

Crystal and Molecular Structure of a Polymeric 2-Aminobenzophenone–Mercury(II) Bromide (1:2) Adduct

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Abstract

The preparation of a mercury adduct, (2abf)·2HgBr₂ (2abf = 2-aminobenzophenone), and the determination of its structure by single-crystal X-ray analysis is described. The structure may be considered as being built up by two different HgBr₂ units, each containing short covalent Hg–Br bonds (a short Hg–N bond is also present) which are linked together by longer metal–bromine interactions in a polymeric structure. The interpretation of far-infrared and Raman spectra is also discussed.

Introduction

There has recently been much interest [1–4] in the coordination behavior of the benzophenones due to the presence of both aromatic rings and a carbonyl group. With the introduction on the benzophenone of another potential binding site, *i.e.* an amino group, the coordination of the metal ions is preferentially obtained through this latter group [5, 6].

We noted that 2-aminobenzophenone (2abf), a ligand that may form 6-membered chelate rings, reacts with Cu(II) ions to form compounds of the type CuX₂(2abf)₂ (X = Cl, Br) in which the amino-benzophenone acts both as monodentate (through the N atom) and a chelating ligand [7].

To further investigate the behavior of the 2abf ligand we have studied its coordination mode with Hg(II) ions; we report here a structural and spectroscopic investigation of the adduct of 2abf with HgBr₂ having the unusual stoichiometric metal-to-ligand molar ratio of 2:1.

The choice of Hg(II) ions for these studies is also suggested by considering that, having filled the 4f and 5d shells, its coordination is affected considerably by factors such as ionic radii, polarizability and differences in electronegativity rather than by ligand field effects.

Experimental

Preparation of the (2abf)·2HgBr₂ Adduct

On adding small amounts of petroleum ether to a toluene solution of mercury(II) bromide and the ligand in metal-to-ligand ratios ranging from 3:1 to 1:3, pale yellow crystals separated after few days. The same compound in microcrystalline form was also separated from ethanol. Found: C, 17.01; H, 1.19; N, 1.51%. Calcd. for C₁₃H₁₁Br₄NOHg₂: C, 16.99; H, 1.20; N, 1.52%.

Structural Determination

A pale-yellow prismatic crystal (approximate dimensions 0.3 × 0.2 × 0.2 mm) was chosen for the X-ray analysis and was mounted on a glass fiber in a random orientation. Space-group was $P\bar{1}$; the cell constants reported in the crystal data were determined from a least squares fit of the 2θ values of 20 high-angle reflections ($2\theta \geq 20^\circ$) measured on a Philips PW 1100 diffractometer, subsequently used for the data collection.

Crystal Data: C₁₃H₁₁Br₄NOHg₂, $M = 918.03$, triclinic, space group $P\bar{1}$, $a = 9.444(7)$, $b = 10.652(8)$, $c = 10.449(8)$ Å, $\alpha = 102.8(2)$, $\beta = 110.6(3)$, $\gamma = 102.9(2)^\circ$, $V = 906(1)$ Å³, $Z = 2$, $D_{\text{calc}} = 3.37$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu(\text{Mo K}\alpha) = 256.6$ cm⁻¹. Intensities were collected using graphite monochromated MoK α radiation up to $2\theta = 50^\circ$, using an $\omega/2\theta$ scan technique. The scan speed was 0.04° s⁻¹ and the scan width used, kept constant through the entire θ -range, was 1.10°. Two background counts were measured for 8 s at each side of the peaks and subsequently averaged. Three standard reflections were measured every 180' to check the stability of the experimental conditions and of the crystal. No significant variations were detected. 3181 independent reflections were collected, of which 2106 were considered as observed having $I_{\text{net}} \geq 3\sigma(I)$ ($\sigma(I)$ based on counting statistics), and were used for the structure determination and

TABLE I. Final Positional and Thermal Parameters. The e.s.d.s are given in parentheses and refer to the last significant figure. The anisotropic temperature factors are expressed as: $T = \exp[-\frac{1}{4}(B_{11}a^*{}^2h^2 + B_{22}b^*{}^2k^2 + \dots + 2B_{12}a^*b^*hk + \dots)]$.

	x/a	y/b	z/c	B_{11}, B_{1so}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg1	0.31547(3)	0.53147(10)	0.07735(11)	5.23(5)	3.49(4)	3.18(4)	2.59(3)	2.24(3)	1.69(3)
Hg2	0.07254(12)	0.47359(10)	0.34074(10)	3.50(4)	3.74(4)	3.00(3)	2.23(3)	1.68(3)	1.07(3)
Br1	0.26615(35)	0.39837(28)	-0.16092(27)	5.91(14)	4.11(12)	3.08(10)	2.75(11)	2.16(10)	1.41(9)
Br2	0.37032(27)	0.68229(23)	0.30960(24)	3.30(9)	3.23(10)	3.09(9)	2.00(8)	1.48(8)	1.56(8)
Br3	-0.02075(28)	0.33524(25)	0.08509(25)	3.07(9)	3.90(10)	2.71(9)	1.78(8)	1.04(7)	1.20(8)
Br4	0.13656(28)	0.68054(22)	0.54637(25)	3.94(10)	2.48(8)	3.66(10)	1.71(7)	2.36(8)	1.46(8)
N	0.2896(20)	0.3816(17)	0.4560(18)	2.43(29)					
O	0.4324(18)	0.3732(16)	0.2780(17)	3.23(28)					
C1	0.2571(23)	0.2408(20)	0.4152(21)	2.23(33)					
C2	0.2850(22)	0.1734(19)	0.2939(20)	1.97(31)					
C3	0.2479(28)	0.0288(24)	0.2492(25)	3.27(42)					
C4	0.1885(31)	-0.0510(27)	0.3232(28)	4.07(49)					
C5	0.1593(30)	0.0182(26)	0.4390(27)	3.73(46)					
C6	0.1898(28)	0.1592(24)	0.4815(25)	3.27(42)					
C7	0.3622(24)	0.2490(21)	0.2214(22)	2.48(35)					
C8	0.3596(23)	0.1750(21)	0.0786(21)	2.38(34)					
C9	0.5068(25)	0.2142(21)	0.0698(23)	2.62(36)					
C10	0.5099(27)	0.1446(24)	-0.0589(25)	3.24(41)					
C11	0.3755(28)	0.0529(24)	-0.1744(25)	3.35(42)					
C12	0.2270(32)	0.0206(28)	-0.1628(29)	4.27(51)					
C13	0.2272(27)	0.0831(23)	-0.0284(24)	3.09(40)					

TABLE II. Selected Bond Lengths (Å) and Angles (deg) for the Compound (e.s.d.'s on the last significant digit in parentheses).

Bond Lengths					
Hg(1)–Br(1)	2.399(3)	Hg(2)–Br(2)	3.335(3)	N–C(1)	1.39(3)
Hg(1)–Br(2)	2.400(3)	Hg(2)–Br(3)	2.472(2)	N–O	2.65(2)
Hg(1)–Br(1) ^I a	3.592(4)	Hg(2)–Br(4)	2.498(2)	O–C(7)	1.23(2)
Hg(1)–Br(3) ^{II} a	3.487(3)	Hg(2)–Br(4) ^{III} a	3.005(3)	C(2)–C(7)	1.47(3)
Hg(1)–Br(3)	3.427(3)	Hg(2)–N	2.51(2)	C(7)–C(8)	1.51(3)
Hg(1)–O	3.04(2)			(C–C) _{Ph} ^b	1.40(3)
Bond Angles					
Hg(1)–Br(2)–Hg(2)	93.17(8)	Br(1)–Hg(1)–Br(3)	96.07(9)	Br(2)–Hg(2)–N	81.9(4)
Hg(1)–Br(3)–Hg(2)	89.70(8)	Br(1)–Hg(1)–Br(1) ^I	86.4(1)	Br(2)–Hg(2)–Br(4) ^{III}	164.59(8)
Br(1)–Hg(1)–Br(2)	174.91(8)	Br(1)–Hg(1)–Br(3) ^{II}	87.85(9)	Br(4) ^{III} –Hg(2)–N	90.2(4)
Br(1) ^I –Hg(1)–Br(3)	147.74(6)	Br(1)–Hg(1)–O	107.0(3)	Br(3)–Hg(2)–Br(4)	156.31(6)
Br(3)–Hg(1)–Br(3) ^{II}	76.37(7)	Br(2)–Hg(1)–Br(3)	87.50(8)	Br(2)–Hg(2)–Br(3)	88.45(8)
Br(1) ^I –Hg(1)–Br(3) ^{II}	135.89(5)	Br(2)–Hg(1)–Br(1) ^I	92.49(8)	Br(2)–Hg(2)–Br(4)	81.26(8)
Br(3)–Hg(1)–O	74.3(3)	Br(2)–Hg(1)–Br(3) ^{II}	89.48(8)	Br(3)–Hg(2)–Br(4) ^{III}	105.92(8)
Br(3) ^{II} –Hg(1)–O	148.3(1)	Br(2)–Hg(1)–O	77.4(3)	Br(3)–Hg(2)–N	99.2(4)
Br(1) ^I –Hg(1)–O	74.2(3)			Br(4)–Hg(2)–Br(4) ^{III}	87.25(8)
				Br(4)–Hg(2)–N	100.4(4)
N–C(1)–C(2)	119.3(1.5)	C(1)–C(2)–C(7)	122.5(1.4)	C(3)–C(2)–C(7)	117.8(1.5)
N–C(1)–C(6)	122.8(1.4)	C(1)–C(2)–C(3)	119.5(1.5)	C(7)–C(8)–C(9)	114.2(1.6)
O–C(7)–C(2)	120.0(1.5)	C(2)–C(1)–C(6)	117.9(1.6)	C(7)–C(8)–C(13)	122.0(1.6)
O–C(7)–C(8)	119.7(1.6)	C(2)–C(7)–C(8)	120.3(1.4)	(C–C–C) _{Ph} ^b	120.0(2.5)
Internal Rotation Angles (deg.)					
Br(1)–Hg(1)–Br(2)–Hg(2)	141.7(1.0)	Hg(2)–N–C(1)–C(2)	89.2(1.9)	O–C(7)–C(8)–C(9)	43.0(2.1)
Br(2)–Hg(2)–N–C(1)	-133.8(1.5)	N–C(1)–C(2)–C(7)	6.6(2.2)	C(1)–C(2)–C(7)–C(8)	-168.0(2.0)
Hg(2)–N–C(1)–C(6)	-87.2(1.8)	O–C(7)–C(2)–C(1)	13.4(2.0)		

^aRoman numeral superscripts refer to the following symmetry operations: I) $1 - x, 1 - y, -z$; II) $-x, 1 - y, -z$; III) $-x, 1 - y, 1 - z$. ^bAverage values. Values in parentheses refer to the standard deviation on the mean.

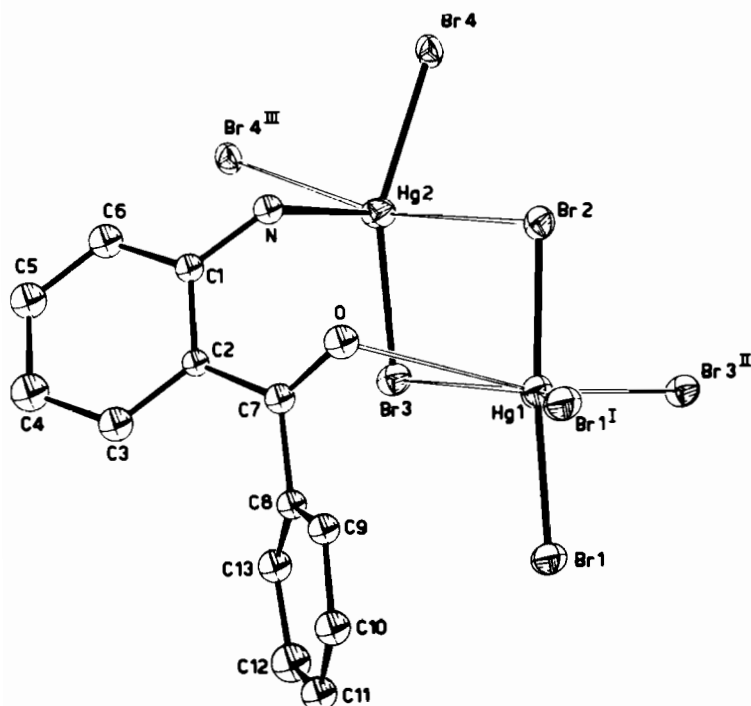


Fig. 1. ORTEP view of the asymmetric unit with the numbering scheme.

refinement. Data were corrected for Lorentz and polarization factors and an empirical absorption correction was applied to the data using the azimuthal ψ scan method.

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares using anisotropic temperature factors for Hg and Br atoms, isotropic for the others. Scattering factors were taken from ref. [8] and the correction from the real part of the anomalous dispersion was taken into account for Hg and Br atoms [8]. The function minimized was $\sum w(|F_o| - (1/k)|F_c|)^2$ using a Cruickshank [9] weighting scheme. The contribution of the H atoms in their idealized calculated positions (C-H = 1.08 Å) was taken into account in the final least squares cycles, but not refined. The final difference map showed no significant features. The final conventional agreement factor R ($R = \sum \|F_o| - (1/k)|F_c|\| / \sum |F_o|$) was 0.076 for the observed reflections. A list of final refined coordinates and thermal parameters for the non-H atoms is given in Table I, while some relevant bond lengths, bond and torsion angles are given in Table II.*

Physical Measurements

Infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer in KBr pellets (4000–

250 cm^{-1}) or in polythene pellets (600–100 cm^{-1}); partial decomposition of the adduct was observed on mulling with nujol. Raman spectra were recorded on solid samples with a Jobin–Yvon instrument equipped with an argon laser.

Results and Discussion

Molecular Structure

An ORTEP [10] view of the asymmetric unit is given in Fig. 1. The packing of the molecules in the unit cell is given in Fig. 2.

The structure may be considered as being built up by the two different units Br(1)–Hg(1)–Br(2) and Br(3)–Hg(2)–Br(4), with strong covalent Hg–Br bonds which are linked together by metal–bromine interactions (in the range 3.33–3.59 Å) resulting in a polymeric structure.

The coordination geometry is best described by considering the two metal centers separately. Hg(1) is symmetrically bound to Br(1) and Br(2) atoms in an almost linear coordination (Br(1)–Hg(1)–Br(2) = 174.91(8)°). The Hg–Br bond distances (2.399(3) and 2.400(3) Å, respectively) are rather short and may be compared with those found in HgBr₂ for the axial ligands (2.48 Å) [11], but are shorter than the values of 2.554(5) and 2.615(5) found in the strongly coordinated [tris(*o*-diphenylarsinophenyl)arsine]–HgBr₂ complex, which is monomeric and which contains a tetrahedrally-coordinated mercury atom [12].

*Calculated hydrogen coordinates and a table of observed and calculated structure factors are available from the authors upon request.

TABLE III. Equations of Least-squares Planes with Distances (Å) of Relevant Atoms from the Planes Given in Square Brackets.

Plane A:	Hg(1), Br(3) ^{II} , Br(1) ^I $0.02024x + 0.64894y + 0.76057z = 2.26980$ [Br(3) -0.035(3); O 0.608(17); Br(1) -2.378(3); Br(2) 2.397(3)]
Plane B:	Hg(2), Br(2), Br(4) ^{III} , N $0.14948x + 0.67766y + 0.72003z = 4.83632$ [Hg(2) -0.248(2); Br(2) 0.127(3); Br(4) ^{III} 0.140(3); N -0.020(18); Br(3) -2.686(3); Br(4) 2.150(3)]
Plane C:	C(1) through C(6) $0.93913x + 0.12447y + 0.32021z = 2.56996$ [Hg(1) -1.488(2); Hg(2) -2.207(2); N 0.004(20); O 0.467(18); C(7) 0.110(25); C(8) -0.183(28)]

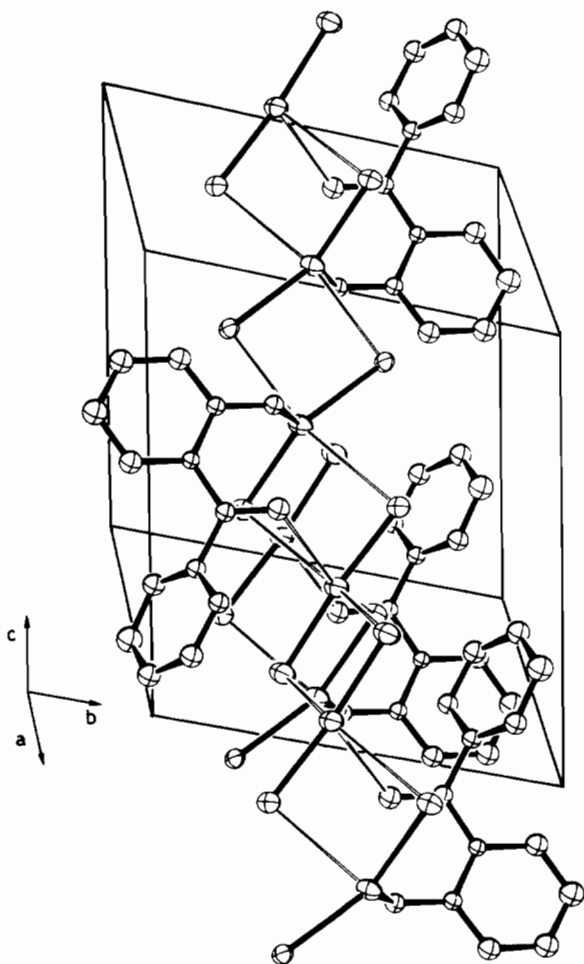


Fig. 2. The packing of the molecules in the unit cell.

Assuming the following values for the Van der Waals radii: mercury = 1.75 Å [13, 14], bromine = 1.87 Å [15], oxygen = 1.42 Å [16], the coordination about Hg(1) is completed by other four ligands, three bromines and the oxygen of the 2abf ligand. All distances are slightly shorter than the sum of the

Van der Waals radii: the Hg...Br(3), Hg...Br(1)^I, Hg...Br(3)^{II}, and Hg...O distances (in the range 3.0–3.6 Å) are thus consistent with weak bonding interactions. The coordination around Hg(1) may be described as a highly distorted octahedron with equatorial angles Br–Hg–L (L = Br, O) in the range 74–136°; it is noteworthy that the Hg and the three Br atoms lie on the same least-squares plane, while the oxygen atom is 0.6 Å away from it (cf. Table III).

While it has long been recognized that two different sets of coordination distances are present around mercury (both long and short) [16, 17], the Van der Waals radius of mercury has been much discussed from a lower limit of 1.50 Å to an upper limit of 1.76 Å [13, 14, 17]. From the coordination sphere in the present compound the choice of the upper value of 1.76 Å is substantiated.

The coordination sphere of Hg(2) atom is also characterized by two different sets of distances, on the one hand the short Hg(2)–Br(3), Hg(2)–Br(4) and Hg(2)–N bond distances, on the other those involving Br(2) and Br(4)^{III} atoms.

A similar coordination geometry has also been found in the polymeric compound dibromo(2,4-dimethylpyridine)Hg(II) (A) [18]. The angle Br(3)–Hg(2)–Br(4) (156.31(6)°) shows a significant distortion which may be due to the influence of the coordinated 2-aminobenzophenone ligand; this value may be compared with the values of similar bond angles in (A) 164.9(3)° or in HgINO₃ (158.66(4)°) [19].

The other three ligands N, Br(2), Br(4)^{III}, and the Hg(2) atom lie approximately (see Table III) in a plane; the Br–Hg–L (L = Br, N) angles are in the range 82 to 165°. Thus the coordination polyhedron around Hg(2) is severely distorted and the deviations from the ideal angular values are such to prevent its description as (elongated) trigonal bipyramidal [20].

The bond lengths and angles in the 2-aminobenzophenone ligand are unexceptional and compare with those found in other coordinated aminobenzophenone

TABLE IV. Relevant IR Bands for (2abf)·2HgBr₂, 2abf and 2abf·HCl.

	(2abf)·2HgBr ₂	2abf	2abf·HCl
$\nu(\text{NH}_2)$, cm ⁻¹	3440m 3320m	3440s 3320s	2940vsb 2550s
$\nu(\text{CO})$, cm ⁻¹	1630vs	1625vs	1662vs 1630vs
$\delta(\text{NH}_2)$, cm ⁻¹	1612s	1575vs	1560s
$\nu(\text{Hg}(1)\text{Br}_2)_{\text{as}}$, cm ⁻¹	262s		
$\nu(\text{Hg}(1)\text{Br}_2)_{\text{s}}$, cm ⁻¹	204s(Raman)		
$\nu(\text{Hg}(2)\text{Br}_2)_{\text{as}}$, cm ⁻¹	218s		
$\nu(\text{Hg}(2)\text{Br}_2)_{\text{s}}$, cm ⁻¹	178s(Raman)		
$\nu(\text{Hg}(2)\text{N})$, cm ⁻¹	250m		

phenones [7]. The conformation of the aminobenzophenone ligand is defined by the torsion angles reported in Table II. The N···O distance of 2.65(2) Å is indicative of an intramolecular hydrogen-bond interaction.

Spectroscopic Results

The more relevant IR bands (Table IV) are unambiguously assigned on comparing the spectra of the present complex with those of the free ligand, its hydrochloride salt, the copper(II) halide complexes previously examined [7], and their deuterated analogues. In the HgBr₂ adduct the ligand bands appear to be modified by coordination to a lesser extent than in the CuX₂ adducts.

It may be expected that the differences in bond lengths and angles in the two HgBr₂ units, one being approximately linear (Br(1)–Hg(1)–Br(2) = 174.91(8)°) and the other severely distorted (Br(3)–Hg(2)–Br(4) = 156.31(6)°), will also be reflected in their IR spectra; the symmetric stretching vibration, $\nu_1(\Sigma_g^+)$ (Raman active) and the antisymmetric mode, $\nu_3(\Sigma_u^+)$ (IR active) should appear at higher energies for the Hg(1)Br₂ moiety, being almost linear with a shorter Hg–Br bond distance. Therefore the IR band at 263 cm⁻¹ and the Raman band at 204 cm⁻¹ are assigned, respectively, to the antisymmetric and symmetric stretching vibrations of the linear Hg(1)Br₂ unit, while the IR band at 218 cm⁻¹ and the Raman band at 178 cm⁻¹ are assigned to the antisymmetric and symmetric stretching vibrations of the Hg(2)Br₂ moiety.

These assignments compare well with those reported for HgBr₂ ($\nu_{\text{as}}(\text{Hg–Br})$ at 250 cm⁻¹ and $\nu_{\text{s}}(\text{Hg–Br})$ at 188 cm⁻¹), with a Br–Hg–Br angle of approx-

imately 180°, but longer Hg–Br bond distances (2.48 Å) [21] than in our Hg(1)Br₂ unit.

The IR frequency at 250 cm⁻¹ may arise from a Hg(2)–N stretching vibration [22].

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