As1—C121	1.932 (4)	B—F3	1.362 (6)
As1—C131	1.937 (3)	B—F2	1.364 (6)
As1—C111	1.939 (4)	B—F4	1.385 (6)
As2—C221	1.931 (4)		
C1—Rh—O2	173.73 (14)	C111—As1—Rh	114.07 (11)
C1—Rh—As2	90.05 (12)	C221—As2—C231	104.3 (2)
O2—Rh—As2	87.95 (8)	C221—As2—C211	102.7 (2)
C1—Rh—As1	88.68 (12)	C231—As2—C211	101.5 (2)
O2—Rh—As1	93.71 (8)	C221—As2—Rh	112.88 (12)
As2—Rh—As1	176.00 (2)	C231—As2—Rh	114.22 (12)
C121—As1—C131	104.1 (2)	C211—As2—Rh	119.39 (12)
C121—As1—C111	103.0 (2)	O1—C1—Rh	177.6 (4)
C131—As1—C111	100.58 (15)	Rh—O2—H2*A*	111 (3)
C121—As1—Rh	119.39 (11)	Rh—O2—H2*B*	120 (3)
C131—As1—Rh	113.47 (10)	H2*A*—O2—H2*B*	114 (4)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*B*···F2	0.95	1.71 (2)	2.647 (7)	170 (3)
O2—H2*A*···F4^{i}	0.95	1.73 (2)	2.679 (7)	177 (3)
C226—H226···F2	0.93	2.48 (2)	3.335 (7)	153 (3)
C234—H234···F1^{ii}	0.93	2.38 (2)	3.276 (7)	163 (3)
C12—H12*B*···F3^{iii}	0.97	2.48 (2)	3.189 (7)	130 (3)

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

The unit-cell and intensity data were recorded at 150 K on a FAST area detector diffractometer using *MADNES* software (Pflugrath & Messerschmidt, 1989); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). All calculations were performed on a 486DX2/66 personal computer. The two H atoms bonded to the water molecule were located experimentally and refined with O—H distances constrained to 0.95 Å; other H atoms were included in idealized positions (C—H = 0.93 Å); U_{iso}'s for all H atoms were freely refined.

Data collection: *MADNES MADONL* (Plugrath & Messerschmidt, 1989). Cell refinement: *MADNES REFINE*. Data reduction: *MADNES ABSURD*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene-κ^2N^2,N^6)mercury(II) Tetrakis(trifluoroacetato)mercury(II) Dichloromethane Solvate

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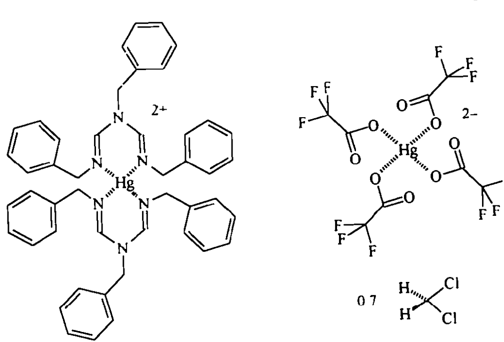
Abstract

The title compound, $[Hg(C_{23}H_{23}N_3)_2][Hg(C_2F_3O_2)_4].0.7CH_2Cl_2$, is ionic with Hg forming complex anions and cations. The cation contains two neutral ligand (*L* = 4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene) molecules giving HgL_2^{2+}, and the anion incorporates four trifluoroacetate ions giving $Hg(tfa)_4^{2-}$. Coordination around Hg in the cation is elongated tetrahedral with Hg—N 2.20 (2), 2.24 (3), 2.22 (2) and 2.30 (3) Å; the bite angles to the two bidentate ligands (*L*) are 84.9 (9) and 82.3 (9)°. In the anion, the shortest Hg—O contacts to the four tfa groups are 2.41 (2), 2.33 (4), 2.22 (2) and 2.38 (4) Å; the coordination is irregular and can only be described as approximately tetrahedral. The solvent molecule, dichloromethane, occupies a cavity in the structure.

Comment

The preparation of the ligand 4-benzyl-1,7-diphenyl-2,4,6-triazahepta-2,5-diene, *L*, and the crystal structure of the product of the reaction of *L* with copper(II) acetate have been described previously (Breuer & Small, 1991). It was of interest to examine the product of the reaction of *L* with mercury(II) trifluoroacetate since the latter reagent has been found to complex readily with N-donor ligands to give a variety of stereochemical configurations around the Hg atom, depending upon the ligand geometry. In general, trifluoroacetate groups have been found to relinquish primary coordination to the Hg atom in favour of any donor N atoms; in this context the behaviour of the bulky bidentate ligand *L* would be of special interest. A preliminary account of this work has been reported (Breuer & Small, 1983).

The distances and angles around the two independent Hg atoms in the title structure, (I) (Table 2), show that Hg1 forms bonds only to four N atoms belonging to two molecules of the ligand *L*, and that Hg2 has bonds only to the O atoms of four trifluoroacetate groups. The two atoms Hg1 and Hg2 are, thus, at the centres of a complex cation and a complex anion, respectively, and are screened from further interactions by an outer shell of six phenyl groups in the case of Hg1, and the F atoms of four trifluoroacetate groups in the case of Hg2.



(I)

The coordination polyhedron around Hg1 in the cation is a tetrahedron elongated in the direction N2···N5 of the two chelating ligands. Bond distances and angles within these ligands are not sufficiently accurate to permit discussion; the torsion angles (Table 2) show a similarity of conformation in the two ligand molecules with respect to the two outer benzyl groups and, further, that there is approximate left–right twofold symmetry of the outer benzyl groups in each molecule. This is also apparent in Fig. 3, which includes a comparable view of the same ligand in the copper acetate complex. In comparison with the copper compound where the outer wings of the ligand are more spread out, it should be noted that in the present compound the four outer benzyl groups of the two ligands are folded in a symmetrical manner so that the phenyl rings enclose and shield the central Hg1 atom. The possibility of some secondary interaction between the central Hg1 and the benzene rings arises. Hg···C(benzene ring) distances of 3.33 Å have been cited as evidence of secondary Hg–π-electron interactions in other structures, *e.g.* (2-benzylpyridine)-methylmercury(II) nitrate (Canty, Chaichit & Gatehouse, 1980). The interaction in the present structure can, however, only be weak as the closest distances from Hg to benzene ring C atoms are to C6 3.41 (3), C7 3.51 (3), C18 3.53 (3), C19 3.64 (3), C29 3.30 (3), C34 3.44 (3), C41 3.60 (3) and C46 3.81 (3) Å.

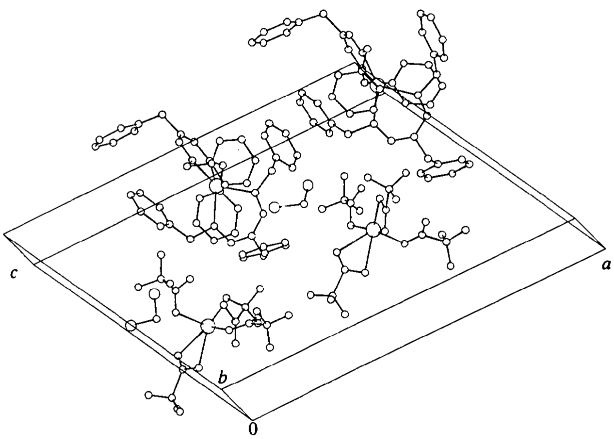


Fig. 1. Projection of unit cell and contents on to (010).

Around Hg2 in the anion, the coordination geometry is less regular (Fig. 2). Considering the bonds from Hg2 to the nearest O atom of each trifluoroacetate group, *i.e.* O2, O3, O5 and O8, the deviation from tetrahedral is quite appreciable (O—Hg—O angles are in the range 81.0–138.3°). The angles involving Hg2—O5, the shortest bond, and each of the other three bonds are greater than 120°, while the other three angles are in the range 81.0–90.2°, thus describing an elongated trigonal pyramid. However, the second O atom of each trifluoroacetate group might also be considered to be sufficiently close to involve interaction with the Hg, as is certainly the case with O1 (Hg2—O1 = 2.59 Å). If the angles to the midpoints of each pair of O atoms are then considered, the coordination is somewhat nearer to tetrahedral with angles in the range 92.2–126.3°. It is not obvious why the coordination of four equivalent trifluoroacetate groups should be so irregular.

Structures in which Hg is involved as a complex ion are not uncommon. Of 1014 organic structures involving Hg listed in the Cambridge Structural Database (Allen *et al.*, 1991), there are 135 in which Hg forms a cation and 161 involving an anion. Only eight structures have been reported in which Hg is present as both an anion and a cation. All of these contain a halogeno–Hg^{II} ion; in six of these there are weak halogen-atom bridges between the Hg atoms of the anions and cations. The remaining two, bromo[2,15-dimethyl-3,7,10,14,20-pentaazabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene]-mercury(II) hexabromodimercury(II) (Drew, McFall & Nelson, 1979) and chloro(1,4,8,11-tetraazacyclotetradecane)mercury(II) tetrachloromercury(II) (Alcock, Curson, Herron & Moore, 1979), involve discrete anions and only electrostatic bonding between the ions. The present structure (Fig. 1) is thus fairly unique in respect of involving Hg atoms complexed with relatively bulky groups in both the anion and the cation.

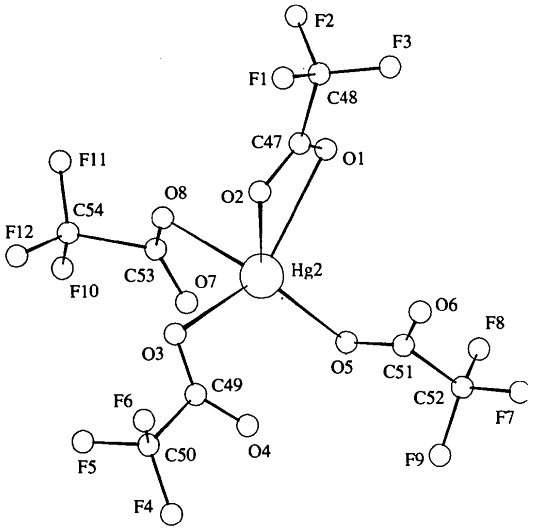


Fig. 2. The anion $[Hg(CF_3COO)_4]^{2-}$ showing atom labelling and coordination around Hg2.

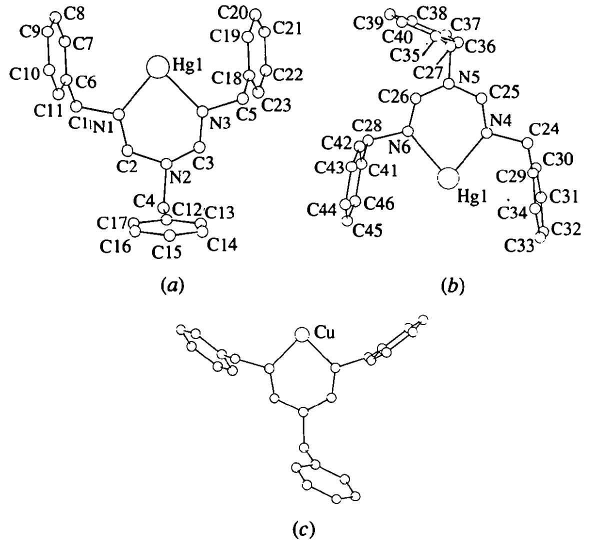


Fig. 3. Coordination around Hg1 showing the atom labelling: the two ligands are shown separately, (*a*) and (*b*), for clarity. (*c*) The same ligand as found in the analoguous Cu^{II} acetate complex for comparison.

Experimental

Crystals of the title compound formed readily on mixing equimolar solutions of the ligand *L* and mercury(II) trifluoroacetate in dichloromethane. On removal from solution, rapid decomposition occurred as the crystals are hygroscopic. The only surviving crystal of the batch was one sealed in a Lindemann capillary tube. This was quite unchanged over a period of several months.

Crystal data

$[Hg(C_{23}H_{23}N_3)_2]$-
$[Hg(C_2F_3O_2)_4].0.7CH_2Cl_2$
$M_r = 1595.7$
Monoclinic
Pc
$a = 15.12\,(1)$ Å
$b = 10.72\,(1)$ Å
$c = 21.58\,(2)$ Å
$\beta = 119.23\,(10)°$
$V = 3053.9\,(10)$ Å^3
$Z = 2$
$D_x = 1.73$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 20 reflections
$\theta = 5$–$20°$
$\mu = 4.96$ mm^{-1}
$T = 288$ K
Prism
$0.46 \times 0.16 \times 0.16$ mm
Colourless

Data collection

Stoe Stadi-2 diffractometer
Variable ω scan, $2\theta'$ fixed
Absorption correction: point-by-point integration (*SHELX76*; Sheldrick, 1976)
$T_{min} = 0.438$, $T_{max} = 0.531$
2910 measured reflections
2829 independent reflections
1986 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.041$
$\theta_{max} = 21.0°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 20$
1 standard reflection per layer monitored every 20 reflections
intensity decay: maximum 5%, corrected by interpolation

Refinement

Refinement on *F*
$R = 0.049$
$wR = 0.045$
$S = 1.676$
1986 reflections
384 parameters (two blocks)
H atoms not located (effect too weak with Hg present)
$w = 1/[\sigma^2(F) + 0.000369F^2]$
$(\Delta/\sigma)_{max} = 0.035$

$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B) for C, H, Cl, F, N and O, and Cromer & Mann (1968) for Hg

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Hg, F and solvent C55 and Cl.

	x	*y*	*z*	U_{eq}/U_{iso}
Cl1	0.323 (1)	0.523 (2)	0.470 (1)	0.14 (1)
Cl2	0.275 (2)	0.368 (3)	0.357 (1)	0.27 (4)
C55	0.358 (4)	0.462 (7)	0.408 (3)	0.13 (9)
Hg1	0.000	0.2521 (2)	0.000	0.075 (1)
Hg2	0.5311 (1)	0.1764 (1)	0.3480 (1)	0.082 (1)
C1	−0.109 (2)	0.517 (3)	−0.067 (2)	0.08 (1)
N1	−0.129 (2)	0.381 (2)	−0.049 (1)	0.06 (1)
C2	−0.225 (3)	0.354 (3)	−0.070 (2)	0.08 (1)
N2	−0.258 (2)	0.230 (2)	−0.062 (1)	0.06 (1)
C4	−0.371 (2)	0.250 (3)	−0.079 (2)	0.08 (1)
C3	−0.212 (2)	0.123 (3)	−0.037 (2)	0.06 (1)
N3	−0.117 (2)	0.109 (2)	−0.015 (1)	0.07 (1)
C5	−0.081 (2)	−0.026 (3)	0.010 (2)	0.06 (1)
C24	0.141 (2)	0.312 (3)	0.167 (2)	0.09 (1)
N4	0.147 (2)	0.273 (2)	0.099 (1)	0.06 (1)
C25	0.240 (2)	0.253 (3)	0.111 (2)	0.07 (1)
N5	0.260 (2)	0.216 (2)	0.060 (1)	0.05 (1)
C27	0.372 (3)	0.192 (3)	0.086 (2)	0.09 (1)
C26	0.202 (2)	0.204 (2)	−0.011 (2)	0.06 (1)
N6	0.104 (2)	0.210 (2)	−0.047 (1)	0.06 (1)
C28	0.055 (2)	0.186 (3)	−0.126 (2)	0.08 (1)
C29	0.062 (2)	0.240 (2)	0.169 (1)	0.07 (1)
C30	0.075 (2)	0.117 (2)	0.193 (1)	0.11 (1)
C31	−0.005 (2)	0.053 (2)	0.194 (1)	0.12 (2)

C32	−0.098 (2)	0.113 (2)	0.171 (1)	0.10 (1)
C33	−0.111 (2)	0.235 (2)	0.146 (1)	0.11 (1)
C34	−0.031 (2)	0.299 (2)	0.146 (1)	0.09 (1)
C35	0.378 (2)	0.049 (1)	0.083 (1)	0.07 (1)
C36	0.370 (2)	−0.028 (1)	0.131 (1)	0.09 (1)
C37	0.380 (2)	−0.157 (1)	0.129 (1)	0.09 (1)
C38	0.399 (2)	−0.209 (1)	0.077 (1)	0.10 (1)
C39	0.407 (2)	−0.132 (1)	0.028 (1)	0.07 (1)
C40	0.397 (2)	−0.003 (1)	0.031 (1)	0.08 (1)
C12	−0.382 (2)	0.265 (2)	−0.015 (1)	0.06 (1)
C17	−0.383 (2)	0.389 (2)	0.004 (1)	0.09 (1)
C16	−0.387 (2)	0.416 (2)	0.066 (1)	0.11 (1)
C15	−0.390 (2)	0.319 (2)	0.109 (1)	0.10 (1)
C14	−0.389 (2)	0.196 (2)	0.089 (1)	0.11 (1)
C13	−0.386 (2)	0.168 (2)	0.027 (1)	0.08 (1)
C18	−0.036 (2)	−0.071 (2)	−0.035 (1)	0.08 (1)
C19	0.069 (2)	−0.071 (2)	−0.007 (1)	0.10 (1)
C20	0.110 (2)	−0.123 (2)	−0.047 (1)	0.10 (1)
C21	0.047 (2)	−0.175 (2)	−0.113 (1)	0.09 (1)
C22	−0.057 (2)	−0.175 (2)	−0.141 (1)	0.10 (1)
C23	−0.099 (2)	−0.123 (2)	−0.101 (1)	0.10 (1)
C41	−0.005 (2)	0.301 (2)	−0.167 (1)	0.09 (1)
C42	0.046 (2)	0.405 (2)	−0.173 (1)	0.12 (1)
C43	−0.008 (2)	0.508 (2)	−0.212 (1)	0.12 (1)
C44	−0.114 (2)	0.509 (2)	−0.245 (1)	0.10 (1)
C45	−0.165 (2)	0.405 (2)	−0.238 (1)	0.10 (1)
C46	−0.110 (2)	0.302 (2)	−0.199 (1)	0.11 (1)
C6	−0.026 (2)	0.569 (2)	0.000 (1)	0.09 (1)
C7	0.072 (2)	0.566 (2)	0.010 (1)	0.08 (1)
C8	0.153 (2)	0.612 (2)	0.072 (1)	0.11 (1)
C9	0.136 (2)	0.661 (2)	0.125 (1)	0.15 (2)
C10	0.038 (2)	0.664 (2)	0.116 (1)	0.16 (2)
C11	−0.043 (2)	0.617 (2)	0.053 (1)	0.10 (1)
O1	0.566 (2)	0.287 (2)	0.464 (1)	0.09 (1)
O2	0.676 (2)	0.153 (2)	0.464 (1)	0.12 (1)
C47	0.641 (3)	0.230 (3)	0.491 (2)	0.08 (1)
C48	0.705 (5)	0.234 (6)	0.572 (3)	0.14 (2)
F1	0.772 (3)	0.150 (3)	0.604 (2)	0.27 (5)
F2	0.655 (2)	0.266 (3)	0.605 (1)	0.18 (5)
F3	0.766 (2)	0.339 (4)	0.589 (1)	0.18 (4)
O3	0.614 (2)	0.018 (3)	0.324 (2)	0.13 (1)
O4	0.593 (2)	0.142 (3)	0.238 (1)	0.12 (1)
C49	0.618 (3)	0.043 (3)	0.270 (2)	0.07 (1)
C50	0.666 (4)	−0.050 (4)	0.246 (2)	0.08 (1)
F4	0.617 (2)	−0.077 (4)	0.183 (2)	0.22 (5)
F5	0.681 (4)	−0.155 (3)	0.282 (3)	0.30 (10)
F6	0.749 (2)	−0.019 (3)	0.249 (3)	0.24 (6)
O5	0.452 (2)	0.327 (2)	0.270 (1)	0.09 (1)
O6	0.601 (2)	0.432 (2)	0.335 (1)	0.11 (1)
C51	0.516 (3)	0.418 (3)	0.285 (2)	0.08 (1)
C52	0.473 (4)	0.513 (5)	0.232 (3)	0.11 (1)
F7	0.420 (3)	0.492 (3)	0.172 (1)	0.21 (4)
F8	0.548 (3)	0.582 (5)	0.236 (3)	0.27 (7)
F9	0.445 (4)	0.604 (3)	0.248 (2)	0.26 (8)
O7	0.335 (2)	0.076 (3)	0.269 (2)	0.15 (1)
O8	0.445 (2)	0.016 (3)	0.374 (2)	0.12 (1)
C53	0.358 (4)	0.007 (5)	0.316 (3)	0.12 (2)
C54	0.299 (4)	−0.099 (5)	0.316 (3)	0.12 (2)
F10	0.225 (3)	−0.130 (3)	0.261 (2)	0.21 (5)
F11	0.259 (4)	−0.077 (5)	0.351 (2)	0.27 (8)
F12	0.351 (3)	−0.195 (4)	0.351 (4)	0.38 (9)

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

Hg1—N1	2.20 (2)	Hg2—O3	2.33 (4)
Hg1—N3	2.24 (3)	Hg2—O4	2.97 (3)
Hg1—N4	2.22 (2)	Hg2—O5	2.22 (2)
Hg1—N6	2.30 (3)	Hg2—O6	3.00 (3)
Hg2—O1	2.59 (3)	Hg2—O7	2.82 (3)
Hg2—O2	2.41 (2)	Hg2—O8	2.38 (4)
N1—Hg1—N3	84.9 (9)	O1—Hg2—O5	101 (1)
N4—Hg1—N6	82.3 (9)	O1—Hg2—O8	89 (1)
N1—Hg1—N4	129.6 (8)	O2—Hg2—O3	81 (1)
N3—Hg1—N4	123.9 (9)	O2—Hg2—O5	138 (1)
N6—Hg1—N1	123.3 (10)	O2—Hg2—O8	90 (1)
N6—Hg1—N3	117.5 (9)	O3—Hg2—O5	121 (1)
O1—Hg2—O2	52 (1)	O3—Hg2—O8	87 (1)
O1—Hg2—O3	133 (1)	O5—Hg2—O8	124 (1)
C1—N1—C2—N2	176 (3)	C29—C24—N4—C25	−134 (3)
C6—C1—N1—C2	130 (4)	N4—C24—C29—C34	−100 (3)
N1—C1—C6—C7	99 (4)	N4—C25—N5—C27	−177 (3)
N1—C2—N2—C4	169 (3)	C25—N5—C27—C35	109 (3)
C2—N2—C4—C12	−98 (4)	N5—C27—C35—C36	−74 (4)
N2—C4—C12—C13	−81 (4)	N5—C26—N6—C28	−177 (2)
N2—C3—N3—C5	180 (3)	C26—N6—C28—C41	−120 (3)
C3—N3—C5—C18	122 (4)	N6—C28—C41—C46	105 (4)
C24—N4—C25—N5	179 (4)		

The crystal was accurately set for rotation about the *b* axis on the diffractometer, which employs equi-inclination Weissenberg geometry; layers $k = 0–10$ were measured. The angle θ' referred to above is the projection of θ onto the equatorial plane. A separate standard is required for each reciprocal lattice layer measured; interlayer scale factors are usually refined and then fixed at a later stage of the structure refinement.

Hg-atom positions were obtained from Patterson maps; the coordinates of one Hg atom were defined as $(0,y,0)$ as required by the space group. Other non-H atoms were located from the ΔF map.

Hg, F and solvent atoms only were refined anisotropically. Phenyl C atoms were constrained as rigid hexagons with C—C = 1.395 Å and refined with individual $U_{\rm iso}$ values. Inclusion of H atoms at calculated positions resulted in only marginal improvement in the R value, as might be expected, and hindered convergence; they were not included in the final cycles of refinement. Hg and solvent atoms were refined in each cycle, ligand and trifluoroacetato groups in alternate cycles.

After initial refinement, until $R = 0.072$, a region of significant electron density remote from other atoms was noted on the ΔF map; this was interpreted as a molecule of the solvent, dichloromethane. After the inclusion of coordinates and U_{ij}'s for the solvent atoms, Cl1, Cl2 and C55, refinement proceeded. Anisotropic U_{ij}'s of all F atoms were also included and found to be large in magnitude; this is a common feature of the trifluoroacetate group and has been the subject of an investigation described elsewhere (Gleghorn & Small, 1995). At an intermediate stage, site occupancy of the solvent molecule was refined and eventually fixed at 0.70; interlayer scale factors were also refined and fixed in the final cycles of refinement.

Data collection: Stoe Stadi-2 diffractometer software. Data reduction: *DATR* (Small, 1977). Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELX*76. Molecular graphics: *SNOOPI* (Davies, 1983).

We acknowledge the use of the Cambridge Structural Database and of the EPSRC Chemical Database Service at Daresbury.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: LI1135). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(2,4-dinitrophenolato)(triethanolamine)-calcium(II)

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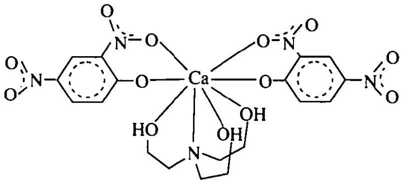
Abstract

The title complex, bis(2,4-dinitrophenolato-*O*,O^2)-(2,2′,2″-nitrilotriethanol-*N*,*O*,*O*′,*O*″)calcium(II), $[Ca(C_6H_3N_2O_5)_2(C_6H_{15}NO_3)]$, is monomeric and the Ca^{2+} ion is eight-coordinate. Both dinitrophenolate ligands coordinate to the metal ion by their phenolic O atoms and one O atom of the *ortho*-nitro group. Ca is further coordinated by all the O atoms and the N atom of triethanolamine, the O atoms of which are also hydrogen-bond donors. The phenolic O atoms and one O atom of a *para*-nitro group take part in intermolecular hydrogen bonding.

Comment

Chemical and X-ray structural studies on systems of the type M^{z+}(anions)(ligand)(H_2O), where M^{z+} is an alkali or alkaline earth cation, the anions are picrate, *o*-nitrophenolate, 3,5-dinitrobenzoate and 2,4-dinitrophenolate (dnp), and the ligands are triethanolamine (tea), diethanolamine (dea), 1,10-phenanthroline, tetraethylene gylcol (teg) and triethylene glycol (treg), have revealed that the metal–ligand interaction is more affected by the nature of the counter anion than is known in the case of transition metal cations (Bajaj & Poonia, 1988). It has also been found that the hydrogen bonding of the anion in the system aids the complexation of the *s*-block metal ions. This led us to investigate ligands such as ethanolamines which can coordinate with the cation and stabilize the anion at the same time. The X-ray structural results for $Ba(picrate)_2(tea)_2$ and $Ba(dnp)_2(tea)_2$ have been reported (Kanters, de Koster, Schouten, Venkatasubramanian & Poonia, 1985; Kanters, Smeets, Venkatasubramanian & Poonia, 1984); those of the title compound, (I), are presented here as part of our investigation of the discrimination among Ca^{2+}, Sr^{2+} and Ba^{2+} ions in Group II.



(I)

An *ORTEP* (Johnson, 1965) diagram of the molecule is shown in Fig. 1. Ca is eightfold coordinated by the two dnp molecules and one tea molecule. Both dnp anions are coordinated through their phenolic O atoms and one of the O atoms of the *o*-nitro groups. The tea ligand coordinates using all four potential donor atoms, *i.e.* three O atoms and one N atom. The important bond distances, angles and torsion angles are given in Table 2. The Ca—O distances are in the range 2.343 (5)–2.547 (7) Å and the Ca—N distance is 2.600 (7) Å. The coordination polyhedron of Ca can be classified as a distorted square antiprism.

Corresponding bond lengths in the two dnp ligands do not show significant differences, the largest being 0.028 Å for the N—O bonds. The C—O bond lengths of 1.279 (9) and 1.283 (8) Å are comparable to those of 1.273 (5) and 1.283 (6) Å found in the Ba complex (Kanters *et al.*, 1984). In both dnp residues, the two C—C bonds at the phenolic site are long [average 1.430 (11) Å] and two out of the remaining bonds are short [average 1.362 (12) Å], whereas the bond angles at the phenolic site are smaller than 120°