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Crystal structure analysis and synthesis of Di-iodobis(3- methylpyridine)mercury(II)

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Abstract : Single crystals of Di-iodobis(3-methylpyridine)mercury(II) were grown by slow evaporation method and X-ray diffraction analysis reveals monoclinic *P21/n* space group with unit cell dimensions of a = 9.569(5) Å, b= 15.242(5) Å, c= 11.380(5) Å and β= 100.966(5)°. The geometry surrounded by two I atoms in the equatorial plane. The benzene rings are planar and make a dihedral angle of 82.4(2)°. Crystal data were collected using BRUKER SMART APEX II CCD X-ray diffractometer. The structure was solved by direct method and refined on F^2 by full-matrix least-squares procedure to the final R1 of 0.024 using SHELXL programs.
Key Words: Methylpyridine, Mercury(II), Crystal packing and Crystal structure.

Introduction

The solid-state structures of the bis(pyridine) complexes of mercury(II) halides have been studied extensively by spectroscopic and diffraction methods[1]. The more recent vibrational studies suggest the iodide analogues to be monomeric with four co-ordinate mercury[2]. Crystallographic reports about mercury (II) complexes containing thioamides establish that these ligands are coordinated via the sulfur atom [3, 4, 5].

Experimental

X-ray Structure Determination

Single crystal of the compound suitable for x-ray diffraction was obtained by slow evaporation method. Three dimensional intensity data were collected on a Bruker[6] SMART APEX CCD Diffractometer using graphite monochromatized Mo-Kα radiation (λ= 0.71073 Å) at Department of chemistry, Pondicherry University, Pondicherry 605 014, India. The structure was solved by direct methods and refined on F^2 by full-

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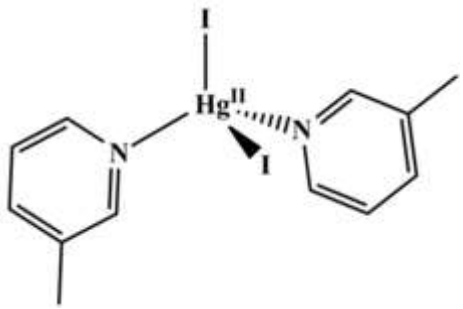
matrix least-squares procedures using the SHELXL programs[7]. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with ORTEP-3[8].The crystallographic data for the compound are listed in Table 1.

Table 1: Crystal data and structure refinement of the titled compound

Compound	**Parameters**
Empirical formula	C12 H14 Hg I2 N2
Formula weight	640.64
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, *P21/n*
Unit cell dimensions	a = 9.569(5) Å alpha = 90.000(5)º.
	b = 15.242(5) Å beta = 100.966(5)º.
	c = 11.380(5) Å gamma = 90.000(5)º.
Volume	1629.5(12) A^3
Z, Calculated density	4, 2.611 Mg/m^3
Absorption coefficient	13.218 mm^{-1}
F(000)	1144
Crystal size	0.35 x 0.30 x 0.20 mm
Theta range for data collection	4.10 to 29.07º.
Limiting indices	-11<=h<=12, -17<=k<=20, -15<=l<=14
Reflections collected / unique	8843 / 3755 [R(int) = 0.0216]
Completeness to theta = 25.00	99.00%
Max. and min. transmission	0.1774 and 0.0905
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3755 / 0 / 156
Goodness-of-fit on F2	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0545
R indices (all data)	R1 = 0.0277, wR2 = 0.0556
Largest diff. peak and hole	0.805 and -1.455 e. $Å^{-3}$

Synthesis of the compound

Mercury iodide (0.3 g) was dissolved in excess of 3-methylpyridine. The solvent was dried by treatment with 3-A molecular sieves. Pale yellow crystals of title compound were obtained by slow cooling of the saturated solution. The resulting solution was subjected to Crystallization by slow evaporation of the solvent resulting in single crystals suitable for X-ray crystallographic studies.



Results and Discussion

The title molecule is shown in Fig. 1. The benzene ring plane is approximately planar, with maximum deviation from the least-squares plane being 0.0327(1) Å for atom C6 and 0.0415(1) Å for atom C12. The dihedral angle between the two benzene ring moiety is 82.4(2)º. The bond distances Hg---I1 and Hg---N1 are 2.6539(2) Å and 2.387(3) Å, and the bond angles I1---Hg---I2 and N1---Hg---N2 are 141.50(1)º and 95.15(11)º.

All bond lengths and bond angles in (I) are in the range of expected values. All the H atoms are involved in C---H...I hydrogen bonds, which serve to link the cations and anions into generating sheets along the c-axis. The crystal packing also features ***π*---*π*** interactions between the benzene rings, with centroid - centroid separations of 3.944(3) Å.

Table 2: Hydrogen-bond geometry [Å]

D—H…A	D—H	H…A	D…A	D—H…A
C9—H9…I2	0.93	3.06	3.974	169

Symmetry code: 5/2-x,1/2+y,1/2-z

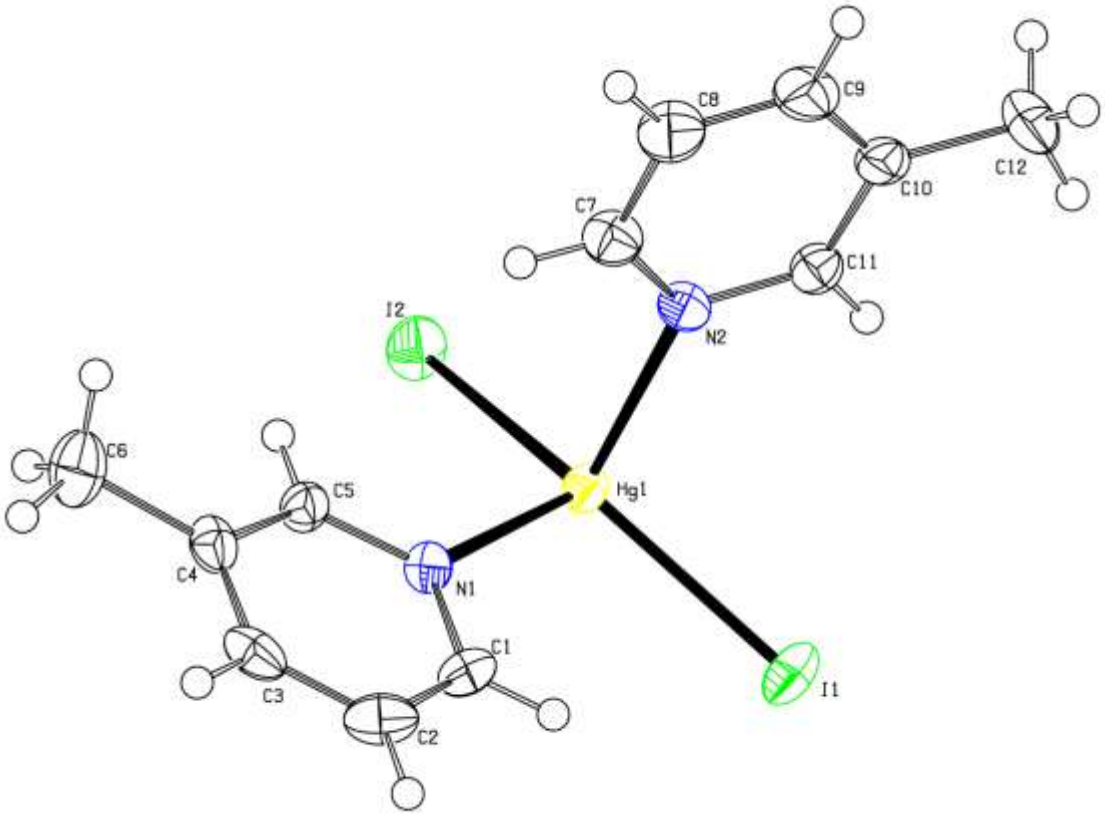


Fig 1. The molecular structure of the title compound, with atom labeling. Displacement ellipsoids are drawn at the 30% probability level.

Table 3: Selected Bond lengths (Å)

Atom	lengths (Å)
C(1)-C(2)	1.381(6)
C(1)-H(1)	0.93
C(2)-C(3)	1.377(6)
C(2)-H(2)	0.93
C(3)-C(4)	1.382(6)
C(3)-H(3)	0.93
C(4)-C(5)	1.385(6)
C(4)-C(6)	1.501(6)
C(5)-N(1)	1.336(5)
C(5)-H(5)	0.93
C(6)-H(6A)	0.96
C(6)-H(6B)	0.96
C(6)-H(6C)	0.96
C(7)-N(2)	1.329(5)
C(7)-C(8)	1.385(6)
C(7)-H(7)	0.93
C(8)-C(9)	1.368(6)
C(8)-H(8)	0.93
C(9)-C(10)	1.393(7)
C(9)-H(9)	0.93
C(10)-C(11)	1.379(6)
C(10)-C(12)	1.506(6)
C(11)-N(2)	1.339(5)
C(11)-H(11)	0.93
C(12)-H(12A)	0.96
C(12)-H(12B)	0.96
C(12)-H(12C)	0.96
N(1)-Hg(1)	2.386(3)

Table 3: Selected Bond angles (º)

Atom	Angle
C(4)-C(3)-H(3)	119.5
C(3)-C(4)-C(5)	116.2(4)
C(3)-C(4)-C(6)	122.8(4)
C(5)-C(4)-C(6)	120.9(4)
N(1)-C(5)-C(4)	124.2(4)
N(1)-C(5)-H(5)	117.9
C(4)-C(5)-H(5)	117.9
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
N(2)-C(7)-C(8)	122.1(4)
N(2)-C(7)-H(7)	118.9
C(8)-C(7)-H(7)	118.9
C(9)-C(8)-C(7)	118.8(4)
C(9)-C(8)-H(8)	120.6
C(7)-C(8)-H(8)	120.6
C(8)-C(9)-C(10)	120.3(4)
C(8)-C(9)-H(9)	119.8
C(10)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	116.6(4)
C(11)-C(10)-C(12)	120.8(4)
C(9)-C(10)-C(12)	122.6(4)
N(2)-C(11)-C(10)	123.9(4)
N(2)-C(11)-H(11)	118
C(10)-C(11)-H(11)	118

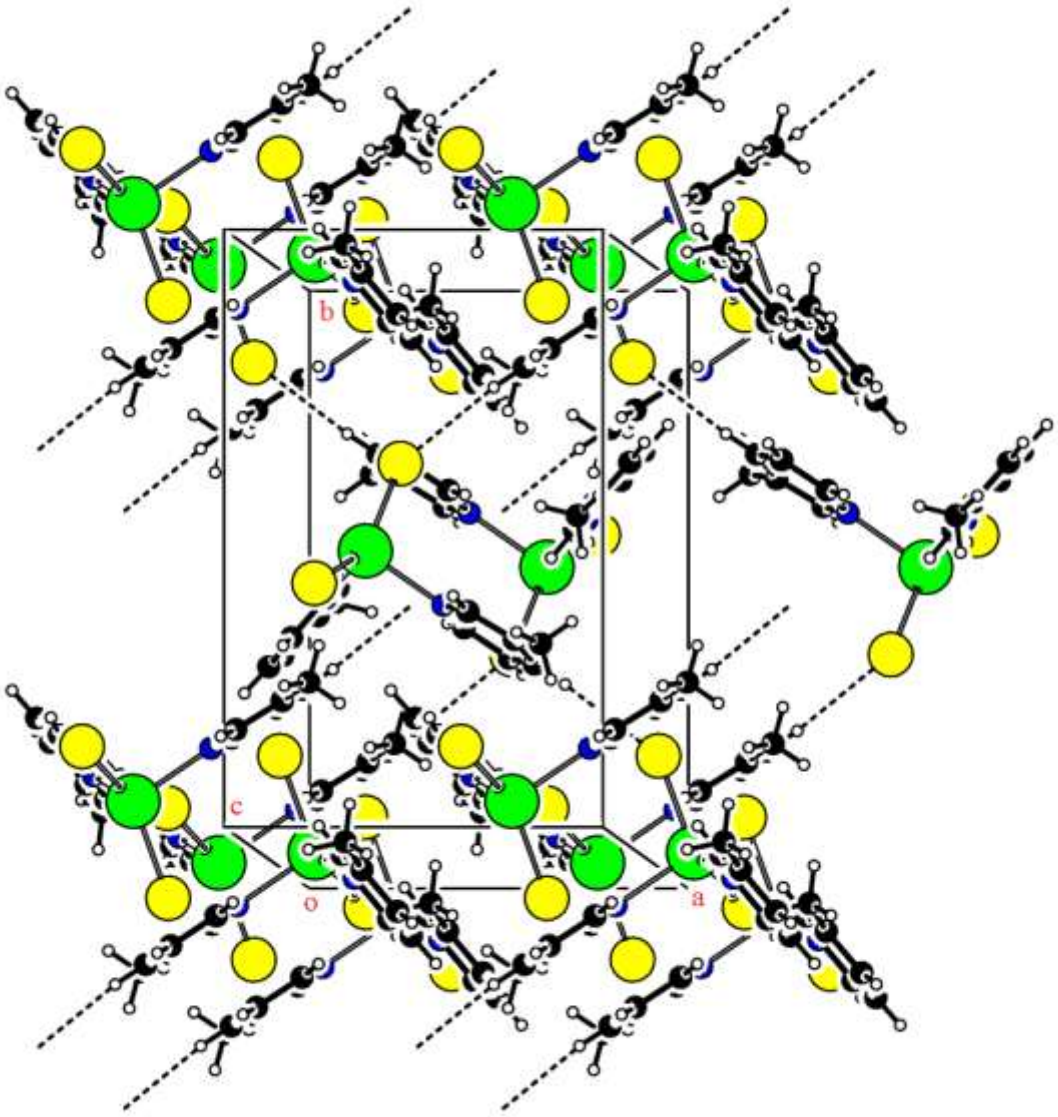


Fig 2. A crystal packing diagram of the title compound, viewed along the c axis. The hydrogen bonds are shown as dashed lines (see Table 2 for details).

Conclusion

The crystal structure analysis of a novel methylpyridine and Mercury(II) compound was studied using x-ray diffraction method. The geometry surrounded by two I atoms in the equatorial plane. All the H atoms are involved in C---H...I hydrogen bonds, which serve to link the cations and anions into generating sheets along the c-axis.

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References

1. Canty, A.J., Raston, C. L., Skelton, B. W., White, A. H., (1982). J. Chem. Soc. Dalton, 15-18.
2. Persson, I., Sandstrom, M., Goggin, P. L. & Mosset, A., (1985). J. Chem. Soc. Dalton Trans. 1597-1604.
3. Popovic, Z., Pavlovic, G., Matkovic-Calogovic, D., Soldin, Z., Rajic, M., Vikic-Topic, D. & Kovacek, D. (2000). Inorg. Chim. Acta,306, 142--152.
4. Popovic, Z., Soldin, Z., Pavlovic, G., Calogovic, D. M. & Rajic, M. M. S. (2002). Struct. Chem.13, 425--436.
5. Jiang, X. N., Xu, D., Yuan, D. R., Yu, W. T., Lu, M. K., Gu, S. Y., Zu, G. H. & Fu, Q. (2001). Chin. Chem. Lett.12, 279—282.
6. Bruker (2008), APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, US.
7. Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
8. Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849—854.

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