

Crystal and Molecular Structure of Bis[(μ -benzotriazolato-N1,N2)methylmercury(II)]

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Benzotriazole, 1, (BTAH; the conjugate base is denoted by BTA) is a technologically important corrosion inhibitor for copper and its alloys with which it reacts to form surface-phase coordination compounds [1, 2] which act as barriers to cathodic reactions. Notwithstanding this, the structures of only three of its copper complexes have been reported: $[\text{Cu}(\text{BTA})_2\text{Cl}_2]_2 \cdot \text{H}_2\text{O}$, [3], the mixed valence copper cluster $\text{Cu}_5(\text{BTA})_6(\text{t-C}_4\text{H}_9\text{NC})_4$, 2, [4] and $[\text{Cu}_2[\text{tris}(\text{methylbenzimidazol-2-ylmethyl})\text{amine}]_2(\text{BTA})(\text{NO}_3)_3]$, 3 [5]. In fact, the structural chemistry of benzotriazole coordination compounds is quite complex, in part because both BTAH and BTA are polydentate ligands which may exhibit multiple bonding modes. Monodentate η_1 coordination via N3 to iridium occurs in $\text{Ir}(\text{CO})(\text{PPh}_3)_2(\text{BTA})$ [6]. Behavior as a η_2 ligand with coordination to N1 and N2 is seen in $\text{M}_3(\text{BTA})_6(\text{CH}_2=\text{CH}-\text{CH}_2\text{NH}_2)_6(\text{Ph}_3\text{PO})_2$ ($\text{M} = \text{Co}, \text{Ni}$) [7, 8] and to N1 and N3 in 3. In $\text{Ti}(\text{BTA})$ [9] and in 2, benzotriazole

serves as a tridentate ligand with all three heterocyclic atoms participating in metal–nitrogen bonding. We have conducted an extensive study of benzotriazole metal complexes in order to generate well characterized compounds which could serve as models for BTAH and BTA surface complexes [10]. One of the materials reported earlier, $\text{CH}_3\text{Hg}(\text{BTA})$, 4, which is the subject of this paper, has now been structurally characterized. It is not monomeric as originally proposed but, in the solid state, dimerizes in such a way that η_2 -benzotriazolato bonding leads to a T-shaped coordination about mercury.

Description of the Structure

The $\text{CH}_3\text{Hg}(\text{BTA})$ molecules crystallize as centrosymmetric dimers with one short and one long Hg–N bond. An ORTEP view is shown in Fig. 1. Positional parameters are listed in Table I and bond distances and angles are given in Table II. The Hg–

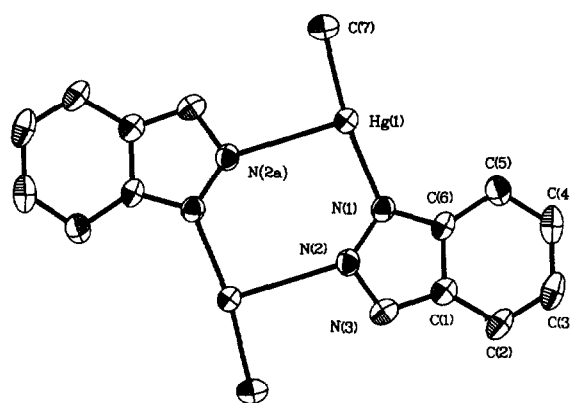


Fig. 1. ORTEP drawing of the centrosymmetric dimer of 4 showing the numbering scheme. Ellipsoids are shown as 50% probability surfaces.

TABLE I. Final Positional Parameters with their e.s.d. in Parentheses for the Non-hydrogen atoms. $U(\text{eq}) = 1/3(U_{11} + U_{22} + U_{33})$.

Atom	x	y	z	$U(\text{eq})$
Hg(1)	0.23417(2)	0.01410(1)	0.08125(5)	0.0415(1)
N(1)	0.1112(4)	-0.0636(3)	0.2915(9)	0.036(1)
N(2)	-0.0302(5)	-0.0628(3)	0.2787(9)	0.038(1)
N(3)	-0.0819(5)	-0.1124(3)	0.461(1)	0.044(1)
C(1)	0.0276(6)	-0.1455(3)	0.602(1)	0.039(1)
C(2)	0.0308(7)	-0.2014(3)	0.811(1)	0.048(1)
C(3)	0.1559(7)	-0.2242(3)	0.908(1)	0.052(1)
C(4)	0.2803(7)	-0.1920(4)	0.801(1)	0.053(1)
C(5)	0.2813(6)	-0.1371(4)	0.593(1)	0.046(1)
C(6)	0.1507(5)	-0.1140(3)	0.493(1)	0.034(1)
C(7)	0.3824(7)	0.0840(4)	-0.096(2)	0.071(2)

TABLE II. Relevant Bond Distances (Å) and Angles (°).

(a) Bond distances					
Hg(1)–N(1)	2.074(4)	N(2)–N(3)	1.324(7)	C(3)–C(4)	1.42(1)
Hg(1)–N(2a) ^a	2.707(4)	N(3)–C(1)	1.372(7)	C(4)–C(5)	1.38(1)
Hg(1)–C(7)	2.072(7)	C(1)–C(2)	1.393(8)	C(5)–C(6)	1.400(8)
N(1)–N(2)	1.361(6)	C(1)–C(6)	1.404(7)		
N(1)–C(6)	1.353(7)	C(2)–C(3)	1.35(1)		
(b) Bond angles					
N(1)–Hg(1)–N(2a)	95.1(1)	N(3)–C(1)–C(2)	131.0(5)		
N(1)–Hg(1)–C(7)	171.2(2)	N(3)–C(1)–C(6)	107.8(5)		
N(2a)–Hg(1)–C(7)	93.6(2)	C(2)–C(1)–C(6)	121.2(5)		
Hg(1)–N(1)–N(2)	122.9(3)	C(1)–C(2)–C(3)	118.0(6)		
Hg(1)–N(1)–C(6)	127.9(4)	C(2)–C(3)–C(4)	120.8(6)		
N(2)–N(1)–C(6)	108.5(4)	C(3)–C(4)–C(5)	122.8(6)		
Hg(1a)–N(2)–N(1)	138.9(3)	C(4)–C(5)–C(6)	115.7(5)		
Hg(1a)–N(2)–N(3)	109.3(3)	N(1)–C(6)–C(1)	106.2(5)		
N(1)–N(2)–N(3)	110.0(4)	N(1)–C(6)–C(5)	132.4(5)		
N(2)–N(3)–C(1)	107.6(5)	C(1)–C(6)–C(5)	121.4(5)		

^aa denotes an atom related by the inversion center.

TABLE III. Least-Squares Planes.^a

I: $-1.608(5)x + 12.96(2)y + 3.099(4)z + 0.0(-) = 0$ Hg(1)* 0.058(2); N(1)* $-0.099(5)$; N(2)* 0.099(5); Hg(1a)* $-0.058(2)$; N(1a)* 0.099(5); N(2a)* $-0.099(5)$
II: $-0.326(25)x + 12.632(35)y + 3.270(9)z - 0.121(7) = 0$ N(1)* $-0.007(10)$; N(2)* 0.007(9); N(3)* $-0.005(11)$; C(1)* 0.001(12); C(6)* 0.003(11); Hg(1) 0.247(9); Hg(1a) $-0.488(9)$

^aPlane equations through the atoms with asterisk in terms of fractional coordinates. Deviations in Å.

N1 separation, 2.074(4) Å, is quite comparable to the d(Hg–N) values of 2.06 Å in Hg[NHC(O)–CH₃]₂ [11] and 2.05 Å in Hg(NSF₂)₂ [12] and substantially shorter than the 2.14–2.64 Å range of Hg–N distances in the seven coordinate mercury complex [(1,8-naphthyridine)₃HgClO₄][ClO₄] [13]. The separation between mercury and the central nitrogen, N2, is 2.706(4) Å, about 0.3 Å shorter than the sum of the van der Waals radii [14] and, in agreement with the solution phase properties of **4**, must be considered to be a rather weak bond. Nevertheless, the Hg–N interactions combine to significantly perturb the stereochemistry about mercury so that <C7–Hg–N1 is 171.2(2)°, the coordination geometry about the metal thus being approximately T-shaped. Distortions from 180° by equatorial ligand interactions for nominally linear Hg(II) occur in C₆H₅Hg(CN)(phenanthroline) [15], with <C–Hg–C = 167.5° and Hg–N contacts of 2.66–2.68 Å and in CH₃Hg(methionine), with <C–Hg–N = 173° and Hg–O contacts of 2.67–2.72 Å [16]. More recently, similar T-shaped geometries have been observed in phenylmercury dithizonate [17] and in [CH₃Hg(di-2-pyridylmethane)]NO₃ [18]. In

both of these compounds, d(Hg–C) is 2.10(2) Å, in agreement with the 2.072(7) Å distance in **4**. In CH₃Hg(BTA), the benzotriazolot(1–) group is bonded to mercury through both N1 and N2. It therefore functions as a bidentate ligand utilizing adjacent nitrogen sites as has been observed in Ni[(BTA)₃Ni(allylamine)]₂(Ph₃PO)₂ [7, 8] and polymeric Zn₂(BTA)₄ [19]. Both N–N and C–N distances in the triazole ring are the same within experimental error, *cf.* Table III, indicating that charge in this ring is effectively delocalized. In agreement with this, the C1, C6, N1, N2, N3 rings are essentially planar with displacements from their least-squares planes being less than 0.01 Å (*cf.* Table III).

The six membered ring in CH₃Hg(BTA) formed by N1, N2 Hg1 and the symmetry-related N1A, N2A and Hg1A is nearly planar. The 0.09 Å atomic displacements from the calculated least-squares plane alternate in sign proceeding around the ring, giving it an overall 'ruffled' appearance. The packing of the dimeric units is illustrated in Fig. 2. Stacking interactions are present in directions perpendicular to the *a*-axis. The benzene rings are separated by

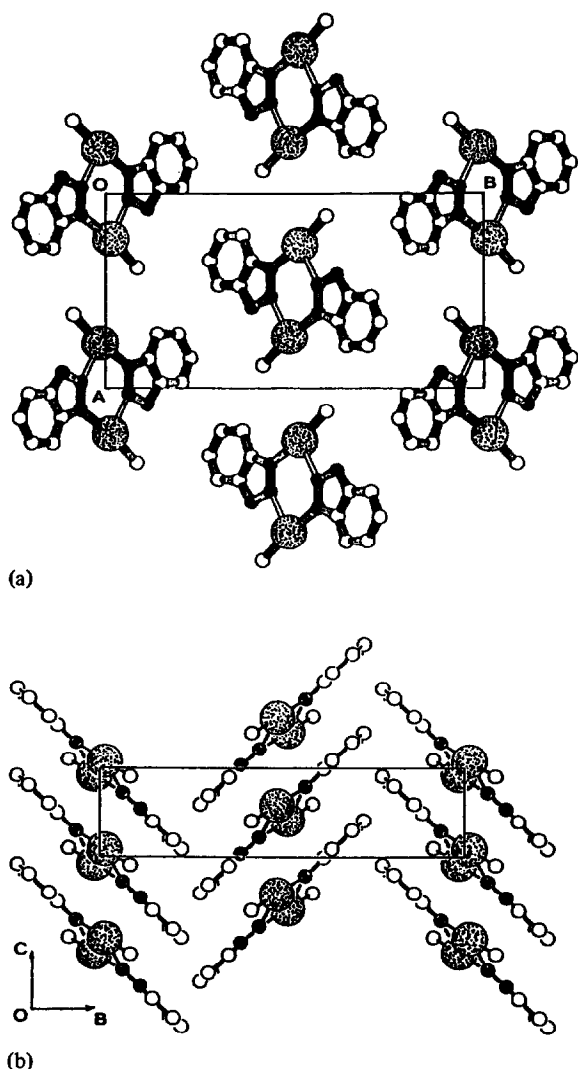


Fig. 2. Packing of the dimers as seen along the *c*-axis (a) and *a*-axis (b). Mercury atoms are represented by dotted circles and nitrogen atoms by black circles. Hydrogen atoms have been omitted for clarity.

3.31 Å. There is a short Hg–N contact between molecules stacked in the *c* direction, viz. Hg1–N3 $[-x, -y, 1 - z] = 3.111(5)$ Å, with N1–Hg1 \cdots N(3) $[-x, -y, 1 - z] = 79.1(2)^\circ$ and N2 $[-x, -y, -z] - \text{Hg1} \cdots \text{N3} [-x, -y, 1 - z] = 83.1(1)^\circ$.

Dimeric $[\text{CH}_3\text{Hg}(\text{BTA})]_2$ dissociates in chloroform solution, most likely by rupture of the long Hg–N2 bond, to form monomeric $\text{CH}_3\text{Hg}(\text{BTA})$. Thus, its molecular weight in this solvent, determined by vapor pressure osmometry, is 335, compared with a calculated value of 333. Similarly, $^2J_{\text{Hg}-\text{C}-\text{H}}$ is 212 Hz, a result consistent with two coordinate mercury in solution.

Experimental

Crystals of **4** suitable for X-ray crystallography were grown by slow cooling of a solution of the compound in hot (*ca.* 100 °C) toluene. A transparent, colorless needle shaped (*c*-axis) specimen was mounted on a glass fiber. Data were collected on an ENRAF-NONIUS CAD4F diffractometer. Crystal data and additional experimental details are given in Table IV. The unit cell dimensions were derived from the setting angles of 25 carefully centered reflections. The space group was determined to be $P2_1/n$ from the observed systematic extinctions ($0\ k\ 0$ for $k = 2n + 1$ and $h\ 0\ l$ for $h + l = 2n + 1$). The observed orthorhombic metrical symmetry is not supported by a corresponding symmetry in the reciprocal lattice (preliminary attempts at a structure solution using crystals grown from acetone were unsuccessful in view of nearly perfect twinning, giving rise to pseudo-orthorhombic Laue symmetry). The intensities for a half sphere of reflections were collected and corrected for absorption by an empirical method [19]. The data were averaged into a unique set and corrected for Lorentz and polarization effects and long term linear decay.

TABLE IV. Crystal Data and Details of the Structure Determination.

(a) Crystal data	
Formula	$\text{C}_7\text{H}_7\text{HgN}_3$
Mol. Wt.	333.75
Space group	$P2_1/n$; No. 14
Crystal system	Monoclinic
<i>a</i> , Å	9.618(2)
<i>b</i> , Å	18.134(1)
<i>c</i> , Å	4.563(2)
β , °	90.00(2)
<i>Z</i>	4
<i>D</i> (calc), g cm^{-3}	2.785

(continued overleaf)

TABLE IV. (continued)

$F(000)$, electrons	600
$\mu(\text{MoK}\alpha)$, cm^{-1}	185.8
Crystal size, mm	$0.15 \times 0.19 \times 1.08$
(b) Data Collection	
θ_{min} , θ_{max} , °	1.1, 27.5
Radiation, Å	MoK α (Zr-filtered), 0.71069
Horizontal and vertical aperture, mm.	3, 3
Max time per reflection, seconds	120
reference reflections	1 2 5; 1 $\bar{2}$ $\bar{5}$; 2 0 0
Decay, hours of X-ray exposure time	14%, 107
Data set	+ h , + k , + l
Total measured reflections	4022
Total unique reflections	1724
Observed data ($I > 2.5\sigma(I)$)	1527
Empirical absorption correction (minimum and maximum correction)	0.762, 1.311
(c) Refinement	
Number of refined parameters	102
Number of reflections	1527
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.035 F^2$
$R = \Sigma F_o - F_c / \Sigma F_o $	0.0271
$R_w = \{\Sigma w(F_o - F_c)^2 / \Sigma w F_o ^2\}^{1/2}$	0.0376
Extinction-parameter x from $F^* = F(1 - 0.0001 * x * F^2 / \sin(\theta))$	0.0007(1)
S =	1.25
min. and max. residual density $e \text{ \AA}^{-3}$	-1.1, 1.4

The mercury atom was located from a Patterson map and the remainder of the structure from a difference synthesis. Full-matrix least-squares refinement converged at $R = 0.0271$. Hydrogen atoms (excluding those on the methyl group) were located on calculated positions and refined in the riding mode with one overall temperature factor. The final difference synthesis did not show any significant features apart from some residual electron density near the mercury atom. Literature scattering factors for Hg, N and C [20] and H [21] were employed. Anomalous dispersion corrections were made by the method of Cromer and Liberman [23].

Calculations were carried out on either the CDC Cyber 175 at the University of Utrecht using the APOLLO (data reduction and correction) and EUCLID (calculation of geometrical data and preparation of illustrations, including an extended version of PLUTO) [24] programs or on the in-house Data General Eclipse S/230 mini-computer using programs of the ILIAS package (an adaptation and extension by A.L.S. of the SHELX-76 [25] package). Final atomic coordinates are listed in Table I along with overall thermal parameters. Anisotropic thermal parameters, hydrogen atom parameters and a list of observed and calculated

structure factors are available as supplementary material.

Supplementary Material Available

Tables of positional and thermal parameters and their estimated standard deviations, bond distances and angles, and a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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