C(13)	2*i*	0.2871(9)	1.1749(7)	0.8475(6)	0.086(6)	0.048(4)	0.052(4)	−0.031(4)	0.018(4)	−0.021(3)
C(12)	2*i*	0.273(1)	1.0816(8)	0.9467(6)	0.111(7)	0.066(5)	0.045(4)	−0.040(5)	0.025(4)	−0.029(4)
C(11)	2*i*	0.2722(9)	0.9718(7)	0.9512(6)	0.076(5)	0.049(4)	0.033(3)	−0.021(4)	0.014(3)	−0.013(3)
C(10)	2*i*	0.2835(6)	0.9536(5)	0.8566(5)	0.032(3)	0.035(3)	0.035(3)	−0.008(2)	−0.002(2)	−0.007(2)
C(15)	2*i*	0.2997(7)	1.0479(6)	0.7572(5)	0.042(3)	0.046(3)	0.034(3)	−0.020(3)	0.003(3)	−0.014(3)
C(9)	2*i*	0.2746(8)	0.8398(6)	0.8545(5)	0.053(4)	0.041(3)	0.034(3)	−0.014(3)	−0.002(3)	−0.010(3)
C(1)	2*i*	0.1271(7)	0.6814(7)	1.0412(6)	0.045(4)	0.063(5)	0.043(4)	−0.019(3)	0.006(3)	−0.019(3)
C(2)	2*i*	0.2858(7)	0.6570(6)	1.0384(5)	0.039(3)	0.042(3)	0.037(3)	−0.018(3)	0.003(3)	−0.013(3)
C(8)	2*i*	0.5015(7)	0.6778(6)	0.9781(5)	0.039(3)	0.042(3)	0.039(3)	−0.016(3)	0.005(3)	−0.015(3)
C(7)	2*i*	0.6173(7)	0.7124(6)	0.9193(6)	0.048(4)	0.050(4)	0.049(4)	−0.023(3)	0.013(3)	−0.017(3)
C(6)	2*i*	0.7583(8)	0.6414(8)	0.9677(7)	0.046(4)	0.072(5)	0.067(5)	−0.031(4)	0.019(4)	−0.029(4)
C(5)	2*i*	0.7839(8)	0.5379(7)	1.0703(7)	0.034(3)	0.064(5)	0.070(5)	−0.011(3)	0.005(3)	−0.028(4)
C(4)	2*i*	0.6701(7)	0.5024(7)	1.1271(6)	0.042(4)	0.050(4)	0.051(4)	−0.013(3)	0.006(3)	−0.016(3)
C(3)	2*i*	0.5278(7)	0.5738(6)	1.0797(5)	0.039(3)	0.036(3)	0.042(3)	−0.013(3)	0.007(3)	−0.020(3)
O(1)	2*i*	0.0070(6)	0.2267(5)	0.2257(4)	0.079(4)	0.078(4)	0.048(3)	−0.019(3)	−0.003(3)	−0.026(3)
N(5)	2*i*	0.0604(6)	0.1568(5)	0.4104(5)	0.049(3)	0.056(4)	0.042(3)	−0.018(3)	0.001(3)	−0.017(3)
C(26)	2*i*	0.2189(9)	0.1210(9)	0.4068(8)	0.057(5)	0.085(6)	0.087(6)	−0.013(5)	−0.002(5)	−0.046(5)
C(25)	2*i*	0.002(1)	0.148(1)	0.5146(7)	0.091(7)	0.115(8)	0.053(5)	−0.043(6)	0.017(5)	−0.033(5)
C(27)	2*i*	−0.0294(9)	0.2090(7)	0.3182(7)	0.055(4)	0.061(5)	0.058(5)	−0.015(4)	−0.002(4)	−0.021(4)
C(17)	2*i*	0.2991(7)	1.5198(6)	0.5944(6)	0.042(4)	0.045(4)	0.056(4)	−0.013(3)	0.001(3)	−0.017(3)
Br(2)	2*i*	0.55465(8)	0.23007(7)	1.39035(6)	0.0511(4)	0.0456(4)	0.0597(4)	−0.0091(3)	0.0063(3)	−0.0133(3)
Br(1)	2*i*	0.10174(8)	0.45672(8)	1.34859(8)	0.0444(4)	0.0709(5)	0.0829(6)	−0.0270(4)	0.0157(4)	−0.0146(4)
Hg(1)	2*i*	0.36454(3)	0.44304(2)	1.29664(2)	0.0429(2)	0.0414(2)	0.0503(2)	−0.0171(1)	0.0094(1)	−0.0111(1)

References

1. Isele, K.; Franz, P.; Ambrus, C., Bernardinelli, G.; Decurtins, S.; Williams, A. F.: Self-Assembly and Interconversion of Tetranuclear Copper(II) Complexes. Inorg. Chem. **44** (2005) 3896-3906.
2. Sun, W.; Shao, C.; Chen, Y.; Hu, H.; Sheldon, R. A.; Wang, H.; Leng, X.; Jin, X.: Controllable Supramolecular Assembly by $\pi\cdots\pi$ Interactions: Cobalt(II) and Copper(II) Complexes with Benzimidazole Derivatives. Organometallics **21** (2002) 4350-4355.
3. Jang, J. J.; Li, L.; Yang, T.; Kuang, D. B.; Wang, W.; Su, C. Y.: Self-assembly of 2D Borromean networks through hydrogen-bonding Recognition. Chem. Commun. (2009) 2387-2389.
4. Dong, Y.-B.; Zhang, Q.; Liu, L. L.; Ma, J.- P.; Tang, B.; Huang, R.-Q.: $[Cu(C_{24}H_{22}N_4O_3)]\cdot CH_2Cl_2$: A Discrete Breathing Metallamacrocycle Showing Selective and Reversible Guest Adsorption with Retention of Single Crystallinity. J. Am. Chem. Soc. **129** (2007) 1514-1515.
5. Raehm, L.; Mimassi, L.; Guyard-Duhayon, C.; Amouri, H.; Crucial Role of the Counteranion on the Templation of Metallomacrocycles and a 3D Network: Synthesis, Characterization, and Structural Analysis. Inorg. Chem. **42** (2003) 5654-5659.
6. Fox, M. A.; Hughes, A. K.: Cage C–H···X interactions in solid-state structures of icosahedral carboranes. Coord. Chem. Rev. **248** (2004) 457-476.
7. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.