Crystal structure and Hirshfeld surface analysis of bis[(ethoxymethanethioyl)sulfanido](N,N,N',N'-tetramethylethane-1,2-diamine)mercury(II)

Adnan M. Qadir,* Sevgi Kansiz,b* Necmi Degec and Eiad Saif,d,e*

*Department of Chemistry, College of Science, Salahaddin University, Erbil, 44001, Iraq, b*Samsun University, Faculty of Engineering, Department of Fundamental Sciences, 55420, Samsun, Turkey, cOndokuz Mayis University, Faculty of Arts and Sciences, Department of Physics, 55139, Samsun, Turkey, dDepartment of Computer and Electronic Engineering Technology, Sanaa Community College, Sanaa, Yemen, and eDepartment of Electrical and Electronic Engineering, Faculty of Engineering, Ondokuz Mayis University, 55139, Samsun, Turkey. *Correspondence e-mail: sevgi.kansiz@samsun.edu.tr, eiad.saif@scc.edu.ye

The title four-coordinate mononuclear complex, \([\text{Hg}(\text{C}_3\text{H}_5\text{OS}_2)_2(\text{C}_6\text{H}_{16}\text{N}_2)]\) or \([\text{Hg}(\text{C}_3\text{H}_5\text{OS}_2)_2(\text{tmeda})]\) (tmeda: N,N,N,N0-tetramethylethylenediamine), has a distorted tetrahedral geometry. The HgII ion is coordinated to two N atoms of the N,N,N,N0-tetramethylethylenediamine ligand and two S atoms from two ethylxanthate xanthate ligands. In the crystal, molecules are linked by weak C—H···S hydrogen bonds, forming a two-dimensional supramolecular architecture in the ab plane. The most important contributions for the crystal packing are from H···H (59.3%), S···H (27.4%) and O···H (7.5%) interactions.

1. Chemical context

Xanthates (dithiocarbonates) attract the interest of many researchers in the field of coordination chemistry owing to their antidotal, antioxidant and antitumor activities (Shahzadi et al., 2009; Perluigi et al., 2006; Larsson & Oberg, 2011). These ligands exhibit different coordination modes such as monodentate, isobidentate or anisobidentate. Cellulose xanthate has been used for the separation of alcohols by the chromatographic method (Friebolin et al., 2004). It has been reported that metal xanthates exhibit cytotoxic activity on human cancer cells and have the ability to inhibit both DNA and RNA viruses in vitro (Efrima & Pradhan, 2003). Mercury represents one of the most toxic heavy metals found in solid and liquid waste from oil refineries and the mining industry. We report herein the synthesis and crystal structure of a new HgII xanthate containing N,N,N',N'-tetramethylethylenediamine, including the results of a Hirshfeld surface analysis.
2. Structural commentary

The asymmetric unit of the title complex (Fig. 1) comprises one Hg\textsuperscript{II} ion, one half \(N,N,N',N'\)-tetramethylethylenediamine ligand and one ethylxanthate ligand. The Hg\textsuperscript{II} ion is coordinated by two N atoms of the \(N,N,N',N'\)-tetramethylethylenediamine ligand and two S atoms from two ethylxanthate xanthate ligands in a distorted tetrahedral environment. The Hg—N and Hg—S bond lengths (Table 1) are 2.531 (8) and 2.416 (3) Å, respectively, whereas the bond angles around the central Hg\textsuperscript{II} ion are in the range 73.8 (3)–149.91 (18)°. The bond lengths and angles of the HgN\textsubscript{2}S\textsubscript{2} coordination units correspond to those in the structures of mixed-ligand Hg\textsuperscript{II} coordination compounds (see Database survey). The C1—O1 and C2—O1 bond lengths are 1.355 (11) to 1.460 (12) Å, respectively, although all of the C—O bonds show single-bond character. In the \(S_2C\) section of the xanthate ligands, the C1—S1 distance is 1.727 (9) Å, which is typical of a single bond, whereas the C1═S2 distance of 1.633 (10) Å is typical of a carbon-to-sulfur double bond. The C—N and C—C bond lengths in the \(N,N,N',N'\)-tetramethylethylenediamine ligand are normal (Qadir et al., 2020).

3. Supramolecular features

In the crystal, there is a weak intermolecular hydrogen bonding (Table 2) between S atoms and the H atoms of the methylene groups \([C4—H4B···S1 (x – \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2})]\), Fig. 2 illustrates the two-dimensional wave-like structure extending in the \(ab\) plane formed by hydrogen-bonding interactions in \([\text{Hg(C}_{3}\text{H}_{5}\text{S}_{2}\text{O}_{1})_{2}(\text{tmeda})]\).

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.42, update of November 2020; Groom et al., 2016) for the title complex revealed five similar complexes: \([\text{Hg(C}_{14}\text{H}_{26}\text{O}_{2}\text{S}_{4}]_{n}\) (BATXOJ; Cox & Tiekink, 1999), \([\text{Hg(C}_{5}\text{H}_{4}\text{NSe})_{2}(\text{C}_{6}\text{H}_{16}\text{N}_{2})]\) (EKODAK; Sharma et al., 2011), \([\text{Hg(C}_{6}\text{H}_{16}\text{N}_{2})(\text{C}_{9}\text{H}_{13}\text{NS})_{2}]_{2}(\text{PF}_{6})_{2}\) (POTJOY; Tang et al., 2009), \([\text{HgCl(C}_{7}\text{H}_{7}\text{S})(\text{C}_{6}\text{H}_{16}\text{N}_{2})]\) (TEVQAM; Kra¨uter et al., 1996) and \([\text{HgCl}_{2}(\text{C}_{6}\text{H}_{16}\text{N}_{2})]\) (ZZZAJM; Htoon & Ladd, 1976). In BATXOJ, the coordination geometry is distorted tetrahedral with the independent Hg—S distances being 2.413 (5) and 2.842 (5) Å. The range of S—Hg—S angles is 81.8 (2)–150.8 (3)° with the wider angle involving the more tightly bound S1 atoms. In EKODAK, the corresponding mercury complex adopts a severely distorted tetrahedral configuration defined by the two monodentate selenolate and chelating tmeda ligands. The Hg—N bond lengths are in the range 2.573 (17)–2.601 (18) Å. In POTJOY, intermolecular C—H···S hydrogen bonds are important in the crystal packing. Similarly, the molecules are connected to each other via C—H···S hydrogen bonds in the title complex. In TEVQAM, the Hg—N and Hg—S bond lengths are 2.54 and 2.34 Å, respectively, comparable to those in the title compound.

5. Hirshfeld surface analysis

A Hirshfeld surface analysis (Spackman & Jayatilaka, 2009) was carried out using CrystalExplorer\textsuperscript{17.5} (Turner et al., 2017) to quantify the various intermolecular interactions. The Hirshfeld surface mapped over \(d_{norm}\) is illustrated in Fig. 3 and the associated two-dimensional fingerprint plots in Fig. 4. The...
major contributions to the crystal structure are from H···H (59.3%), S···H (27.4%) and O···H interactions (7.5%). The large number of H···H interactions suggest that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing. C···H (3.4%) and S···O (1.9%) contacts are also observed.

6. Synthesis and crystallization

Potassium ethylxanthate (4 mmol, 0.64 g) in hot ethanol (10 mL) was added to a hot solution of Hg(CH$_3$CO$_2$)$_2$ (2 mmol, 0.64 g) in ethanol (10 mL) under stirring. The formed precipitate was filtered off, washed with water and air-dried. The precipitate was suspended in hot ethanol (10 mL) and tetramethylethylenediamine (2 mmol, 0.23 g) was added under stirring. The colour changed to dark brown. The precipitate was filtered off and dried and then recrystallized from ethanol. Brown rods were formed.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. C-bound H atoms were positioned geometrically (C—H = 0.96 and 0.97 Å) and refined using a riding model, with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and $1.2U_{eq}(C)$ for all others.

Table 3

| Crystal data                              | [Hg(C$_5$H$_7$OS)$_2$C$_6$H$_6$N$_2$] |
|-------------------------------------------|--------------------------------------|
| Chemical formula                          | [Hg(C$_5$H$_7$OS)$_2$C$_6$H$_6$N$_2$] |
| $M_r$                                      | 559.18                               |
| Crystal system, space group               | Orthorhombic, Pbcn                   |
| Temperature (K)                           | 296                                  |
| $a$, $b$, $c$ (Å)                         | 12.235 (7), 8.017 (5), 21.251 (17)   |
| $V$ (Å$^3$)                               | 2084 (2)                             |
| $Z$                                       | 4                                    |
| Radiation type                            | Mo Kα                                |
| $\mu$ (mm$^{-1}$)                         | 7.79                                 |
| Crystal size (mm)                         | 0.71 × 0.38 × 0.06                   |

Data collection

Diffractometer                              | Bruker D8 Quest with Photon II CPADs detector |
Absorption correction                       | Multi-scan (SADABS; Krause et al., 2015)   |
$T_{min} \ T_{max}$                         | 0.041, 0.627                             |
No. of measured, independent and observed | 8974, 1946, 1265                          |
$R_{int}$                                   | 0.139                                 |
$R(F^2 > 2\sigma(F^2)), wR(F^2), S$        | 0.053, 0.147, 1.00                      |
No. of reflections                          | 1946                                  |
No. of parameters                           | 99                                    |
H-atom treatment                           | H-atom parameters constrained         |
$\Delta p_{max}, \Delta p_{min}$ (e Å$^{-3}$)| 1.01, -2.73                           |

Computer programs: APEX3 and SAINT (Bruker, 2017), SHELXT2016/2 (Sheldrick, 2015a), SHELXL2017/1 (Sheldrick, 2015b), PLATON (Spek, 2020) and WinGX (Farrugia, 2012).

Acknowledgements

Author contributions are as follows. Conceptualization, SK, AMQ and ES; synthesis, AMQ; writing (review and editing of the manuscript), SK and AMQ, formal analysis, SK, AMQ and ND, validation, SK, AMQ and ND, project administration, SK, AMQ and ES.

Funding information

Funding for this research was provided by: Ondokuz Mayıs University under Project No. PYO.FEN.1906.19.001.
References

Bruker (2017). APEX3 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.

Cox, M. J. & Tiekink, E. R. T. (1999). Z. Kristallogr. Cryst. Mater. 214, 486–491.

Efrima, S. & Pradhan, N. (2003). C. R. Chim. 6, 1035–1045.

Farrugia, L. J. (2012). J. Appl. Cryst. 45, 849–854.

Friebolin, W., Schilling, G., Zöller, M. & Amtmann, E. (2004). J. Med. Chem. 47, 2256–2263.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). Acta Cryst. B72, 171–179.

Htoon, S. & Ladd, M. F. C. (1976). J. Cryst. Mol. Struct. 6, 55–58.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.

Kräuter, G., Neumüller, B., Goedken, V. L. & Rees, W. S. (1996). Chem. Mater. 8, 360–368.

Larsson, A. C. & Öberg, S. (2011). J. Phys. Chem. A, 115, 1396–1407.

Perluigi, M., Joshi, G., Sultana, R., Calabrese, V., De Marco, C., Coccia, R. & Butterfield, D. A. (2006). Neuroscience, 138, 1161–1170.

Qadir, A. M., Kansiz, S., Dege, N., Rosair, G. M. & Iskenderov, T. S. (2020). Acta Cryst. E76, 1038–1041.

Shahzadi, S., Ali, S., Jabeen, R. & Khosa, M. K. (2009). Turk. J. Chem. 33, 307–312.

Sharma, R. K., Kedarnath, G., Wadawale, A., Jain, V. K. & Vishwanadh, B. (2011). Inorg. Chim. Acta, 365, 333–339.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.

Spackman, M. A. & Jayatilaka, D. (2009). CrystEngComm, 11, 19–32.

Spek, A. L. (2020). Acta Cryst. E76, 1–11.

Turner, M. J., Mackinnon, J. J., Wolff, S. K., Grimwood, D. J., Spackman, P. R., Jayatilaka, D. & Spackman, M. A. (2017). CrystalExplorer17.5. University of Western Australia. http://hirshfeldsurface.net.
Crystal structure and Hirshfeld surface analysis of bis[(ethoxymethane-thioyl)sulfanido](N,N,N’,N’-tetramethylethane-1,2-diamine)mercury(II)

Adnan M. Qadir, Sevgi Kansiz, Necmi Dege and Eiad Saif

Computing details

Data collection: APEX3 (Bruker, 2017); cell refinement: SAINT (Bruker, 2017); data reduction: SAINT (Bruker, 2017); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2017/1 (Sheldrick, 2015b); molecular graphics: PLATON (Spek, 2020); software used to prepare material for publication: WinGX (Farrugia, 2012).

Bis[(ethoxymethanethioyl)sulfanido](N,N,N’,N’-tetramethylethane-1,2-diamine)mercury(II)

Crystal data

\[\text{[Hg(C}_3\text{H}_5\text{OS}_2)\text{2(C}_6\text{H}_1\text{6N}_2)]}\]

\(M_r = 559.18\)

Orthorhombic, \(Pbcn\)

\(a = 12.235 \ (7) \ \text{Å}\)

\(b = 8.017 \ (5) \ \text{Å}\)

\(c = 21.251 \ (17) \ \text{Å}\)

\(V = 2084 \ (2) \ \text{Å}^3\)

\(Z = 4\)

\(F(000) = 1088\)

Data collection

Bruker D8 Quest with Photon II CPADs
detector
diffractometer
Radiation source: Incoatec microfocus source
Detector resolution: 7.4074 pixels mm\(^{-1}\)
Detector resolution: 7.4074 pixels mm\(^{-1}\)
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)

\(T_{\min} = 0.041, T_{\max} = 0.627\)

Refinement

Refinement on \(F^2\)
Least-squares matrix: full
\(R[F^2 > 2\sigma(F^2)] = 0.053\)
\(wR(F^2) = 0.147\)
\(S = 1.00\)
1946 reflections
99 parameters
0 restraints
Primary atom site location: dual

Hydrogen site location: inferred from
eighbouring sites
H-atom parameters constrained

\(\Delta \sigma_{\text{max}} = 0.001\)
\(\Delta \rho_{\text{max}} = 1.01 \ \text{e Å}^{-3}\)
\(\Delta \rho_{\text{min}} = -2.73 \ \text{e Å}^{-3}\)
**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|   | x     | y     | z     | Uiso* | Ueq  |
|---|-------|-------|-------|-------|------|
| Hg1 | 0.500000 | 0.59649 (6) | 0.750000 | 0.0605 (2) |
| S1  | 0.6620 (2) | 0.6747 (4) | 0.69202 (12) | 0.0807 (9) |
| S2  | 0.4722 (2) | 0.7975 (5) | 0.61444 (14) | 0.0815 (8) |
| O1  | 0.6840 (6) | 0.8337 (10) | 0.5917 (3) | 0.0753 (19) |
| N1  | 0.4366 (6) | 0.3441 (10) | 0.6885 (3) | 0.0580 (18) |
| C1  | 0.6025 (8) | 0.7760 (12) | 0.6290 (4) | 0.063 (2) |
| C6  | 0.5057 (9) | 0.3204 (18) | 0.6319 (5) | 0.087 (4) |
| H6A | 0.502245 | 0.418481 | 0.606101 | 0.131* |
| H6B | 0.479686 | 0.226095 | 0.608454 | 0.131* |
| H6C | 0.579968 | 0.301191 | 0.644595 | 0.131* |
| C4  | 0.4462 (8) | 0.1997 (13) | 0.7314 (5) | 0.069 (2) |
| H4A | 0.441367 | 0.097608 | 0.707118 | 0.083* |
| H4B | 0.385492 | 0.201216 | 0.760778 | 0.083* |
| C3  | 0.7614 (16) | 0.9572 (16) | 0.5016 (5) | 0.101 (5) |
| H3A | 0.747525 | 1.015326 | 0.462895 | 0.152* |
| H3B | 0.795996 | 0.852358 | 0.492616 | 0.152* |
| H3C | 0.808505 | 1.023299 | 0.527706 | 0.152* |
| C5  | 0.3232 (9) | 0.3668 (17) | 0.6701 (5) | 0.090 (4) |
| H5A | 0.280086 | 0.390950 | 0.706757 | 0.136* |
| H5B | 0.296750 | 0.266672 | 0.650617 | 0.136* |
| H5C | 0.317899 | 0.457818 | 0.640942 | 0.136* |
| C2  | 0.6563 (11) | 0.9271 (15) | 0.5349 (5) | 0.091 (4) |
| H2A | 0.621592 | 1.031988 | 0.545653 | 0.109* |
| H2B | 0.606886 | 0.863221 | 0.508546 | 0.109* |

**Atomic displacement parameters (Å²)**

|   | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|---|-----|-----|-----|-----|-----|-----|
| Hg1 | 0.0589 (4) | 0.0689 (4) | 0.0536 (3) | 0.000 | 0.0023 (2) | 0.000 |
| S1  | 0.0618 (15) | 0.113 (2) | 0.0676 (13) | −0.0248 (17) | −0.0088 (11) | 0.0231 (15) |
| S2  | 0.0674 (17) | 0.096 (2) | 0.0811 (16) | 0.0098 (16) | −0.0023 (13) | 0.0141 (16) |
| O1  | 0.082 (5) | 0.085 (5) | 0.059 (3) | −0.011 (4) | 0.009 (3) | 0.013 (3) |
| N1  | 0.056 (5) | 0.064 (5) | 0.054 (4) | 0.000 (4) | 0.002 (3) | 0.000 (3) |
| C1  | 0.075 (6) | 0.059 (6) | 0.056 (5) | −0.015 (5) | 0.004 (4) | 0.000 (4) |
| C6  | 0.103 (9) | 0.088 (9) | 0.071 (6) | −0.008 (8) | 0.012 (5) | −0.024 (6) |
| C4  | 0.057 (6) | 0.067 (6) | 0.084 (6) | −0.023 (6) | −0.006 (5) | −0.010 (5) |
| C3  | 0.142 (13) | 0.083 (10) | 0.079 (7) | 0.005 (8) | 0.037 (7) | 0.015 (7) |
| C5  | 0.075 (8) | 0.123 (11) | 0.073 (6) | −0.013 (7) | −0.019 (6) | −0.003 (6) |
| C2  | 0.115 (10) | 0.090 (8) | 0.067 (6) | 0.005 (8) | 0.018 (7) | 0.025 (5) |

*Acta Cryst. (2021). E77, 1126-1129*
### Geometric parameters (Å, °)

| Bond/Angle | Value (Å/°) |
|-----------|-------------|
| Hg1—S1    | 2.416 (3)   |
| Hg1—S1\(^{i}\) | 2.416 (3)   |
| Hg1—N1    | 2.531 (8)   |
| Hg1—N1\(^{i}\) | 2.531 (8)   |
| S1—C1     | 1.727 (9)   |
| S2—C1     | 1.633 (10)  |
| O1—C1     | 1.355 (11)  |
| O1—C2     | 1.460 (12)  |
| N1—C5     | 1.452 (13)  |
| N1—C4     | 1.479 (13)  |
| N1—C6     | 1.481 (13)  |
| C6—H6A    | 0.9600      |
| C6—H6B    | 0.9600      |
| S1—Hg1—S1\(^{i}\) | 149.91 (18) |
| S1—Hg1—N1 | 101.26 (18) |
| S1\(^{i}\)—Hg1—N1 | 102.70 (19) |
| S1—Hg1—N1\(^{i}\) | 102.70 (19) |
| S1\(^{i}\)—Hg1—N1\(^{i}\) | 101.26 (18) |
| N1—Hg1—N1\(^{i}\) | 73.8 (3)   |
| C1—S1—Hg1 | 99.9 (3)   |
| C1—O1—C2 | 119.2 (9)   |
| C5—N1—C4 | 109.8 (9)   |
| C5—N1—C6 | 110.1 (8)   |
| C4—N1—C6 | 110.8 (9)   |
| C5—N1—Hg1| 109.3 (7)   |
| C4—N1—Hg1| 106.4 (5)   |
| C6—N1—Hg1| 110.3 (6)   |
| C1—C1—S2 | 124.9 (7)   |
| O1—C1—S1 | 107.7 (7)   |
| S2—C1—S1 | 127.4 (5)   |
| N1—C6—H6A| 109.5       |
| N1—C6—H6B| 109.5       |
| H6A—C6—H6B| 109.5      |
| N1—C6—H6C| 109.5       |
| H6A—C6—H6C| 109.5      |
| H6B—C6—H6C| 109.5      |
| N1—C4—C4\(^{i}\) | 112.7 (7)  |
| C2—O1—C1—S2 | 1.9 (13)   |
| C2—O1—C1—S1 | −179.2 (8) |
| Hg1—S1—C1—O1 | 178.2 (6)  |
| Hg1—S1—C1—S2 | −3.0 (7)   |
| S1—Hg1—S1\(^{i}\) | N1—C4—C4\(^{i}\) | 162.2 (10) |
| S1—Hg1—N1 | C6—N1—C4—C4\(^{i}\) | 75.9 (12) |
| S1\(^{i}\)—Hg1—N1 | Hg1—N1—C4—C4\(^{i}\) | −44.0 (11) |
| S1—Hg1—N1\(^{i}\) | C1—O1—C2—C3 | −174.4 (9) |

Symmetry code: \((i)\) \(-x+1, y, -z+3/2\).
### Hydrogen-bond geometry (Å, °)

|         | D—H | H···A | D···A     | D—H···A |
|---------|-----|-------|-----------|---------|
| C4—H4B···S1\textsuperscript{ii} | 0.97 | 2.92  | 3.845 (11) | 160     |

Symmetry code: (ii) \(x-1/2, y-1/2, -z+3/2\).