$S = 1.08$
6069 reflections
272 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 3.7698P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXTL95*
Extinction coefficient: 0.0021 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

W—N1	1.973 (4)	W—C19	2.182 (5)
W—N2	2.013 (4)	W—Cl	2.422 (1)
W—N3	1.741 (4)	N3—C1	1.388 (6)
N1—W—N2	82.62 (15)	N3—W—N2	126.6 (2)
N3—W—C19	108.8 (2)	N1—W—Cl	160.2 (1)
N1—W—C19	88.0 (2)	N2—W—Cl	86.4 (1)
N2—W—C19	124.5 (2)	C19—W—Cl	84.7 (1)
N3—W—Cl	95.9 (1)	C1—N3—W	165.1 (4)
N3—W—N1	103.9 (2)		

H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.96 and 0.97 Å were used for methyl and secondary C atoms, respectively. A distance of 0.93 Å was used for sp^2-C atoms. H-atom displacement parameters were $1.2U_{eq}$ ($1.5U_{eq}$ for methyl atoms) of the parent C atom. A hemisphere of frames, 0.3° in ω, were collected. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. The average e.s.d. for a C—C bond was 0.007 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART* and *SAINT* (Siemens, 1995). Data reduction: *SHELXTL95* (Sheldrick, 1995). Program(s) used to solve structure: *SHELXTL95*. Program(s) used to refine structure: *SHELXTL95*. Molecular graphics: *SHELXTL95*. Software used to prepare material for publication: *SHELXTL95*.

KAA wishes to acknowledge the National Science Foundation for funding of the purchase of the X-ray equipment.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1269). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Mercury(II) Trifluoroacetate–Bipyridyl System

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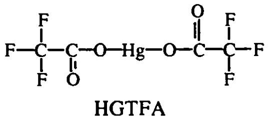
Abstract

Three complexes of mercury(II) trifluoroacetate and 2,2′-bipyridyl, of different stoichiometry, have been investigated and their structures compared with the previously published structure of bis[(2,2′-bipyridyl-*N*,*N*′)bis(trifluoroacetato-*O*)mercury(II)], $[Hg(C_2F_3O_2)_2(C_{10}H_8N_2)]_2$ (BHG). The complete series, AHG {(2,2′-bipyridyl-*N*,*N*′)(trifluoroacetato-*O*)mercury(II) hemi[tetrakis(trifluoroacetato-*O*)mercury(II)], $[Hg(C_2F_3O_2)(C_{10}H_8N_2)][Hg(C_2F_3O_2)_4]_{0.5}$}, BHG, GHG {bis(2,2′-bipyridyl-*N*,*N*′)(trifluoroacetato-*O*)mercury(II) (2,2′-bipyridyl-*N*,*N*′)tris(trifluoroacetato-*O*)mercury(II), $[Hg(C_2F_3O_2)(C_{10}H_8N_2)_2][Hg(C_2F_3O_2)_3(C_{10}H_8N_2)]$}, and DHG {bis(2,2′-bipyridyl-*N*,*N*′)mercury(II) bis(trifluoroacetate), $[Hg(C_{10}H_8N_2)_2](C_2F_3O_2)_2$}, shows the progressive replacement of trifluoroacetate by bidentate 2,2′-bipyridyl. Within the series, mercury may be coordinated to zero, one or two bidentate bipyridyl groups. In the extreme case, *i.e.* DHG, the complex ion $[Hg(bipyridyl)_2]^{2+}$ is formed with exclusion of trifluoroacetate from the mercury coordination.

Comment

On account of the ease with which the trifluoroacetyl group may be replaced, mercury(II) trifluoroacetate (HGTFA) has proved to be a valuable reagent in the study of the stereochemical configuration around mercury particularly by N-donor and certain O-donor ligands.


$F_3C{-}C({=}O){-}O{-}Hg{-}O{-}C({=}O){-}CF_3$

HGTFA

The structures of the products of the complexation of HGTFA with monodentate N-donors, *e.g.* bis(pyridine) (Halfpenny, Small & Thorpe, 1978), tris(pyridine) (Halfpenny & Small, 1978, 1995), a bidentate N-donor, 4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene (Breuer & Small, 1995), a bi- and tridentate N-donor, 2,4,6-tri(2-

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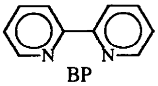
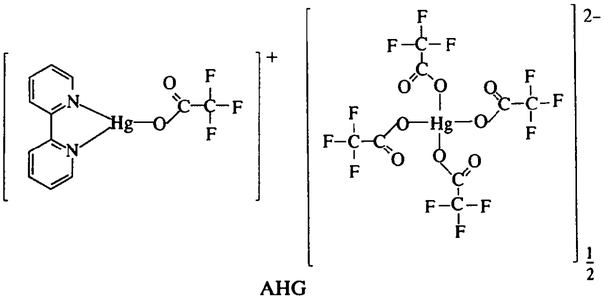
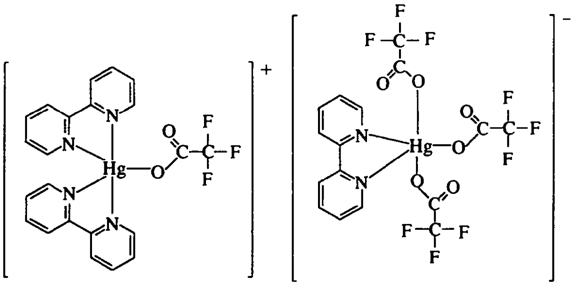
pyridyl)-1,3,5-triazine (Halfpenny & Small, 1982), and the O-donor ligands 1,4-dioxane (Small, 1982) and pyridine *N*-oxide (Halfpenny & Small, 1991), indicate that N-donors are more effective than O-donor ligands in displacing trifluoroacetate groups from the primary sphere of coordination around mercury. This is particularly the case with bidentate ligands such as 2,2′-bipyridyl (BP).


BP

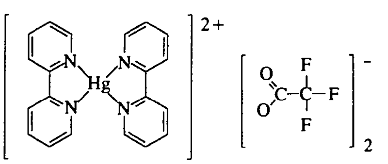
The structure of BHG, the equimolar complex of HGTFA and bipyridyl, has already been described (Halfpenny, 1982). BHG is formed from an equimolar solution of both components in dichloromethane. It was found that by varying the composition of this solution, compounds with four different stoichiometries could be crystallized (see Table 1). The four compounds are: AHG {$(HGTFA)_{1.5}(BP)$, (2,2′-bipyridyl)(trifluoroacetato)mercury(II) hemi[tetrakis(trifluoroacetato)-mercury(II)]}, BHG {$(HGTFA)_2(BP)_2$, bis[(2,2′-bipyridyl)bis(trifluoroacetato)mercury(II)]}, GHG {$(HGTFA)_2(BP)_3$, bis(2,2′-bipyridyl)(trifluoroacetato)mercury(II) (2,2′-bipyridyl)tris(trifluoroacetato)mercury(II)} and DHG {$(HGTFA)(BP)_2$, bis(2,2′-bipyridyl)mercury(II) bis(trifluoroacetate)}. These formulations are based on the the crystal structure determinations reported here; elemental analyses are unreliable in the presence of mercury and fluorine. A preliminary report, without details, of the structures of these compounds (Halfpenny & Small, 1981) is superseded by the present account of the structures of AHG, GHG and DHG, and that of Halfpenny (1982) on BHG.



AHG



GHG



DHG

The structures of AHG, GHG and DHG are shown in Figs 1, 3 and 4, respectively. For ease of comparison, the structure of BHG is also reproduced in Fig. 2. Principal bond distances and angles are given in Tables 2, 3 and 4. The structures illustrate the irregular and diverse features of mercury stereochemistry. As in the case of BHG, AHG and GHG both contain two structurally distinct mercury centres, but DHG contains only one. In all, within the four compounds, there are seven unique mercury coordination schemes. In two of these, two bipyridyl ligands bond to one Hg atom, in four cases, a Hg atom is bound to one bipyridyl ligand, and in one case, the Hg atom forms no bond to a bipyridyl ligand. The bipyridyl molecules are always coordinated to mercury in a regular bidentate manner, with bite angles in the range 70.8–73.0°, the largest deviation of the Hg atom from the mean bipyridyl plane being 0.19 (6) Å. The Hg—N distances fall within the range 2.18–2.39 Å, which is typical for N-donor complexes of mercury. In GHG and DHG, where two bipyridyl ligands bond to one Hg atom, the angles between the two bipyridyl mean planes are similar with values of 39.8 (5) and 38.2 (6)°, respectively. Coordination around the Hg atom is completed by an O atom of trifluoroacetate (TFA) groups. In compounds of this type, Hg—O bond distances have been found to range from the covalent bonding value (2.0–2.2 Å) up to the van der Waals contact distance (around 3.1 Å). The Hg—O ionic separation has been estimated as 2.54 Å (Halfpenny & Small, 1978), but distances lying between this value and 3.1 Å frequently occur; they are likely to be weakly electrostatic in character. In the three present compounds (and BHG), Hg—O bonds having these characteristics are encountered; it is useful to consider them in relation to the number of bipyridyl molecules bonded to the relevant Hg atom. In AHG, the Hg1 atom lies on a symmetry centre and forms no bonds to bipyridyl, only to two centrosymmetrically related pairs of TFA groups. The Hg1—O3 bond may be identified as covalent from its length. The other TFA group which is bidentate has almost equal Hg—O distances; the bonds could be ionic or covalent involving the two resonant possibilities. Overall, the Hg1 atom is at the centre of a complex $[Hg(TFA)_4]^{2-}$ ion and is shielded from further interactions.

A similar ion has been reported in bis(4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene)mercury(II) tetrakis-(trifluoroacetato)mercury(II) dichloromethane solvate (Breuer & Small, 1995). The counterion in AHG (with an overall charge of +1) is the Hg2 atom covalently bound to one bipyridyl and one TFA ligand. These groups do not completely shield the Hg2 atom which interacts with the outer O atom of the anion as seen in the close approach of Hg2 to the O4, O6 and O2″ atoms. The structure, bound through the sequence -O2-Hg2-O1-O2-Hg2-, is thus weakly polymeric. In BHG, the two Hg atoms are each bound differently to one bipyridyl and two TFA ligands covalently, and are thus almost neutral; incomplete shielding allows very weak polymeric bonding involving both Hg atoms. There are two quite differently coordinated Hg atoms in GHG. The Hg1 atom bonds to one bipyridyl and to three TFA groups. To one of these TFA groups, the Hg1—O3 bond has the typical covalent distance. A second TFA group has a slightly longer but nevertheless covalent bond, Hg1—O1, the lengthening being compensated for by a shortening of Hg1—O2 to less than the van der Waals value. The third TFA group involves unequal bidentate bonding that is possibly ionic. Overall, this moiety centred around the Hg1 atom will bear a charge of about −1. The Hg2 atom is closely coordinated by two bipyridyl groups which hinder further close approaches, the nearest being a TFA group, with Hg—O distances of 2.69 (1) and 2.86 (2) Å, which can only be ionic. The charge on the moiety around the Hg2 atom is thus +1. A further weak interaction links the Hg2 atom to the O4 atom of the anion.

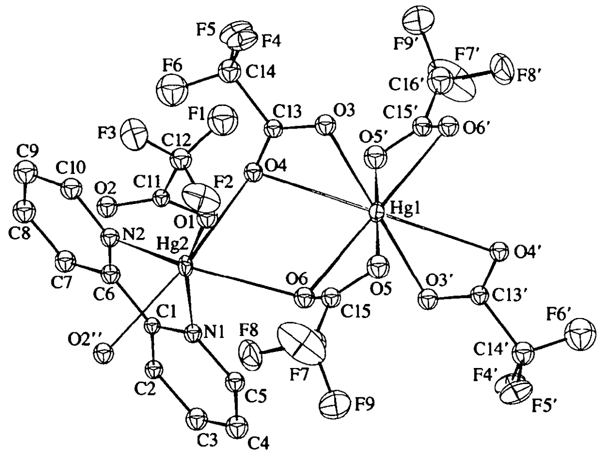


Fig. 1. View of AHG showing the unit cell and one unit of structure plus the centrosymmetric moiety around the special position (Hg1). Displacement ellipsoids of the Hg atom are shown at 50% probability levels, while those of the F atoms are shown at 10% probability levels. The F1 and F6 atoms, as well as all other atoms, are isotropic.

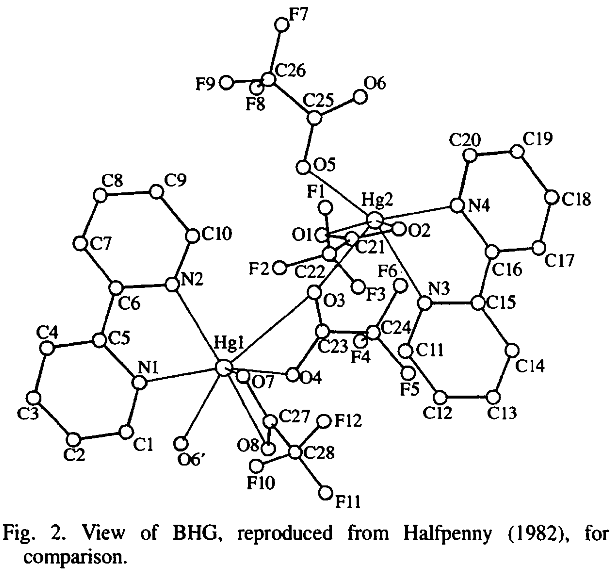


Fig. 2. View of BHG, reproduced from Halfpenny (1982), for comparison.

DHG has the simplest structure with mercury closely coordinated by two bipyridyl ligands. The two TFA groups are quite distant from the Hg atom, but must necessarily be ionically bound to them, although the Hg—O distances are in excess of the estimated ionic value; in effect, the coordination of the two bipyridyl ligands increases the ionic radius of Hg^{2+} by forming a complex ion.

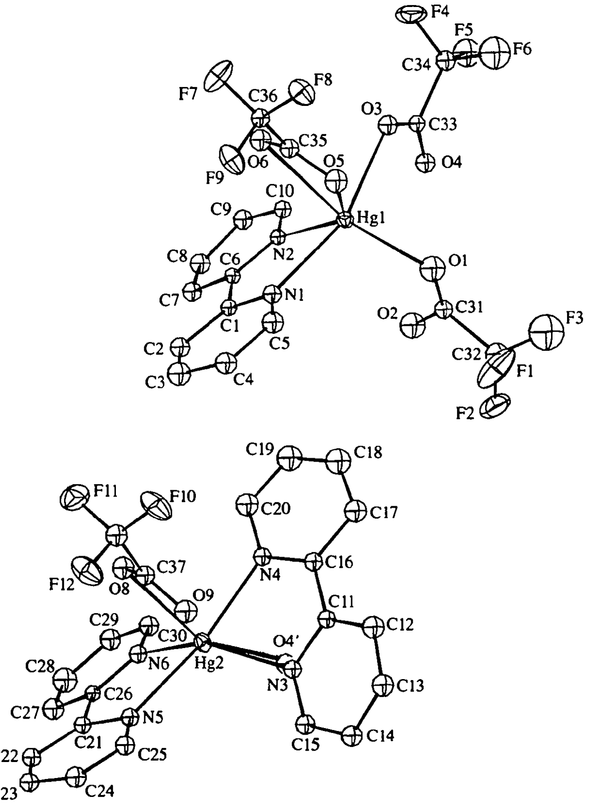


Fig. 3. View of GHG showing the unit cell and one unit of structure. Displacement ellipsoids of the Hg atom are shown at 50% probability levels, while those of the F atoms are shown at 10% probability levels. The F3, F5 and F6 atoms, as well as all other atoms, are isotropic.

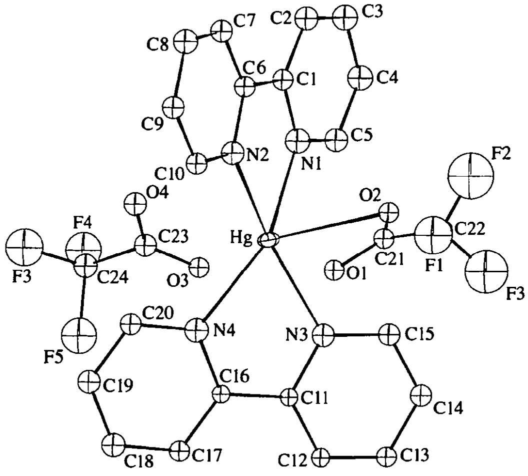


Fig. 4. View of DHG showing the unit cell and one unit of structure. The displacement ellipsoid of the Hg atom is shown at the 50% probability level. All other atoms are isotropic.

Experimental

AHG, GHG and DHG were crystallized from dichloromethane. Table 1 shows the composition of the products obtained from four different solutions.

Table 1. *Composition of the products (mole fraction HGTFA)*

	AHG	BHG	GHG	DHG
Crystals	0.600	0.500	0.400	0.333
Solution	0.667	0.500	0.400	0.333

AHG

Crystal data

$[Hg(C_2F_3O_2)(C_{10}H_8N_2)]$-$[Hg(C_2F_3O_2)_4]_{0.5}$
$M_r = 796.1$
Triclinic
$P\bar{1}$
$a = 11.72\,(1)$ Å
$b = 9.57\,(1)$ Å
$c = 10.69\,(1)$ Å
$\alpha = 100.42\,(10)°$
$\beta = 110.81\,(10)°$
$\gamma = 103.55\,(10)°$
$V = 1042.6\,(10)$ Å^3
$Z = 2$
$D_x = 2.536$ Mg m^{-3}
$D_m = 2.567$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 5$–$20°$
$\mu = 10.73$ mm^{-1}
$T = 288$ K
Acicular along **a**
0.420 × 0.134 × 0.084 mm
Colourless

Data collection

Stoe Stadi-2 diffractometer
Variable ω scan; $2\theta'$ fixed
Absorption correction: integration (*SHELX76*; Sheldrick, 1976)
$T_{\min} = 0.237$, $T_{\max} = 0.458$

$\theta_{\max} = 21°$
$h = 0 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$
1 standard reflection per layer

2135 measured reflections
1987 independent reflections
1661 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.016$

every 20 reflections
intensity decay: maximum 5%, corrected by interpolation

Refinement

Refinement on F
$R = 0.046$
$wR = 0.050$
$S = 2.375$
1661 reflections
204 parameters
H atoms not refined; see below
$w = 1/[\sigma^2(F) + 0.000381F^2]$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.21$ e Å^{-3}
$\Delta\rho_{\min} = -1.48$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV) and Cromer & Mann (1968) (Hg)

Table 2. *Selected geometric parameters (Å, °) for AHG*

Hg1—O3	2.277 (13)	Hg2—O1	2.089 (13)
Hg1—O4	2.795 (13)	Hg2—O2	3.029 (14)
Hg1—O5	2.499 (15)	Hg2—O2$^{\rm i}$	2.774 (14)
Hg1—O6	2.542 (13)	Hg2—O4	2.631 (12)
Hg2—N1	2.178 (14)	Hg2—O6	2.654 (14)
Hg2—N2	2.331 (15)		
O3—Hg1—O4	50.6 (4)	N1—Hg2—O4	99.8 (4)
O3—Hg1—O5	93.3 (5)	N1—Hg2—O6	82.9 (5)
O3—Hg1—O6	98.6 (4)	N1—Hg2—O2$^{\rm i}$	85.4 (5)
O3—Hg1—O4$^{\rm ii}$	129.4 (4)	N2—Hg2—O1	127.0 (6)
O3—Hg1—O5$^{\rm ii}$	86.7 (4)	N2—Hg2—O4	87.4 (4)
O3—Hg1—O6$^{\rm ii}$	81.4 (4)	N2—Hg2—O6	145.4 (4)
O4—Hg1—O5	106.5 (4)	N2—Hg2—O2$^{\rm i}$	89.6 (4)
O4—Hg1—O6	71.8 (4)	O1—Hg2—O4	79.4 (5)
O4—Hg1—O5$^{\rm ii}$	73.5 (5)	O1—Hg2—O6	77.6 (5)
O4—Hg1—O6$^{\rm ii}$	108.2 (4)	O1—Hg2—O2$^{\rm i}$	97.4 (5)
O5—Hg1—O6	50.8 (5)	O4—Hg2—O6	72.8 (4)
O5—Hg1—O6$^{\rm ii}$	129.2 (5)	O4—Hg2—O2$^{\rm i}$	172.9 (6)
N1—Hg2—N2	72.8 (6)	O6—Hg2—O2$^{\rm i}$	112.8 (6)
N1—Hg2—O1	159.8 (6)		

Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $-x, -y, -z$.

GHG

Crystal data

$[Hg(C_2F_3O_2)(C_{10}H_8N_2)_2]$-$[Hg(C_2F_3O_2)_3(C_{10}H_8N_2)]$
$M_r = 1321.8$
Triclinic
$P\bar{1}$
$a = 12.78\,(1)$ Å
$b = 16.06\,(2)$ Å
$c = 10.58\,(1)$ Å
$\alpha = 86.46\,(9)°$
$\beta = 90.18\,(9)°$
$\gamma = 80.29\,(8)°$
$V = 2136.1\,(16)$ Å^3
$Z = 2$
$D_x = 2.055$ Mg m^{-3}
$D_m = 2.099$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 5$–$20°$
$\mu = 7.00$ mm^{-1}
$T = 288$ K
Triclinic prism
0.50 × 0.18 × 0.10 mm
Colourless

Data collection

Stoe Stadi-2 diffractometer
Variable ω scan; $2\theta'$ fixed
Absorption correction: integration (*SHELX76*; Sheldrick, 1976)
$T_{\min} = 0.364$, $T_{\max} = 0.516$

$\theta_{\max} = 20°$
$h = 0 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -10 \rightarrow 10$
1 standard reflection per layer

4013 measured reflections
3796 independent reflections
2902 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.027$

every 20 reflections
intensity decay: maximum 5%, corrected by interpolation

Refinement

Refinement on F
$R = 0.049$
$wR = 0.053$
$S = 2.227$
2902 reflections
336 parameters (2 blocks)
H atoms not refined; see below
$w = 1/[\sigma^2(F) + 0.000444F^2]$

$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 1.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.87$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV) and Cromer & Mann (1968) (Hg)

Table 3. *Selected geometric parameters (Å, °) for GHG*

Hg1—N1	2.318 (15)	Hg1—O6	2.766 (12)
Hg1—N2	2.391 (12)	Hg2—N3	2.305 (13)
Hg1—O1	2.355 (16)	Hg2—N4	2.250 (15)
Hg1—O2	2.862 (16)	Hg2—N5	2.309 (14)
Hg1—O3	2.246 (13)	Hg2—N6	2.273 (13)
Hg1—O4	3.156 (15)	Hg2—O7	2.848 (14)
Hg1—O5	2.572 (14)	Hg2—O8	2.687 (13)
N1—Hg1—N2	70.8 (5)	O3—Hg1—O5	85.2 (5)
N1—Hg1—O1	97.9 (6)	O3—Hg1—O6	78.6 (4)
N1—Hg1—O2	81.9 (5)	O5—Hg1—O6	48.8 (4)
N1—Hg1—O3	160.7 (4)	N3—Hg2—N4	73.0 (5)
N1—Hg1—O5	86.6 (5)	N3—Hg2—N5	106.3 (5)
N1—Hg1—O6	82.8 (4)	N3—Hg2—N6	150.2 (5)
N2—Hg1—O1	135.2 (5)	N3—Hg2—O7	72.6 (4)
N2—Hg1—O2	87.7 (4)	N3—Hg2—O8	117.3 (4)
N2—Hg1—O3	104.5 (4)	N4—Hg2—N5	161.0 (5)
N2—Hg1—O5	137.8 (4)	N4—Hg2—N6	118.1 (5)
N2—Hg1—O6	92.2 (4)	N4—Hg2—O7	80.8 (5)
O1—Hg1—O2	47.5 (6)	N4—Hg2—O8	81.6 (5)
O1—Hg1—O3	98.1 (5)	N5—Hg2—N6	72.3 (5)
O1—Hg1—O5	81.6 (5)	N5—Hg2—O7	81.0 (5)
O1—Hg1—O6	130.4 (5)	N5—Hg2—O8	82.2 (5)
O2—Hg1—O3	117.0 (5)	N6—Hg2—O7	134.2 (4)
O2—Hg1—O5	124.8 (5)	N6—Hg2—O8	92.3 (4)
O2—Hg1—O6	163.8 (5)	O7—Hg2—O8	47.0 (4)

DHG

Crystal data

$[Hg(C_{10}H_8N_2)_2](C_2F_3O_2)_2$
$M_r = 739.0$
Triclinic
$P\overline{1}$
$a = 16.54$ (2) Å
$b = 11.06$ (1) Å
$c = 7.59$ (1) Å
$\alpha = 98.6$ (10)°
$\beta = 87.7$ (9)°
$\gamma = 67.2$ (7)°
$V = 1258.2$ (10) Å^3
$Z = 2$
$D_x = 1.950$ Mg m^{-3}
$D_m = 1.979$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 5$–20°
$\mu = 5.95$ mm^{-1}
$T = 288$ K
Acicular along **c**
0.27 × 0.13 × 0.08 mm
Colourless

Data collection

Stoe Stadi-2 diffractometer
Variable ω scan; $2\theta'$ fixed
Absorption correction: integration (*SHELX76*; Sheldrick, 1976)
$T_{\rm min} = 0.425$, $T_{\rm max} = 0.657$
2456 measured reflections
2214 independent reflections
1950 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.014$

$\theta_{\rm max} = 21.0°$
$h = -15 \rightarrow 15$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 7$
1 standard reflection per layer
every 20 reflections
intensity decay: maximum 5%, corrected by interpolation

Refinement

Refinement on F
$R = 0.052$
$wR = 0.057$
$S = 2.267$
1950 reflections
200 parameters
H atoms not refined; see below
$w = 1/[\sigma^2(F) + 0.000623F^2]$

$(\Delta/\sigma)_{\rm max} = 0.018$
$\Delta\rho_{\rm max} = 1.78$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.02$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV) and Cromer & Mann (1968) (Hg)

Table 4. *Selected geometric parameters (Å, °) for DHG*

Hg—N1	2.297 (13)	Hg—O1	2.977 (12)
Hg—N2	2.327 (12)	Hg—O2	2.680 (12)
Hg—N3	2.282 (12)	Hg—O3	2.894 (12)
Hg—N4	2.330 (13)	Hg—O4	2.987 (15)
N1—Hg—N2	71.7 (4)	N3—Hg—O1	81.2 (4)
N1—Hg—N3	119.8 (4)	N3—Hg—O2	81.3 (4)
N1—Hg—N4	154.1 (4)	N3—Hg—O3	80.8 (4)
N1—Hg—O1	116.7 (4)	N3—Hg—O4	121.2 (4)
N1—Hg—O2	77.0 (4)	N4—Hg—O1	86.8 (4)
N1—Hg—O3	84.8 (4)	N4—Hg—O2	128.9 (4)
N1—Hg—O4	80.4 (4)	N4—Hg—O3	74.1 (4)
N2—Hg—N3	157.7 (4)	N4—Hg—O4	74.0 (4)
N2—Hg—N4	106.1 (4)	O1—Hg—O2	45.7 (3)
N2—Hg—O1	76.6 (4)	O1—Hg—O3	157.0 (4)
N2—Hg—O2	83.4 (4)	O1—Hg—O4	142.2 (4)
N2—Hg—O3	120.6 (4)	O2—Hg—O3	143.4 (4)
N2—Hg—O4	77.9 (4)	O2—Hg—O4	154.3 (4)
N3—Hg—N4	72.0 (4)	O3—Hg—O4	44.1 (4)

Although HGTFA is hygroscopic and unstable in air, the bipyridyl compounds were found to be quite stable. For the compounds AHG, GHG and DHG, intensity data were collected on a two-circle diffractometer employing equi-inclination Weissenberg geometry. A uniform procedure was adopted for all three compounds as described below. The angle θ' referred to is the projection of θ onto the equatorial plane. The crystal was set with the axis indicated accurately aligned along the diffractometer ω axis. A separate standard is required for each reciprocal lattice layer measured; interlayer scale factors were refined and then fixed at a later stage of the structure refinement. Hg-atom positions were obtained from Patterson maps. Other non-H atoms were located from the ΔF map and included in the refinements. C, N and O atoms were treated isotropically. Anisotropic U^{ij} values of all F atoms were also included and found to be large in magnitude; this is a common feature of structures involving the trifluoroacetate group and has been the subject of an investigation elsewhere (Gleghorn & Small, 1995). H atoms were included at calculated positions (C—H 1.08 Å) but not refined. The most prominent features on the final ΔF maps were in the near vicinity of the Hg atoms; these were attributed to series termination errors arising from incomplete data sets in respect of high-angle scattering by mercury or deficiencies in the calculated absorption factors.

For all compounds, data reduction: *DATR* (Small, 1977); program(s) used to solve structures: *SHELX76* (Patterson) (Sheldrick, 1976); program(s) used to refine structures: *SHELX76*; molecular graphics: *SNOOPI* (Davies, 1983)

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: LI1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structural Investigation of Ni$^{\rm II}$ Complexes. XI. Dichlorobis(4-methylpiperidine-*N*)(4-methylpyridine-*N*)nickel(II)

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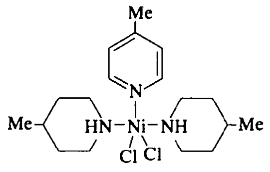
Abstract

Molecules of the title compound, [NiCl$_2$(C$_6$H$_7$N)(C$_6$H$_{13}$N)$_2$], lie on crystallographic twofold axes which pass through each Ni atom and 4-methylpyridine ligand. The coordination polyhedron around the Ni$^{\rm II}$ centre is distorted trigonal bipyramidal with an N$_3$Cl$_2$ coordination sphere; the equatorial plane is formed by two chloride ions and the N atom of the 4-methylpyridine ligand, while the axial positions are occupied by the N atoms of the 4-methylpiperidine groups.

Comment

The stoichiometry and stereochemistry of Ni$^{\rm II}$ complexes with various piperidine ligands have been studied. The title compound, [NiCl$_2$(4-Mepip)$_2$(4-Mepy)], (I), where 4-Mepip is 4-methylpiperidine and 4-Mepy is 4-methylpyridine, was prepared from the NiCl$_2$/4-Mepip system. The 4-Mepy moiety was formed in the reaction mixture by dehydrogenation (Koman, Ďurčanská, Jóna & Ondrejovič, 1991).



(I)

Spectroscopic and magnetic measurements were consistent with the presence of pentacoordination about the Ni$^{\rm II}$ atom, but could not distinguish between square-pyramidal and trigonal-bipyramidal coordination (Koman, Jóna & Ďurčanská, 1986). Our results show that the coordination polyhedron around the Ni$^{\rm II}$ atom is intermediate between trigonal bipyramidal and square pyramidal (Addison, Rao, Reedijk, Rijn & Verschoor, 1984). Molecules of (I) lie on crystallographic twofold axes (Fig. 1). In the trigonal-bipyramidal complex, the equatorial plane is formed by the N2, Cl and Cl$^{\rm i}$ atoms [symmetry code: (i) $-x, y, \frac{1}{2} - z$] and the axial ligands are 4-Mepip. In the square-pyramidal complex, two 4-Mepip ligands and two chloride ions define the basal plane, with the apical site occupied by an 4-Mepy ligand. The Ni$^{\rm II}$ ion lies 0.578 (1) Å from this mean basal plane defined by the Cl, Cl$^{\rm i}$, N1 and N1$^{\rm i}$ atoms, in the direction of the N2 atom.

The interatomic distances in the coordination polyhedron of the title complex are in agreement with average interatomic distances in pentacoordinate complexes of nickel(II) with neutral N-donor and chloride ligands (Melník, Šramko, Dunaj-Jurčo, Sirota & Holloway, 1994). Comparison of the Ni—N interatomic distances with those in the complexes [Ni(NCS)$_2$(3,5-diMepip)$_3$] (Koman, Jóna & Ďurčanská, 1992), [Ni(NCS)$_2$(py)$_4$] (Valach, Sivý & Koreň, 1984), [Ni(NCS)$_2$(pip)$_4$] (Koman, Handlovič, Ďurčanská & Gažo, 1983) and [Ni(NCS)$_2$(pip)$_2$(py)(H$_2$O)].2pip (Koman, Ďurčanská, Handlovič & Gažo, 1983) shows that those involving non-aromatic heterocyclic ligands are somewhat longer than those to aromatic ligands.

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