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LETTER

Terpyridine complexes of $Hg(OCOCF_3)_2$ and $Hg(BF_4)_2$. Crystal and molecular structure of mercuric trifluoroacetato-2,2′:6′,2″-terpyridine

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Hg–L bonds in most Hg(II) structures are essentially covalent but, since they have different bond orders, various coordination polyhedra appear around the mercury atom. They are conveniently systematized according to their characteristic and effective ligancy [1]. In order to find out the mercury coordination preferences we have examined the mercury response toward 2,2′:6′,2″-terpyridine known as a rather rigid tridentate ligand. The only known structures of mercury(II) complexes with terpyridine are $[MeHg(Et_3terpy)](NO_3)$ [2] and $Hg(CF_3)_2\cdot$terpy [3]. The analogous complexes with mercuric halides, perchlorate and nitrate were identified only by means of chemical analysis and IR spectroscopy [4]. The five-coordinated mercury atom in the halide and nitrate complexes, $HgX_2\cdot$terpy ($X = Cl^-$, Br^-, I^-, NO_3^-) and six-coordinated mercury atom in the perchlorate complex have been presumed by the authors.

We report here the preparation of the terpyridine complex with mercuric trifluoroacetate (**I**) and tetrafluoroborate (**II**), respectively, as well as the crystal and molecular structure of complex **I**. Assuming terpyridine in the function of a tridentate ligand, mercury is apparently forced to the coordination of six by the presence of ionically bound tetrafluoroborate as in **II**. From this point of view, the crystal structure of **II**, or of the mercuric perchlorate complex with terpyridine, seemed to be interesting. Our attempts to crystallize the perchlorate complex as crystals suitable for X-ray investigation have failed so far, but a preliminary X-ray investigation of **II** gave a well recognized pattern of two short mercury-to-nitrogen bonds and four longer ones but the structure could not be refined to an *R* value of less than 0.24 [5].

Experimental

Preparation of $Hg(OCOCF_3)_2\cdot$terpy (I)

A solution of terpyridine (0.39 g in 6 ml of ethanol) was added slowly to an aqueous solution of mercuric trifluoroacetate (0.639 g in 25 ml of H_2O with a few drops of trifluoroacetic acid). The precipitated prismatic crystals were left to stand overnight, then filtered off, washed with cold water and dried. Yield 0.95 g (96%). *Anal.* Calc.: Hg, 30.40; C, 34.58; H, 1.86. Found: Hg, 30.36; C, 35.18; H, 2.15%. IR max. (cm^{-1}): 2959(w), 2927(vs), 2916(s), 1674(s), 1636(m), 1592(m), 1583(m), 1576(w), 1559(m), 1541(m), 1522(w), 1508(w), 1480(m), 1453(w), 1420(m), 1362(w), 1339(w), 1322(w), 1255(w), 1187(s), 1169(s), 1136(s), 1013(m), 844(m), 793(m), 778(s), 726(s), 668(w), 658(w), 650(w), 640(w), 472(w).

Preparation of $Hg(BF_4)_2\cdot 2$terpy (II)

To a warm (30 °C) aqueous suspension of yellow mercuric oxide (0.3 g in 6 ml of H_2O) an etheral solution of tetrafluoroboric acid was added slowly drop by drop (0.5 ml, 54 wt.%). To this clear and still warm solution of mercuric tetrafluoroborate, an ethanolic solution of terpyridine was added slowly (0.66 g in 12 ml) and the reaction mixture left to stand overnight. Colourless crystals sometimes with a pinkish shade were filtered off, washed with cold ethanol and dried. Yield 1.1 g (95%). *Anal.* Calc.: Hg, 23.86; C, 42.86; H, 2.64; N, 10.00. Found: Hg, 23.88; C, 42.60; H, 3.18; N, 9.76%. IR max. (cm^{-1}): 2954(s), 2933(vs), 2924(s), 2012(s), 1594(s), 1584(s), 1480(s), 1454(s), 1437(m), 1318(m), 1251(m), 1195(s), 1170(m), 1110(s), 1063(vs), 1020(s), 827(m), 772(vs), 650(m), 638(m), 520(m).

Structure determination

Crystal data and data collection parameters are listed in Table 1. The space group was determined by preliminary oscillation and Weissenberg photographs. A transparent colourless single crystal bonded by planes {100}, {010}, {110}, $\{1\bar{1}0\}$, {101}, and $(\bar{1}01)$, $(1\bar{3}\bar{4})$, with dimensions of $0.39 \times 0.24 \times 0.09$ mm was glued on the top of a glass fibre. Data were collected on a Philips PW 1100 diffractometer at 295 K. The unit cell dimensions were determined by the least-squares procedure from 24 automatically centred reflections in the range of $16 < 2\theta < 24°$. Crystal alignment and decomposition were monitored

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TABLE 1. Crystal data and data collection parameters

Formula	$HgC_{19}H_7O_4N_3F_6H_8$
Molecular weight	659.89
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	14.594(7)
b (Å)	16.173(7)
c (Å)	8.661(6)
β (°)	93.47(3)
V (Å^3)	2040.5
$F(000)$	1248
Z	4
D_{calc} (g cm^{-3})	2.148
D_{obs} (g cm^{-3})	2.100
Crystal size (mm)	0.39×0.24×0.09
μ(Mo Kα) (cm^{-1})	76.22
Radiation	Mo Kα (λ=0.7107 Å) graphite monochromator
Scan method	$\theta/2\theta$
Collection range, 2θ (°)	4–60
Total unique data	4540
Data with $F_o > 4\sigma(F_o)$	3604
No. parameters	176
R (unit weight)	0.062
Goodness-of-fit	4.6

throughout data collection by measuring three standard reflections ($\bar{7}03$, 320, 035) every 2 h. Only random variations of the intensities during data collection were observed. The intensities were corrected for Lorentz and polarization effect as well as for absorption. Transmission factors ranged from 0.434 to 0.700 for the full data set. A total of 4540 intensities was measured within the range of $2 < \theta < 30°$. Average equivalents gave 4262 unique reflections (R_{int} 0.033), of which 3604 with $F_o > 4\sigma(F_o)$ were used for the final Crysruler package calculation [6]. Scattering factors were taken from the International Tables [7]. The structure was solved by the heavy-atom method starting from the three-dimensional Patterson analysis. Successive Fourier syntheses gave coordinates of all non-hydrogen atoms, which were refined by means of isotropic least-squares calculation to $R = 0.11$. Several cycles in two blocks with anisotropic thermal parameters for all atoms except for those of trifluoromethyl groups (atoms C22, F1, F2, F3; C32, F11, F12, F13) were treated isotropically with a constrained and average C–F bond of 1.283(12) Å and F–F bond of 2.057(20) Å, respectively, and a final R of 0.0624 was obtained. The insertion of hydrogen atoms at their expected positions did not give any improvement. The final atomic coordinates and isotropic thermal parameters are given in Table 2, and interatomic distances and angles in Table 3.

TABLE 2. Fractional coordinates (×10^4) and thermal parameters (Å^2×10^4)

Atom	x/a	y/b	z/c	U_{eq}[a]
Hg	2373(1)	1411(1)	1929(1)	449(1)
N1	3466(8)	2368(7)	1095(13)	447(37)
N2	1636(8)	2547(7)	687(13)	443(33)
N3	782(8)	1191(8)	1583(15)	550(45)
C1	4387(10)	2227(10)	1243(17)	518(49)
C2	5013(11)	2813(12)	907(21)	652(66)
C3	4713(11)	3581(12)	410(21)	683(61)
C4	3758(11)	3745(10)	274(19)	584(52)
C5	3166(10)	3106(9)	576(17)	476(46)
C6	2144(10)	3196(9)	308(16)	465(47)
C7	1727(11)	3923(10)	−299(19)	596(50)
C8	779(13)	3926(11)	−524(21)	672(64)
C9	269(12)	3237(12)	−132(20)	650(65)
C10	726(9)	2561(9)	476(17)	471(45)
C11	252(10)	1778(10)	910(17)	502(48)
C12	−687(10)	1662(12)	612(21)	683(65)
C13	−1082(12)	934(14)	1023(24)	774(78)
C14	−534(12)	312(13)	1717(22)	727(70)
C15	412(12)	458(12)	2011(23)	714(66)
O1	2844(8)	1722(7)	4463(11)	598(36)
O2	1897(8)	720(7)	5023(15)	737(45)
O3	2660(8)	97(8)	1156(16)	873(52)
O4	3976(10)	380(9)	2258(20)	1044(65)
C21	2461(9)	1252(9)	5345(17)	460(42)
C31	3437(12)	−22(11)	1492(20)	614(55)
C22	2737(14)	1411(15)	7017(23)	1130(91)*
C32	3799(10)	−861(9)	850(16)	723(48)*
F1	2611(18)	769(13)	7829(34)	3045(128)*
F2	3573(12)	1596(12)	7379(22)	1800(71)*
F3	2302(16)	2026(15)	7581(35)	2985(134)*
F11	4591(9)	−1066(10)	1419(16)	1390(56)*
F12	3277(9)	−1480(9)	1142(16)	1251(48)*
F13	3833(9)	−830(9)	−636(13)	1123(43)*

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. Starred items = isotropic thermal parameters.

Results and discussion

Description of the structure of Hg(OCOCF$_3$)$_2$·terpy (I)

The molecular structure, shown in Fig. 1, could be interpreted on the basis of a distorted (O1)(O3)Hg(N1)(N3) tetrahedron in which the (O1)Hg(O3) plane is roughly perpendicular to the (N1)Hg(N3) plane, the corresponding angles being 115.6(4) and 137.7(4)°, respectively. The pyridine rings of the ligand are not in the same plane. Almost equally long Hg–N bonds of 2.367(12), 2.356(11) and 2.350(12) Å differ in length from the analogous bonds in similar terpyridine complexes examined so far, e.g. in [MeHg(Et$_3$terpy)](NO$_3$) (2.25 to 2.52 Å) [2], or in Hg(CF$_3$)$_2$·terpy (2.62 to 2.70 Å) [3]. The Hg–O1 and Hg–O3 distances of 2.315(10) and 2.275(13) Å are in the range typical for the covalent Hg–O values

TABLE 3. Bond distances (Å) and angles (°) with e.s.d.s in parentheses

Hg–N1	2.367(12)	C9–C10	1.369(23)
Hg–N2	2.356(11)	C10–C11	1.502(21)
Hg–N3	2.350(12)	C11–C12	1.392(21)
Hg–O1	2.315(10)	C12–C13	1.368(29)
Hg–O3	2.275(13)	C13–C14	1.398(28)
N1–C1	1.362(19)	C14–C15	1.409(25)
N1–C5	1.340(18)	O1–C21	1.235(18)
N2–C6	1.337(19)	O2–C21	1.212(18)
N2–C10	1.330(18)	O3–C31	1.170(21)
N3–C11	1.336(20)	O4–C31	1.191(23)
N3–C15	1.363(23)	C21–C22	1.502(25)
C1–C2	1.360(24)	C31–C32	1.570(23)
C2–C3	1.377(27)	C22–F1	1.274(33)
C3–C4	1.417(23)	C22–F2	1.277(27)
C4–C5	1.382(22)	C22–F3	1.292(34)
C5–C6	1.503(21)	C32–F11	1.273(20)
C6–C7	1.411(22)	C32–F12	1.292(20)
C7–C8	1.385(25)	C32–F13	1.292(18)
C8–C9	1.393(26)		
Hg...O2	3.023(13)	Hg...O4	2.873(15)
O1–Hg–O3	115.6(4)	C8–C9–C10	118.5(16)
N3–Hg–O3	91.1(4)	N2–C10–C9	121.7(14)
N3–Hg–O1	112.8(4)	C9–C10–C11	123.3(13)
N2–Hg–O3	132.9(4)	N2–C10–C11	115.0(12)
N2–Hg–O1	111.4(4)	N3–C11–C10	116.4(13)
N2–Hg–N3	68.8(4)	C10–C11–C12	122.1(14)
N1–Hg–O3	112.4(4)	N3–C11–C12	121.5(15)
N1–Hg–O1	88.9(4)	C11–C12–C13	119.6(16)
N1–Hg–N3	137.7(4)	C12–C13–C14	119.5(17)
N1–Hg–N2	69.4(4)	C13–C14–C15	119.1(18)
Hg–N1–C5	118.2(9)	N3–C15–C14	119.8(17)
Hg–N1–C1	122.8(9)	Hg–O1–C21	109.7(9)
C1–N1–C5	118.8(13)	Hg–O3–C31	105.9(12)
Hg–N2–C10	120.0(9)	O1–C21–O2	128.4(15)
Hg–N2–C6	118.7(9)	O2–C21–C22	118.8(14)
C6–N2–C10	121.1(12)	O1–C21–C22	112.7(14)
Hg–N3–C15	120.1(11)	O3–C31–O4	130.3(18)
Hg–N3–C11	119.3(10)	O4–C31–C32	116.4(15)
C11–N3–C15	120.5(13)	O3–C31–C32	113.3(15)
N1–C1–C2	122.4(15)	C21–C22–F3	112.8(19)
C1–C3–C4	119.4(15)	C21–C22–F2	118.3(17)
C2–C3–C4	119.2(17)	C21–C22–F1	110.7(18)
C3–C4–C5	117.9(15)	F2–C22–F3	102.2(20)
N1–C5–C4	122.3(14)	F1–C22–F3	109.2(23)
C4–C5–C6	121.6(13)	F1–C22–F2	102.9(21)
N1–C5–C6	116.1(13)	C31–C32–F13	110.7(13)
N2–C6–C5	116.5(13)	C31–C32–F12	112.7(13)
C5–C6–C7	122.7(13)	C31–C32–F11	113.9(13)
N2–C6–C7	120.8(14)	F12–C32–F13	106.5(13)
C6–C7–C8	117.4(15)	F11–C32–F13	107.9(13)
C7–C8–C9	120.4(17)	F11–C32–F12	104.7(14)

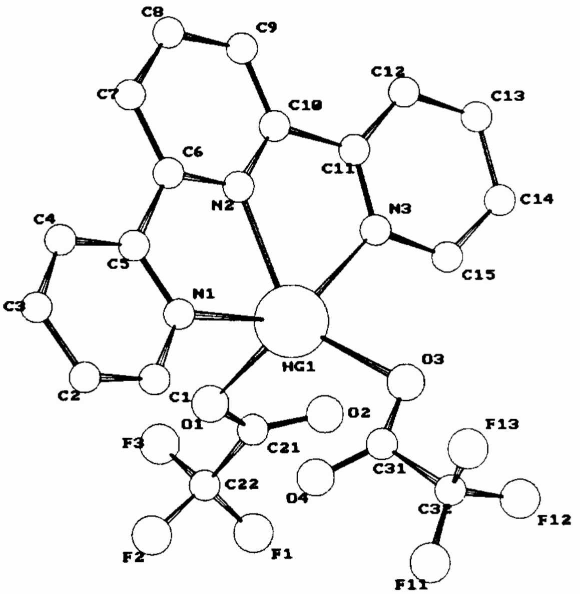

Fig. 1. The molecule of mercuric trifluoroacetato-2,2′:6′,2″-terpyridine.

(2.0 to 2.3 Å). At the same time they are much shorter than those found in mercuric trifluoroacetate complexes [8–10]. The other two oxygen atoms, O2 and O4, at distances of 3.023(13) and 2.873(15) Å, make the mercury atom effectively seven-coordinated [1]. A seven-coordinated mercury atom was also found in $Hg(py)_2(OCOCF_3)_2$ [9] and in tetraethyleneglycol(dimethylether)mercury(II) chloride [11]. The mercury coordination polyhedron is similar to that found in $Hg(CF_3)_2 \cdot$terpy [3]. The interatomic distances and bond angles in the terpyridine molecule are comparable with those found in similar complexes. Fluorine atoms in both trifluoroacetate ions have high thermal parameters also found in all mercuric trifluoroacetate complexes examined so far, and appear to indicate some persistent disorder of the trifluoromethyl group [3, 8–10].

IR spectra

The shift of the 'ring breathing' vibrations due to chelation observed at 1020 cm^{-1} with respect to the free ligand at 988 cm^{-1}, could be taken as a measure of the metal–ligand interaction [12]. Thus, from $\Delta\nu$ (cm^{-1}) of 25 for **I** and 32 for **II**, one can predict a stronger metal–ligand interaction in the latter. Terpyridine bands (C=N, C=C) are observed at 1592 and 1583 cm^{-1} for **I** and at 1594 and 1587 cm^{-1} for **II**, respectively. The other terpyridine vibrations are observed in the region between 1480–1430 cm^{-1}. Very strong absorptions due to ring hydrogens are observed at 778 and 772 cm^{-1} for **I** and **II**, respectively, as well as slightly weaker ones at 844 and 827 cm^{-1}.

Supplementary material

Atomic coordinates and further details of the crystal structure investigations are available from the authors on request.

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