

# Crystal and Molecular Structure at 298 and 183 K of Hexakis(pyridine)mercury(II) Trifluoromethanesulfonate, $[\text{Hg}(\text{NC}_5\text{H}_5)_6](\text{CF}_3\text{SO}_3)_2$ , and Thermal Analyses of Hexapyridine Solvates of Mercury(II)

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Åkesson, R., Sandström, M., Stålhandske, C. and Persson, I., 1991. Crystal and Molecular Structure at 298 and 183 K of Hexakis(pyridine)mercury(II) Trifluoromethanesulfonate,  $[\text{Hg}(\text{NC}_5\text{H}_5)_6](\text{CF}_3\text{SO}_3)_2$ , and Thermal Analyses of Hexapyridine Solvates of Mercury(II). – Acta Chem. Scand. 45: 165–171.

The compound  $[\text{Hg}(\text{NC}_5\text{H}_5)_6](\text{CF}_3\text{SO}_3)_2$  crystallizes with two formula units in its unit cell in the triclinic space group  $P\bar{1}$  with  $a = 10.890(4)$  [10.799(5)],  $b = 11.206(6)$  [11.128(8)],  $c = 17.736(7)$  [17.695(5)] Å,  $\alpha = 85.10(4)$  [85.14(7)],  $\beta = 89.38(3)$  [89.32(4)],  $\gamma = 60.57(3)$  [59.90(4)]°,  $V = 1877(2)$  [1832(2)] Å<sup>3</sup> at 298 [183] K. The structural parameters were refined by least-squares methods to conventional  $R$ -values of 0.045 [0.030]. The structure is built up from discrete hexakis(pyridine)-mercury(II) complex ions and trifluoromethanesulfonate ions. The six Hg–N bonds in the range 2.42–2.48 [2.402–2.499] Å, at 298 [183] K form a tetragonally elongated octahedron with two opposite Hg–N bonds somewhat longer (average value 2.48<sub>s</sub> [2.50] Å) than the other four (average 2.44 [2.42] Å). This structural feature appears to be consistent with a thermogravimetric (TG) analysis, which showed that the pyridine molecules leave in pairs in a stepwise decomposition leading to  $[\text{Hg}(\text{NC}_5\text{H}_5)_2](\text{CF}_3\text{SO}_3)_2$ . A similar behaviour was found for the hexakis(pyridine)-mercury(II) perchlorate.

Pyridine solvates rarely crystallize with six ligands coordinated to the metal. We have found only two such crystal structures described in the literature. In the iron(II) compound  $[\text{Fe}(\text{py})_6][\text{Fe}_4(\text{CO})_{13}]$ , with a unit cell of  $P\bar{1}$  symmetry, the cation has the idealised point group symmetry  $T_h$  with each pair of *trans* pyridine molecules lying in three mutually perpendicular planes.<sup>1</sup> The magnesium compound  $[\text{MgBr}_2(\text{py})_4] \cdot 2\text{py}$  is built up from discrete octahedral  $[\text{MgBr}_2(\text{py})_4]$  complexes with two additional pyridine molecules inserted in the structure. The coplanar *trans* pyridine ligands are twisted relative to the octahedral axes.<sup>2</sup>

Mercury(II) complexes with an almost regular octahedral ligand configuration have previously only been found in a few oxygen-coordinated hexasolvates ( $\text{H}_2\text{O}$ , DMSO and pyridine-*N*-oxide).<sup>3–5</sup> With softer donor atoms such as nitrogen and sulfur, complexes with a few strongly bonded ligands very often are formed, typically two (in linear or slightly bent configurations), three (trigonal) or four (tetrahedral), often with with some additional weak interactions within the coordination sphere of the mercury atom.<sup>6,7</sup>

The pronounced tendency of two short and strong bonds in mercury(II) compounds is evident from some previously reported structures of pyridine solvates. In the bispyridine

compounds  $\text{Hg}(\text{py})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  and  $\text{Hg}(\text{py})_2(\text{CF}_3\text{COO})_2$ ,\* almost linear  $\text{NHgN}$  entities are formed with Hg–N distances between 2.11 and 2.14 Å.<sup>8,9</sup> The coordination sphere around mercury also contains four and five equatorial oxygen atoms, respectively, at 2.6 Å or longer distances. In the trispyridine compound  $\text{Hg}(\text{py})_3(\text{CF}_3\text{COO})_2$ , a bent  $\text{NHgN}$  unit (161°) can be distinguished with a mean Hg–N distance of 2.28 Å.<sup>10</sup> A third nearly perpendicular Hg–N bond is found at 2.38 Å, and four weak Hg–O interactions (2.5–2.8 Å) complete the coordination.

Six almost equal Hg–N bonds at a mean distance of 2.40 Å are found in the TFMS salt of tris(1,10-phenanthroline) mercury(II). The bidentate ligand causes a considerable deviation from a regular octahedral symmetry, however, with a mean *trans* N–Hg–N angle of 154.5°.<sup>11</sup>

The presently studied compound, as well as other solid hexapyridinemerccury(II) solvates, readily lose up to four pyridine molecules in air, forming stable bispyridine derivatives.<sup>12</sup> Thermogravimetric (TG) analyses may offer additional information about the relative bond strengths in the molecule. Such a study has previously been performed on various hexapyridine perchlorate compounds, and the ex-

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\* In the following the abbreviations  $\text{py} = [\text{NC}_5\text{H}_5]$  and TFMS =  $[\text{CF}_3\text{SO}_3]^-$  are used.

istence of  $[\text{Hg}(\text{py})_4](\text{ClO}_4)_2$  as an intermediate step in the thermal decomposition of  $[\text{Hg}(\text{py})_6](\text{ClO}_4)_2$  to  $[\text{Hg}(\text{py})_2](\text{ClO}_4)_2$  was suggested.<sup>12</sup>

It has been proposed that the observed preference in mercury(II) chemistry to form two strong and short bonds is a result of the rather small energy separation between the valence shell 6s and the occupied 5d<sub>z<sup>2</sup></sub> atomic Hg orbitals, giving some d-character to the binding molecular orbitals because of configurational mixing.<sup>13,14</sup> This effect can also be explained in terms of a vibronic coupling of electronic states, a second-order (or pseudo) Jahn–Teller (SOJT) effect.<sup>15,16</sup> A strong SOJT effect could in an octahedral field give rise to geometrical distortions, in a similar way as for first-order JT effects, e.g. in the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion.<sup>17</sup> However, results from Hartree–Fock SCF calculations on isolated  $[\text{Hg}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Hg}(\text{H}_2\text{S})_6]^{2+}$  clusters gave the lowest energy for a regular hexacoordination of the ligands, although a “softened” ground state was found in both cases, with a large amplitude of the stretching  $E_g$  vibrations, consistent with a weak SOJT effect.<sup>18</sup> Large-angle X-ray scattering (LAXS) studies on the hexasolvated mercury(II) ions formed in aqueous and DMSO solutions give a radial distribution function (RDF) with a broad peak corresponding to an average of the six Hg–O bonds for the hexasolvated mercury(II) ions in aqueous and DMSO solutions,<sup>19</sup> in contrast to the RDF of the  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ion, where the main peak corresponds to four Cu–O bonds.<sup>20</sup> The Debye–Waller factor of the Hg–O bond is, however, anomalously large.<sup>19</sup> This is again in accord with a weak SOJT effect, although the approximations involved in theoretical calculations, in particular the absence of environmental effects such as hydrogen bonds, make detailed comparisons with results from condensed phases difficult.

In stronger ligand fields more pronounced SOJT effects would be expected. The Gibbs free energy,  $\Delta G_{\text{tr}}^\circ$ , and the enthalpy of transfer,  $\Delta H_{\text{tr}}^\circ$ , of the  $\text{Hg}^{2+}$  ion from water to pyridine,  $-79$  and  $-161$  kJ mol<sup>-1</sup>, respectively,<sup>21,22</sup> show that the  $\text{Hg}^{2+}$  ion is much more strongly solvated in pyridine than in water. Owing to the rather low solubility of non-complex-forming mercury(II) compounds in pyridine, it has not been possible to obtain reliable LAXS data (the EXAFS method will provide a better possibility) on the  $\text{Hg}^{2+}$  solvation. In order to study possible structural effects of the SOJT in a nitrogen-coordinated compound, the crystal structure of  $[\text{Hg}(\text{py})_6](\text{TFMS})_2$  was studied. A previous attempt to solve the structure of  $[\text{Hg}(\text{py})_6](\text{ClO}_4)_2$  at ambient temperature could not be brought to completion, probably because of disorder in the structure.<sup>23</sup> Another nitrogen-donor ligand,  $\text{NH}_3$ , with still more strongly coordinating properties towards mercury,<sup>24</sup> is also being investigated. Preliminary results from a crystal-structure investigation of mercury(II) perchlorate crystallized from liquid ammonia show that a  $[\text{Hg}(\text{NH}_3)_4](\text{ClO}_4)_2$  solvate is formed with a distorted tetrahedral coordination around the mercury atom.<sup>23</sup>

## Experimental

Anhydrous mercury(II) trifluoromethanesulfonate, prepared and analysed as described previously,<sup>25</sup> gave colourless crystals of the title compound from a saturated pyridine solution.  $[\text{Hg}(\text{py})_6](\text{ClO}_4)_2$  was prepared by recrystallization of  $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$  from pyridine, as has been described before.<sup>12</sup> In studying the solvation of mercury(II) and the stabilities of, e.g., the mercury(II) halide systems in organic solvents,<sup>25</sup> TFMS, which also has a low tendency for ion-pairing, is a more suitable anion than perchlorate for two reasons: (i) it is easy to prepare a water-free mercury(II) TFMS salt; (ii) the ever-present danger of explosions with organic solvates of perchlorate compounds is avoided.<sup>19,25</sup>

Rounded  $[\text{Hg}(\text{py})_6](\text{TFMS})_2$  crystals enclosed in capillaries with some mother liquid were used for the X-ray

Table 1. Crystal and experimental data from the determination of the  $[\text{Hg}(\text{NC}_5\text{H}_5)_6](\text{CF}_3\text{SO}_3)_2$  structure.

T/K	298	183
Diffractometer	Syntex P2 <sub>1</sub>	CAD-4
No. of reflections and their 2θ range (in °) for lattice parameters	17	25
Space group	$P\bar{1}$	$P\bar{1}$ (triclinic)
a/Å	10.980(4)	10.799(5)
b/Å	11.206(6)	11.128(8)
c/Å	17.736(7)	17.695(5)
α/°	85.10(4)	85.14(7)
β/°	89.08(3)	89.32(4)
γ/°	60.57(3)	59.90(4)
V/Å <sup>3</sup>	1877(2)	1832(2)
Z	2	2
D <sub>c</sub> /g cm <sup>-3</sup>	1.67	1.71
Data collection (2θ) <sub>max</sub>	41	50
Scan mode	θ–2θ	ω–2θ
Scan width (in °)	1.10	0.75+0.50 tan θ
Standard reflections (% variation)	112, 423, 222 ±11 <sup>a</sup>	557, 505, 176 ±7
No. of measured reflections	3846	7048
No. of unique reflections	3455	6334
Reflections in refinements	3048 [ <i>I</i> >6.0σ( <i>I</i> )]	5595 [ <i>I</i> >3.0σ( <i>I</i> ) <sup>b</sup>
Least-squares parameters	478	328
Range of relative transmission	0.58–1.00	–
Weights in refinements ( <i>w</i> <sup>-1</sup> )	σ <sup>2</sup> ( <i>F</i> <sub>o</sub> )+(0.01 <i>F</i> <sub>o</sub> ) <sup>2</sup>	σ <sup>2</sup> ( <i>F</i> <sub>o</sub> )+(0.03 <i>F</i> <sub>o</sub> ) <sup>2</sup> +3.0
Largest Δ/σ in final cycle	0.10	0.08
Δρ <sub>max</sub> /e Å <sup>-3</sup>	0.7 <sup>c</sup>	1.2
<i>R</i> <sup>d</sup>	0.045	0.030
<i>R</i> <sub>w</sub> <sup>e</sup>	0.053	0.039

<sup>a</sup>Larger variations during first 10% of data collection. <sup>b</sup>Five strong low-angle reflections omitted (affected by secondary extinction). <sup>c</sup>In addition there are also six peaks near Hg with Δρ<sub>max</sub> ≈ 1.50 e Å<sup>-3</sup>. <sup>d</sup> $R = \sum |F_o| - |F_c| / \sum |F_o|$ . <sup>e</sup> $R_w = [\sum w_j (F_o - |F_c|)^2 / \sum w_j |F_o|^2]^{1/2}$ .

Table 2. Fractional atomic coordinates and isotropic temperature factors at 298 and 183 K (below) with estimated standard deviations in parenthesis.

Atom	x	y	z	$U_{\text{eq}}$
Hg	0.04258(6)	0.00011(6)	0.24872(3)	0.0467(2)
	0.04324(2)	-0.00017(2)	0.24861(1)	0.0223(1)
N1	-0.0671(11)	-0.0817(12)	0.1631(1)	0.054(3)
	-0.0675(4)	-0.0798(4)	0.1626(2)	0.029(2)
N2	-0.0726(11)	0.2190(12)	0.1656(5)	0.055(3)
	-0.0771(4)	0.2241(4)	0.1659(2)	0.029(2)
N3	-0.1509(12)	0.0780(12)	0.3356(6)	0.056(4)
	-0.1467(4)	0.0732(5)	0.3368(2)	0.029(2)
N4	0.1548(12)	-0.2200(13)	0.3308(6)	0.065(4)
	0.1606(4)	-0.2278(4)	0.3286(3)	0.030(2)
N5	0.2505(12)	-0.0956(13)	0.1738(6)	0.056(3)
	0.2536(4)	-0.0971(4)	0.1735(2)	0.027(2)
N6	0.1541(13)	0.0968(13)	0.3238(6)	0.058(4)
	0.1549(4)	0.0979(4)	0.3227(2)	0.029(2)
C11	-0.0311(16)	-0.0921(17)	0.0910(8)	0.070(5)
	-0.0290(6)	-0.0944(6)	0.0900(3)	0.032(1) <sup>a</sup>
C12	-0.0876(18)	-0.1420(17)	0.0391(8)	0.078(5)
	-0.0844(6)	-0.1426(6)	0.0386(3)	0.038(1) <sup>a</sup>
C13	-0.1835(19)	-0.1824(17)	0.0639(10)	0.082(6)
	-0.1829(7)	-0.1796(6)	0.0633(3)	0.042(1) <sup>a</sup>
C14	-0.2221(19)	-0.1703(18)	0.1392(10)	0.086(6)
	-0.2237(7)	-0.1653(7)	0.1382(4)	0.046(1) <sup>a</sup>
C15	-0.1619(16)	-0.1199(16)	0.1885(8)	0.066(5)
	-0.1638(6)	-0.1148(6)	0.1853(3)	0.034(1) <sup>a</sup>
C21	-0.1910(15)	0.2590(16)	0.1237(8)	0.061(4)
	-0.1925(6)	0.2622(5)	0.1210(3)	0.031(1) <sup>a</sup>
C22	-0.2450(16)	0.3716(17)	0.0701(8)	0.068(5)
	-0.2445(6)	0.3746(6)	0.0658(3)	0.034(1) <sup>a</sup>
C23	-0.1768(17)	0.4499(16)	0.0601(8)	0.070(5)
	-0.1761(6)	0.4517(6)	0.0562(3)	0.035(1) <sup>a</sup>
C24	-0.0567(15)	0.4109(16)	0.1056(8)	0.065(5)
	-0.0585(6)	0.4149(6)	0.1027(3)	0.035(1) <sup>a</sup>
C25	-0.0094(16)	0.2977(15)	0.1576(8)	0.062(4)
	-0.0136(5)	0.3024(5)	0.1570(3)	0.030(1) <sup>a</sup>
C31	-0.1194(15)	0.0412(18)	0.4103(8)	0.075(5)
	-0.1176(6)	0.0318(5)	0.4117(3)	0.033(1) <sup>a</sup>
C32	-0.2228(19)	0.0936(20)	0.4631(8)	0.087(6)
	-0.2210(6)	0.0799(6)	0.4645(6)	0.040(1) <sup>a</sup>
C33	-0.3599(17)	0.1788(19)	0.4399(10)	0.080(6)
	-0.3605(7)	0.1747(6)	0.4421(3)	0.042(1) <sup>a</sup>
C34	-0.3927(16)	0.2097(20)	0.3633(10)	0.090(6)
	-0.3914(7)	0.2167(7)	0.3660(4)	0.045(1) <sup>a</sup>
C35	-0.2827(16)	0.1610(17)	0.3139(8)	0.073(5)
	-0.2823(6)	0.1646(6)	0.3152(3)	0.036(1) <sup>a</sup>
C41	0.0779(15)	-0.2800(17)	0.3577(9)	0.068(5)
	0.0856(6)	-0.2870(5)	0.3573(3)	0.032(1) <sup>a</sup>
C42	0.1356(18)	-0.3943(17)	0.4113(10)	0.076(5)
	0.1430(6)	-0.4008(6)	0.4116(3)	0.038(1) <sup>a</sup>
C43	0.2761(18)	-0.4517(17)	0.4361(9)	0.076(5)
	0.2819(6)	-0.4562(6)	0.4369(3)	0.034(1) <sup>a</sup>
C44	0.3548(16)	-0.3976(17)	0.4052(8)	0.067(5)
	0.3613(6)	-0.3987(6)	0.4065(3)	0.034(1) <sup>a</sup>
C45	0.2926(15)	-0.2825(16)	0.3529(8)	0.063(4)
	0.2968(6)	-0.2854(5)	0.3532(3)	0.031(1) <sup>a</sup>
C51	0.2991(16)	-0.2239(17)	0.1534(8)	0.065(5)
	0.3061(6)	-0.2276(5)	0.1541(3)	0.032(1) <sup>a</sup>
C52	0.4079(17)	-0.2824(18)	0.1030(10)	0.081(5)
	0.4136(6)	-0.2852(6)	0.1032(3)	0.040(1) <sup>a</sup>
C53	0.4619(17)	-0.2007(23)	0.0714(9)	0.084(6)
	0.4697(7)	-0.2065(6)	0.0711(3)	0.043(1) <sup>a</sup>
C54	0.4157(17)	-0.0703(19)	0.0930(9)	0.077(5)
	0.4177(6)	-0.0734(6)	0.0909(3)	0.039(1) <sup>a</sup>

contd

Table 2. (contd)

Atom	x	y	z	$U_{\text{eq}}$
C55	0.3071(15)	-0.0196(15)	0.1436(8)	0.060(4)
	0.3095(5)	-0.0213(5)	0.1415(3)	0.029(1) <sup>a</sup>
C61	0.2958(16)	0.0356(15)	0.3342(9)	0.065(5)
	0.2968(6)	0.0387(5)	0.3331(3)	0.031(1) <sup>a</sup>
C62	0.3560(18)	0.0794(18)	0.3860(10)	0.078(5)
	0.3603(6)	0.0830(6)	0.3819(3)	0.039(1) <sup>a</sup>
C63	0.2715(25)	0.1889(24)	0.4243(10)	0.094(7)
	0.2728(7)	0.1943(6)	0.4230(4)	0.044(19) <sup>a</sup>
C64	0.1266(23)	0.2572(19)	0.4126(10)	0.085(6)
	0.1250(6)	0.2587(6)	0.4123(3)	0.042(19) <sup>a</sup>
C65	0.0694(17)	0.2080(17)	0.3602(9)	0.069(5)
	0.0715(6)	0.2073(5)	0.3617(3)	0.032(1) <sup>a</sup>
S1	0.39742(43)	0.30646(46)	0.12697(32)	0.0704(12)
	0.39938(14)	0.30735(13)	0.12851(8)	0.0322(5)
S2	0.29385(47)	0.30224(49)	0.62278(24)	0.0761(13)
	0.28581(13)	0.30300(13)	0.61991(7)	0.0300(5)
C1	0.2894(22)	0.4197(20)	0.1953(10)	0.084(6)
	0.2834(7)	0.4225(6)	0.1972(3)	0.038(2)
C2	0.2798(25)	0.4084(25)	0.6920(1)	0.109(7)
	0.2761(7)	0.4059(7)	0.6958(4)	0.050(3)
F11	0.1816(12)	0.5301(12)	0.1635(7)	0.128(4)
	0.1721(4)	0.5365(4)	0.1637(3)	0.059(2)
F12	0.3603(12)	0.4599(11)	0.2360(5)	0.113(4)
	0.3523(5)	0.4661(4)	0.2398(2)	0.055(2)
F13	0.2414(16)	0.3568(15)	0.2431(6)	0.155(5)
	0.2316(6)	0.3596(5)	0.2450(2)	0.073(3)
F21	0.2820(15)	0.5188(15)	0.6679(9)	0.158(6)
	0.2819(5)	0.5188(4)	0.6705(3)	0.075(2)
F22	0.1636(15)	0.4482(14)	0.7298(7)	0.151(5)
	0.1544(5)	0.4485(5)	0.7327(3)	0.076(2)
F23	0.3894(15)	0.3337(19)	0.7429(7)	0.199(6)
	0.3843(5)	0.3306(6)	0.7469(3)	0.080(2)
O11	0.3036(10)	0.2754(11)	0.0884(8)	0.075(3)
	0.3056(4)	0.2730(4)	0.0898(2)	0.037(2)
O12	0.4326(13)	0.3993(14)	0.0797(6)	0.109(4)
	0.4380(5)	0.3968(5)	0.0825(3)	0.052(2)
O13	0.5082(15)	0.1984(13)	0.1698(8)	0.141(5)
	0.5136(5)	0.1937(5)	0.1734(3)	0.067(2)
O21	0.4192(92)	0.2744(11)	0.5850(5)	0.070(3)
	0.4212(4)	0.2703(4)	0.5866(2)	0.037(2)
O22	0.2850(15)	0.1921(13)	0.6572(8)	0.129(5)
	0.2799(5)	0.1858(4)	0.6568(3)	0.052(2)
O23	0.1643(12)	0.4018(16)	0.5740(7)	0.130(5)
	0.1621(4)	0.3989(5)	0.5726(2)	0.047(2)

<sup>a</sup>Isotropically refined  $U_{\text{iso}}$  values, all other  $U_{\text{eq}}$  calculated from the anisotropic parameters according to the formulas:

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j = a^2 b^2 c^2 [B_{11} \sin^2 \alpha + B_{22} \sin^2 \beta +$$

$$B_{33} \sin^2 \gamma + 2B_{12} \sin \alpha \sin \beta \cos \gamma + 2B_{13} \sin \alpha \cos \beta \sin \gamma + 2B_{23} \cos \alpha \sin \beta \sin \gamma] / (24\pi^2 V)^2,^{33} \text{ and } \sigma^2(U_{\text{eq}}) = \frac{1}{3} \{[\sigma^2(U_{11}) + \sigma^2(U_{22}) + \sigma^2(U_{33})][1 - (ab + ac + bc)/2(a^2 + b^2 + c^2)]\}^{1/2}.^{34}$$

diffraction studies. Intensity data collections were carried out at 298 and 183 K. The low-temperature device used is described elsewhere.<sup>26</sup> Graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) was used. All reflections were corrected for Lorentz and polarisation effects and converted into scaled  $|F_o|$  values by means of a data reduction

Table 3. Selected interatomic distances (in Å) and angles (in °) with estimated standard deviations in parenthesis.

	298 K	183 K
Coordination polyhedron:		
Hg–N1	2.45(2)	2.422(4)
Hg–N2	2.48(1)	2.497(5)
Hg–N3	2.44(2)	2.402(4)
Hg–N4	2.49(1)	2.499(5)
Hg–N5	2.42(2)	2.410(4)
Hg–N6	2.46(2)	2.442(4)
N1–Hg–N6	174.3(5)	173.3(1)
N2–Hg–N4	179.0(5)	178.2(1)
N3–Hg–N5	173.5(5)	172.3(1)
Trifluoromethanesulfonate ions:		
S1–O11	1.43(2)	1.446(4)
S1–O12	1.48(2)	1.449(5)
S1–O13	1.38(2)	1.428(5)
S2–O21	1.42(2)	1.449(4)
S2–O22	1.38(2)	1.439(5)
S2–O23	1.52(2)	1.439(5)
S1–C1	1.81(2)	1.818(6)
S2–C2	1.75(3)	1.806(7)
C1–F11	1.30(3)	1.328(7)
C1–F12	1.31(3)	1.340(7)
C1–F13	1.34(3)	1.342(8)
C2–F21	1.37(4)	1.330(8)
C2–F22	1.27(4)	1.336(8)
C2–F23	1.33(4)	1.342(8)

program. A semi-empirical absorption correction method was used in the same way as before for the data collected at 298 K.<sup>27</sup> No absorption correction was applied to the low-temperature data, as the crystal was dissolved in the mother liquid when the temperature was raised. An attempt to correct the observed data for absorption with the program ABSORB<sup>28</sup> gave neither better *R*-values nor lower standard deviations in the coordinates. A summary of the parameters of the single-crystal X-ray diffraction experiments is given in Table 1.

Patterson methods were used to localize the six Hg–N vectors, and the S, F, O and C atoms were identified from

subsequent Fourier difference syntheses. A conventional *R*-value of 0.080 was obtained with all atoms isotropic for the data collected at 298 K. The final least-squares refinements of 478 variables (53 anisotropic atoms and one scale factor) based on 3048 independent reflections yielded an *R*-value of 0.045. No hydrogen atoms were included.

The positional parameters found from the room-temperature data were used as start values for the treatment of the low-temperature data. In this case the final least-squares refinement was performed with 328 parameters and 5595 reflections. Anisotropic temperature factors were applied for mercury, nitrogen and all the TFMS atoms, and isotropic ones for the remaining atoms. Hydrogen atoms were included with fixed parameters in calculated positions [ $d(\text{C–H}) = 0.95 \text{ \AA}$ ]. Structural parameters are given in Table 2 and selected interatomic distances and angles in Table 3.\*

Differential scanning calorimetry (DSC) curves were obtained with a Perkin-Elmer DSC-2c instrument with a ca. 15 mg sample enclosed in a steel cell designed to withstand a high internal pressure. An empty cell was used as the reference. The temperature region 298–423 K was scanned at a rate of 2.5 K min<sup>-1</sup>. TG curves were recorded with samples between 7 and 15 mg in platinum cups under nitrogen flow at heating rates of 2.5 and 10 K min<sup>-1</sup> in the temperature range 300–550 K with the use of a Perkin-Elmer TGS-2 instrument.

### Description and discussion of the structure

*X-Ray data.* The mercury(II) atom is coordinated to six nitrogen atoms, forming discrete hexakis(pyridine)mercury(II) ions (Fig. 1). The pyridine rings show the normal geometry with mean distances of C–C 1.39<sub>2</sub> and C–N 1.35<sub>5</sub> Å. At the lower temperature the average C–N distance is 1.34<sub>2</sub> Å. The opposite pairs, N1–N6 and N3–N5, of the pyridine molecules, are twisted along the pseudo-octahedron.

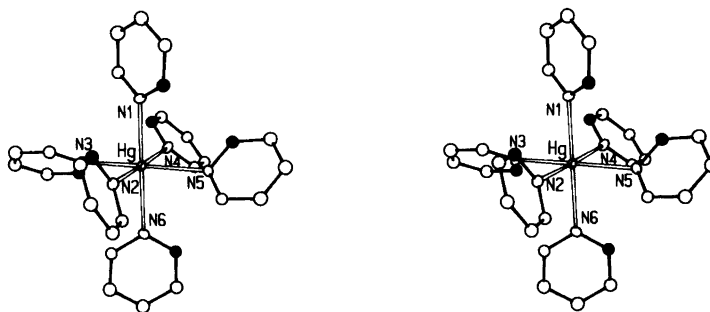


Fig. 1. The hexakis(pyridine)mercury(II) ion. For clarity the H atoms have been omitted and only the Hg and N atoms are labelled. The C<sub>11</sub>, C<sub>21</sub>, ..., C<sub>61</sub> atoms are filled and the other C atoms are numbered consecutively. (The first index number on the H and C atoms denotes the pyridine ligand.) The angles between opposite pyridine planes (defined by the normal directions) are: N1–N6, 54.1(2); N2–N4, 20.6(3)° and N3–N5, 75.6(1)°.

\* Lists of thermal and hydrogen-atom parameters and of observed and calculated structure factors are available from M.S. on request.

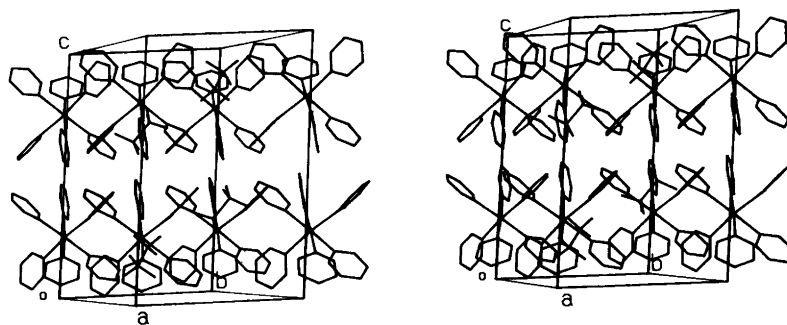


Fig. 2. A stereoscopic view of the triclinic unit cell.

dral axes in opposite directions, rather like the arms of a windmill. In the N2–N4 pair, however, the pyridine rings are twisted in the same direction, which gives approximately overall  $C_2$  symmetry to the hexakis(pyridine)mercury(II) ion (Fig. 1). The six Hg–N bonds in the range 2.4 to 2.5 Å, average 2.45 Å, are comparatively long,<sup>7</sup> in agreement with the high coordination number. They are also longer than the 2.40 Å mean value in the six-coordinated tris(1,10-phenanthroline)mercury(II) complex.<sup>11</sup> There is no sign of a shortening of two opposite Hg–N distances, as was found in the bis- and trispyridine salts.<sup>8–10</sup> On the contrary, two longer Hg–N bonds were found for the pair N2–N4 (Table 3). This interesting feature, already noticeable at room temperature, prompted us to make a study at low temperature in order to ascertain the significance in the difference. The temperature ellipsoids of the N atoms are fairly isotropic and not abnormally large, indicating an absence of static or dynamic disorder.

Some rather short H···H distances are found between the *ortho* hydrogen atoms of adjacent pyridine rings. The shortest are calculated to be H<sub>45</sub>–H<sub>61</sub> 2.35 Å, H<sub>25</sub>–H<sub>55</sub> 2.40 Å, H<sub>15</sub>–H<sub>41</sub> 2.49 Å and H<sub>21</sub>–H<sub>35</sub> 2.51 Å.<sup>†</sup> Thus all *ortho* hydrogens from the two pyridine ligands with longer Hg–N bonds are involved in rather close H···H contacts. This may be a reason for the different direction of twist of these pyridine rings, but is not a probable explanation for the long Hg–N bonds. It is also of interest to note that, while the pyridine ligands coordinated to the closed-shell Hg(II) and Mg(II) ions<sup>2</sup> are twisted around the metal–nitrogen bond, those coordinated to the  $d^6$  ion Fe(II) are not.<sup>1</sup> For a metal ion with an incompletely filled d-shell, the  $T_h$  configuration of a hexapyridine complex allows maximum overlap of a bonding ligand  $\pi$ -orbital with an empty  $d_\pi$ -orbital of the metal ion. The lack of this stabilizing influence in the  $[\text{Hg}(\text{py})_6]^{2+}$  ion, in the presence of some asymmetry in its surroundings, is a possible reason for the different configurations of the complexes.

The two trifluoromethanesulfonate ions in the asymmetric unit have rather large and anisotropic temperature factors, especially at the higher temperature, indicating libra-

tional movements consistent with a lack of hydrogen bonds in the structure. The ions have a staggered conformation with approximate  $C_{3v}$  symmetry, and with torsion angles O–S–C–F varying between 178.5 and 179.7° at 183 K for the O and F atoms in *trans* positions. The  $-\text{CF}_3$  groups have an almost regular tetrahedral conformation, with average S–C–F and F–C–F angles of 111.6 and 107.1°, respectively, and with an average C–F distance of 1.336(3) Å. For the  $-\text{SO}_3$  groups the corresponding C–S–O and O–S–O angles are 103.3 and 114.9°, respectively, and the average S–O distance is 1.442(3) Å. These distances and angles do not differ significantly from previously determined values,<sup>29–32</sup> although some of the bonds appear to be shorter at room temperature than at 183 K, an expected effect of large librational motions of the TFMS ions.<sup>30</sup>

A stereoscopic view of the unit cell is shown in Fig. 2. We observe some rather short intermolecular O, F···C interactions, the shortest being F<sub>22</sub>–C<sub>25</sub> 3.23 Å. It seems unlikely, however, that crystal packing forces could explain the differences found between the intramolecular Hg–N bonds.

**Thermogravimetric analyses.** In order to investigate the effect of the unexpected structural feature of two significantly longer Hg–N bonds, the thermal decomposition of the compound was studied. TG curves offer immediate information about the thermal stability of the compound, which in turn can illustrate the relative bond strengths within the molecule.

The  $[\text{Hg}(\text{py})_6](\text{TFMS})_2$  compound starts to decompose at room temperature. With a heating rate of 2.5 K min<sup>-1</sup> under a slow nitrogen flow the decomposition to  $[\text{Hg}(\text{py})_2](\text{TFMS})_2$  is complete at 355 K. A dip, enhanced in the derivative, in the TG curve at about 333 K indicates that the thermal decomposition of  $[\text{Hg}(\text{py})_6](\text{TFMS})_2$  occurs in two steps, each of which is associated with a weight loss corresponding to two pyridine molecules. We therefore conclude that  $[\text{Hg}(\text{py})_4](\text{TFMS})_2$  has a transient existence in the decomposition.

The thermogram obtained with the faster scan rate, 10 K min<sup>-1</sup>, had a similar appearance (Fig. 3), although with the inflexion points of the TG curve shifted by 10–20 K towards higher temperature. The bispyridine compound  $[\text{Hg}(\text{py})_2]$

<sup>†</sup> The first index number on the H and C atoms denotes the pyridine ligand.

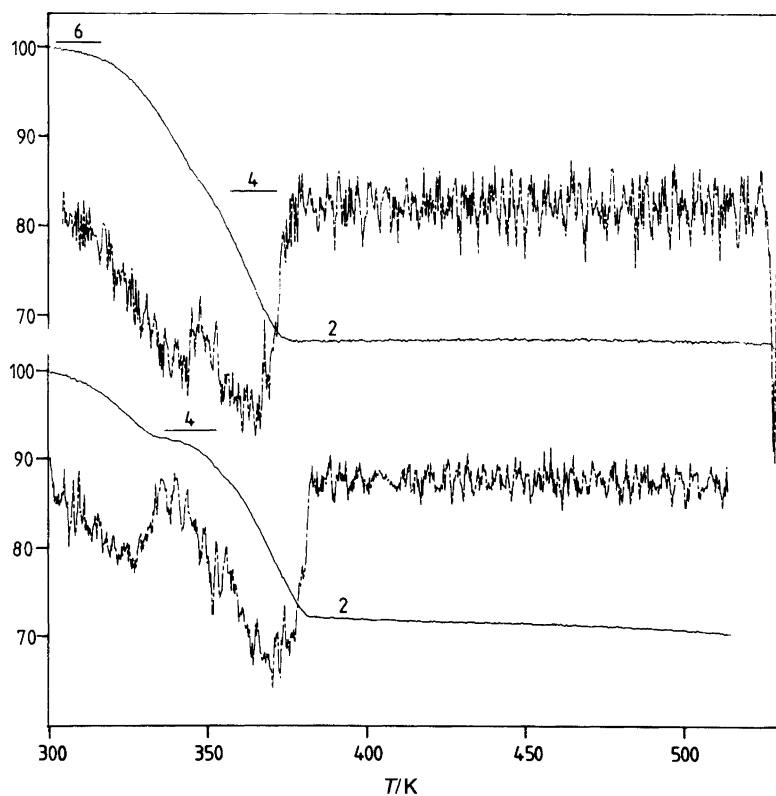


Fig. 3. TG curves of  $[\text{Hg}(\text{py})_6](\text{TFMS})_2$  (upper part) and  $[\text{Hg}(\text{py})_6](\text{ClO}_4)_2$  (lower part) at a heating rate of  $10 \text{ K min}^{-1}$ . The solid lines show the weight loss,  $\Delta m$ , and the dashed line its derivative,  $d\Delta m = f(T)$ . Assuming that the horizontal parts of the TG curves correspond to the bispyridine solvates, the calculated levels corresponding to compositions with four and six pyridine ligands are indicated in the figure. At loading the compounds were exposed to air for a short time, which caused some loss of pyridine, especially in the perchlorate compound. The 100 % level of Fig. 3 (sample weights 13.2027 and 7.0500 mg for the TFMS and perchlorate salts, respectively) therefore does not correspond to a pure hexapyridine composition.

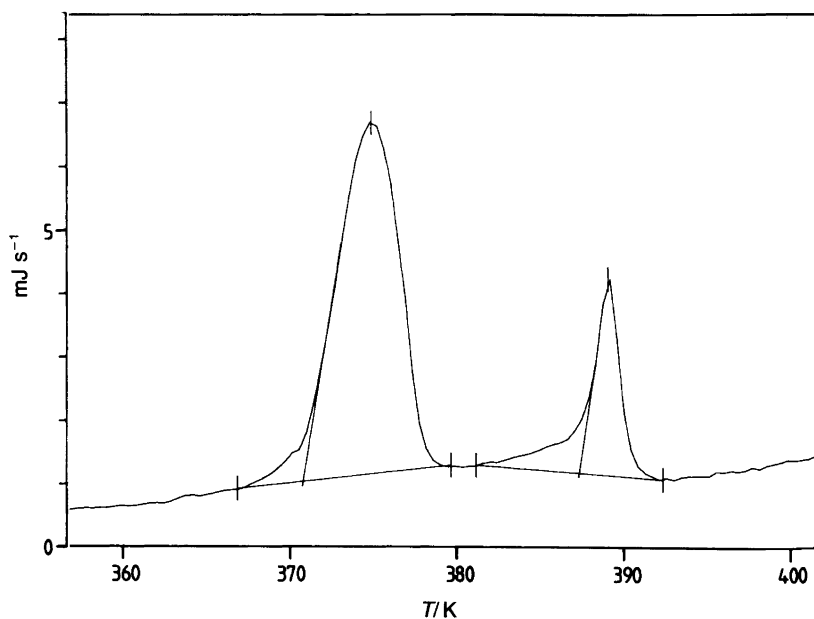
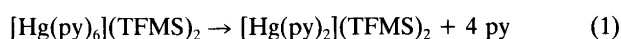


Fig. 4. DSC curve of  $[\text{Hg}(\text{py})_6](\text{TFMS})_2$  (sample weight at loading 14.60 mg) at a heating rate of  $2.5 \text{ K min}^{-1}$ .

(TFMS)<sub>2</sub> is stable up to about 530 K, where it decomposes rapidly.

We also made a TG analysis of [Hg(py)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>. The presence of the tetrapyridine compound [Hg(py)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub>, as previously proposed by Chudinova,<sup>12</sup> was shown by a plateau in the curve (Fig. 3). Its stability is markedly higher than that of the corresponding tetrapyridine TFMS compound. The bispyridine TFMS salt is also less stable than the bispyridine perchlorate, [Hg(py)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, which is reported to decompose explosively at 601 K.<sup>12</sup>

The DSC curve for [Hg(py)<sub>6</sub>](TFMS)<sub>2</sub> displayed two endothermic peaks at the onset temperatures 371 and 387 K (Fig. 4). Both peaks showed good reproducibility, and the first was assigned to the overall decomposition reaction (1).



The corresponding enthalpy of reaction was 43.5 kJ mol<sup>-1</sup>. The second peak is probably caused by vaporization of the released pyridine, as the temperature corresponds well to its boiling point.

### Concluding remarks

For the first time six-coordination of mercury(II) with nitrogen donor atoms in an almost regular octahedral symmetry has been verified. An interesting feature is the two opposite longer Hg–N bonds in the [Hg(py)<sub>6</sub>](TFMS)<sub>2</sub> structure. Thermogravimetric studies of this compound show that the pyridine molecules leave the hexapyridine solvate pairwise, also an indication of two weaker Hg–N bonds. These observations may be an effect of a vibronic mixing of closely lying electronic states in the valence shell of the mercury(II) ion, a SOJT effect, which can cause tetragonal distortions of a regular octahedral coordination.

*Acknowledgements.* We wish to thank Professor Mats Nygren and coworkers, Department of Inorganic Chemistry, University of Stockholm, for their kind assistance with the thermal analyses. The Swedish Natural Council is gratefully acknowledged for its support.

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Received June 18, 1990.