C(14)	−0.1253 (2)	−0.1578 (3)	0.2239 (2)	0.045 (1)
C(15)	−0.1447 (2)	−0.0950 (3)	0.3022 (2)	0.043 (1)
C(16)	−0.2037 (2)	−0.1337 (3)	0.3523 (2)	0.056 (1)
C(17)	−0.2188 (2)	−0.0692 (3)	0.4238 (2)	0.062 (1)
C(18)	−0.1766 (2)	0.0325 (3)	0.4435 (2)	0.059 (1)
C(19)	−0.1185 (2)	0.0669 (3)	0.3910 (2)	0.055 (1)
N(21)	0.0422 (1)	0.1800 (2)	0.3196 (2)	0.043 (1)
C(20)	0.0797 (2)	0.1736 (3)	0.3939 (2)	0.051 (1)
C(21)	0.0911 (2)	0.2738 (3)	0.4434 (2)	0.056 (1)
C(22)	0.0655 (2)	0.3862 (3)	0.4156 (2)	0.061 (1)
C(23)	0.0299 (2)	0.3958 (3)	0.3381 (2)	0.056 (1)
C(24)	0.0193 (2)	0.2901 (2)	0.2916 (2)	0.041 (1)
Cl(1)	0.3241 (1)	−0.0087 (1)	0.3642 (1)	0.061 (1)
O(1)	0.3360 (2)	−0.0728 (4)	0.2919 (2)	0.124 (2)
O(2)	0.2499 (2)	0.0451 (3)	0.3623 (2)	0.103 (1)
O(3)	0.3812 (2)	0.0834 (4)	0.3734 (3)	0.133 (2)
O(4)	0.3315 (2)	−0.0861 (5)	0.4326 (2)	0.151 (2)

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

Zn(1)—N(11)	2.166 (2)	Zn(1)—N(12)	2.172 (3)
Zn(1)—N(21)	2.135 (2)	N(11)—C(10)	1.341 (4)
N(11)—C(14)	1.345 (4)	N(12)—C(15)	1.339 (4)
N(12)—C(19)	1.346 (4)	C(10)—C(11)	1.379 (5)
C(11)—C(12)	1.370 (5)	C(12)—C(13)	1.377 (5)
C(13)—C(14)	1.390 (5)	C(14)—C(15)	1.485 (4)
C(15)—C(16)	1.390 (4)	C(16)—C(17)	1.384 (5)
C(17)—C(18)	1.368 (5)	C(18)—C(19)	1.389 (5)
N(21)—C(20)	1.359 (4)	N(21)—C(24)	1.343 (4)
C(20)—C(21)	1.367 (5)	C(21)—C(22)	1.379 (5)
C(22)—C(23)	1.392 (5)	C(23)—C(24)	1.388 (4)
C(24)—C(24^i)	1.492 (5)		
N(11)—Zn(1)—N(12)	75.8 (1)	N(11)—Zn(1)—N(21)	169.5 (1)
N(12)—Zn(1)—N(21)	95.2 (1)	N(11)—Zn(1)—N(11^i)	88.1 (1)
N(12)—Zn(1)—N(11^i)	93.9 (1)	N(21)—Zn(1)—N(11^i)	98.1 (1)
N(12)—Zn(1)—N(12^i)	165.8 (1)	N(12)—Zn(1)—N(21^i)	95.9 (1)
N(21)—Zn(1)—N(21^i)	77.2 (1)	Zn(1)—N(11)—C(10)	125.9 (2)
Zn(1)—N(11)—C(14)	115.7 (2)	Zn(1)—N(12)—C(15)	115.1 (2)
Zn(1)—N(12)—C(19)	124.7 (2)	Zn(1)—N(21)—C(20)	125.5 (2)
Zn(1)—N(21)—C(24)	115.2 (2)	C(10)—N(11)—C(14)	118.2 (3)
C(15)—N(12)—C(19)	119.4 (3)	N(11)—C(10)—C(11)	123.5 (3)
C(10)—C(11)—C(12)	117.9 (3)	C(11)—C(12)—C(13)	119.8 (3)
C(12)—C(13)—C(14)	119.3 (3)	N(11)—C(14)—C(13)	121.3 (3)
N(11)—C(14)—C(15)	115.8 (2)	C(13)—C(14)—C(15)	122.9 (3)
N(12)—C(15)—C(14)	116.2 (2)	N(12)—C(15)—C(16)	121.0 (3)
C(14)—C(15)—C(16)	122.8 (3)	C(15)—C(16)—C(17)	119.3 (3)
C(16)—C(17)—C(18)	119.8 (3)	C(17)—C(18)—C(19)	118.4 (3)
N(12)—C(19)—C(18)	122.1 (3)	C(20)—N(21)—C(24)	118.6 (2)
N(21)—C(20)—C(21)	122.5 (3)	C(20)—C(21)—C(22)	118.7 (3)
C(21)—C(22)—C(23)	119.8 (3)	C(22)—C(23)—C(24)	118.4 (3)
N(21)—C(24)—C(23)	121.8 (3)	N(21)—C(24)—C(24^i)	115.4 (2)
C(23)—C(24)—C(24^i)	122.7 (2)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

A crystal of suitable size was cut and mounted on a glass fibre for data collection. Lp corrections were applied. The structure was solved by direct methods using *SAPI*91 (Fan, Yao, Zheng, Gu & Qian, 1991) and refined anisotropically with *SHELXL*93 (Sheldrick, 1993). The H atoms were generated geometrically (C—H 0.96 Å), assigned isotropic displacement parameters and included in structure-factor calculations.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexakis(dimethyl sulfoxide)mercury(II) Trifluoromethanesulfonate, a Standard for Solid-State ^{199}Hg NMR

James M. Hook

NMR Facility, University of New South Wales, Sydney, NSW 2052, Australia

Philip A. W. Dean

Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

David C. R. Hockless

Research School of Chemistry, Institute of Advanced Studies, Australian National University, Canberra, ACT 0200, Australia

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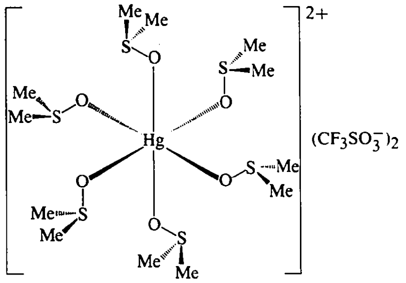
Abstract

In the title compound, $[Hg\{(CH_3)_2SO\}_6](CF_3SO_3)_2$, the discrete cations have $\bar{3}$ symmetry. For the octahedral HgO_6 kernel, the compression ratio and polar angle are 1.39 and 58.1°, respectively. Within the cations, intramolecular Hg···H distances range from 4.00 to 5.48 Å, while there are no intermolecular Hg···H distances shorter than 4.34 Å.

Comment

The title compound, (1), was first synthesized by Peringer (1980). Its physical, chemical and NMRspectroscopic properties make it attractive as a standard for solid-state cross-polarization magic-angle-spinning ^{199}Hg NMR experiments (Hook, Van Gorkom & Dean, 1995). However, no structural data are available for (1), though preliminary X-ray diffraction data have been reported (Peringer, 1980). The structure consists of discrete $[Hg(dmso)_6]^{2+}$ cations and $CF_3SO_3^-$ anions, as shown in Fig. 1.



(1)

The geometry of the anions is unexceptional. Selected bond distances and angles for the cation are given in Table 2. Of these dimensions, only the S—O distance falls significantly outside the ranges that were established for the centrosymmetric cations in $[Hg(dmso)_6](ClO_4)_2$, (2) (Sandström & Persson, 1978). The S—O distance in (1) [1.543 (5) Å] is marginally larger than the largest S—O distance in (2) [1.522 (6) Å]. The HgO_6 kernel of the cation of (1) is compressed along the threefold axis, with a compression ratio and polar angle (Steifel & Brown, 1972) of 1.39 and 58.1°, respectively. The $\bar{3}$ symmetry of the cation is consistent with the axial symmetry implied by the ^{199}Hg NMR spectrum of the powder. The range of intramolecular Hg···H distances in (1) is 4.00–5.48 Å, compared with a range of 3.32–5.50 Å that can be calculated for (2). Both salts also have comparatively short intermolecular Hg···H distances, for example below 5 Å, 4.34 Å for (1), and 4.35 and 4.61 Å for (2). Hg···H distances are an important factor in determining the efficiency of ^{1}H–^{199}Hg polarization transfer for the NMR experiments. On the basis of its shorter intramolecular Hg···H interactions alone, (2) is expected to show more efficient cross polarization. However, its potentially explosive character renders it inappropriate for use as a standard.

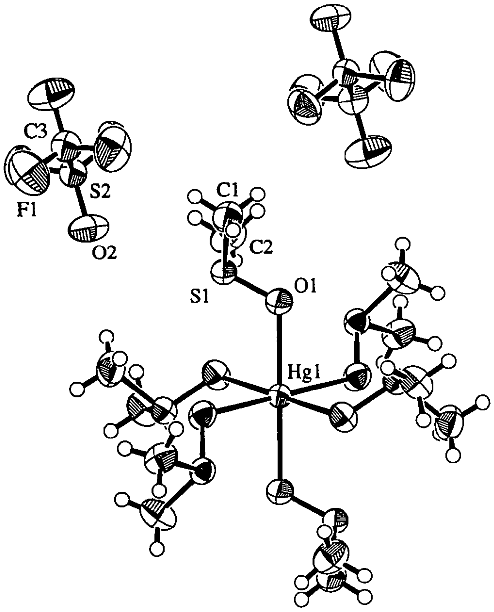


Fig. 1. View of $[Hg\{(CH_3)_2SO\}_6](CF_3SO_3)_2$ showing the labelling of all unique non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as circles of arbitrary radii.

Experimental

The literature synthesis (Peringer, 1980) produced (1) in crystalline form.

Crystal data

$[Hg(C_2H_6OS)_6](CF_3SO_3)_2$
$M_r = 967.49$
Trigonal
$P\bar{3}$
$a = 12.195\ (1)$ Å
$c = 6.713\ (2)$ Å
$V = 864.6\ (2)$ Å^3
$Z = 1$
$D_x = 1.858$ Mg m^{-3}
Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 48.8$–$50.0°$
$\mu = 12.76$ mm^{-1}
$T = 293$ K
Block
0.150 × 0.120 × 0.100 mm
Colourless

Data collection

Rigaku AFC-6*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical
$T_{min} = 0.157$, $T_{max} = 0.354$
1498 measured reflections
869 independent reflections
859 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.081$
$\theta_{max} = 60.12°$
$h = 0 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = 0 \rightarrow 7$
3 standard reflections monitored every 150 reflections
intensity decay: 10.79%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.046$
$S = 2.69$
859 reflections
64 parameters
H-atom parameters not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.009F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.0030$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -1.20$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: $2\ (2) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg(1)	0	0	0	0.0376 (3)
S(1)	0.2141 (2)	−0.0540 (2)	0.2176 (3)	0.042 (1)
S(2)	2/3	1/3	−0.3568 (5)	0.051 (1)
F(1)	0.6628 (7)	0.2316 (6)	−0.7020 (9)	0.098 (4)
O(1)	0.1832 (5)	0.0528 (5)	0.1848 (7)	0.050 (3)
O(2)	0.5516 (6)	0.2214 (6)	−0.3095 (9)	0.078 (4)
C(1)	0.2999 (9)	−0.0130 (8)	0.443 (1)	0.059 (5)
C(2)	0.3391 (9)	−0.0235 (10)	0.053 (1)	0.069 (5)
C(3)	2/3	1/3	−0.626 (2)	0.061 (6)

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

Hg(1)—O(1)	2.347 (5)	Hg(1)···H(1*c*)	4.80
S(1)—O(1)	1.543 (5)	Hg(1)···H(2*a*)	5.05
S(1)—C(1)	1.766 (8)	Hg(1)···H(2*b*)	4.00
S(1)—C(2)	1.764 (9)	Hg(1)···H(2*c*)	4.73
Hg(1)···H(1*a*)	5.48	Hg(1)···H(1*c*^{i})	4.73
Hg(1)···H(1*b*)	5.11		
O(1)—Hg(1)—O(1^{ii})	94.6 (2)	C(1)—S(1)—C(2)	98.6 (5)
O(1)—S(1)—C(1)	104.1 (3)	Hg(1)—O(1)—S(1)	116.4 (3)
O(1)—S(1)—C(2)	106.5 (4)		

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

The θ-scan width used was $(1.30 + 0.30 \tan\theta)^\circ$ at a speed of 8.0° min^{-1} in ω. The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with 2:1 ratio of peak to background counting time.

The structure can be solved by inference: since the Laue class is $\bar{3}$ and $Z = 1$, the Hg atom must have site symmetry $\bar{3}$ and be centered at the origin [Wyckoff position (1*c*)]. Likewise, the anion has 3 symmetry and hence must be oriented about (*c*) or (*d*). The structure was expanded by Fourier techniques (Beurskens *et al.*, 1992). This is the three-dimensional analogue of the method used by Robertson & Woodward (1940) to solve the structure of Pt phthalocyanine. Methyl H atoms were fixed at ideal positions [$U_{iso} = 1.2U_{eq}$(C)].

Data collection and cell refinement were performed using *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989). All other calculations, including data reduction and structure refinement, were performed using *TEXSAN* (Molecular Structure Corporation, 1993).

We would like to thank Dr Marcia Scudder and Mr Don Craig (UNSW) for their assistance with data analysis.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1049). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraaqua(3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetato)dizinc(II)–Water (1/2)

M. Hernandez-Padilla, S. Dominguez and A. Mederos*

Departamento de Química Inorgánica, Universidad de La Laguna, Tenerife, Canary Islands, Spain

J. M. Arrieta

Departamento de Química Inorgánica, Universidad del País Vasco, Bilbao, Spain

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Abstract

The simplest unit of the title compound, [$Zn_2(C_{15}H_{14}N_2O_8)(H_2O)_4$].2$H_2O$, is a dinuclear Zn^{II} complex bridged by the O atoms of one carboxylate moiety of the 3,4-toluenediamine-*N*,*N*,*N*′,*N*′-tetraacetate ligand (3,4-tdta). The coordination geometry of the zinc-3,4-tdta moiety is close to trigonal prismatic, whereas the other zinc ion is in a nearly O_h environment comprising two O atoms from carboxylate groups of different ligands and four water molecules. The other two water molecules are waters of crystallization in the polynuclear complex [Zn-μ-(3,4-tdta)-Zn(H_2O)$_4$]$_n$.2H_2O_n.

Comment

3,4-tdta acid (Mederos, Herrera, Felipe & Quesada, 1984) is similar to *o*-phdta acid (*o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic) (Nakasuka, Kunimatsu, Matsumura & Tanaka, 1985) derived from *o*-phenylenediamines. The octahedral structure is quite common in metal complexes of potentially hexadentate aminopolycarboxylates such as ethylenediaminetetraacetate (edta). This is, however, not the case for the complexes of *o*-phdta and 3,4-tdta acids, since the substitution of the ethylenic