Tableau 3. *Interactions* Na···*nigéricine* (Å)

| | | | |
|---|---|---|---|
| $Na^+\cdots O(43)$ | 2,38 (1) | $Na^+\cdots O(47)$ | 2,25 (1) |
| $Na^+\cdots O(44)$ | 2,52 (1) | $Na^+\cdots O(49)$ | 2,44 (1) |
| $Na^+\cdots O(45)$ | 2,48 (1) | | |

que $F_o < F_c < 3F_o$ et 0,050 pour les seules réflexions considérées comme observées.*

**Discussion.** Les coordonnées des atomes C,O,Na sont données dans le Tableau 1. La configuration de la molécule est représentée sur la Fig. 1.

Les longueurs de liaisons sont réunies dans le Tableau 2(*a*) et les angles de liaisons dans le Tableau 2(*b*). Les longueurs des liaisons C—C se distribuent autour d'une valeur moyenne de 1,530 (0,020) Å, celles des liaisons C—O dans les hétérocycles autour de 1,447 (0,021) Å.

Le Tableau 3 donne les principales distances impliquées dans l'interaction sodium–nigéricine. La très courte distance (2,25 Å) entre le cation et l'oxygène O(47) du groupement carboxylique montre que l'on a affaire à un sel complexe, comme dans le complexe nigéricine–argent.

La fermeture du macrocycle autour du cation est assurée par deux liaisons hydrogène: $O(48)\cdots O(50) =$ 2,55 Å et $O(47)\cdots O(51) =$ 2,75 Å.

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* Les listes des facteurs de structure, des paramètres thermiques anisotropes et des coordonnées des atomes d'hydrogène non affinés ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 35002: 24 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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# The Structure of Phenyl(pyridine)mercury(II) Trifluoroacetate

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**Abstract.** $[Hg(C_6H_5)(C_5H_5N)]C_2F_3O_2$, $C_{11}H_{10}HgN^+.C_2F_3O_2^-$, orthorhombic, $Pca2_1$, $a$ = 34·43 (3), $b$ = 7·404 (7), $c$ = 10·64 (1) Å, $D_m$ = 2·216, $D_x$ = 2·212 Mg m$^{-3}$ with $Z$ = 8. The structure has been determined from 1256 diffractometer-measured intensities with least-squares refinement to $R$ = 0·057. In the structural unit there are two independent $[HgPhpy]^+$ ions and two $CF_3CO_2^-$ ions. N and C attached to Hg could not be reliably differentiated; Hg—C(N) distances are: to Hg(1), 2·01 (4), 2·11 (4) Å; to Hg(2), 2·09 (4), 2·19 (4) Å. There are seven $Hg\cdots O$ contacts within the range 2·66 to 2·98 Å.

**Introduction.** Mercury trifluoroacetate readily reacts with benzene to give phenyl(trifluoroacetato)mercury(II), the structure of which has been determined (Grdenić, Kamenar & Hergold-Brundić, 1976). Recrystallization of this compound from pyridine gave lath-like crystals of the title compound, the forms {100}, {010}, {001} being observed. Weissenberg photographs, taken with Cu $K\alpha$ radiation ($\lambda$ = 1·542 Å), were used for the determination of the unit-cell dimensions and space group. Crystals were mounted with $b$ aligned on the axis of a Stoe STADI-2 automatic two-circle diffractometer; 1556 independent intensities in the range $4° < 2\theta < 40°$ were measured with Mo $K\alpha$ radiation ($\lambda$ = 0·7107 Å). Irradiation with X-rays caused decomposition of the crystals with progressive diminution of intensity and broadening of reflexions: it was necessary to use three crystals to collect data from the layers $k$ = 0 to 7. Separate absorption corrections ($\mu$ = 10·53 mm$^{-1}$) were made for each crystal using the *SHELX* program (Sheldrick, 1976). During data reduction, intensities for which $I < 3\sigma(I)$ were eliminated and the 1256 values remaining were used in the structure determination and refinement. Subsequent calculations were made with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

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Coordinates for the two independent Hg atoms were obtained from Patterson maps and were used to phase $(F_o - F_c)$ maps which eventually gave the remaining atomic positions (other than H). The origin was defined by restraining $z_{\mathrm{Hg}(1)}$ at 0·0. Refinement of atomic parameters proceeded using anisotropic $U_{ij}$ values for Hg atoms and isotropic $U$'s for C, O, (N) and F. No attempt was made to distinguish between the phenyl and pyridine rings as the estimated standard deviations of bond distances and the variation of peak heights were too large in relation to the expected differences between N and C atoms; all ring atoms were therefore treated as C. During later cycles individual scale factors for the layers $k = 0$ to 7 were refined. When the ratio of shift to e.s.d. of parameters was less than 0·1, the $R$ value was 0·057 and no significant features were present on a final $(F_o - F_c)$ map. Atomic scattering factors for Hg, including anomalous scattering, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970); those for other atoms were from *International Tables for X-ray Crystallography* (1962). Final coordinates and temperature factors are given in Table 1.*

Table 1. *Final atomic parameters* ($\times 10^3$; *for* Hg $\times 10^4$) *and temperature factors* ($U \times 10^3$; $U_{ij} \times 10^4$)

| | $x$ | $y$ | $z$ | $U$ (Å$^2$) |
|---|---|---|---|---|
| C(1) | 174 (1) | 449 (5) | 235 (4) | 45 (10) |
| C(2) | 178 (1) | 528 (5) | 139 (4) | 61 (12) |
| C(3) | 217 (1) | 552 (7) | 78 (5) | 85 (15) |
| C(4) | 245 (2) | 455 (8) | 147 (6) | 106 (18) |
| C(5) | 238 (1) | 372 (6) | 259 (5) | 82 (16) |
| C(6) | 201 (1) | 368 (6) | 306 (6) | 80 (14) |
| C(7) | 55 (1) | 436 (6) | 359 (4) | 59 (12) |
| C(8) | 45 (2) | 313 (7) | 450 (5) | 93 (16) |
| C(9) | 3 (1) | 307 (6) | 485 (6) | 91 (15) |
| C(10) | −21 (1) | 402 (6) | 425 (5) | 82 (15) |
| C(11) | −13 (2) | 541 (7) | 317 (7) | 111 (18) |
| C(12) | 29 (1) | 537 (6) | 289 (6) | 80 (14) |
| C(13) | 214 (1) | 931 (6) | 459 (4) | 55 (12) |
| C(14) | 228 (1) | 852 (5) | 351 (4) | 63 (12) |
| C(15) | 267 (1) | 858 (6) | 318 (6) | 81 (13) |
| C(16) | 293 (1) | 953 (6) | 396 (5) | 69 (13) |
| C(17) | 279 (1) | 1050 (6) | 498 (6) | 78 (13) |
| C(18) | 240 (1) | 1046 (6) | 526 (6) | 98 (17) |
| C(19) | 101 (1) | 931 (5) | 584 (4) | 37 (9) |
| C(20) | 94 (1) | 1006 (7) | 691 (5) | 75 (14) |
| C(21) | 54 (2) | 991 (7) | 744 (5) | 87 (16) |
| C(22) | 27 (2) | 899 (8) | 685 (6) | 105 (19) |
| C(23) | 32 (2) | 812 (7) | 569 (6) | 107 (18) |
| C(24) | 72 (1) | 834 (6) | 518 (6) | 92 (16) |
| C(25) | 118 (1) | 953 (7) | 233 (5) | 68 (13) |
| C(26) | 103 (3) | 6 (13) | 94 (10) | 191 (35) |
| C(27) | 145 (1) | 441 (6) | 605 (4) | 62 (11) |
| C(28) | 134 (1) | 487 (6) | 733 (5) | 65 (14) |
| O(1) | 124 (1) | 69 (5) | 296 (5) | 100 (10) |
| O(2) | 119 (1) | 795 (5) | 270 (3) | 100 (12) |
| O(3) | 149 (1) | 566 (4) | 535 (4) | 91 (10) |
| O(4) | 151 (1) | 288 (4) | 581 (3) | 87 (10) |
| F(1) | 63 (1) | 18 (6) | 96 (5) | 182 (17) |
| F(2) | 107 (1) | 854 (7) | 26 (6) | 183 (20) |
| F(3) | 116 (1) | 108 (7) | 41 (7) | 190 (22) |
| F(4) | 108 (2) | 431 (6) | 788 (7) | 206 (20) |
| F(5) | 153 (1) | 624 (6) | 772 (5) | 155 (17) |
| F(6) | 158 (1) | 392 (6) | 809 (5) | 155 (16) |
| Hg(1) | 8433 (1) | 649 (2) | 0 | |
| Hg(2) | 8867 (1) | 5617 (2) | 8009 (2) | |

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Hg(1) | 613 (11) | 717 (11) | 681 (12) | −34 (9) | 39 (11) | 51 (16) |
| Hg(2) | 524 (10) | 728 (12) | 732 (12) | −37 (9) | −6 (11) | 89 (16) |

**Discussion.** A view of one unit of structure is shown in Fig. 1; the distances and angles involving the Hg atoms are listed in Table 2. Each Hg is covalently bound to two six-membered rings; the two bonds to Hg(1) are appreciably non-linear, unlike those to Hg(2). It will be noted that each Hg has one bond shorter than the other by 0·1 Å and although it would be possible to identify the nearer atoms as carbon and thereby distinguish the phenyl groups from the pyridines, this has not been done in view of the e.s.d. (0·04 Å) of the bonds involved. In contrast to these covalent bonds, those to O are all in excess of the covalent value (normally within the range 2·0 to 2·2 Å) and have magnitudes similar to those found in tris(pyridine)mercury(II) bis(trifluoroacetate) (Halfpenny & Small, 1978) and bis(pyridine)mercury(II) bis(trifluoroacetate) (Halfpenny, Small & Thorpe, 1978). The coordination of each Hg follows the pattern found in many organomercury compounds, involving two approximately linear covalent bonds to Hg and a number of longer equatorially disposed bonds. The structure of the present compound may be compared with that of the parent compound, phenyl(trifluoroacetato)mercury(II) (Grdenić, Kamenar & Hergold-Brundić, 1976) in

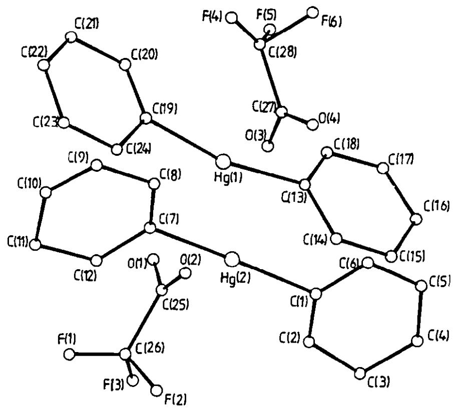

Fig. 1. View of one unit of the structure showing the atom-numbering scheme.

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* Lists of structure factors and distances and angles involving atoms other than Hg have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35034 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *around the* Hg *atoms*

| | | | |
|---|---|---|---|
| Hg(1)–C(13) | 2·01 (4) | Hg(1)–O(2) | 2·97 (4) |
| Hg(1)–C(19) | 2·11 (4) | Hg(1)–O(3) | 2·88 (3) |
| Hg(1)–O(1) | 2·66 (5) | Hg(1)–O(4) | 2·87 (3) |
| C(13)–Hg(1)–C(19) | 167 (2) | C(19)–Hg(1)–O(4) | 80 (1) |
| C(13)–Hg(1)–O(1) | 104 (1) | O(1)–Hg(1)–O(2) | 44 (1) |
| C(13)–Hg(1)–O(2) | 104 (1) | O(1)–Hg(1)–O(3) | 117 (1) |
| C(13)–Hg(1)–O(3) | 96 (1) | O(1)–Hg(1)–O(4) | 81 (1) |
| C(13)–Hg(1)–O(4) | 99 (1) | O(2)–Hg(1)–O(3) | 73 (1) |
| C(19)–Hg(1)–O(1) | 88 (1) | O(2)–Hg(1)–O(4) | 124 (1) |
| C(19)–Hg(1)–O(2) | 87 (1) | O(3)–Hg(1)–O(4) | 153 (1) |
| C(19)–Hg(1)–O(3) | 81 (1) | | |
| Hg(2)–C(1) | 2·19 (4) | Hg(2)–O(1) | 2·87 (4) |
| Hg(2)–C(7) | 2·09 (4) | Hg(2)–O(2) | 2·78 (4) |
| | | Hg(2)–O(3) | 2·94 (4) |
| C(1)–Hg(2)–C(7) | 178 (2) | C(7)–Hg(2)–O(2) | 96 (1) |
| C(1)–Hg(2)–O(1) | 85 (1) | C(7)–Hg(2)–O(3) | 99 (1) |
| C(1)–Hg(2)–O(2) | 82 (1) | O(1)–Hg(2)–O(2) | 166 (1) |
| C(1)–Hg(2)–O(3) | 82 (1) | O(1)–Hg(2)–O(3) | 107 (1) |
| C(7)–Hg(2)–O(1) | 97 (1) | O(2)–Hg(2)–O(3) | 75 (1) |

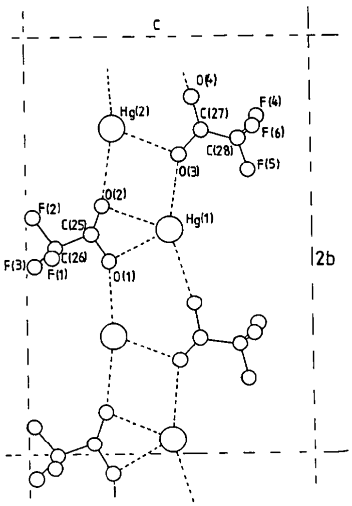

Fig. 2. Projection of part of the structure along *a* showing Hg···O coordination (phenyl and pyridine rings have been omitted for clarity).

which one O of the trifluoroacetate group is covalently bound to Hg (at 2·13 Å) almost collinearly with the phenyl ligand. In the present compound pyridine molecules displace trifluoroacetate anions and form the cations [HgPh(pyridine)]$^+$, indicating that pyridine is a more favourable ligand for bonding to Hg than the trifluoroacetate ion. The angle between the planes of the two rings of the Hg(1) group is 8(1)° and in the Hg(2) group, 12 (1)°. These values can be compared with those in diphenylmercury (Grdenić, Kamenar & Nagl, 1977), which is centrosymmetric, and the [Hg(pyridine)$_2$]$^{2+}$ group in bis(pyridine)mercury(II) bis(trifluoroacetate) (Halfpenny, Small & Thorpe, 1978), which has an angle of 31°.

The cations have their long directions parallel to *a* and are bound into continuous bands parallel to *b* by a system of Hg···O bonds involving the trifluoroacetate counter ions. The arrangement is shown in Fig. 2; each anion is bound to three Hg atoms. The ion defined by O(1), O(2) differs from that defined by O(3), O(4) in that the former is bound in a bidentate manner to Hg(1) whereas the latter is tilted so that only one of the Hg···O distances to Hg(2) can be considered as a bond, the other being considerably in excess (3·45 Å) of the van der Waals separation, using the most recent estimate of the van der Waals radius of Hg (1·75 Å; Barr, Goldstein, Hairs, McPartlin & Markwell, 1974). Hg(1) thus has four O atoms coordinated equatorially, with an effective overall coordination of six, while Hg(2) has three equatorial O atoms and an effective coordination of five.

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