Crystal and Molecular Structure of Bis(2-amino-5-methyl-1,3,4-thiadiazole-N^3)dibromomercury(II).† A Spectroscopic Study and INDO Calculations

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The crystal structure of the compound $Hg(amtz)_2Br_2$(amtz= 2-amino-5-methyl-1,3,4-thiadiazole) was determined by *X*-ray crystallography. The compound crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions a = 9.133(2), b = 11.002(2), c = 8.404(2) Å, α = 102.65(2), β = 116.80(2), γ = 93.87(2)°, and Z = 2. The structure was solved by the heavy-atom method and refined by least-squares calculations. The structure consists of monomeric discrete molecules, in which the Hg atom is co-ordinated in a distorted tetrahedral geometry by two bromine ions and by two nitrogens of the 2-amino-5-methyl-1,3,4-thiadiazole ligands. Infrared bands are assigned, the ^1H, ^{13}C, and ^{199}Hg n.m.r. spectra of the complex have been recorded, and INDO calculations are discussed.

Complexes containing 2,5-disubstituted 1,3,4-thiadiazole have recently received considerable attention because of the pharmacological and antileukaemic properties of the free ligand.[1–3] Crystal-structure results on solid complexes, which could provide support for structural hypotheses, are lacking. This work considers the ligand 2-amino-5-methyl-1,3,4-thiadiazole (amtz).

Interest in mercury chemistry is increasing considerably because of its unpredictable stereochemistry since, depending on its co-ordination number, a large variety of stereochemistries can occur. The commonest co-ordination arrangements are linear or tetrahedral, although five- and six-co-ordination are also known. This behaviour is due to characteristic co-ordination, where the mercury–donor atom bond distance is close to the sum of the appropriate covalent radii, and to effective co-ordination, where the mercury–donor atom distance is within the sum of the van der Waals radii;[4] namely, the co-ordination sphere of Hg^{II} usually contains both close and distantly bound atoms.[5]

Experimental

All chemicals were reagent grade and used as received. The complex was prepared as described in ref. 6. Suitable crystals were obtained by sealing a saturated ethanolic solution in a phial at 40 °C for 1 month. Transparent crystals were collected.

I.r. spectra were recorded on the solid in KBr discs (4 000—250 cm^{-1}) and in Nujol mulls on Polythene (400—50 cm^{-1}).

All n.m.r. spectra were recorded on a VARIAN XL-200 spectrometer (4.7 T) at 200.053, 50.3, and 35.65 MHz for proton, carbon-13, and mercury-199 respectively. Measurements for the ligand amtz and the complex $Hg(amtz)_2Br_2$ were recorded in the 15—35 °C range in $[^2H_6]$acetone solution (Carlo Erba Cod. 550891 99.9% isotopic grade), the only solvent in which sufficient solubility for n.m.r. investigation could be obtained. Lower temperature measurements were not possible because of the decreasing solubility of the compound with decreasing temperature. The chemical shift data given are referred to 21 °C. The internal reference for ^1H and ^{13}C was $SiMe_4$, while for ^{199}Hg the external reference was $HgBr_2$ in $[^2H_6]$acetone solution.

Crystal Data.—$C_6H_{10}Br_2HgN_6S_2$, M = 590.7, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 9.133(2), b = 11.002(2), c = 8.404(2) Å, α = 102.65(2), β = 116.80(2), γ = 93.87(2)°, U = 721.9 Å^3, Z = 2, D_c = 2.72 (D_m = 2.70) g cm^{-3}, $F(000)$ = 539.9, graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 159.6 cm^{-1}, and crystal dimensions 0.10 × 0.10 × 0.55 mm.

The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer with the ω–2θ scan technique in the θ range 2—27°, at a lowest scan speed of 1.27° min^{-1}. Three standard reflections were measured every 4 h, and their intensities showed no significant changes. All data were corrected for Lorentz and polarization effects, and an empirical absorption correction, based on the ψ scan was applied[7] (max., min. transmission factors: 0.99, 0.50). A total of 2 706 reflections were measured which, after merging equivalent data, gave 2 552 reflections with $I > 3\sigma(I)$ which were used in the structure determination.

The structure was solved by conventional Patterson and Fourier methods and refined through full-matrix least-squares calculations. Non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were included as fixed contributors at calculated positions assuming a bond distance of 1.0 Å and $U_H = U_C + 1.0$ Å^2 or $U_H = U_N + 1.0$ Å^2. This model converged to $R = 0.039$ and $R' = 0.044$ $\{w = 1.1/[\sigma^2(F) + 0.0003 F_o^2]\}$.

During refinement, zero weights were assigned to five strong low-order reflections, which may be affected by secondary extinctions.

Complex neutral-atom scattering factors[8] were employed throughout; major calculations were carried out on a VAX 11/750 computer, using the SHELX 76[9] program package and the ORTEP[10] plotting program.

Final fractional co-ordinates for non-hydrogen atoms are given in Table 1. Bond distances and angles are given in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises the H-atom co-ordinates and thermal parameters.

Results and Discussion

Description of the Structure.—The crystal structure consists of discrete mononuclear molecules (Figure), linked by hydrogen bonding interactions. The mercury atom is co-ordinated to two

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Final positional parameters for $Hg(amtz)_2Br_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Hg	0.479 15(5)	0.193 99(3)	0.186 04(5)
Br(1)	0.252 3(1)	0.007 4(1)	−0.063 3(1)
Br(2)	0.601 5(2)	0.346 3(1)	0.069 7(2)
S(1)	0.812 5(3)	0.025 9(2)	0.678 0(3)
S(2)	0.186 7(4)	0.476 8(3)	0.430 3(4)
N(1)	0.636 1(9)	0.140 2(6)	0.447(1)
N(4)	0.353(1)	0.324 3(7)	0.339(1)
N(2)	0.742(1)	0.236 6(7)	0.611(1)
N(5)	0.295(1)	0.268 5(7)	0.438(1)
N(3)	0.568(1)	−0.081 6(7)	0.329(1)
N(6)	0.343(1)	0.506 2(7)	0.231(1)
C(1)	0.659(1)	0.025 8(7)	0.462(1)
C(4)	0.307(1)	0.432 1(8)	0.326(1)
C(2)	0.839(1)	0.190 2(9)	0.742(1)
C(5)	0.207(1)	0.335 9(9)	0.496(2)
C(3)	0.958(1)	0.268(1)	0.929(2)
C(6)	0.126(2)	0.300(1)	0.603(3)

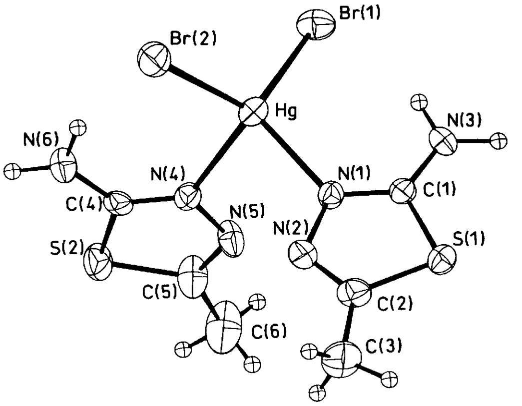

Figure. ORTEP view of $Hg(amtz)_2Br_2$ showing the atom numbering and thermal motion ellipsoids (50%) for the non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius

Table 2. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

Hg–Br(1)	2.554(1)	C(5)–N(5)	1.29(1)
Hg–N(1)	2.245(7)	Hg–Br(2)	2.541(1)
N(1)–N(2)	1.41(1)	Hg–N(4)	2.407(7)
C(1)–N(3)	1.34(1)	C(1)–N(1)	1.32(1)
C(1)–S(1)	1.72(1)	C(2)–S(1)	1.73(1)
C(2)–N(2)	1.30(1)	C(2)–C(3)	1.46(1)
N(4)–N(5)	1.39(1)	C(4)–N(4)	1.30(1)
C(4)–N(6)	1.37(1)	C(5)–S(2)	1.75(1)
C(4)–S(2)	1.73(1)	C(5)–C(6)	1.49(2)
Br(1)–Hg–Br(2)	116.0(1)	N(1)–Hg–Br(1)	111.6(2)
N(1)–Hg–Br(2)	122.3(2)	N(4)–Hg–Br(1)	107.7(2)
N(4)–Hg–Br(2)	103.6(2)	N(4)–Hg–N(1)	90.8(3)
C(2)–S(1)—C(1)	88.0(4)	C(5)–S(2)–C(4)	86.6(5)
N(2)–N(1)–Hg	119.1(5)	C(1)–N(1)–Hg	127.6(6)
C(1)–N(1)–N(2)	112.6(7)	N(5)–N(4)–Hg	116.0(5)
C(4)–N(4)–Hg	131.0(6)	C(4)–N(4)–N(5)	112.2(7)
C(2)–N(2)–N(1)	111.7(7)	C(5)–N(5)–N(4)	112.9(8)
N(1)–C(1)–S(1)	113.3(6)	N(3)–C(1)–S(1)	122.2(7)
N(3)–C(1)–N(1)	124.2(9)	N(4)–C(4)–S(2)	114.6(7)
N(6)–C(4)–S(2)	120.4(7)	N(6)–C(4)–N(4)	125.0(8)
N(2)–C(2)–S(1)	114.1(7)	C(3)–C(2)–S(1)	122.1(9)
C(3)–C(2)–N(2)	123.7(10)	N(5)–C(5)–S(2)	113.7(8)
C(6)–C(5)–S(2)	120.9(8)	C(6)–C(5)–N(5)	125.3(10)

Table 3. M.o. indices* for 2-amino-5-methyl-1,3,4-thiadiazole

Atoms	q^{tot}	q	F_N
C(1, 4)	0.4177	0.1240	0.2086
C(2, 5)	0.2584	0.0113	0.3745
C(3, 6)	0.0233		0.0184
N(1, 4)	−0.2363	−0.3198	0.5487
N(2, 5)	−0.1193	−0.1306	0.2471
N(3, 6)	−0.2313	0.1662	0.4843
S(1, 2)	−0.3875		0.0228

* Atomic unit. F represents the frontier electron density values of the highest occupied m.o.

bromine and two *endo*-nitrogen atoms in a distorted tetrahedral geometry. The two Hg–Br bond distances [2.554(1) and 2.541(1) Å, respectively] do not differ significantly, and are close to the sum of the covalent radii of Hg and Br (1.48 + 1.11 = 2.59 Å) (of the possible covalent radii of mercury[4] we refer to that of Pauling[11]). Furthermore, their values compare well with those reported for other tetrahedral mercury(II) dibromide complexes.[12–15] The two Hg–N bond lengths of 2.245(7) and 2.407(7) Å are significantly different, and only the lowest value is close to the sum of the covalent radii of 2.23 Å.[11] Such a difference could be interpreted as due to the largest angular deviation from the ideal tetrahedral geometry, which involves the N–Hg–N bond angle [90.8(3)°]. The Hg atom is displaced by 0.641 Å from the mean plane through the five-membered ring of the N(4) atom, the corresponding deviation from the ring plane of N(1) being 0.180 Å. The extent of the tetrahedral distortion of the co-ordination polyhedron may also be evaluated by means of the dihedral angle between the Br–Hg–Br and N–Hg–N planes; our value of 73.6° is markedly less than that of 90° for the tetrahedral co-ordination.

There are no significant differences between corresponding bond distances and angles of the two crystallographically independent amtz molecules. Their five-membered rings are planar within ± 0.007 Å and none of the exocyclic C and N atoms deviates by more than 0.062 Å from the mean planes. Our bond distances and angles compare very well with those reported for 1,3,4-thiadiazole,[16] and the 2-amino-5-mercapto- and 2,5-dimercapto-substituted derivatives.[17] This means that the metal binding does not affect the relevant double-bond character of all the cyclic bonds, and of the exocyclic C–N bond. The rotation of the thiadiazole ring planes about the Hg–N bond appears to be mainly determined by intramolecular hydrogen-bond interactions between the NH_2 group and Br atoms; the dihedral angle between the planes is 97.8°. Furthermore, intermolecular hydrogen bond contacts, on which the crystal packing depends, occur between the NH_2 group and unco-ordinated endocyclic N atoms, with N • • • H separations of 2.21 and 2.32 Å and subtended N–H • • • N angles of 143 and 145°, respectively.

Molecular Orbital Calculation.—The preference of N(1) [and N(4)] as the co-ordinating agent can be explained by means of a semi-empirical all valence-electron molecular orbital (m.o.) calculation, with INDO approximation and parametrization.[18] The applicability and usefulness of INDO indices for the prediction of the reactivity have recently been stressed.[19] The m.o. indices of amtz calculated in the present study are reported in Table 3. The indices chosen to represent the main features of the electronic structure of the ligand are: the total ($\sigma + \pi$) net charge and the π net charge of the ring atoms and of the nitrogen

Table 4. N.m.r. spectra in [$^2H_6$]acetone solutions (chemical shifts in p.p.m.)

	amtz			Hg(amtz)$_2$Br$_2$			HgBr$_2$
^{1}H	CH_3		NH_2	CH_3		NH_2	
	2.46		6.33	2.54		7.18	
^{13}C	C^1	C^2	C^3	C^1	C^2	C^3	
	168.82	154.57	15.21	171.51	155.83	15.33	
^{199}Hg					+445.65		0

atom of the NH_2 group, together with the frontier electron density values of the highest occupied m.o. (h.o.m.o.) on the same atoms. From the analysis of the electron distribution and the m.o. features of the h.o.m.o. {which shows a strong localization on the N(1) [and N(4)] atom} N(1) [and N(4)] offers the greatest chance of co-ordination towards the mercury(II) ion.

I.r. Spectra.—Only one ν(Hg–Br) band at 177 cm^{-1} can be safely assigned, and agrees with other values for terminal Hg–X bonds in a tetrahedral structure.[20] New bands, compared to the non-co-ordinated ligand, are present in the complex (406 and 225 cm^{-1}) which can be due to the same ν(Hg–N) stretching mode. The $\nu(NH_2)$ ligand frequencies measured in $CHCl_3$ solution decrease significantly in the complex. This is not due to co-ordination of the amine group but to the hydrogen bonds still remaining in the solid state after complexation of the ligand.

N.M.R. Spectra.—No significant results were obtained from the measurement of the ^{15}N spectra, probably due to the low obtainable concentration and to the very long spin–lattice relaxation time of the sp^2 nitrogen atom. The n.m.r. results are summarized in Table 4. Comparative inspection of the n.m.r. data shows a downfield shift of the proton signals of the CH_3 and NH_2 groups, as well as of the ^{13}C signals of all the carbon atoms of the co-ordinated ligand, with respect to the free ligand.

The observed deshielding of the various molecular sites strongly depends on the distance from the mercury atom. A downfield shift of the ^{199}Hg signal in the complex, compared with $HgBr_2$, is also observed. Furthermore, complexation through amtz causes signal broadening of the ^{199}Hg resonance {$\Delta\nu_{\frac{1}{2}}[HgBr_2] \simeq 50$ Hz, $\Delta\nu_{\frac{1}{2}}[Hg(amtz)_2Br_2] \simeq 400$ Hz} and the ^{13}C resonances for C^1 and C^2 {$\Delta\nu_{\frac{1}{2}}$ (amtz) $\simeq$ 15 Hz, $\Delta\nu_{\frac{1}{2}}[Hg(amtz)_2Br_2] \simeq 45$ Hz}. No significant signal broadening of the ^{13}C resonance of the C^3 atom and of ^{1}H resonances of the CH_3 and NH_2 groups are observed. In the indicated temperature range a sharpening of the ^{199}Hg and ^{13}C signals is observed on going from lower (470,53 Hz) to higher (270,25 Hz) temperature respectively. This could mean the presence of exchange equilibria in solution rather than a ^{14}N quadrupolar effect.

In conclusion, the deshieldings observed and, in particular, the ^{199}Hg deshielding in the complex, with respect to $HgBr_2$, suggest that the metal is co-ordinated to the ligand by two ring nitrogen atoms. This result is consistent with the *X*-ray structure of the complex.

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References

1 G. Maffei, E. Testa, and R. Ettore, *Il Farmaco*, 1957, **13**, 187.
2 M. M. Ciotti, S. R. Humphries, J. M. Venditti, N. O. Kaplan, and A. Goldin, *Cancer Res.*, 1960, **20**, 1195.
3 E. Testa, G. C. Gallo, and F. Weber, *Gazz. Chim. Ital.*, 1958, **88**, 812.
4 D. Grdemić, *Q. Rev. Chem. Soc.*, 1965, **19**, 303.
5 A. F. Wells, 'Structural Inorganic Chemistry,' 2nd edn., Oxford University Press, Oxford, 1960, pp. 631—634.
6 A. C. Fabretti, G. C. Franchini, and G. Peyronel, *Spectrochim. Acta, Part A*, 1979, **35**, 1009.
7 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
8 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—101 and 149—150.
9 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, 1976.
10 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965.
11 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.
12 G. Dyer, D. C. Goodall, R. H. B. Mais, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 1110.
13 A. J. Canty, C. L. Raston, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1982, 15.
14 H. B. Buergi, E. Fisher, R. W. Kunz, M. Parvez, and P. S. Pregosin, *Inorg. Chem.*, 1982, **21**, 1246.
15 I. Persson, M. Sandström, P. L. Goggin, and A. Mosset, *J. Chem. Soc., Dalton Trans.*, 1985, 1597.
16 T. la Cour, *Acta Crystallogr., Sect. B*, 1974, **30**, 1642.
17 T. C. Downie, W. Harrison, and E. S. Raper, *Acta Crystallogr., Sect. B*, 1972, **28**, 1584.
18 J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289.
19 R. E. Brown and A. M. Simas, *Theor. Chim. Acta*, 1982, **1**, 62.
20 A. C. Fabretti, G. C. Pellacani, and G. Peyronel, *Gazz. Chim. Ital.*, 1973, **103**, 1259.

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